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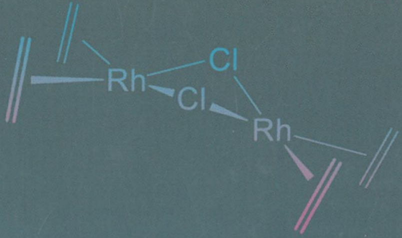

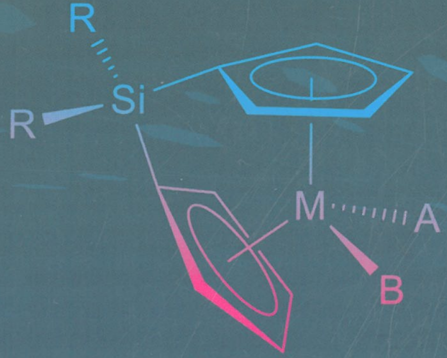

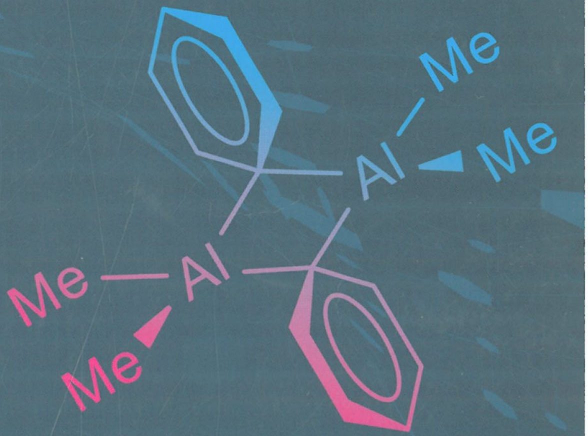

MANFRED BOCHMANN

ORGANOMETALLICS AND CATALYSIS

AN INTRODUCTION

Organometallics and Catalysis

An Introduction

Manfred Bochmann
University of East Anglia

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Preface

Organometallic chemistry can be described as the interface of two rather different scientific fields: the reactivity and structure of the metallic and semi-metallic elements, which is the classical domain of inorganic chemistry and metallurgy, and the chemistry of carbon compounds. The result is an instructive and surprising insight into the diversity of the chemical bond, some of which continues to challenge conventional views, and a powerful toolbox for the selective making and breaking of carbon–carbon and carbon–element bonds. Organometallic compounds of the s- and p-block elements contain polarized metal–carbon bonds of superb reactivity, while the availability of d-orbitals in the transition metals offer low energy pathways for catalytic transformations. The overwhelming majority of all products of the world's chemical industry pass through a catalytic step at some stage of their manufacture, and many of these steps involve a metal–carbon bond. Catalysis is the basis of large-scale industrial processes, as well as of laboratory-scale syntheses of fine chemicals and pharmaceuticals. This book aims to provide an introductory overview of the main types of compound classes and reactions in organometallic chemistry, and to provide a basis for understanding synthetic possibilities and catalytic reaction mechanisms.

This text is based on two slim volumes that appeared in 1994 as part of the Oxford Chemistry Primers series, which provided an introduction to the chemistry of transition metal complexes with σ-bonds ('Organometallics 1') and with π-bonds ('Organometallics 2'). The concept of these booklets was to give a lecture-note style introduction, with copious illustrations and examples, which would make it easy for the student to get the flavour of the scientific concepts without being overwhelmed with detail. The approach proved popular, but important aspects were lacking—in particular there was no coverage of s- and p-block elements, no space for more than a cursory mention of some catalytic reactions, and of course many areas have moved on significantly since then.

A fresh start was needed. The result is the present text, which gives more comprehensive coverage arranged into three parts: (1) organometallic chemistry of the Main Group elements, (2) complexes of the transition elements, and (3) catalytic mechanisms, applications, and processes. The underlying philosophy of the Oxford Chemistry Primers has remained the same however: to enable moderately experienced students to come to grips with the concepts and way of thinking in organometallic chemistry and to appreciate the applicability of the material they have learned. The scope, it is hoped, will be adequate to provide the basis for university lecture courses at undergraduate and Masters level, and wide enough to allow flexibility in coverage. It is assumed that students will have completed introductory courses of general and inorganic chemistry, in which the structure of the Periodic Table and concepts such as electronegativity, Lewis acidity, and simple molecular orbital (MO) theory have been introduced. Postgraduate students at the beginning of their PhD degrees may also find aspects of this book a useful refresher.

There are a number of more comprehensive (and necessarily more heavy-weight) textbooks on organometallic chemistry and homogeneous catalysis which offer more detailed treatment; some of these are listed in the section on Further Reading. Here we tried to sieve out those aspects that seem to us fundamental or that best illustrate the main points; the main challenge therefore was not what to include but rather what to leave out. It is hoped that the resulting text fits into a student's pocket, is light enough to have around, and is sufficiently well structured to be an easy reference.

The structure of the Main Group part follows the Periodic Table, starting with a discussion of organometallic compounds of the s- and p-elements. Here, in the interest of brevity, it was decided to exclude coverage to the heavier members of Groups 15 and 16 which, although metallic, are electron rich and have more in common with their non-metallic congeners. Within the range of elements covered, emphasis is given to those with the greatest synthetic, catalytic, or industrial utility. The section on transition metals is preceded by a discussion of the main ligand types and the reaction steps relevant to the understanding of catalytic cycles. The chapters are ordered according to ligand classes, with those having particularly widespread roles, such as CO, being discussed first.

At various intervals, shaded boxes are inserted as excursions which provide additional information that can be left out on first reading. They also illustrate snippets of interest of a more specialized nature. Margin notes are added as 'bookmarks' and also add further detail. The main take-home message of each chapter is briefly summarized in a box headed 'Key points', followed by some Exercise questions that aim to encourage readers to review the chapter content in their minds and to help students to assimilate the material and build up confidence. Appendices provide general information, such as common abbreviations and properties of solvents. Finally, a Further Reading section lists comprehensive texts, review articles, and specific literature references of material included in the text. For a text of this level and brevity it was felt it would not be helpful to include comprehensive primary literature citations.

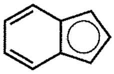
M. Bochmann
Norwich, 2014

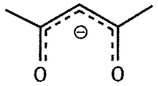
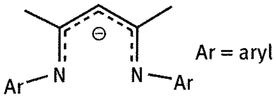
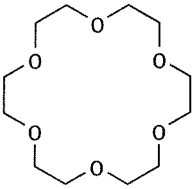
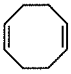
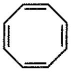
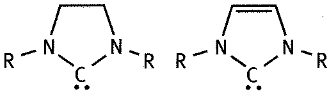
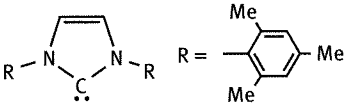
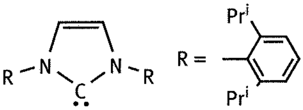
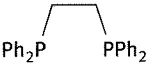
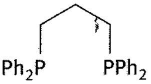
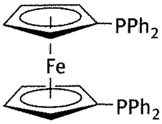
General Information

Given below are abbreviations that are commonly used in this book as well as in the scientific literature on organometallic compounds and catalysts.

The isolation and handling of organometallic reagents and compounds relies on the appropriate use of solvents. For readers less familiar with the field, **Appendix 1** gives a list of common solvents and their properties, which may prove useful.

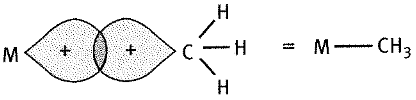
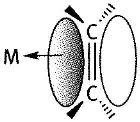
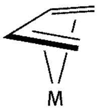
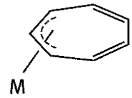
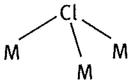
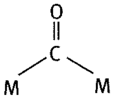
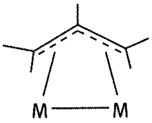
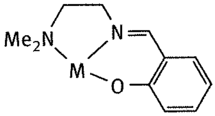
Commonly used abbreviations in organometallic chemistry:

Formula	Name	Systematic name	Common abbreviation
CH_3	methyl	methyl	Me
CH_3CH_2	ethyl	ethyl	Et
Me_2CH	isopropyl	1-methylethyl	Pr^i
$CH_3CH_2CH_2$	*n*-propyl	*n*-propyl	Pr^n
Me_2CHCH_2	isobutyl	2-methylpropyl	Bu^i
$MeCH_2CH(Me)$	*sec*-butyl	2-butyl	Bu^s
Me_3CH	*tert*-butyl	1,1-dimethylethyl	Bu^t
$H_2C{=}CH{-}CH_2$	allyl	2-propenyl	
$H_2C{=}C(Me){-}CH_2$	methallyl	2-methyl-2-propenyl	
C_5H_5	cyclopentadienyl	1-cyclopenta-2,4-dienyl	Cp
C_5Me_5	pentamethyl-Cp	pentamethylcyclopentadienyl	Cp*
	indenyl	1-indenyl	Ind
C_6H_5	phenyl	phenyl	Ph
$C_6H_5CH_2$	benzyl	benzyl	Bn, $PhCH_2$
$2\text{-}MeC_6H_4$	*ortho*-tolyl	2-methylphenyl	*o*-tol
$2,4,6\text{-}Me_3C_6H_2$	mesityl	2,4,6-trimethylphenyl	mes
$2,6\text{-}Pr^i{}_2C_6H_3$	isityl	2,6-di(isopropyl) phenyl	Dipp
$2,4,6\text{-}Pr^i{}_3C_6H_2$		2,4,6-tri(isopropyl)phenyl	Tripp
C_6H_{11}	cyclohexyl	cyclohexyl	Cy
$H_2C{=}CH{-}$	vinyl	1-ethenyl	
CH_3COO^-	acetate	ethanoate	OAc

CF_3COO^-	trifluoroacetate	trifluoroethanoate	OAc^F, tfa
$CF_3SO_3^-$	triflate	trifluoromethane sulfonate	OTf
	acetylacetonate	2,4-pentanedionato	acac
	*N*-aryl-beta-diketiminato	2,4-pentanediiminato	nacnac
	18-crown-6	1,4,7,10,13,16-hexaoxacyclo-octadecane	18-c-6
	cyclooctadiene	*cis*-1,5-cyclooctadiene	COD
	cyclooctatetraene	1,3,5,7-cyclooctatetraene	COT
	N-heterocyclic carbene		NHC
		1,3- dimesityl imidazolylidene	IMes
		bis(di-isopropylphenyl) imidazolylidene	IPr
		1,2-bis(dimethylphosphino)ethane	dmpe
		1,2-bis(diphenylphosphino)ethane	dppe
		1,3-bis(diphenylphosphino)-propane	dppp
		1,1′-bis(diphenylphosphino)-ferrocene	Dppf

Ligand Nomenclature

Ligand types and the bonding mode of ligands in complexes are described by a number of symbols and conventions. These are used throughout this text.

σ-ligand, σ-bond	Bond directed along the axis connecting two atoms, made by overlap of orbital lobes pointing at one another: the 2-electron-2-centre bond	
π-bond	Bond made by interaction of the metal with the π-electron system of an unsaturated compound, such as an alkene	
η^n hapticity	Greek 'eta', indicates π-bonding ligand, with superscript *n* denoting the number of C atoms in a π-system bonded to a metal. The η-number gives the number of C atoms that bind to the metal = the **hapticity**. η^2, η^3, η^4-ligands are called **dihapto**, **trihapto**, **tetrahapto**, etc.	 η^4-diene  η^3-allylic bonding (η^3-cycloheptatrienyl)
μ_m	Greek 'mu': indicates ligand bridging *m* metal atoms. The subscript indicates the number of atoms that are bridged.	 μ_3-chloride  μ_2-carbonyl  μ_2,η^3-allyl
κ	Greek 'kappa': indicates coordination of classical coordination ligand, usually N or O donor	 κ^3-*N,N,O* complex
X	General symbol for **anionic ligand**: halide, alkoxide	
L	General symbol for **neutral donor ligand**: such as pyridine, phosphines	
R	General symbol for **hydrocarbyl ligand**: methyl, phenyl, or for substituent in an organic molecule	

Detailed Contents

2. Organometallic Compounds of Transition Metals 81

1

Organometallic Compounds of Main Group Elements

Organometallic chemistry describes the structures and reactivity of compounds with M–C bonds, where M is a metallic or semi-metallic element. Organometallic compounds are frequently involved in the making and breaking of C–C and C–X bonds (X = non-carbon element) and have become an indispensable part of synthetic methodology. The vast majority of all products produced by the chemical industry involves at least one catalytic transformation, and most catalytic cycles involve metal–carbon bonds. Organometallic compounds also demonstrate a surprisingly versatile range of structures and provide intriguing insight into the nature of chemical bonds.

In Part 1 we will concentrate on M–C compounds of the elements in Groups 1, 2, and 12–14 of the Periodic Table (shaded; radioactive elements are excluded).

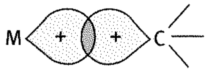
1	2		12	13	14	15	16	17	18
Li 1.0	**Be** 1.6			**B** 2.0	**C** 2.6	**N** 3.0	**O** 3.4	**F** 4.0	**Ne**
Na 0.9	**Mg** 1.3			**Al** 1.6	**Si** 1.9	**P** 2.2	**S** 2.6	**Cl** 3.2	**Ar**
K 0.9	**Ca** 1.0	d-block elements, lanthanides	**Zn** 1.7	**Ga** 1.8	**Ge** 2.0	**As** 2.2	**Se** 2.6	**Br** 3.0	**Kr**
Rb 0.8	**Sr** 1.0		**Cd** 1.7	**In** 1.8	**Sn** 2.0	**Sb** 2.1	**Te** 2.1	**I** 2.7	**Xe**
Cs 0.8	**Ba** 0.9		**Hg** 2.0	**Tl** 2.0	**Pb** 2.3	**Bi** 2.0			

ionic M–C bond ⟺ **covalent M–C bond**

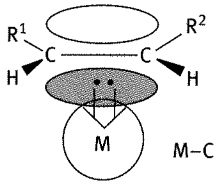
The numbers underneath the element symbols are the ***Pauling electronegativities***, which provide an indication of the M–C bond polarities.

1.1 General and Bonding Considerations

Most of the Main Group organometallic compounds under discussion here contain **metal-carbon σ-bonds** generated by orbital overlap along the M–C axis. There is also the possibility of interaction of the metal with the π-electron systems of unsaturated organic compounds, in particular if the unsaturated moiety carries a negative charge. These π-bonds are, for the most part, weak in Main Group chemistry (although very prominent in transition metal complexes), but can be reinforced by dipole interactions between a positively charged metal centre and the π-electron density.



M–C σ-bond



M–C π-interaction

Bond polarity

One important aspect that governs the reactivity of organometallic species is the polarity of the $M^{\delta+}$–$C^{\delta-}$ bond, which is a reflection of the differences in electronegativity between carbon and metals. The **bond polarity** decreases from left to right across the Periodic Table. The bond polarity also increases on going down the group, i.e. on going from lighter to heavier elements, while at the same time the M–C bond strength decreases.

An M–C bond can be described by two resonance forms:

$$\overset{\oplus}{M}\ \ \overset{\ominus}{CR_3} \longleftrightarrow M{-}CR_3$$

The bonds between alkyl anions and alkali metal cations of Group 1, as the most electropositive elements, are the most ionic, although they retain more covalent character than alkali halides. The polarity readily expresses itself in the reactivity of metal alkyl compounds: while the alkyls of Group 1 and 2 metals are extremely sensitive to hydrolysis and oxidation, those of Group 13 are less so and Group 14 compounds are comparatively unreactive.

Electronegativity (EN)

Electronegativity (EN) is a measure of the ability of an atom to pull the electron density of a bond towards itself. While this is a straightforward concept for simple M–H and M–Cl bonds, the electronegativity of an element such as carbon is not constant, but depends on the amount of s-orbital character that is involved in its bonding, since the s-orbital is more strongly affected by the effective nuclear charge than p-orbitals. Values of EN = 2.5–2.6 are typical of sp^3-hydridized C, whereas sp^2-hydridized carbon has a higher electronegativity (ca. 2.7), and an sp-carbon atom (as in $-C{\equiv}CR$) has an EN comparable to chlorine. This is reflected, on the one hand, in the increase in C–H acidity of hydrocarbons ($C_2H_6 < C_2H_4 << HC{\equiv}CH$) and on the other in the increasing bond strength towards a given metal: sp^3-C < sp^2-C < sp-C.

Similarly, the nature of other atoms bonded to the C atom in question is important, a concept referred to as '**group electronegativity**'. Thus, a CH_3 substituent is significantly less electronegative than CF_3, with its three strongly electron-withdrawing fluorine substituents, so that the EN(CF_3) is comparable to that of oxygen. Similarly, pentafluorophenyl ($-C_6F_5$)

is significantly more electronegative (electron withdrawing) than phenyl ($-C_6H_5$), as discussed further in the section on boron compounds (Section 1.4.1).

Reactivity

The **reactivity** of Main Group metal alkyls, i.e. the ability to transfer the alkyl group to unsaturated organic substrates or to metal halides, decreases with decreasing ionic character of the M–C bond, and with decreasing Lewis acidity of the metal centre:

$$\text{Li–R} > \text{RMgX(X = halide)} > \text{MgR}_2 > \text{AlR}_3 > \text{ZnMe}_2 \approx \text{SnMe}_4.$$

M–C bond strengths

The M–C bonds of some alkyls are too strong (as in BMe_3), or the compounds are insufficiently Lewis acidic (e.g. $SiMe_4$) to be effective alkyl transfer agents.

In terms of thermodynamic stability, the organometallic compounds of most of the lighter elements are comparable, for example, to alkylamines (e.g. NMe_3: heat of formation $\Delta H_f = -24$ kJ mol^{-1}; mean N–C bond dissociation enthalpy $D = 314$ kJ mol^{-1}). Alkyls of heavier elements can be endothermic. Table 1.1 lists representative thermodynamic data.

Mean bond dissociation energies are only a rough guide to reactivity, since the reaction with the first alkyl ligand is very much more facile than with subsequent ones. For example, in reactions of $AlMe_3$ with transition metal halides, usually only one of the three methyl groups can be transferred.

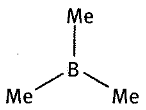
Structural Types. Main Group metal alkyls form a number of structural types, such as A–H:

No bridges:

Me—M—Me

M = Zn, Cd, Hg

A



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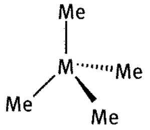
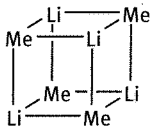


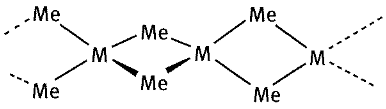
M = C, Si, Ge, Sn, Pb

C

With bridging alkyls:

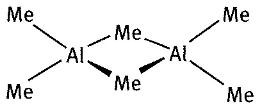


D



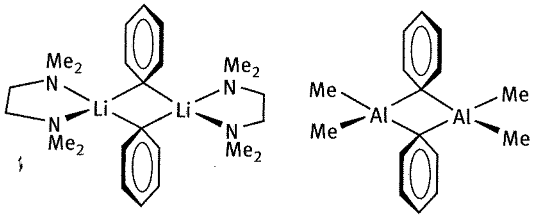
M = Be, Mg

E

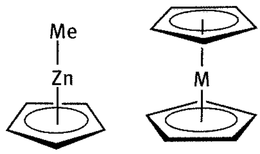


F

With π-ligands:



G



M = Li⁻, Tl⁻, Mg, Al⁺

H

The structures are determined by the number of valence orbitals available on the metal, and by the Lewis acidity of the metal centre. The dialkyls of Zn, Cd, and Hg (**A**) are only weakly Lewis acidic, and although zinc, for example, is in principle capable of accepting

Table 1.1 Thermodynamic data of some Main Group element methyl compounds **in the gas phase** (kJ mol^{-1})[a]

Group	12			13			14	
	MMe_2			MMe_3			MMe_4	
M	ΔH_f	D	**M**	ΔH_f	D	**M**	ΔH_f	D
			B	−123	365	**C**	−167	358
			Al	−81	274	**Si**	−245	311
Zn	+50	177	**Ga**	−42	247	**Ge**	−71	249
Cd	+106	139	**In**	173	160	**Sn**	−19	217
Hg	+94	121	**Tl**	–	–	**Pb**	+136	152

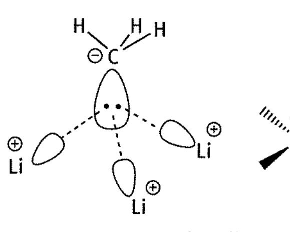
[a] M. E. O'Neill, K. Wade, *Comprehensive Organometallic Chemistry*, **1982**, *1*, 5.

two donor ligands to give tetrahedral structures, the electron donor properties of the methyl ligands render it insufficiently Lewis acidic to form aggregates with bridging methyl ligands; the compounds are therefore monomeric and linear. Trimethylborane (**B**) has a vacant p-orbital and is in principle capable of binding an electron pair, i.e. it is a Lewis acid, but this acidity is weak due to the **+I effect** of the methyl groups. Boron is very small; in consequence, steric repulsion prevents dimerization and the compound is a monomeric gas. The tetramethyl compounds of Group 14 elements (**C**) are **electron-precise** compounds, in which the central element is surrounded by an **electron octet**. These compounds are not Lewis acidic (even though Si and higher congeners can in principle bind anions, X^-, and assume coordination numbers of 5 or 6), and they are relatively unreactive, volatile monomers.

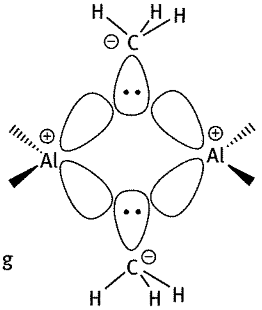
2e3c, 2e4c bonding

On the other hand, where the number of vacant valence shell orbitals exceeds the number of valence electrons, and where steric factors are unimportant, the electron pair of a CH_3^- anion is shared between two or more metal centres. This leads to electron-deficient structures such as in $[LiMe]_4$ (**D**), in which three Li ions compete for one methyl anion and form 2-electron-4-centre (**2e4c**) bonds. Similarly, Be and Mg are more polar and more Lewis acidic than Zn and form dimethyl compounds in which they attain tetrahedral geometries by forming 2-electron-3-centre (**2e3c**) bonds with bridging methyl ligands (**E**). As a result, these compounds are non-volatile polymers. The same bonding type is seen in trimethylaluminium. Aluminium is larger than boron, more electropositive, and a stronger Lewis acid. These factors combine to favour a dimeric structure (**F**): the Al compound, unlike its boron analogue, is a dimer in the solid state and in hydrocarbon solution, while in the gas phase it is in equilibrium with monomeric, trigonal-planar $AlMe_3$.

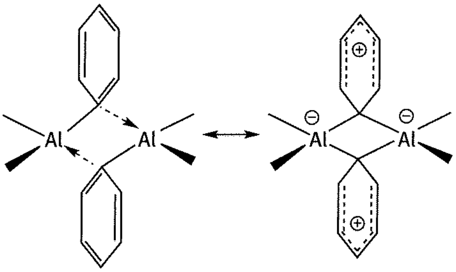
If anions with sp^2-hydridized C atoms are present, as in metal vinyls or aryls, these unsaturated hydrocarbyl moieties adopt bridging positions, as in **G**. In the lithium example, further coordination sites are occupied by tetramethylethylenediamine ligands, to give the Li^+ ion a tetrahedral coordination geometry (sp^3 hybrid). In mixed-ligand aluminium aryl alkyls, it is always the aryl that adopts the bridging position. The aryl bridges are further examples of 2e3c bonds, although participation of the π-electron density of the aryl in the ionic resonance form for $[R_2Al(\mu\text{-}C_6H_5)]_2$ contributes to an octet configuration. The bonding interactions are shown in the following diagram:



2-electron-4-centre bonding interactions in LiMe

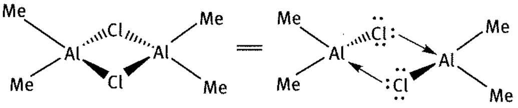


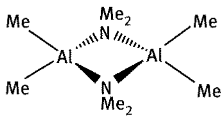
2-electron-3-centre bonds in Al_2Me_6

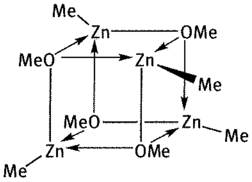


Bonding in bridging aryls. In the ionic resonance form the metal achieves an octet electron configuration.

In other dimeric compounds containing heteroatoms, the heteroatom occupies the bridging positions. Since these atoms contain at least one electron pair, bonding here is not the consequence of electron-deficient multi-centre bonding, but due to n-donor interactions, so that the metal centres achieve octet electron configurations and are **electron-precise** structures, for example:

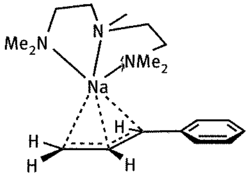




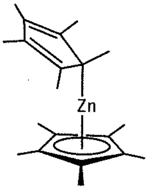


With unsaturated arene anions such as the cyclopentadienyl anion ($C_5H_5^-$, abbreviated Cp^-), **sandwich complexes** of type **H** are formed which include **π-bonding**. A sandwich complex is a compound in which the metal centre is bonded to two ring ligands with delocalized π-electrons. The Cp anion can deliver up to six π-electrons; it is a **6π Hückel aromatic system** and is isoelectronic with benzene. This achieves high electronic saturation, such that in $ZnCp_2$ only one Cp ring is π-bonded (η^5), while the second ring interacts with the metal via only one carbon (η^1).

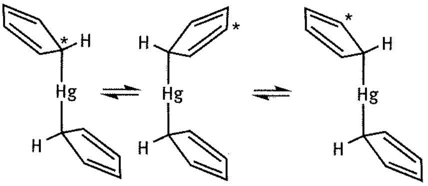
By contrast, the low tendency towards π-coordination in mercury dialkyls means that in $HgCp_2$ both rings form only σ-bonds (η^1); however, these bonds are ***fluxional***, and the metal migrates rapidly over the π-face, so that on average all carbons become metal-bonded. Some examples of Main Group compounds with π-bonded ligands are:



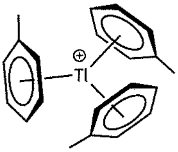
Na(1-phenyl-η^3-allyl)



Zn(η^1,η^5-C_5Me_5)$_2$

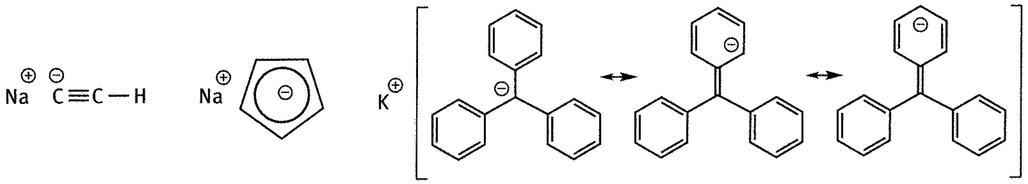


Hg(η^1-C_5H_5)$_2$

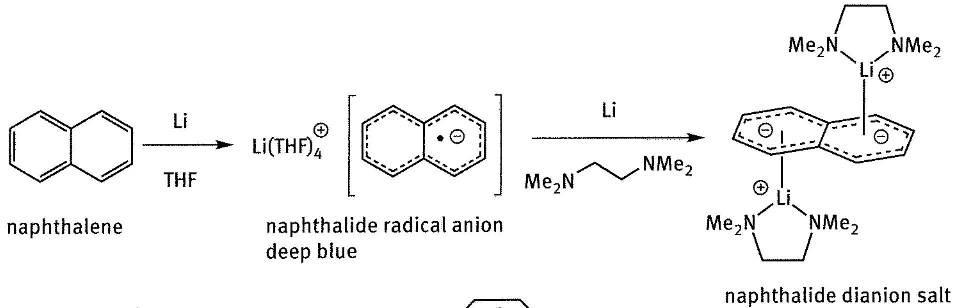


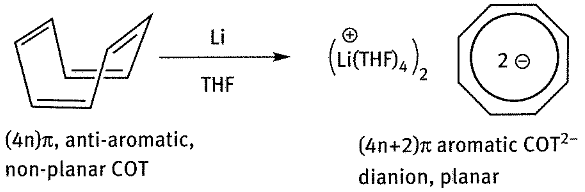
Tl(η^6-toluene)$_3$ cation

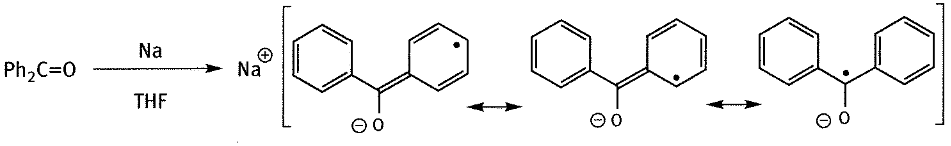
Ionic organometallics. In cases where the organic anion is particularly stable, because it contains electron-withdrawing substituents, or because the negative charge is extensively delocalized, the interaction of the metal cation with the carbanion may be much weaker than with solvent molecules, such that there may or may not be significant direct bonding interactions between the ions in solution. For example, the acetylide anion in NaC_2H is akin to a halide, NaCp contains the cyclopentadienide anion, a 6π-aromatic compound, while in $KCPh_3$ the CPh_3^- anion is stabilized by extensive delocalization of the negative charge over all three phenyl substituents.



The high reduction potential of alkali metals can be used for electron transfer to arenes or polyenes, to generate salts of (usually intensely coloured) radical anions or anionic aromatic systems. Such compounds are readily generated in non-protic polar solvents (such as tetrahydrofuran, THF) and are often employed as convenient reducing agents. The alkali metal cation is solvated, without direct bonds to the anion, although in some cases crystalline salts have been obtained. Heteroaromatics such as pyridine also react with alkali metals to give the purple pyridine radical anion (whereas no such electron transfer takes place with benzene or toluene). Alkali metals reduce cyclooctatetraene (a non-planar, non-aromatic olefin with eight π-electrons) to the $C_8H_8^{2-}$ dianion, which is a planar 10π-aromatic system (and obeys Hückel's $(4n + 2)\pi$ rule). The reduction of benzophenone to the deep purple radical anion makes it an excellent, self-indicating drying agent for the purification and deoxygenation of polar non-protic solvents such as diethyl ether and THF:

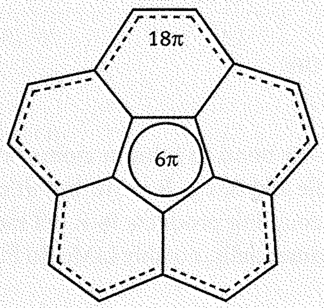




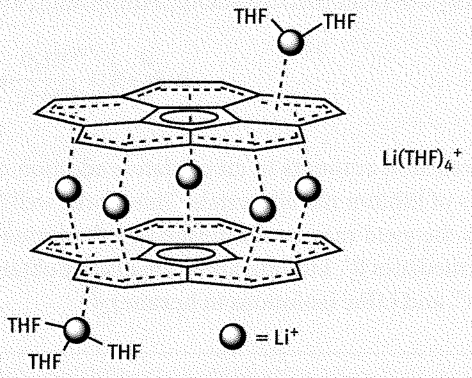


Box 1.1 Lithium ion intercalation

Lithium ions are important as charge carriers in graphitic electrodes. A model for Li^+ intercalation in such structures is the corannulene tetraanion, which intercalates five Li^+ ions to give a sandwich structure. The sandwich is very stable and persists in THF solution; the intercalated Li^+ ions are retained even on addition of crown ethers.



$[corannulene]^{4-}$ anion



Key points

Organometallic compounds of main group elements are mainly used as reagents to generate C–C, C–element, and C–metal bonds. The polarity of Main Group M–C bonds can range from ionic (alkali metals) to essentially covalent (B, Sn). This determines their reactivity, alkylation power, and stability to air. Polar M–C bonds react rapidly with water, and compounds may be pyrophoric.

Exercises

1. Order the following according to increasing polarity of the M–C bonds: $ZnMe_2$, LiMe, $MgMe_2$, BMe_3, $SiMe_4$.
2. Draw the structures of the compounds in question 1 and determine the electron counts of the metal centres. Which of them achieves an electron octet?
3. Why are $C_5H_5^-$ (Cp^-) and benzene said to be isoelectronic?

Li 3
6.941

1.2 Alkali Metal Organometallics: Lithium

1.2.1 Synthesis

Lithium is the hardest of the alkali metals and reacts only slowly with air. It can be hammered into flat sheets and cut with scissors into small pieces for LiR synthesis. Since it reacts with N_2, reactions should be conducted under argon.

Lithium alkyls are made by reacting alkyl halides with lithium metal. The reaction is facilitated by a solvent that can stabilize the lithium ion, such as diethyl ether.

$$\mathrm{R{-}Br + 2\,Li \xrightarrow[20\,^{\circ}C]{Et_2O} LiR + LiBr}$$

The reaction amounts to an oxidative addition of the R–Br bond to lithium atoms on the edges of lithium metal crystals. This works well for simple alkyls, e.g. R = Me, but in some cases the yield may be diminished by the formation of coupling products R–R via radical intermediates $R^{\bullet}$. Lithium alkyls are usually obtained commercially, notably LiMe (in Et_2O), $LiBu^n$, and $LiBu^t$ (solutions in hexane).

Since lithium alkyls are easily hydrolysed, $LiR + H_2O \rightarrow RH + LiOH$, the concentration of LiR needs to be checked. This is conveniently done by double titration: one aliquot of LiR is hydrolysed in distilled water and titrated against a suitable indicator (e.g. bromothymol blue), and another aliquot is treated under nitrogen with an excess of 1,2-dibromoethane before water is added: $LiR + BrC_2H_4Br \rightarrow LiBr + RBr + C_2H_4$. Any LiOH present in this second sample is due to hydrolysis before dibromoethane was added, so the difference in the titration values of the two samples equals the concentration of LiR.

Lithium alkyls can be seen as the salts of deprotonated alkanes. Since alkanes are extremely weak acids, the alkyl anions in LiR are among the **strongest bases available**:

$$\mathrm{LiMe < LiBu^n < LiBu^t}$$

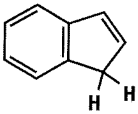
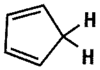
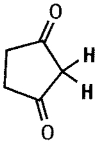
A wide variety of lithium reagents can therefore be conveniently generated by reactions with hydrocarbons containing C–H bonds that are more acidic (more polarized) than either CH_4, *n*-butane, or $HCMe_3$.

$$\mathrm{LiR + R'{-}H \xrightarrow{hexane} LiR' + RH}$$

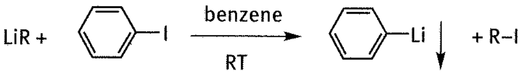
This C–H acidity is exploited for the preparation of new lithium reagents under salt-free conditions; for example, Bu^nLi reacts with toluene to give $PhCH_2Li$ and butane. Methyl-substituted heteroaromatics are even more readily deprotonated; e.g. 2-lutidine (2-methylpyridine) affords deep orange $LiCH_2py$.

Lithium alkyls are also prepared by **metal–halogen exchange**. Iodoarenes react readily, while bromoarenes are usually slow and chloroarenes are unreactive. Choice of the solvent is also important. These are equilibrium reactions, and for a successful synthesis it is helpful to shift the equilibrium by removing one of the products. In the case of the phenyllithium synthesis, this is achieved by using benzene as a solvent in which PhLi is insoluble and precipitates:

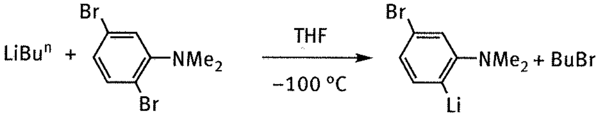
C–H pK_a values of organic compounds in non-aqueous solution (relevant H in bold)

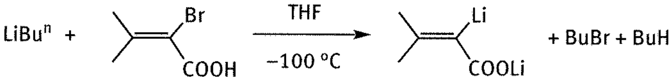
Compound	pK_a	Compound	pK_a
$\mathrm{Me_3C{-}\mathbf{H}}$	47		18.5
$\mathrm{Me{-}\mathbf{CH_3}}$	42		
$\mathrm{CH_4}$	40		
$\mathrm{C_6H_5{-}\mathbf{H}}$	39		15
$\mathrm{C_6H_5{-}\mathbf{CH_3}}$	37	$\mathrm{CH_3COO\mathbf{H}}$	4.7
$\mathrm{H_2C{=}CH{-}\mathbf{CH_3}}$ $\mathrm{Ph_3C{-}\mathbf{H}}$ $\mathrm{HC{\equiv}C{-}\mathbf{H}}$	36.5 32 24		4.5

$$\mathrm{LiR + R'{-}X \rightleftharpoons LiR' + R{-}X}$$



Metal–halogen exchange can be a good route to the selective synthesis of aryl lithium reagents with functional groups and can provide lithium aryls and vinyls in near-quantitative yields, provided the temperature is well controlled:

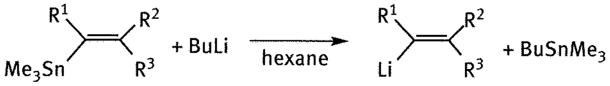




The synthesis of lithium alkyls by **transmetallation** occurs by metal exchange with less electropositive metals (e.g. Hg, Sn, Zn). It is a less common route but can provide lithium compounds under salt-free conditions:

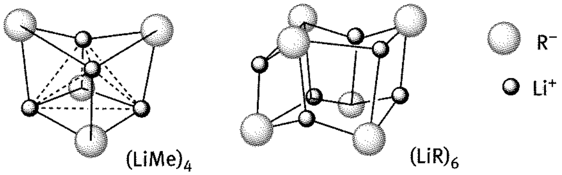
$$\mathrm{R{-}M + Li \longrightarrow R{-}Li + M}$$

$$\mathrm{R{-}M + BuLi \longrightarrow R{-}Li + BuM}$$

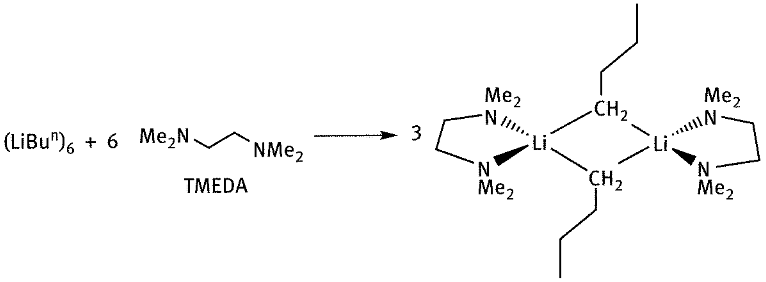


1.2.2 Structure of Lithium Alkyls

Lithium alkyls form aggregates, held together by multi-centre bonding. In spite of the high polarity of the $Li^{\delta+}\cdots C^{\delta-}$ interactions, these aggregates show low polarity overall, and are therefore soluble in non-polar solvents. LiMe, for example, is tetrameric in Et_2O or THF, with a distorted cubic structure. $LiBu^n$ and LiCy are hexameric in hexane solution (Cy = cyclohexyl). The cubic structure of LiMe may also be described as a Li_4 tetrahedron capped by four methyl groups; however, there are no bonds between the Li ions.



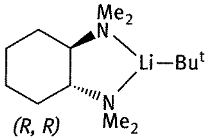
The degree of aggregation is dependent on the solvent, and complex association equilibria may be established. More strongly coordinating solvents such as THF can break up the clusters into smaller units. The addition of chelating non-protic amines, such as $Me_2NC_2H_4NMe_2$ (TMEDA) or $Me_2NC_2H_4N(Me)C_2H_4NMe_2$ (PMDETA), gives dimeric or monomeric compounds, which often display higher reactivity than the aggregates. This explains why, for metallations with lithium reagents, the choice of solvent or solvent mixture is often critical. For example, the addition of TMEDA to $(LiBu^n)_6$ gives a dimer:



Sterically very highly hindered Li alkyls have been found to exist as ion pairs containing **dialkyllithiate anions**, as in $[Li(THF)_3]^+[R\text{–}Li\text{–}R]^-$ $\{R = C(SiMe_3)_3\}$.

Degrees of aggregation of commonly used lithium alkyls

Compound	Solvent or adduct	Degree of association
LiMe	Et_2O, THF, crystal	4
LiPh(PMDETA)	*N,N,N*-chelate adduct	1
Li(η^3-allyl)(PMDETA)	*N,N,N*-chelate adduct	1

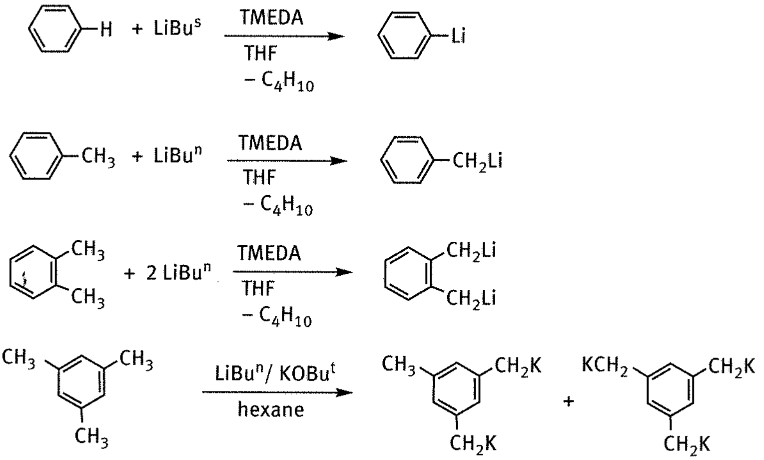
Compound	**Solvent or adduct**	**Degree of association**
Li(n^3-allyl)(TMEDA)	*N,N*-chelate adduct	∞, polymeric chain
$LiPh(Et_2O)$	Base adduct	4
LiPh	Et_2O + THF	2
$LiBu^n$	Hexane, crystal	6
$LiBu^n$	THF	2, 4
$LiBu^t$	hexane, crystal	4
$LiBu^t$	Et_2O, THF	1, 2
	crystal	1

1.2.3 Reactivity of Lithium Alkyls

As strong bases, lithium alkyls are used extensively for the **deprotonation of C–H bonds.** The addition of chelating donor ligands such as TMEDA has proved beneficial and greatly increases the reactivity. For example, although benzene is five orders of magnitude more acidic than *n*-butane, its metallation with $LiBu^n$ in THF proceeds at a useful rate only after TMEDA addition. $LiBu^s$/TMEDA is even more effective. Mixtures of $LiBu^n$ and $KOBu^t$ ('*Lochmann–Schlosser base*') generate the more powerful KBu^n *in situ* and metallate benzene even in the absence of TMEDA; the by-product $LiOBu^t$ is easily removed.

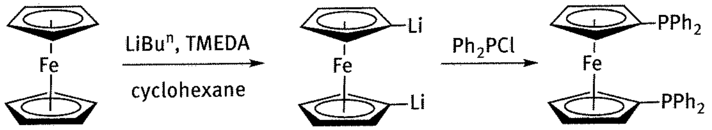
LiR/KOBu^t superbase

The methyl group in toluene is lithiated with $LiBu^n$/TMEDA, while *o*- and *m*-xylenes give dimetallated products. No ring metallation is observed.



See Section 2.4.5 and Box 2.8.1.

By contrast, ferrocene ($FeCp_2$) is readily dimetallated by $LiBu^n$/TMEDA as a route to ferrocenophosphines:

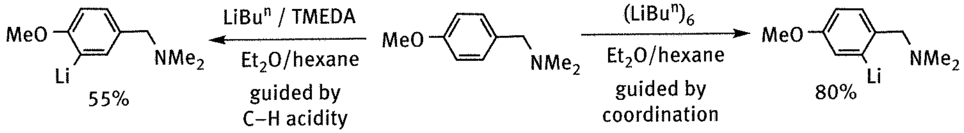


Lithium alkyls are frequently used to deprotonate H–X bonds, where X = N, O, P, etc., under salt-free conditions. This route to phosphides is preferable over the synthesis from R_2PCl + Na.

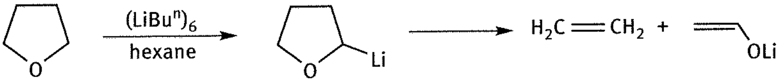
$$\mathrm{LiBu^n + HNPr^i_2 \xrightarrow[-\,butane]{} LiNPr^i_2}$$

$$\mathrm{LiBu^n + HPPh_2 \xrightarrow[-\,butane]{} LiPPh_2}$$

Functional groups capable of coordinating to LiR are frequently used to control the site selectivity of metallation to give *ortho*-lithiated products, which is known as the ***ortho*-directing effect**. If two different substituents are present, one increasing the acidity of the C–H bond in *ortho* position to the substituent, while the other has the stronger coordination ability, the selectivity is guided by the aggregation state and the Lewis acidity of the lithium alkyls. In both cases ring metallation is observed:



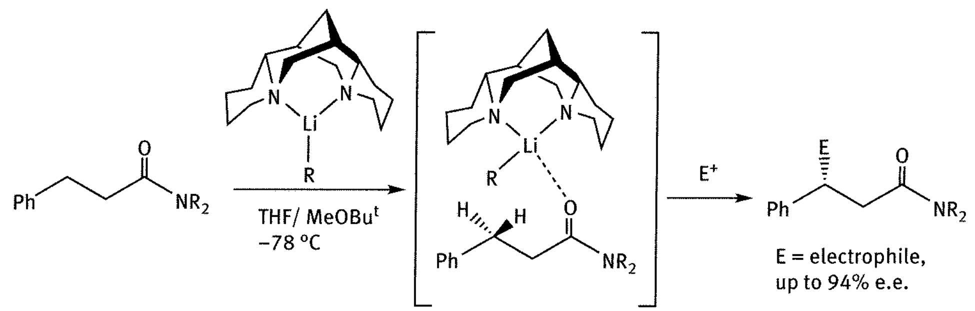
Solvents are readily attacked by lithium alkyls; for example, the half-life of $LiBu^n$ in THF is only about 10 minutes. The addition of THF to hexane solutions of LiR is usually quite exothermic. THF is initially lithiated in the *o*-position, followed by cleavage to give a lithium enolate:



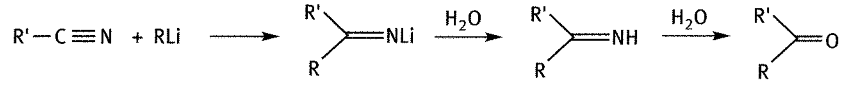
The dimethylamino substituents of amines such as TMEDA can also be metallated under suitable conditions. These reactions are usually controlled by lowering the reaction temperature.

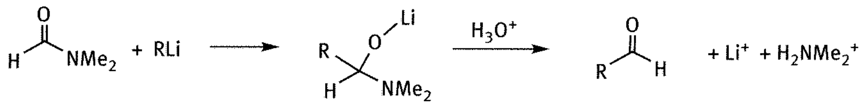
Chiral alkylation

The tendency of Li to coordinate chelating nitrogen bases can be used to provide **stereo-differentiating lithium reagents**, e.g. by using the chiral amine sparteine:



Lithium alkyls undergo **additions to multiple bonds**. Nitriles are converted to ketones (after hydrolysis of the intermediate imines) and carboxylic amides to aldehydes:

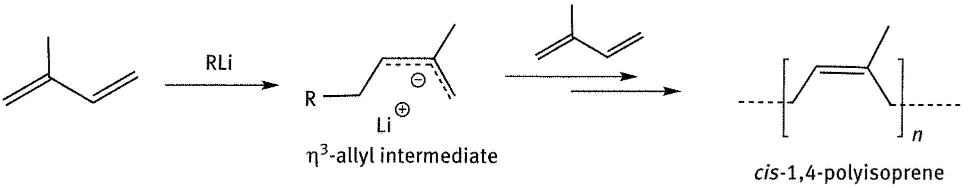




The addition to conjugated dienes leads to lithium **η^3-allyls**, which are the reactive intermediates in **anionic polymerization,** e.g. of isoprene to synthetic rubber. This polymerization can also be effected with other organometallic species. Various stereoisomers of poly(isoprene) are possible (1,4-*cis*, 1,4-*trans*, 1,2, and mixtures of these), and their relative abundance is sensitive to the nature of the initiator and the solvent. The 1,4-*cis* polymer best mimics the properties of natural rubber.

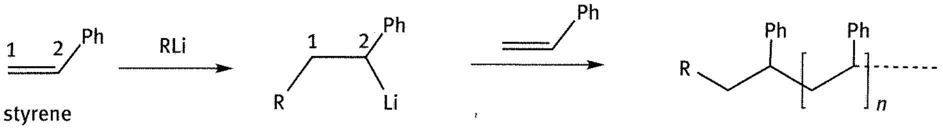
Similarly, lithium and sodium alkyls initiate the anionic polymerization of styrene. The intermediate is a *sec*-alkyl lithium species in which the negative charge is delocalized over the phenyl ring. The polymerization therefore proceeds by a series of 2,1-additions to the C=C bond of styrene, each leading to a new *sec*-alkyl lithium propagating species. Since chain growth is fast and uniform, the molecular weight of these polymers can be precisely controlled by the monomer/RLi ratio.

Polystyrenes of precisely controlled molecular weight produced by anionic polymerization are used as standards for gel permeation chromatography.



η^3-allyl intermediate

cis-1,4-polyisoprene
synthetic rubber



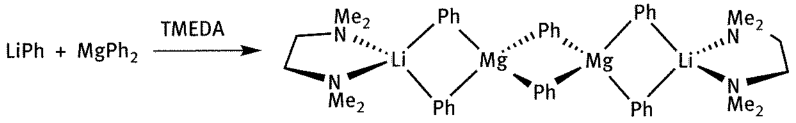
styrene

polystyrene

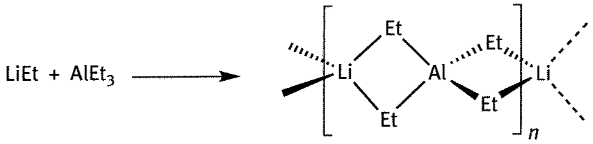
'Ate' complexes

As strong bases, lithium alkyls add to Lewis acidic compounds to form 'ate' complexes, i.e. compounds that contain metallate anions, for example:

$LiMe + BMe_3 \longrightarrow Li[BMe_4]$ tetraalkylborate



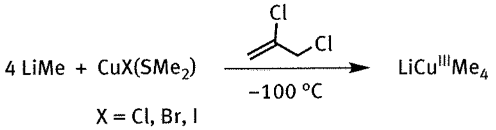
magnesate



aluminate

$LiMe + CuMe \longrightarrow LiCu^{I}Me_2$ homocuprate

$LiMe + CuX \longrightarrow LiCu^{I}(X)Me$ heterocuprate



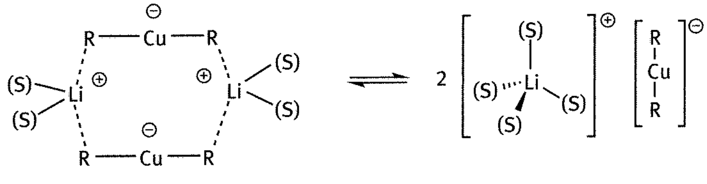
$$4\,LiMe + CuX(SMe_2) \xrightarrow[-100\ °C]{} LiCu^{III}Me_4$$

X = Cl, Br, I

Cu(III) alkyl cuprate
d^8, square-planar
half-life at 0 °C: 7 h

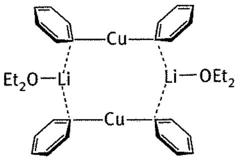
Cuprate reagents

The cuprates are based on linear anions $[R{-}Cu{-}R]^-$ which may form contact ion pairs or solvent-separated ion pairs. The Cu–C bonds are largely covalent.

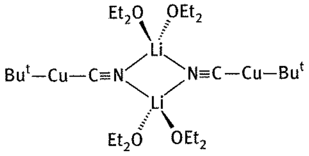


(S) = donor solvent

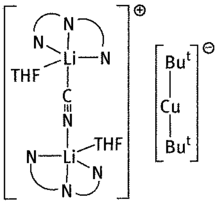
Examples of their structures in a crystal are shown in the following diagram; they dissolve in ethers, where they display fast exchange and solution equilibria. Lithium organocuprates are used for selective alkyl 1,4-addition to conjugated enones, additions to C–C multiple bonds, and substitution reactions.



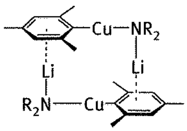
aryl cuprate



alkyl cyanocuprate



NNN = PMTEDA dialkyl cuprate



aryl amidocuprate

1.2.4 Organometallic Compounds of the Heavier Alkali Metals: Na–Cs

11
Na
22.990

As the ionic radius of the alkali metals increases:

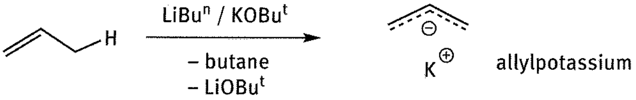
Li^+	Na^+	K^+	Rb^+	Cs^+
0.69	0.97	1.33	1.47	1.67 Å

so does the ionic character of the metal alkyl compounds. Adding a MeLi solution to $MOBu^t$ (M = Na, K) gives NaMe and KMe, respectively. Solid KMe forms an ionic lattice in which the CH_3^- anions are surrounded by six K^+ ions. Solid NaMe is intermediate between LiMe and KMe. Potassium alkyls are rarely isolated and are generally used in synthesis as species prepared *in situ* from LiR + $KOBu^t$; they are capable of metallating activated C–H bonds, e.g. those in allylic positions to C=C bonds:

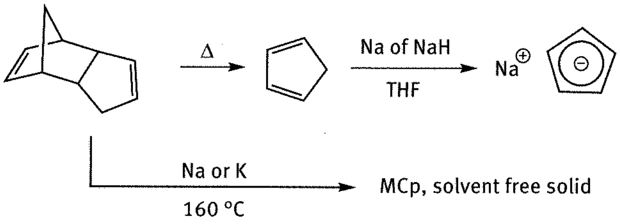
19
K
39.098

37
Rb
85.468

55
Cs
132.905



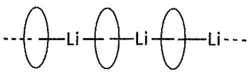
The most important Na and K organometallic compounds, from a synthetic perspective, are the cyclopentadienides. These are accessible either from the metal, the metal hydride, or from Li alkyls. NaCp and KCp are more conveniently and quantitatively made by reacting dicyclopentadiene with the metal directly, without prior cracking into CpH:

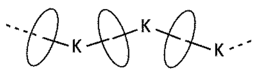


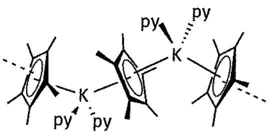
As ionic compounds, these cyclopentadienides dissolve readily in non-protic donor solvents such as THF. In the solid state they form stacks of Cp^- anions and M^+ cations, giving linear or zigzag chains, depending on the ionic radius of the M^+ ions and the presence or absence of donor molecules (ethers, pyridine). Alkali cations are spherical and exert no influence over the relative orientation of the Cp ligands, and the crystal structures are determined by electrostatic and packing forces. With large, stable cations, such as PPh_4^+, sandwich complexes such as $[LiCp_2]^-$ have been isolated.

Alkali metal cyclopentadienides are the key to the synthesis of an important class of transition metal complexes, the 'metallocenes'.

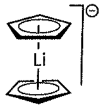
MCp complexes, see Section 2.8





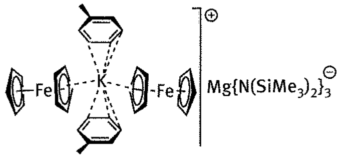


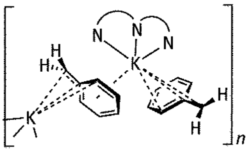
KCp*(pyridine)$_2$



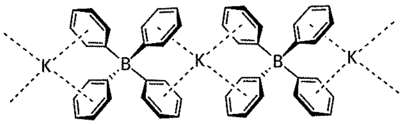
Since alkali metal ions contain no electrons for covalent bonding, readily dissolve in water, and have a high affinity for polar ether solvents, it might be expected that their tendency for coordination to typical hydrocarbon π-ligands is low. This holds true only to a limited extent, and large alkali metal cations frequently bind to aromatic π-systems, particularly when these form part of a counter-anion, even in the presence of strong solvents like THF. In the structure of the salt $[K(toluene)_2(FeCp_2)_2]^+[Mg(NR_2)_3]^-$, for example, coordination to toluene is preferred over formation of an amido bridge to the magnesate anion.

The structures of potassium and rubidium benzyl compounds show η^3- and η^6-type π-interactions of the alkali metal cation with planar benzyl anions. Strong differences in cation–arene interactions are seen in the tetraphenylborate salts $MBPh_4$: whereas the Na^+ salt is highly soluble in water, the potassium analogue is so insoluble that it can be used for the **gravimetric determination of K^+** by precipitation. The compound has a chain structure, as do the Rb^+ and Cs^+ BPh_4^- salts.





[$KCH_2Ph(PMDETA)$]$_n$



[$KBPh_4$]$_n$

Key points

Alkali metals form organometallic compounds M–R with highly polar M–C bonds. They become more ionic in the series from Li to Cs.

Li alkyls LiR are extremely strong bases, with the basicity increasing for $R = Me < Bu^n < Bu^t$. They metallate C–H bonds.

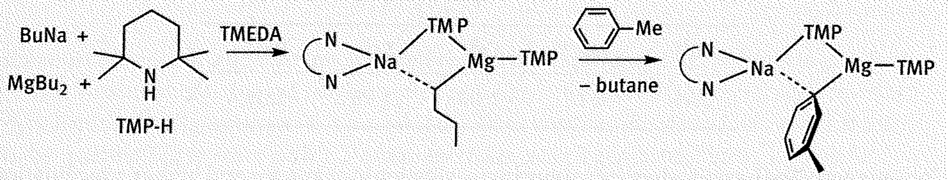
Lithium alkyls and aryls form aggregates with 2e3c or 2e4c bonds; they also add to other metal alkyls to give mixed-metal compounds. Solvent coordination can break up the aggregates and plays an important role in enhancing the reactivity of lithium alkyls.

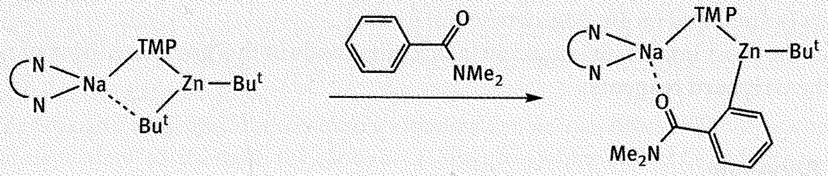
Exercises

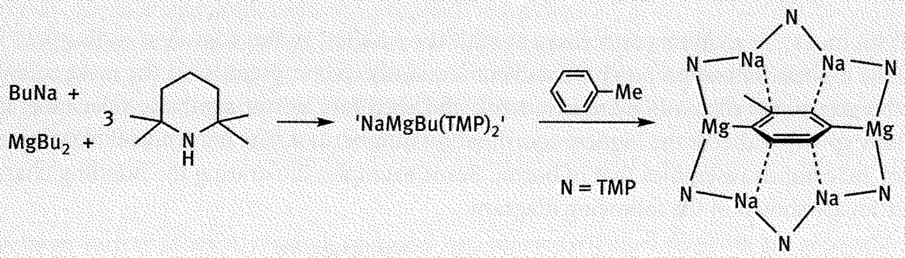
1. Show how lithium reagents can be made from lithium metal. Which solvent should be used? Give the chemical equations.
2. Does BuLi react with iodobenzene, and if so, how? Give the chemical equation and show the mechanism in detail.
3. Butyllithium is a hexamer $[RLi]_6$ in hexane but a dimer when tetramethylethylenediamine ($Me_2N–C_2H_4–NMe_2$, TMEDA) is added. What is the structure of the product? Does the lithium ion achieve an octet electron configuration?
4. Show how sodium hydride reacts with cyclopentadiene. Show structures and equations. Does the product contain ionic or covalent metal–carbon bonds? Which solvent should be used, and why? Give your reasons.

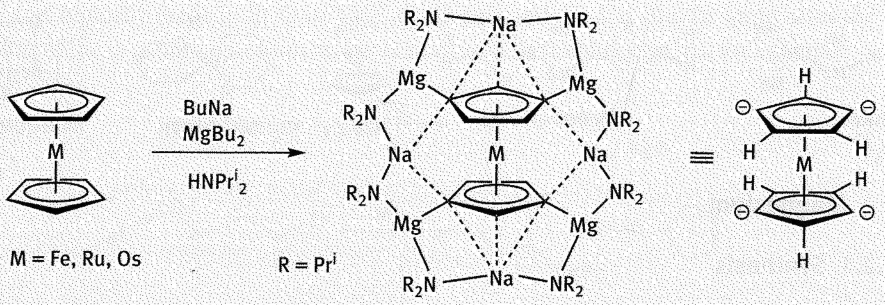
Box 1.2.4 Mixed-metal complexes and superbases

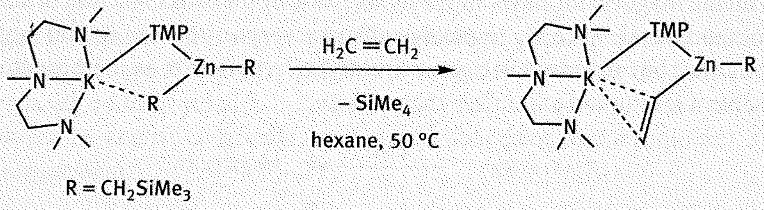
Lithium alkyls have long been known to form adducts with other metal compounds including alkyls and aryls. If such multimetallic mixtures also contain amide ligands, they form aggregates that are described as '**superbases**'; these compounds are particularly effective for the deprotonation of C–H bonds and work in cases where monometallic metal alkyls or amides fail. The products of mixtures of Li, Na, or K alkyls with dialkyls of magnesium or zinc and tetramethylpiperidine (TMP–H), or of KTMP, MgR_2, and a chelating amine, readily and regioselectively react with mono- and bi-metallate arenes, heteroarenes, transition metal sandwich complexes, and even ethylene, for example:











1.3 Organometallic Compounds of Alkaline Earth Metals

Alkaline earth metals have a [noble gas]s^2 electron configuration, and consequently can form two σ-bonds and give compounds MX_2. The oxidation state is +II (with very few exceptions). Alkaline earth elements are more electronegative than the alkali metals and their M–C bonds are more covalent. Since the number of valence orbitals exceeds the number of valence electrons, alkaline earth compounds are **Lewis acids** and can coordinate two or more neutral ligands. This Lewis acidity is responsible for their high reactivity. The ionic radii of six-coordinate M^{2+} ions increase in the series:

Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
0.45	0.72	1.00	1.18	1.35 Å

Consequently the heavier elements show increasing ionic character and higher coordination numbers (tetrahedral for Be, Mg; octahedral for Ca).

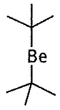
By far the most important organometallic compounds in this group are those of magnesium, the **Grignard reagents**.

Be 4
9.012

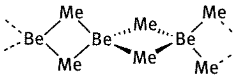
1.3.1 Beryllium

Beryllium, as the alkaline earth element with the smallest radius (covalent radius 0.93 Å), has the highest ionization potential and consequently its compounds are the most colavent in the group. Beryllium is extremely toxic and therefore not of synthetic relevance. It is usually sp^3-hydridized; the highest coordination number is 4. The tendency of beryllium to form 2e3c bonds resembles that of boron. Some examples illustrating the bonding characteristics are shown in the following diagram.

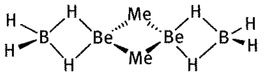
electron deficient:



$BeBu^t_2$

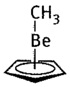


$BeMe_2$

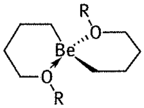


$[MeBeBH_4]_2$

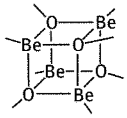
electron precise:



MeBeCp



$Be(C_4H_8OR)_2$



$[BeMe(OMe)]_4$

Mg 12
24.305

1.3.2 Magnesium

1.3.2.1 Synthesis

Direct Grignard synthesis

From Mg metal. Magnesium alkyls and aryls are made by the direct reaction of alkyl halides with magnesium metal. Since Mg organometallics are very sensitive to air and moisture, the preparations must be carried out in rigorously dried solvents under an inert gas atmosphere. An ether solvent is required to stabilize the product:

$$R{-}X + Mg \xrightarrow{Et_2O} RMgX(Et_2O)_n$$

The discovery that RMgX reagents readily react with C=O bonds in organic molecules (Victor Grignard, 1900) has led to the widespread use of magnesium reagents for making C–C bonds.

Box 1.3.2 Grignard reagents

The formation of Grignard reagents is heterogeneous. Magnesium is usually introduced as metal turnings, and the reaction proceeds on the metal surface. Electron transfer from the metal and alkyl radicals may be involved:

$$R{-}X + e^- \rightarrow RX^{\bullet -} \rightarrow R^\bullet + X^-$$

the most prominent side reaction is therefore **Wurtz coupling** of alkyl radicals to give R–R.

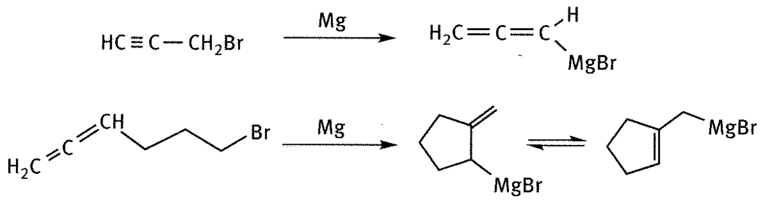
The formation of Grignard reagents often requires 'activation' of the metal surface, either by warming the Mg turnings with a crystal of iodine until the purple iodine vapour is seen, or by reacting Mg in ether with 1,2-dibromoethane, which generates $MgBr_2$ + ethylene. The presence of Lewis acidic species ($MgBr_2$ or MgI_2) catalyses the reaction of Mg with R–X; without it, the formation of Grignard reagents may be retarded by long induction periods. Similarly, the addition of LiCl to the reaction mixture can significantly facilitate the formation of Grignard reagents.

Role of $MgBr_2$, LiCl, amine additives

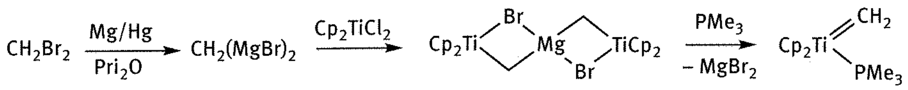
Since Grignard reagents form complexes with donor molecules, their reactivity is strongly solvent-dependent; for example, the addition of NEt_3 gives amine adducts which can react several orders of magnitude faster than amine-free species.

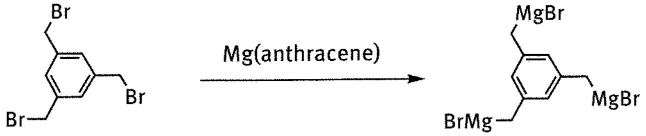
An alternative to Mg turnings is the use of highly reactive Mg powder, e.g. obtained by reducing anhydrous $MgCl_2$ with potassium in refluxing THF or diglyme (Rieke magnesium), or the reduction of $MgCl_2$ with lithium metal in THF at room temperature using naphthalene as electron transfer agent.

A large variety of alkyl, alkenyl, aryl, and heteroaryl Grignard reagents are accessible in this way, typically made in Et_2O or THF as solvents and used in situ. In some cases the formation of the organomagnesium reagents may involve rearrangements, for example:



Di-Grignard reagents are also accessible, although often produced in low yields. Compounds of the type $BrMg(CH_2)_nMgBr$ are generally accessible if $n \geq 3$. $CH_2(MgBr)_2$ can be prepared under carefully controlled conditions and used to make metal methylene complexes. Di-and tri-Grignards are also accessible using Mg(anthracene), a source of activated magnesium:

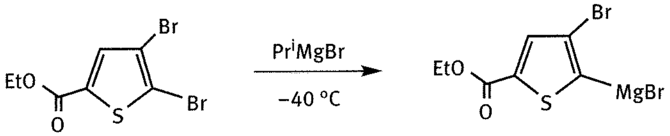


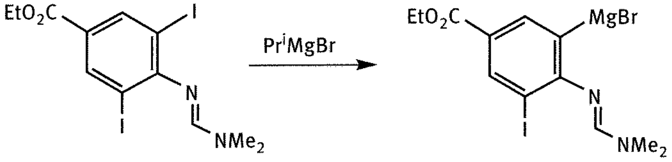


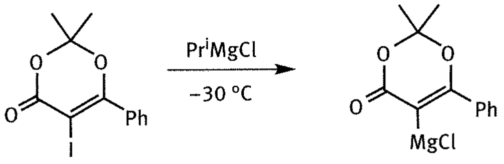
By metal–halogen exchange. Magnesium reagents can also often be prepared by **transmetallation:**

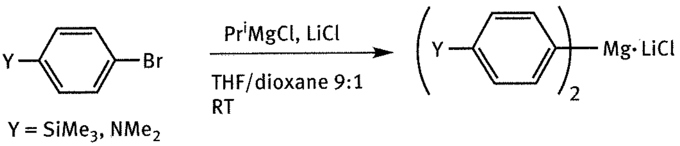
$$RMgX + R'X \longrightarrow R'MgX + RX$$

Mg–sp^3-C bonds are replaced by more stable alkenyl, aryl, or heteroaryl ligands. This can be a convenient way of generating Grignard reagents at much lower temperatures than would be necessary for the direct synthesis from Mg metal. Transmetallation therefore gives access to Mg reagents that would be too unstable under typical Grignard conditions. The reaction is further assisted by LiCl, e.g. using the mixed-metal adduct $Pr^iMgBr \cdot LiCl$ in the presence of O- or N-donors is thought to give rise to equilibrium concentrations of reactive $[Pr^i_2MgCl]^-$ and proceeds with much higher efficiency than with Pr^iMgBr alone. At lower temperatures, numerous functional groups are tolerated without requiring protection; the reaction is also useful for electron-rich arene substrates where the direct Grignard route is normally sluggish, for example:



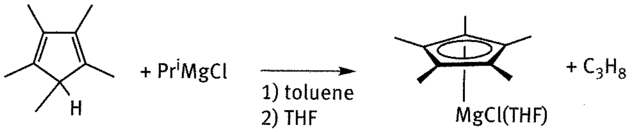


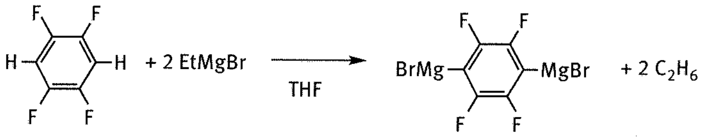




By C–H metallation. Grignard reagents can metallate compounds R–H with sufficiently acidic C–H bonds ($pK_a \le 25$). This is a route to alkynylmagnesium compounds and cyclopentadienyl and indenyl derivatives, and related substrates. The reactions are usually facilitated by strongly coordinating solvents. Magnesium cyclopentadienyl compounds have η^5-bonded Cp rings.

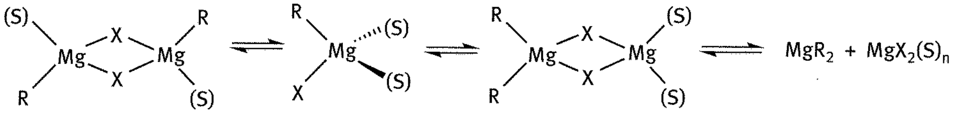
$$R'-C\equiv C-H \;+\; RMgX \longrightarrow R'-C\equiv C-MgX \;+\; RH$$





Magnesium Dialkyls

Grignard reagents form solution equilibria, including the dialkyls MgR_2 (**Schlenk equilibrium**):



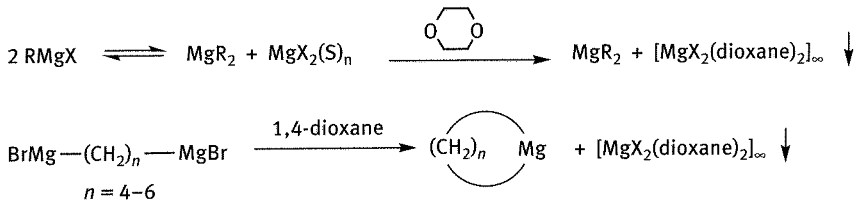
The rates of ligand exchange involved in the Schlenk equilibrium decrease in the sequence X = Cl > Br > I, and sterically hindered R groups exchange more slowly than *n*-alkyls. The existence of such equilibria has been supported by ^1H, ^{13}C, and ^{25}Mg NMR spectroscopic studies. The equilibrium constant K is strongly solvent-dependent and shows that in Et_2O the alkyl halide RMgX is always prevalent, whereas solutions in the more strongly coordinating THF contain MgR_2 concentrations close to the statistical value of 25% ($K = 4$):

Schlenk equilibrium

$$K = \frac{[RMgX]^2}{[MgR_2][MgX_2]}$$

RMgX	Solvent (25 °C)	*K*
MeMgBr	Et_2O	320
	THF	ca. 3.5–4
EtMgBr	Et_2O	480–484
	THF	5.09
EtMgI	Et_2O	>630

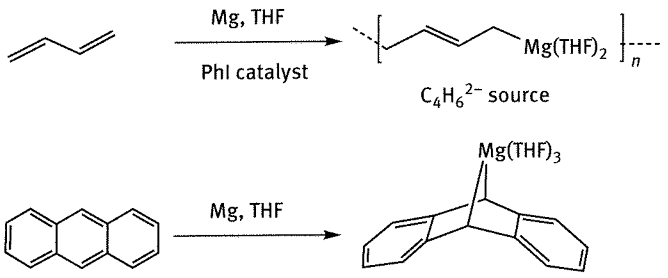
Shifting the Schlenk equilibrium by removing the dihalides MgX_2 through complexation (e.g. with 1,4-dioxane, which gives an insoluble coordination polymer) allows the synthesis of magnesium dialkyls. $MgBu_2$, which is commercially available, is a statistical mixture of $MgBu^n{}_2$ and $MgBu^s{}_2$. Di-Grignard reagents give ring structures:



The addition of strongly coordinating solvents [such as HMPA, $O{=}P(NMe_2)_3$], aza-crown ethers, or multidentate amines such as PMDETA leads to an equilibrium involving **self-ionization** of MgR_2:

$$2\,MgR_2 + n\,L \rightleftharpoons [R-Mg(L)_n]^+\,MgR_3^-$$

Magnesium(0) reduces electron-accepting unsaturated substrates such as butadiene or anthracene to give the corresponding Mg(II) reagents:

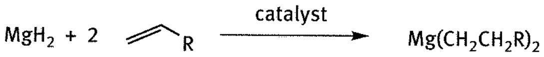


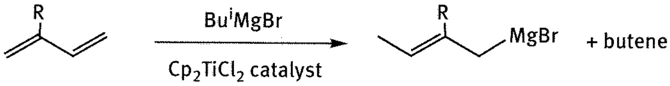
Mixtures of magnesium anthracene and transition metal halides ($TiCl_4$, $CrCl_3$, or $FeCl_2$) catalyse the reaction of Mg metal with H_2 under pressure to give MgH_2. This reaction is reversible, and H_2 can be liberated on heating. MgH_2 has high hydrogen content (7.6 wt %) and is of interest as a hydrogen storage material.

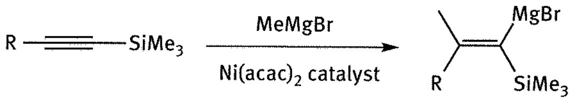
Hydromagnesation

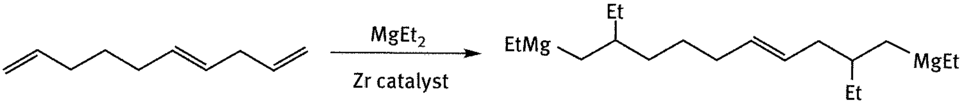
Carbomagnesation

In the presence of transition metal catalysts (e.g. $ZrCl_4$ or Cp_2TiCl_2), MgH_2 reacts with 1-alkenes to give magnesium dialkyls as products of C=C **hydromagnesation**. The reaction probably involves the formation of a transition metal hydride, followed by alkene insertion and transmetallation to Mg. The addition of Mg–C bonds to C=C leads to **carbomagnesation**:

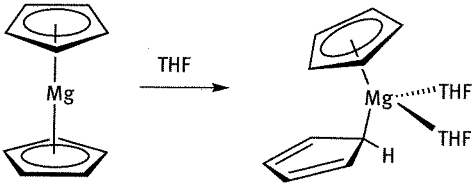






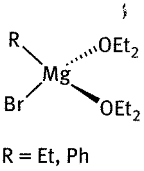


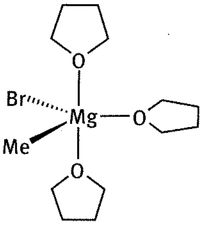
The reaction of cyclopentadiene with $MgBu_2$, or with Mg metal in the presence of $CpTiCl_3$ as catalyst, gives $MgCp_2$ (**magnesocene**) under mild conditions. The compound can also be obtained by vacuum sublimation from CpMgBr. $MgCp_2$ has a metallocene structure with parallel Cp rings. The interaction between Cp^- and Mg^{2+} is largely ionic, as becomes apparent on addition of dimethyl sulfoxide (DMSO), which leads to ionization into $[Mg(DMSO)_6]^{2+}(Cp^-)_2$, with non-coordinated Cp anions. The addition of the less strongly coordinating THF results in displacement of one of the Cp ligands from a pentahapto to a monohapto structure:

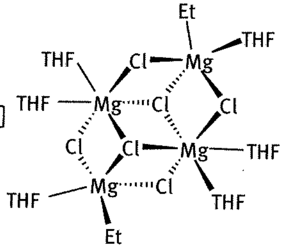


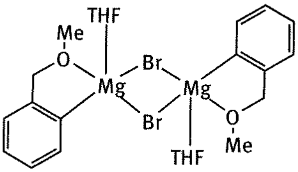
1.3.2.2 Structures of Magnesium Reagents

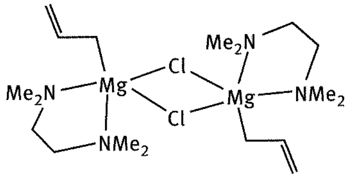
The structures of Grignard reagents depend on the steric requirements of the alkyl or aryl ligand, the halide, and the presence of coordinating solvents. In sterically highly hindered compounds, Mg may have coordination numbers 2 or 3, but in most cases the compounds adopt a distorted tetrahedral structure, although other geometries are also possible. Unlike ionic $LiCPh_3(TMEDA)$, $BrMgCPh_3(OEt_2)_2$ contains a covalent $Mg–CPh_3$ σ-bond. Allyl-Mg reagents contain η^1-bonded allyl ligands, whereas CpMg derivatives are usually η^5-bonded.



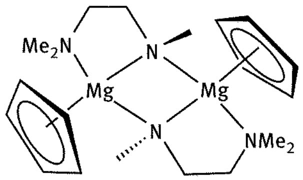




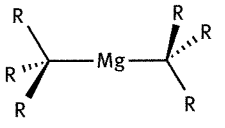




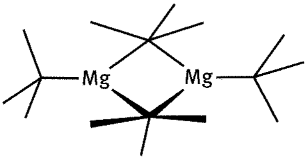
(η¹-allyl)MgCl(TMEDA)



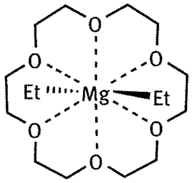
Dialkyl- and diarylmagnesium compounds exhibit **electron-deficient multi-centre bonding** akin to the structures observed for lithium reagents. $[MgMe_2]_n$ is polymeric, with 2e3c bonds. $MgBu^t{}_2$ is a dimer, while the extremely bulky $C(SiMe_3)_3$ ligand only permits a monomeric, two-coordinate structure (Mg–C 2.116(2) Å). Polymeric structures are broken up by donor ligands or by reactions with bulky ligands; e.g. the reaction of $[MgMe_2]_n$ with a sterically demanding diketimine gives a monomeric three-coordinate MeMg(diketiminate). Diphenylmagnesium is a coordination polymer with μ,η^1,η^1-bonded C_6H_5 ligands, while *ortho*-substitution of aryl rings results in dimer formation.



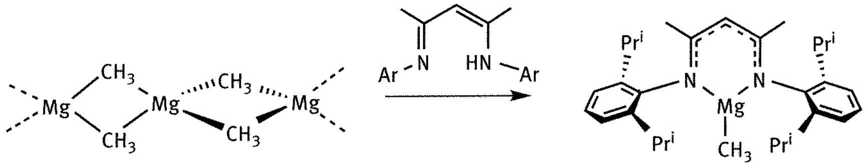
$Mg(CR_3)_2$, R = $SiMe_3$

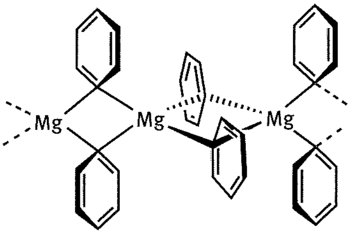


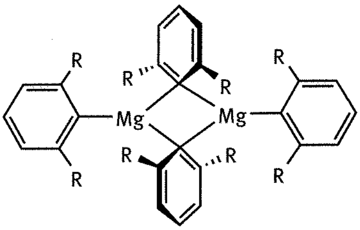
$[Mg(Bu^t)_2]_2$



$MgEt_2$(18-crown-6)

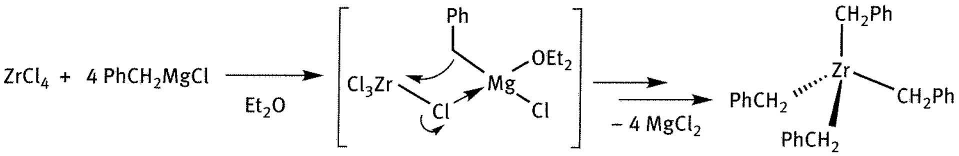


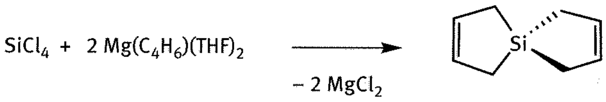


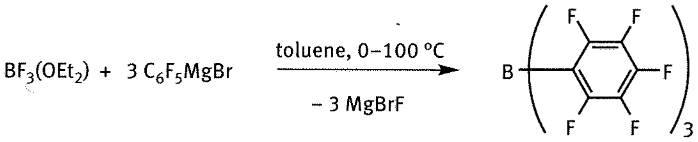


1.3.2.3 Reactions of Magnesium Reagents

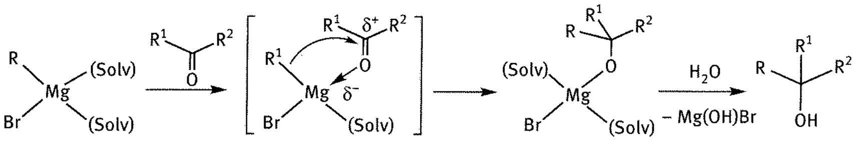
Grignard reagents are commonly used to transfer alkyl or aryl substituents to other elements and to organic substrates; these are standard synthetic methods for a large number of Main Group and transition metal organometallic compounds, for example:

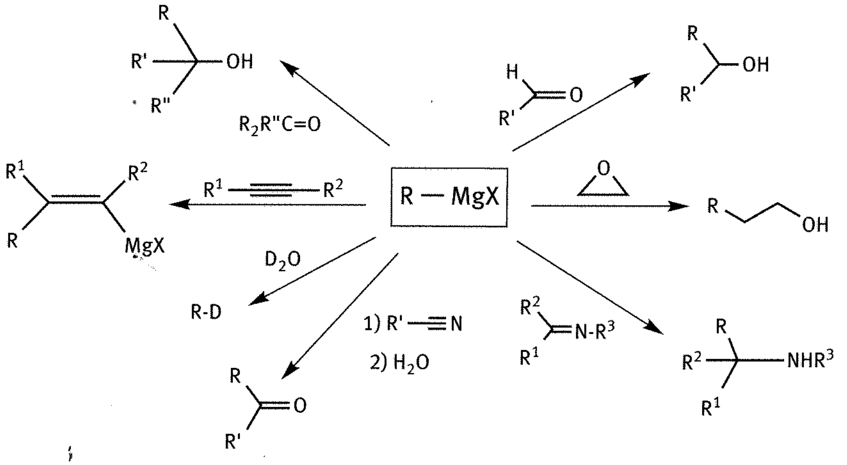






The most common C–C forming application is the reaction with organic carbonyl compounds. The Lewis acidity of the magnesium centre is responsible for the reactivity; coordination of the substrate increases the bond polarity and facilitates transfer of the hydrocarbyl ligand R.





1.3.3 Calcium, Strontium, and Barium

20
Ca
40.078

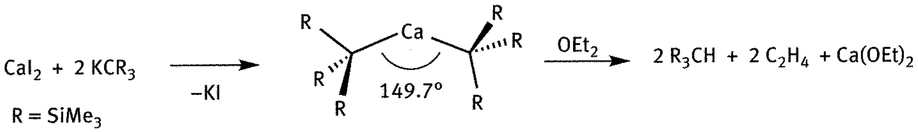
Organometallic derivatives of the heavier alkaline earth metals are more difficult to prepare and handle, are less selective, and in practice are rarely used in synthetic applications.

38
Sr
87.62

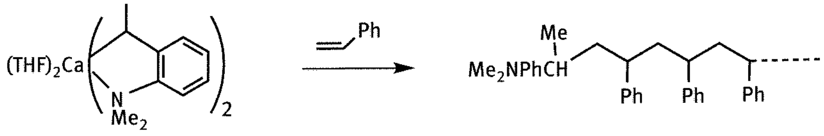
56
Ba
137.327

The larger ionic radii mean that the compounds are less covalent than the Mg analogues, and tend to form octahedral rather than tetrahedral compounds, usually by coordinating more solvent molecules.

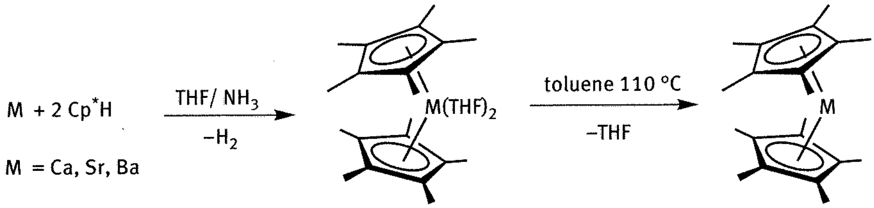
The bulky dialkyl $Ca(CR_3)_2$ (R = $SiMe_3$) is bent, unlike the Mg and Zn analogues, and reacts with ethers. Calcium dibenzyls deprotonate triphenylmethane to give a product with an ion pair structure. Due to their strong basicity, calcium dibenzyls act as initiators for the anionic polymerization of styrene.

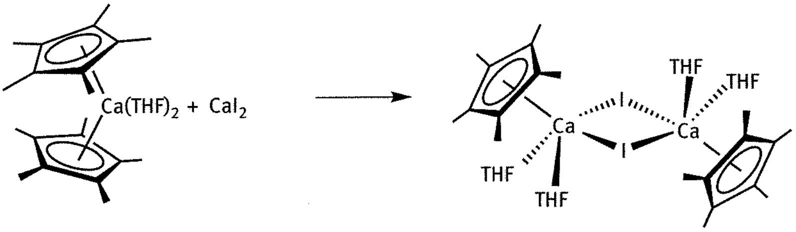


$$CaI_2 + 2\,KCH_2Ph \xrightarrow[-KI]{} Ca(CH_2Ph)_2 \xrightarrow[THF]{HCPh_3} [Ca(THF)_6]_2^{+}(CPh_3^{-})_2$$



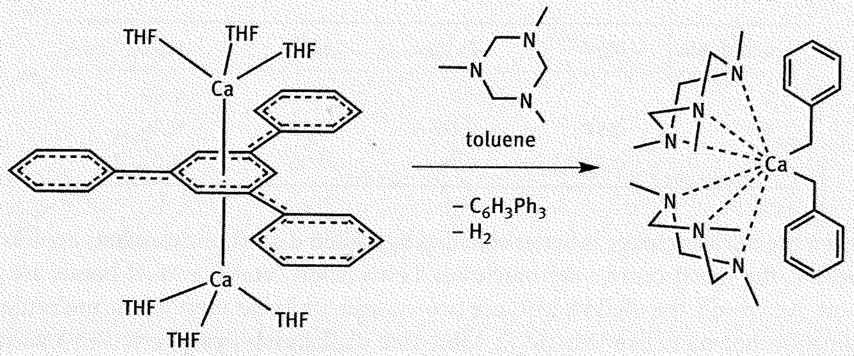
A number of **cyclopentadienyl compounds** are known. The compounds with unsubstituted C_5H_5 rings, MCp_2, are insoluble coordination polymers. C_5Me_5 (Cp*), which is much more strongly electron donating as well as more bulky, gives complexes with a sandwich structure. Unlike $MgCp_2$, these are bent. The compounds can be made from the metals using NH_3 to generate $M(NH_2)_2$ in situ as a reactive intermediate. $BaCp^*_2$ is volatile and can be purified by sublimation. Comproportionation of MCp^*_2 with MI_2 leads to mono-Cp compounds.





Box 1.3.3 Unusual Ca(I) compound

An unusual case of a Ca(I) compound was found in the reaction of bromotriphenylbenzene with activated calcium, which gives $\{Ca(THF)_3\}_2C_6H_3Ph_3$. The pyrophoric complex is deeply coloured due to the small HOMO–LUMO gap in the planar triphenylbenzene dianion, which has a triplet ground state. The compound metallates toluene to give a Ca(II) benzyl complex.



Key points

Alkaline earth organometallic compounds have somewhat less polar M–C bonds than alkali metals. Magnesium reagents are widely used alkylating agents, with sophisticated applications in C–C bond formation. Lewis acidity and solvent coordination are the dominant factors governing reactivity. Ligand exchange equilibria and electron-deficient bonding are characteristic aspects of their chemistry.

Exercises

1. Show how $PhCH_2Cl$ reacts with Mg to give a Grignard reagent. Which solvent should be used, and why?
2. What are the oxidation states of Mg before and after formation of the Grignard reagent? What type of reaction is this?
3. Draw the mechanistic steps involved in the Schlenk equilibrium.
4. How can the Schlenk equilibrium be used for the preparation of magnesium dialkyls?
5. What type of bonding is present in $[MgPh_2]_n$?
6. Which structure would you expect for CpMgBr and why?

1.4 Zinc, Cadmium, and Mercury

Although the Group 12 elements appear at the end of the transition metal block in the Periodic Table, their chemical behaviour strongly resembles that of Group 2 elements, and it is therefore appropriate to include their discussion here. Their ionic radii are comparable to the alkaline earth metals:

Coord. No.	Mg^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}
2				0.69
4	0.57	0.60	0.78	0.96
6	0.72	0.74	0.95	1.02

However, the nuclear charge is better shielded by a filled d-shell, the elements are less electropositive, the metal centres are much less Lewis acidic, and the M–C bonds are more covalent. As a result, the dialkyls MR_2 are two-coordinate linear monomeric molecules, not coordination polymers like $[MgMe_2]_n$. Most zinc dialkyls are pyrophoric and sensitive to hydrolysis. Nevertheless, zinc compounds are less powerful alkylating agents than their Mg analogues and much more tolerant of functional groups, a factor that explains the surge in interest in zinc organometallics and their applications in synthesis in recent years. The stability of Cd and Hg alkyls to air and moisture is an important factor in the high toxicity and biological and environmental impact of these compounds.

1.4.1 Zinc Compounds

30
Zn
65.39

Zinc alkyls were among the first metal alkyls ever to be made (E. Frankland, 1848) and are regarded as the true starting point of organometallic chemistry. Frankland found that methyl and ethyl iodide react with zinc to give RZnI, which on heating decomposes into volatile ZnR_2 and zinc iodide:

$$\mathrm{Zn + R{-}I \longrightarrow [R{-}ZnI]_n \xrightarrow{\Delta} ZnR_2 + ZnI_2}$$

$$\mathrm{R = Me, Et}$$

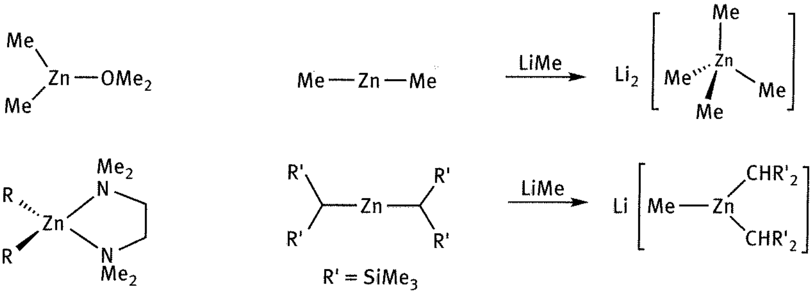
ZnR_2. Zinc dialkyls are accessible by a number of routes, e.g. from zinc metal and alkyl halides, or from $ZnCl_2$. One of the best routes to solvent-free ZnR_2 is the reaction of $Zn(OAc)_2$ with neat AlR_3 in the absence of solvents. The volatile zinc alkyls are easily separated by distillation.

$$\mathrm{ZnX_2 + 2\ R{-}Li \longrightarrow ZnR_2 + 2\ LiX \quad (X = Cl, Br)}$$

$$\mathrm{3\ Zn(OAc)_2 + 2\ AlMe_3 \longrightarrow 2\ ZnMe_2 + 2\ Al(OAc)_3}$$

The alkyls ZnR_2 (R = Me, Et, Pr^i, Bu^t, etc.) are all colourless volatile liquids that spontaneously combust on contact with air. By contrast, the sterically highly hindered tris(trimethylsilyl)methyl complex $Zn\{C(SiMe_3)_3\}_2$ is stable in refluxing THF/water mixtures and can even be steam-distilled without decomposition—a powerful demonstration of the effect of steric stabilization.

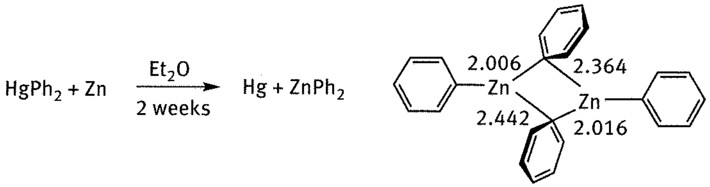
$ZnMe_2$ and other less hindered dialkyls form three- or four-coordinate adducts with dimethyl ether or chelating amines. Similarly, zinc dialkyls react with lithium alkyls to give tri- and tetraalkylzincate salts:

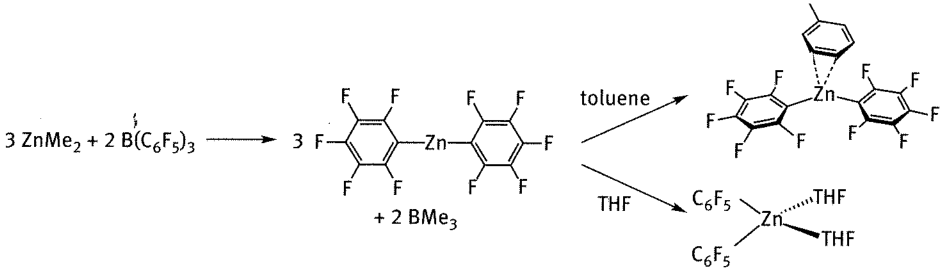


Box 1.4.1 Zinc alkyl purification

Many amine adducts of $ZnMe_2$ and $ZnEt_2$ are labile and complex formation is reversible. This fact is used for the purification of ZnR_2: complexes of involatile diamines are formed, recrystallized to the required degree of purity, and pure $ZnMe_2$ is then released on heating. $ZnMe_2$ of extremely high purity is used for the gas-phase deposition of II–VI semiconductor films such as ZnSe, in the production of electronic devices.

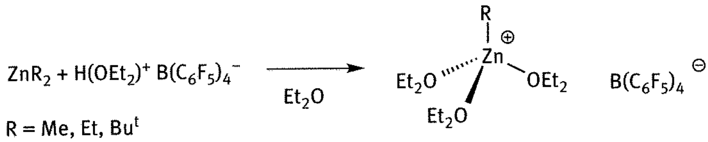
Halide-free $ZnPh_2$ can be obtained by transmetallation from $HgPh_2$; in the crystal it forms a dimer with unsymmetric 2e3c-bridges. Another route to salt-free aryls is the exchange with boron aryls. This is a high-yielding route to $Zn(C_6F_5)_2$, a strong enough Lewis acid to form isolable adducts with arenes (even though this interaction is weak, ca. 25 kJ mol^{-1}).





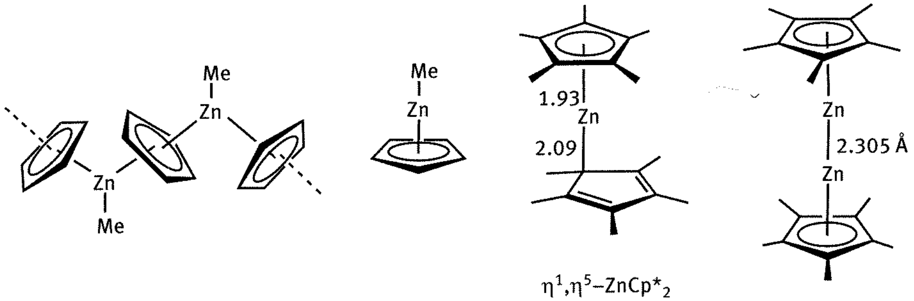
See also R_2AlX for cationic polymerization

The trigonal-planar **triarylzincate** anion $[Zn(C_6F_5)_3]^-$ is sufficiently stable towards electron transfer that it can tolerate carbocations and form crystalline CPh_3^+ salts. Mixtures of $Zn(C_6F_5)_2$ and activated alkyl chlorides RCl (e.g. *t*-BuCl or cumyl chloride $PhCMe_2Cl$) generate equilibrium concentrations of carbocations (R^+), and are capable of initiating the cationic polymerization of isobutene to butyl rubber. Cationic zinc alkyls are accessible by the protolysis of ZnR_2 in Et_2O in the presence of weakly coordinating anions (such as $B(C_6F_5)_4^-$), and have tetrahedral structures:



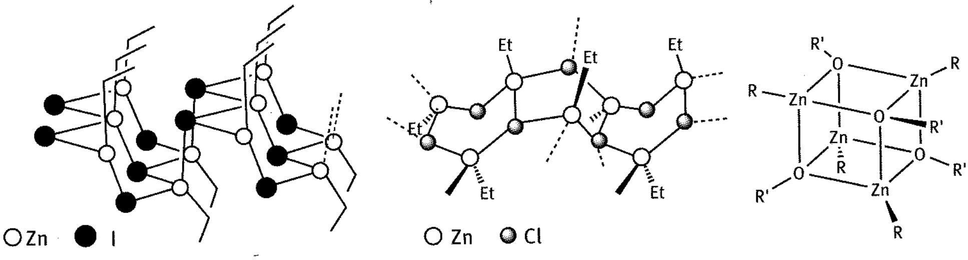
Cyclopentadienyl compounds. Zinc bis(cyclopentadienyl), $ZnCp_2$, is a coordination polymer. MeZnCp is also polymeric in the solid state but a monomer in the gas phase, with an η^5-bonded Cp ligand. The bulkier $ZnCp^*_2$ is monomeric and fluxional; the hapticity of the ligands interchanges rapidly on the NMR time scale, and the compound gives a singlet in the ^1H NMR spectrum.

The reaction of $ZnCp^*_2$ with $ZnEt_2$, or better between KCp^*, $ZnCl_2$, and KH, provided the first example of a **zinc(I) compound** with an unsupported Zn–Zn bond: $Cp^*Zn–ZnCp^*$.

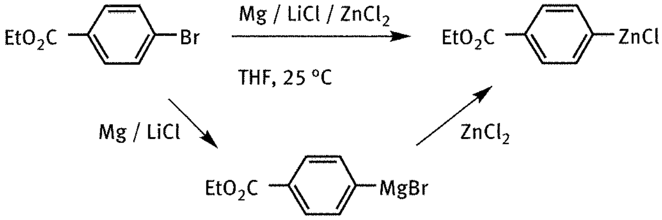


η^1,η^5-$ZnCp^*_2$

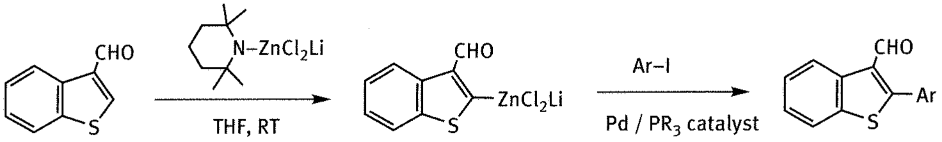
RZnX. Alkylzinc halides have more Lewis acidic metal centres, which adopt polymeric structures with tetrahedral Zn. Frankland's $[EtZnI]_\infty$ forms layers based on linked Zn_3I_3 6-rings in chair conformation, while in $[EtZnCl]_\infty$ these rings have a boat conformation. The alkoxides $[RZn(OR')]_4$ form a cube.



In general, mixed-ligand zinc halides are conveniently prepared by transmetallation from Grignard reagents. The structures of the resulting mixed-metal products are probably more complex than indicated, since Li/Mg/Zn reagents often exhibit higher reactivity than the mono- or bimetallic reagents alone.

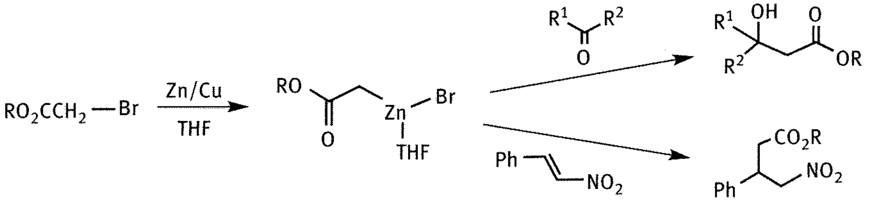


Since zinc reagents tolerate many functional groups and are thermally more robust than the Mg analogues, they are convenient reagents for C–C coupling reactions. For example, it is possible to selectively metallate heterocycles carrying aldehyde functions without protection using zinc amido halide reagents; the resulting zinc aryl can then be used for palladium-catalysed cross-coupling reactions.



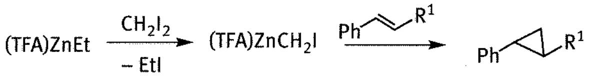
Reformatsky

The best-known functionalized zinc alkyl is the **Reformatsky reagent**, made from α-halomethyl esters. It reacts with carbonyl compounds as well as activated alkenes:

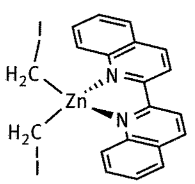


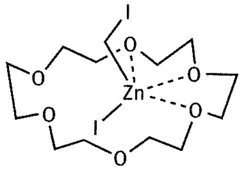
Simmons–Smith

α-Halomethylzinc reagents are employed as CH_2 transfer agents in cyclopropanations (**Simmons–Smith reaction**); these species are therefore referred to as ***zinc carbenoids***. While originally these were produced by reacting CH_2I_2 with Cu-activated zinc to give I–$ZnCH_2I$, there are advantages in using $(X)ZnCH_2I$ (e.g. X = CF_3CO_2, TFA). With X = chiral alkoxide R*O, the reaction may be enantioselective. The crystal structures of a number of crown-ether and bipyridyl-stabilized iodomethyl reagents have been determined.

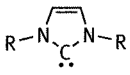


R^1 = H, Me, CH_2OH, Ph

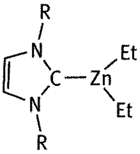


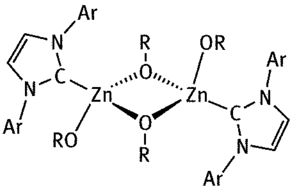


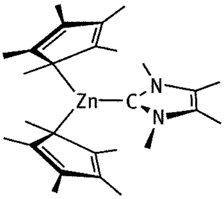
Carbene complexes. N-heterocyclic carbenes (NHCs) are strong σ-donor ligands and are widely used in catalysis in place of electron-rich phosphines. A number of zinc NHC complexes are known; some of these have been studied as initiators for the ring-opening polymerization of cyclic esters such as L-lactide. Due to the presence of a strong electron donor, in ZnCp*$_2$(NHC) the Cp* ligands are both η^1-bonded.



NHC ligand







Cd
48
112.411

1.4.2 Cadmium Compounds

Like ZnR$_2$, cadmium dialkyls CdR$_2$ are linear monomers which comproportionate with CdX$_2$ reversibly to give RCdX. The alkyls are comparable to their mercury analogues, but are thermally and photochemically less stable and highly toxic. They are generally unimportant for synthetic applications.

The reaction of CdMe$_2$ with sources of S, Se, or Te (H$_2$S, H$_2$Se, or Pr$^i{}_2$Te) is used in the electronics industry for the deposition of **II–VI semiconductors,** such as CdS, CdSe, and CdTe. Crystalline solid state films are grown by metal–organic chemical vapour deposition (MOCVD) from the gas phase at 300–400 °C. CdTe doped with mercury is used as an infrared detector in night vision equipment.

$$\mathrm{CdMe_2 + H_2Se} \xrightarrow{300\text{–}400\ ^\circ\mathrm{C}} \mathrm{CdSe + 2\ CH_4}$$

Growth of II–VI semiconductor materials by MOCVD[a]

II–VI compound	Reactants	Growth temperature (°C)
CdS	CdMe$_2$, H$_2$S	300–400
CdSe	CdMe$_2$, H$_2$Se	300–400
CdTe	CdMe$_2$, Pr$^i{}_2$Te	350–400
CdHgTe	CdMe$_2$, Pr$^i{}_2$Te, Hg	350–400

[a] C. J. Carmalt, S. Basharat, *Comprehensive Organometallic Chemistry III*, vol. 12, p. 23.

1.4.3 Mercury Compounds

80
Hg
200.59

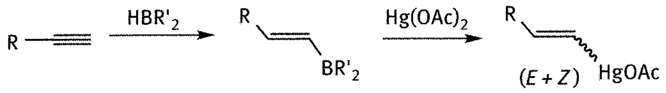
The organometallic chemistry of mercury almost exclusively involves the oxidation state +II. The electronegativities of mercury and carbon are very similar; Hg–C bonds are highly covalent and therefore unreactive to air and moisture, even though they are not thermodynamically strong. They also do not react with typical organic electrophiles such as alkyl halides or carbonyl compounds. They tolerate a wide range of functional groups; for this reason mercury reagents continue to be used in many synthetic procedures.

1.4.3.1 Synthesis

Mercury alkyls and aryls are accessible by alkylation with Li or Mg reagents, as well as by transmetallation from boron or tin reagents. Another route is the thermal decarboxylation of mercury carboxylate compounds:

$$\mathrm{RLi} + \mathrm{HgCl_2} \xrightarrow[-\,\mathrm{LiCl}]{} \mathrm{R{-}HgCl} \xrightarrow[-\,\mathrm{LiCl}]{\mathrm{LiR}} \mathrm{HgR_2}$$

alkylation



transmetallation

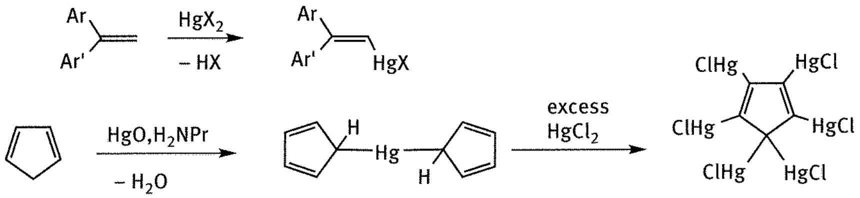
$$\mathrm{Ar{-}SnMe_3} \xrightarrow[-\,\mathrm{XSnMe_3}]{\mathrm{HgX_2}} \mathrm{Ar{-}HgX}$$

transmetallation

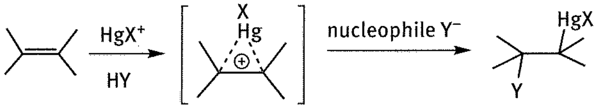
$$\mathrm{RCO_2HgX} \xrightarrow{\Delta} \mathrm{RHgX} + \mathrm{CO_2}$$

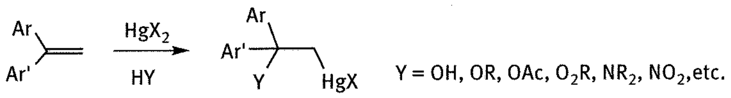
decarboxylation

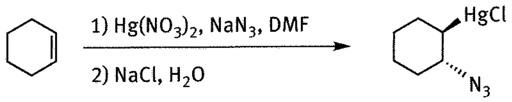
Alkenes can be mono- and polymercurated:

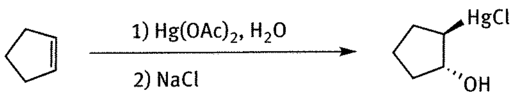


A powerful method for the di-functionalization of alkenes is **solvomercuration**:

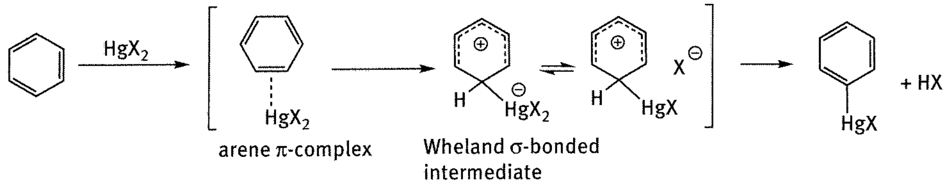




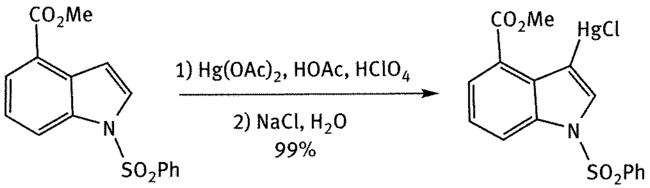


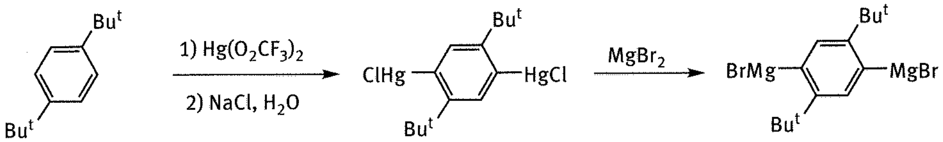


Mercury salts are electrophiles and readily metallate aromatics by **electrophilic substitution**. The classical example is the formation of PhHgOAc from $Hg(OAc)_2$ and benzene. The more electrophilic $Hg(O_2CF_3)_2$ (often in CF_3COOH as solvent) reacts orders of magnitude faster. The reaction proceeds by first forming a mercury(II) arene complex, followed by deprotonation by the weakly basic anion.

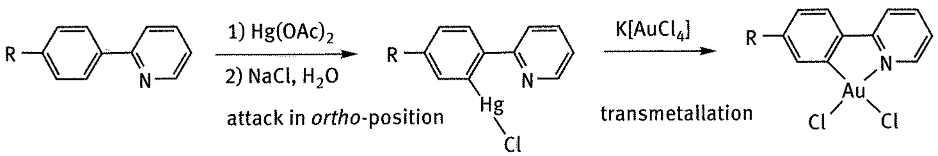


This reaction is usually site-specific and has been applied to the metallation of a large number of 5- and 6-ring aromatics. The mercury can be replaced by other metals, and the method can be used, for example, for the synthesis of Grignard reagents that are difficult to make by other routes. The mercuration takes place preferentially close to a donor substituent which can coordinate to the mercury ion and direct the site of electrophilic attack.

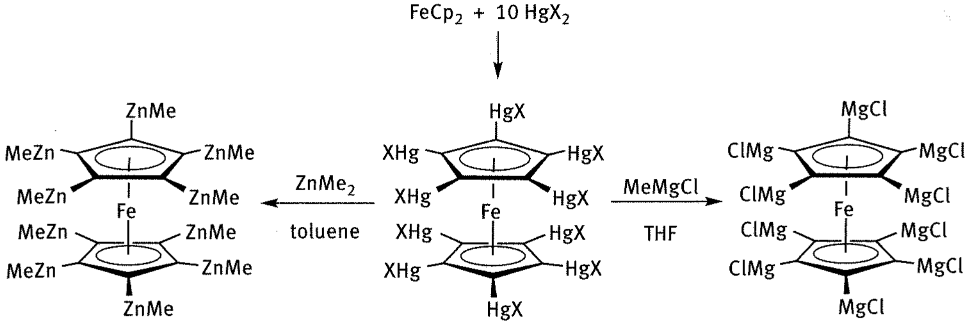




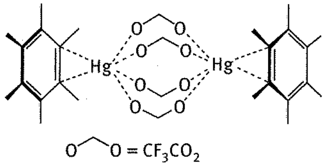
Transmetallation

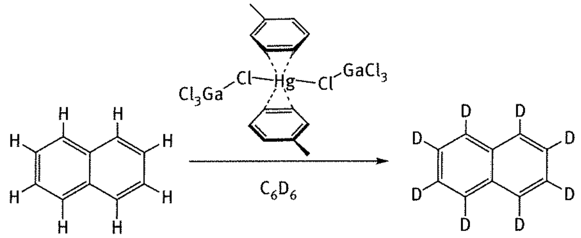


The synthetic potential of mercuration is exemplified by the complete metallation of metallocene complexes such as ferrocene $FeCp_2$:



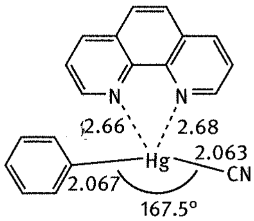
If the anion is insufficiently nucleophilic to bring about H^+-abstraction, the mercury–arene π-complexes can be isolated. Arene exchange is reversible, and the $Hg(GaCl_4)_2$ complex catalyses the electrophilic deuterium exchange between naphthalene and C_6D_6.

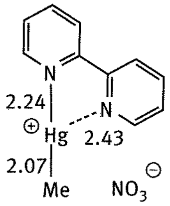


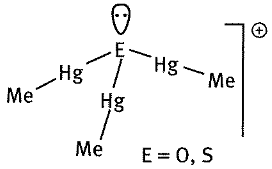


1.4.3.2 Structural Aspects

HgR_2 and RHgX form generally linear molecules. In the solid there may be secondary interactions with donor ligands perpendicular to the R–Hg–X axis but with significantly longer distances; this may result in a T-shaped geometry. Unlike zinc(II), mercury(II) adducts hardly deviate from linearity even with strongly chelating ligands like 2,2′-bipyridyl. Cationic complexes show a tendency to increase the coordination number through these secondary interactions and form asymmetric chelates. The reaction of $(MeHg)_2O$ with strong acids gives salts of the pyramidal $[(MeHg)_3O]^+$ cation ($X = BF_4$, ClO_4, NO_3).



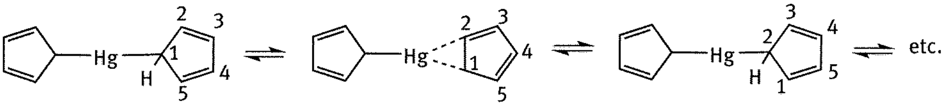




The cyclopentadienyl ligands in $HgCp_2$ are both η^1-coordinated, unlike the zinc analogue. The compound is **fluxional** due to haptotropic migration of Hg over all ring positions. This

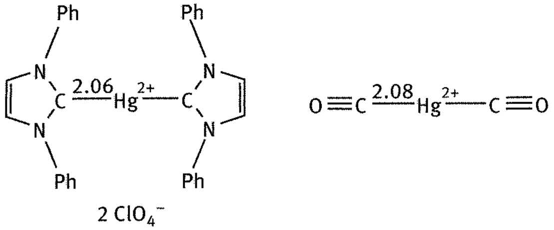
Fluxionality: haptotropic shifts

interchange is fast on the NMR time-scale, so that at ambient temperature the complex gives a single resonance in the ^1H NMR spectrum.



For CO bonding see Section 2.3.1

Different types of Hg(II) complexes are formed with neutral donor or acceptor ligands. N-heterocyclic carbenes or CO both form linear dications $[HgL_2]^{2+}$. The CO complex is isolable only as a salt of the extremely weakly coordinating $Sb_2F_{11}^-$ anion. There is no metal-to-CO back-bonding, and consequently the CO stretching frequency is significantly higher than that of free CO (2279.5 vs. 2143 cm^{-1}).



Box 1.4.3 Organomercury compounds *in vivo*

The Hg–C bond is covalent and is not attacked by water. This means that mercury alkyls can survive under physiological conditions.

Microorganisms methylate Hg^{2+} ions in water by methyl transfer from the vitamin-B_{12} derivative methylcobalamine. The resulting $MeHg^+$ ion forms complexes with any available O, N, and particularly S compounds and can be taken up into the food chain. In higher animals and humans it binds to proteins, such as those in the brain. There is of course a natural background level of mercury in the environment, which is tolerated. However, where there is increased exposure to mercury (as well as other heavy metals, such as cadmium and thallium), typically due to the release of industrial effluents which can enter the food chain, the effect on health can include paralysis and even death. Marine organisms such as mussels and fish are capable of concentrating $MeHg^+$ compounds in their bodies. In the 1950s in Japan, their consumption gave rise to catastrophic health problems ('Minamata disease'). For this reason, the use of mercury in industrial processes (such as in chlor-alkali electrolysis) has been drastically reduced. However, mercury is also used in unregulated gold-winning activities in less-developed parts of the world, where gold particles are extracted as mercury alloy and recovered by evaporation of the mercury. Annually, thousands of tons of mercury are still released into the environment in this way.

Dimethylmercury is lipophilic and can rapidly **penetrate skin as well as latex gloves.** ***The use of simple laboratory gloves therefore offers no protection and may provide a false sense of security***. At least one death of a laboratory worker has been recorded as the result of skin contact with just a few drops of $HgMe_2$. Although most mercury organometallics are involatile and less easily ingested, the handling of mercury compounds requires **awareness, careful handling, and safe disposal**.

Key points

Although organometallic compounds of Zn, Cd, and Hg show similarities to alkaline earth compounds, they have much less polar M–C bonds, lower Lewis acidity, and a low tendency for aggregation. Zn and Hg are important as synthetic reagents. Cadmium alkyls are mainly important as precursors for II–VI semiconductors. Mercury salts are particularly useful for the electrophilic metallation of arene C–H bonds. The Hg–C bond is highly covalent and resistant to air, moisture, and many functional groups, with many applications in organic synthesis.

Exercises

1. Show synthetic routes to $ZnMe_2$ and $[ZnMe_4]^{2-}$ and give balanced chemical equations.
2. Why is $ZnEt_2$ a monomer, but EtZnCl a polymer?
3. Draw the mechanism and intermediates for the mercuration of benzene with mercury(II) acetate.
4. What is the structure of $Zn(C_5Me_5)_2$, and why does the ^1H NMR spectrum at room temperature show only one signal?
5. What is a 'Reformatsky reagent'?
6. How can mercury compounds be useful for the preparation of di-Grignard reagents?
7. What is 'solvomercuration'? Give the reaction scheme and intermediates.

1.5 Organometallic Compounds of the Boron Group

The organometallic chemistry of the Group 13 elements B, Al, Ga, In, and Tl is dominated by boron and aluminium, a reflection of their utility and applications. Boron is a non-metal and has a small radius; it does not form simple ions, and consequently its bonds to carbon are highly covalent. The higher members of the group are metals, with more polar M–C bonds. The electronegativity decreases down the group, as does the stability of the +III oxidation state. As a result, almost all organometallic compounds of B and Al are trivalent, while for In and Tl the oxidation state +I becomes important.

The ionic radii (Å) of Group 13 elements in the +III state are smaller than those of alkaline earth metals. There is a distinct jump from B to Al, which is reflected in differences in bonding behaviour.

Coordination number	B	Al	Ga	In	Tl
4	0.11	0.39	0.47	0.62	0.75
6	0.27	0.54	0.62	0.8	0.89
Covalent radius	0.84	1.21	1.22	1.42	1.45

The stability of the M–C bonds decreases down the group, as shown by the mean M–Me bond dissociation energies $\overline{D}(\text{M–CH}_3)$ (kJ mol^{-1}) of the trimethyls:[a]

B	Al	Ga	In	Tl
369.6	281.4	256.2	218.4	151.2

[a] J. J. Eisch, *Comprehensive Organometallic Chemistry*, 1982, *1*, 618.

B 5
10,811

1.5.1 Boron Compounds

Boron forms organometallic compounds of the types RBX_2, R_2BX, and BR_3, where R = alkyl, alkenyl, or aryl, and X = H, OH, OR′, SR′, NR′$_2$, or halide. Since trivalent boron is Lewis acidic, it may bind anions to give a corresponding series of borates, such as RBX_3^- and BR_4^-.

Boron–carbon σ-bonds are comparable to or slightly stronger than C–C bonds, e.g. 362±11 kJ mol^{-1} in BMe_3 and about 400 kJ mol^{-1} in $MeBF_2$, compared to 347–356 kJ mol^{-1} for C–C.

1.5.1.1 Synthetic Methods

By transmetallation:

$$BF_3(OEt_2) + 3\,RMgX \longrightarrow BR_3 + 3\,MgFX + Et_2O$$

$$B(OMe)_3 + RMgX \longrightarrow RB(OMe)_2 + MgX(OMe)$$

$$2\,B(OEt)_3 + Al_2R_6 \longrightarrow 2\,BR_3 + 2\,Al(OEt)_3$$

$$BBr_3 + PhHgBr \longrightarrow PhBBr_2 + HgBr_2$$

Convenient starting materials are the Et_2O complex of BF_3, the rather hydrolysis sensitive BBr_3, or the much less Lewis acidic alkylborates $B(OR)_3$. The reactivity of various alkylating agents MR_n decreases in the order Na, K > Li > Mg > Zn > Sn, Pb, Hg. Addition of lithium reagents leads to the formation of **tetraalkylborates**:

$$BX_3 + 3\,LiR \xrightarrow[-\,3\,LiX]{} BR_3 \xrightarrow{LiR} Li^+[BR_4]^-$$

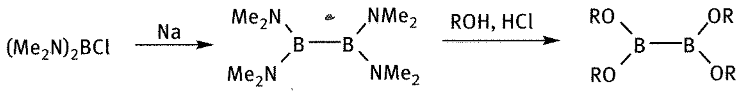
Ligand redistribution

The use of zinc, tin, and mercury alkyls allows the selective synthesis of incompletely alkylated boranes, RBX_2 and R_2BX. These compounds are also accessible by **ligand redistribution**:

$$BX_3 + 2\,BR_3 \longrightarrow 3\,R_2BX$$

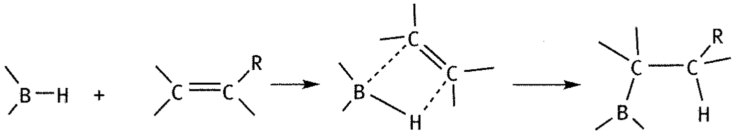
B–B bond

The reduction of R_2BCl gives boron(II) compounds with B–B bonds; those carrying N or O substituents are particularly stable and are used as diborylation reagents.

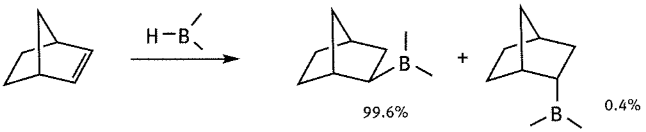


By Hydroboration:

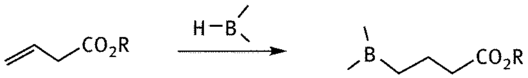
Borane in diethyl ether or THF solution reacts with alkenes to give mono-, bis-, and tris-insertion products BR_nH_{3-n}. The reaction requires a mildly coordinating solvent. The thioether complex $BH_3(SMe_2)$ is also often used; SMe_2 is a labile ligand but helps to make BH_3 easier to handle. Catecholborane has the advantage of greater stability to air and moisture.



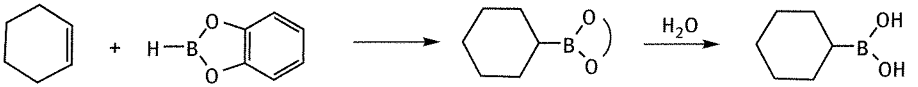
anti-Markovnikov product



stereoselective addition



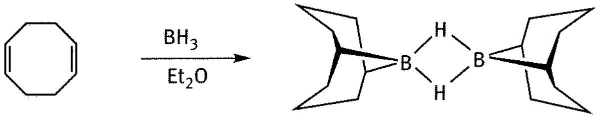
functional group tolerance



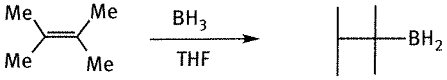
catecholborane

alkylboronic acid

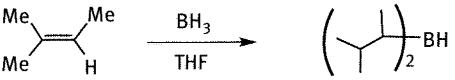
Bulky alkyl hydroboranes give much improved regioselectivity. Commonly used are 9-borabicyclononane (9-BBN) and reagents known as thexylborane and bis(siamyl)borane:



9-BBN



"thexylborane"

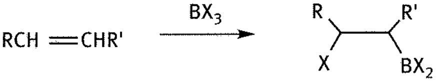


'disiamylborane', Sia_2BH

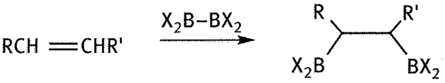
For Pd-catalysed coupling reactions with B reagents, see Chapter 3.6.

Organoboranes BR_3 are fairly stable to water. Hydrolysis of catecholboranes gives the corresponding boronic acids, which are popular reagents in palladium-catalysed C–C coupling reagents because of their stability to air and moisture and ease of handling.

Other methods for the preparation of organoboranes include haloboration and diboration. These are often accompanied by subsequent rearrangements and are of less general utility.



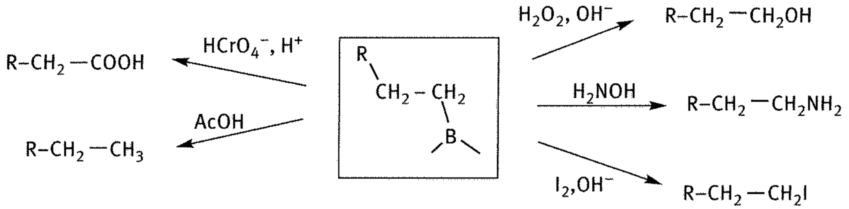
haloboration



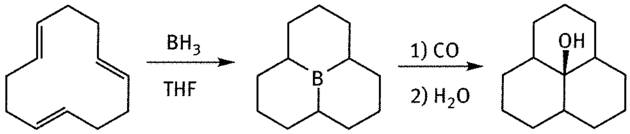
diboration

1.5.1.2 Reactivity of Boron Compounds

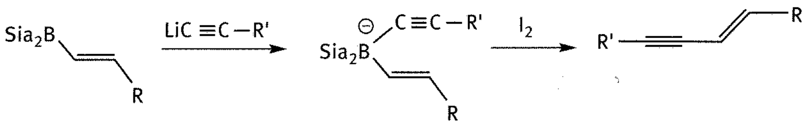
Hydroboration proceeds in an ***anti-Markovnikov*** sense; bulky boranes such as 9-BBN are particularly selective. The method is a versatile route to 1-substituted organic products:



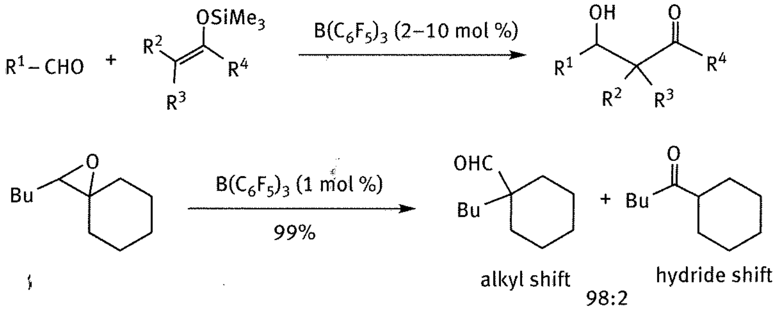
Sec-alkyl boranes are oxidized by pyridinium chlorochromate to ketones, *n*-alkyls to aldehydes. Treatment of BR_3 with CO leads to transfer of all three alkyl groups to C, to give *tert*-alcohols, for example:



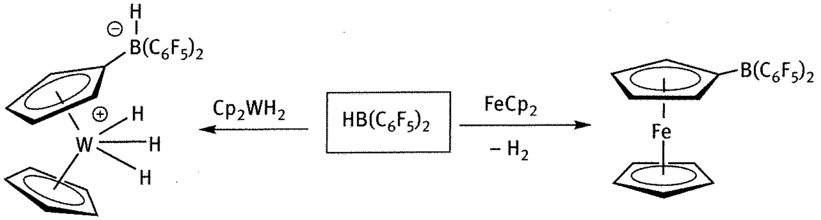
The oxidation of borates can also be utilized for C–C bond formation, e.g. for the formation of dialkynes, enynes, and dienes:



The highly Lewis acidic perfluorophenyl borane $B(C_6F_5)_3$ has been found to be a very effective catalyst for a number of organic synthetic applications, for example:



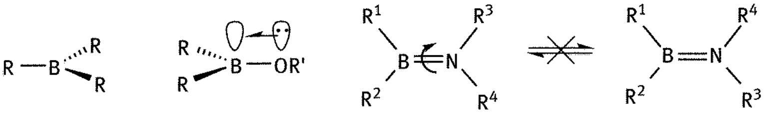
The electrophilic perfluorophenyl boranes $(C_6F_5)_2BH$ and $(C_6F_5)BH_2$ and their more convenient SMe_2 adducts are potent hydroborating agents. They can be made by mixing $BH_3(SMe_2)$ with $B(C_6F_5)_3$ in the required ratios. $(C_6F_5)_2BH$ borylates metallocenes:



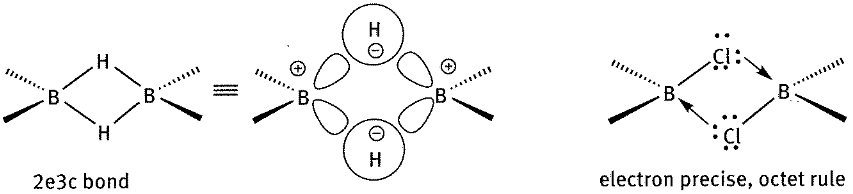
1.5.1.3 Structure and Bonding

Neutral organoboranes are planar and monomeric, with an electron sextet. BMe_3 is a gas; higher simple BR_3 alkyls are liquids which ignite on contact with air and burn with a characteristic green flame. The introduction of aryl, halide, or alkoxide substituents reduces the **Lewis acidity** by π-interaction between the empty p-orbital on boron and the lone pair of the heteroelement. The **π-interaction** in B–E bonds reflects the similarity in energy levels of the boron p-orbital and the lone pair on the heteroelement E, and increases in the order $Cl < S < O < F < N$. The B–N bond is isoelectronic with a C=C bond and has double bond character, as indicated by a high barrier of rotation.

B–E π-bonding



Boranes R_2B–H form H-bridged dimers with 2e3c bonds. Alkyl halides R_2BX are also dimeric, but since the halide contributes a lone pair, the boron centres attain an electron octet, i.e. these compounds are electron-precise:



2e3c bond

electron precise, octet rule

The addition of a negatively charged nucleophile Y^- to boranes gives borates $[BR_3Y]^-$. Addition of NaH or KH to BH_3 or BR_3 gives salts of the **hydroborate** anions BH_4^- and HBR_3^-, respectively, which are frequently used as reducing agents. Borates are **tetrahedral**, have an electron octet, and are isoelectronic with alkanes. $NaBPh_4$ is water-soluble and can be used as an analytical reagent for the determination of K^+ and higher alkali cations, all of which form insoluble BPh_4^- salts.

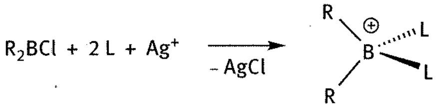
$$4\,NaH + B(OMe)_3 \xrightarrow{250\text{–}270\,°C} Na[BH_4] + 4\,NaOMe$$

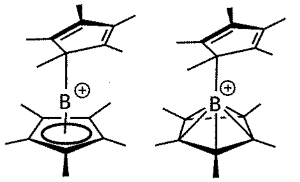
$$LiH + BEt_3 \xrightarrow[Et_2O]{} Li[HBEt_3]$$

$$BR_3 + BH_4^- \longrightarrow [R_3B\text{-}H\text{-}BH_3]^-$$

$$NaBF_4 + 4\,PhMgBr \xrightarrow[Et_2O]{} Na[BPh_4] + 4\,MgBrF$$

The addition of donor ligands to organoboron halides gives boronium ions, again with an electron octet and a tetrahedral structure. The cation $BCp^*{}_2^+$ also has an electron octet; its structure is similar to that of $BeCp^*{}_2$ and $ZnCp^*{}_2$.



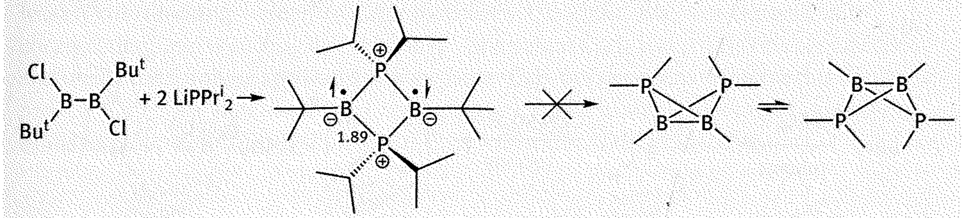


π-complex and carborane cluster views of n^1,n^5-$Cp^*{}_2B^+$

borates BR_4^-

Box 1.5.1.1 The importance of steric factors: stabilization of a transition state

Boron has a very small radius and is therefore strongly influenced by the steric requirements of its substituents. This can lead to unusual bonding situations. For example, the reaction of $B_2Cl_2Bu^t{}_2$ with $LiPPr^i{}_2$ did not produce the expected butterfly-structure but gave a crystalline, stable biradical with a planar B_2P_2 ring. Calculations showed that the structure is a transition state for the inversion of the bicyclic B_2P_2 isomer.

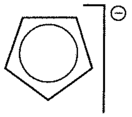


R_2B^+ cations

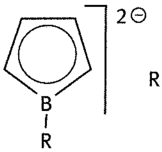
Since C and B^- are isoelectronic, there are many compounds where B and C can be interchanged. For example, there is a series of boron-containing rings analogous to benzene and cyclopentadienyl; incorporation of B leads to a correspondingly higher charge.

A special class of compounds are the carboranes. In polyboranes, electron-deficient bonding leads to cluster formation, and some of the B–H moieties can be replaced by C–R. Coverage of carboranes and their structural diversity is beyond the scope of this text; however, the $C_2B_9H_{11}^{2-}$ dianion should be mentioned since it has bonding characteristics similar to the cyclopentadienyl anion and forms analogous transition metal complexes.

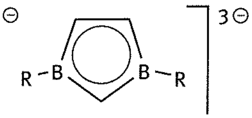
Cp$^-$ analogues



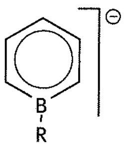
cyclopentadienyl



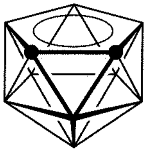
borole dianion



1,3-dibora-Cp



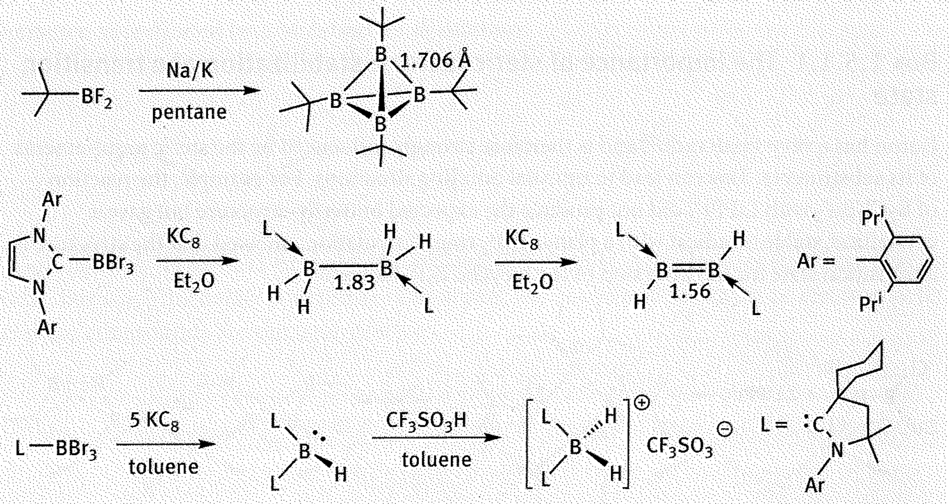
boratabenzene



7,8-isomer of nido-$C_2B_9H_{11}{}^{2-}$

Box 1.5.1.2 Boron in uncommon bonding situations

The reduction of Bu^{t}BF$_2$ leads to a B(I) cluster, B$_4$Bu$^t_4$, a highly electron-deficient structure in which four B atoms are held together by only eight electrons. In the presence of very strong donor ligands such as N-heterocyclic carbenes (NHCs), cluster formation is prevented, and compounds with HB=BH bonds can be isolated. Yet stronger carbene donors prevent even this dimerization and give adducts of borylene (HB:), which contains a lone pair of electrons and can be protonated, in a way rather similar to an amine:



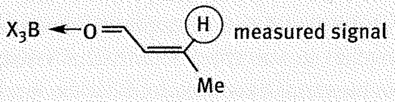
Lewis acidity

Box 1.5.1.3 Determination of Lewis acidity

Boron alkyls, aryls, and halides and analogous aluminium compounds are known as the archetypical Lewis acids. However, whereas the pK_a of Brønsted acids can easily be determined with good accuracy, the determination of the Lewis acid strength of a compound is less straightforward. Methods have been developed which measure the NMR chemical shifts of adducts, on the assumption that the equilibrium constant is a linear function of the Lewis acidity.

$$X_3B + L \overset{K}{\rightleftharpoons} X_3B{-}L$$

A widely used method that gives generally good agreements is the Child method, where the ^1H NMR resonance of the remote proton of crotonaldehyde is measured:

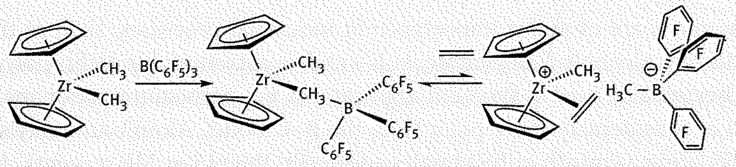


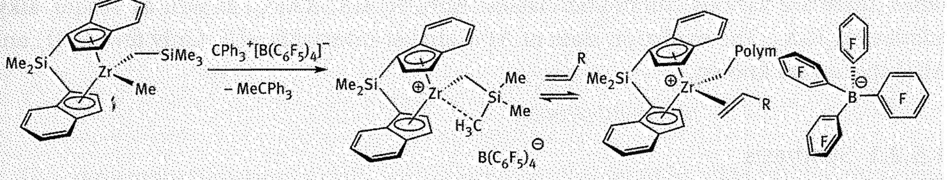
Using this method, a scale can be established which shows that triarylboranes with strongly electron-withdrawing substituents, such as $B(C_6F_5)_3$, compare well with boron and aluminium halides.

MX_3	BBr_3	BCl_3	$AlCl_3$	$B(C_6F_5)_3$	BF_3	$AlEt_3$
Relative acidity	1.00	0.93	0.82	0.77	0.77	0.44

Substituent effects in boranes: C_6F_5 vs. C_6H_5

Replacing the C_6H_5 substituents in BPh_3 by C_6F_5 not only increases the Lewis acidity but also provides stability against chemical attack and particularly against hydrolysis. An even more stable compound is the $[B(C_6F_5)_4]^-$ anion—it is soluble in low polarity solvents, is chemically remarkably inert, and has a very high oxidation potential, so that its NBu_4^+ salt is used as supporting electrolyte in electrochemistry. These properties have turned **$B(C_6F_5)_3$** and **$[B(C_6F_5)_4]^-$** salts into important **catalysts** and **catalyst activators**. Their reactions with Group 4 metallocene dialkyls generate extremely active catalysts for the **polymerization of olefins**. The C_6F_5-substituents make the anions actually larger than the metallocene complexes and distribute the negative charge over a very large volume, so that the anions become **extremely weakly coordinating**—orders of magnitude less nucleophilic than conventional 'non-coordinating' anions such as BF_4^- and SbF_6^-. The parent C_6H_5 compounds are too unstable and ineffective for these applications. Even larger C_6F_5 borate anions reinforce this effect and provide numerous 'super-weakly' coordinating anions, for example diborates containing a bridging group Z, $[(C_6F_5)_3B\text{–}Z\text{–}B(C_6F_5)_3]^-$ (Z = OH, CN, NH_2, imidazolyl).

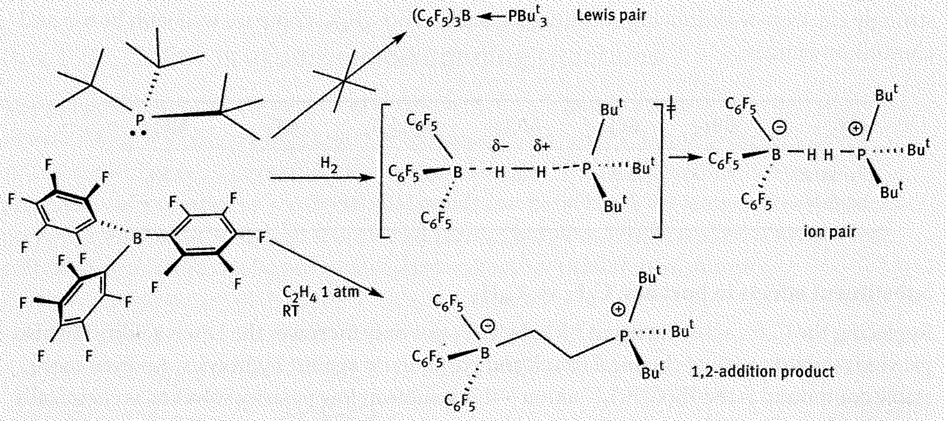




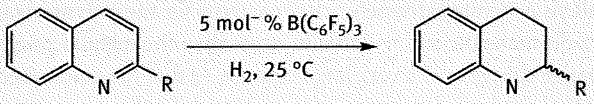
Box 1.5.1.4 The 'frustrated Lewis pair' (FLP) concept

'Frustrated Lewis pairs'

$B(C_6F_5)_3$ is trigonal-planar, with the C_6F_5 arranged propeller-fashion. The compound is sterically quite hindered, and although Lewis acids prefer to form adducts with Lewis bases, some bases are too hindered to do so—an effect described as **'frustrated Lewis pairs' (FLP)**. However, such acid/base combinations have been found to be very effective in the **heterolytic cleavage of H_2**. They also add to ethylene:



These FLP systems catalyse the metal-free hydrogenation of imines, anilines, and heterocycles; in some cases the substrate itself may act as the base, for example:



13
Al
26.982

1.5.2 Aluminium

Aluminium alkyls are of major importance in industrial processes, such as the production of surfactant alcohols ('Ziegler alcohols') and as activators for olefin polymerization catalysts. They are also used in synthetic applications, e.g. carboalumination reactions. The Al–C bond is considerably more polar than the B–C bond. Aluminium alkyls, AlR_3, are stronger alkylating agents than BR_3 but less powerful than Li or Mg reagents. As with boranes, there are various compound classes: AlR_3, R_2AlX, $RAlX_2$, as well as 'sesqui' alkyl halides, $Al_2R_3X_3$. The oxidation state of Al is almost invariably +III. Only few Al(II) and Al(I) species are known.

Sesqui = one and a half, i.e. $AlCl_{1.5}Et_{1.5}$

1.5.2.1 Synthesis

Aluminium trimethyl is made directly from methyl halide and aluminium. The compound is a liquid at room temperature and dimeric; it dissociates in the gas phase into monomeric $AlMe_3$.

$$4\ Al + 6\ MeX \longrightarrow 2\ Al_2Me_3X_3 \xrightarrow[-\ NaX]{Na} Al_2Me_6$$

Aluminium alkyls with longer alkyl chains are made by the **Ziegler process**, which involves the ***hydroalumination*** of alkenes. The reaction is based on the observation that in the presence of Al alkyls, metallic Al reacts with hydrogen, and the Al–H species thus formed insert olefins. The reactivity of Al is increased if it is alloyed with a small amount of titanium.

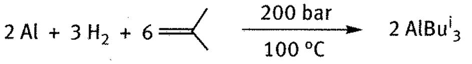
hydroalumination

$$2\ Al + 3\ H_2 + 4\ AlEt_3 \xrightarrow[80\text{–}160\ °C]{100\text{–}200\ bar} 6\ Et_2AlH$$

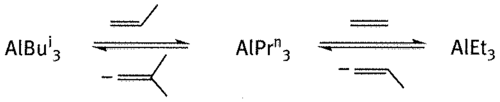
$$6\ Et_2AlH + 6\ C_2H_4 \xrightarrow[80\text{–}110\ °C]{1\text{–}10\ bar} 6\ Et_3Al$$

$$2\ Al + 3\ H_2 + 6\ C_2H_4 \longrightarrow 2\ Et_3Al$$

Similarly, Al, H_2, and isobutene give, depending on the reaction conditions, either diisobutyl aluminium hydride Bu^i_2AlH ('DIBAH') or tri-isobutyl aluminium $AlBu^i_3$ ('TIBA'). Both are in equilibrium, i.e. $AlBu^i_3$ contains small amounts of Bu^i_2AlH; TIBA is used in the activation of certain 1-alkene polymerization catalysts.



The reversibility of the hydroalumination can be used to **interconvert** Al alkyls:



Aluminium alkyls may also be prepared from the **alkylation** of the halides with Grignard or lithium reagents; in these cases ether adducts are formed. An excess of LiR gives an **'ate' complex**:

$$\begin{tikzcd} AlCl_3 + 3\ RMgX \arrow[r, "Et_2O"'] & AlR_3(Et_2O) + 3\ MgXCl \arrow[d, "LiR'"] \\ & \begin{array}{c} Li^+\ [AlR_3R']^- \\ \text{tetraalkylaluminate} \end{array} \end{tikzcd}$$

Aluminates $[AlR_4]^-$

The **comproportionation** of AlR_3 with aluminium halides gives alkyl halides; these may be further alkylated to give mixed-ligand aluminium alkyls. In such cases heating must be avoided to suppress alkyl ligand redistribution.

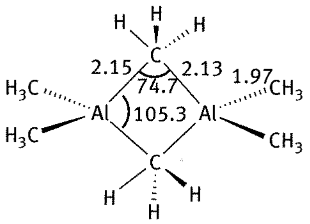
$$AlX_3 + 2\ AlR_3 \xrightarrow[Et_2O]{} 3\ R_2AlX \xrightarrow{LiR'} 3\ R_2AlR'$$

A convenient, salt-free route to aluminium aryls is the **ligand exchange** with boranes. The reaction proceeds by stepwise substitution; however, since BMe_3 is a gas which is easily removed from the reaction mixture, the equilibrium can be shifted to give the Al product quantitatively. Non-polar solvents like toluene allow the preparation of strongly Lewis acidic Al compounds such as $Al(C_6F_5)_3$ (as a labile η^1-toluene adduct), which would form strong adducts with ether solvents if the Grignard route was used.

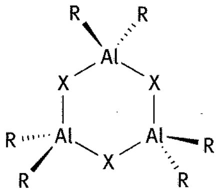
$$AlMe_3 + BAr_3 \rightleftharpoons AlAr_3 + BMe_3\uparrow$$

1.5.2.2 Structures and Properties

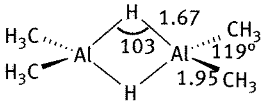
Trimethylaluminium is a dimer in solution and the solid state, unlike BMe_3, since Al is large enough to allow interaction with a fourth methyl ligand. This is a classical example of a **2-electron-3-centre** bonding pattern, as discussed in Section 1.1. The trialkyls AlR_3 (R = Me, Et, Pr^n, Bu^n) are dimeric in hydrocarbon solution, while $AlBu^i_3$, $AlBu^t_3$, $Al(CH_2Ph)_3$ are monomeric.



solid-state structure of Al_2Me_6



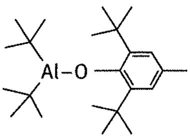
X = H, OMe, NHMe; R = Me, Et, Bu^i
X = Cl; R = Et, Bu^i

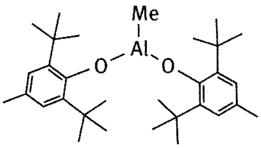


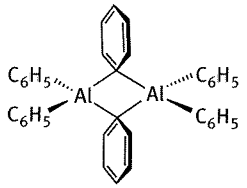
gas-phase electron diffraction structure of $[Me_2AlH]_2$

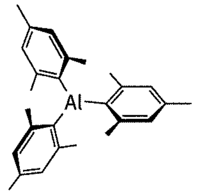
Compounds containing heteroatoms are electron-precise oligomers $[R_2AlX]_n$, where n depends on the steric requirements of R and X; for example, for R = Et, $n = 3$ for X = OMe, NH_2, and NHMe but $n = 2$ for X = OBu^t or NMe_2. Me_2AlF is a tetramer.

$AlBu^t_3$ is monomeric, as are the bulky aryloxides $Bu^t_2Al(OC_6H_3Bu^t_2)$ and $MeAl(OC_6H_3Bu^t_2)_2$; the latter has been used as an impurity scavenger in olefin polymerization catalysis. $AlPh_3$ is a dimer with bridging phenyl ligands and 2e3c bonds, whereas more bulky aryls are planar monomers. $Al(mesityl)_3$ forms only a labile adduct with THF (mesityl = 2,4,6-$Me_3C_6H_2$). By contrast, $Al(C_6F_5)_3$ is a much stronger Lewis acid; it forms adducts with THF (and even weak η^2-adducts with cyclohexene) and reacts with F^- to give the extremely weakly coordinating fluoride-bridged anion $[(C_6F_5)_3Al(\mu\text{-}F)Al(C_6F_5)_3]^-$.

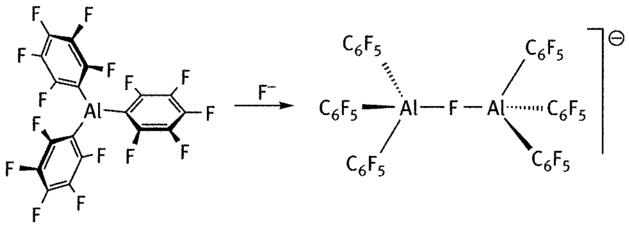






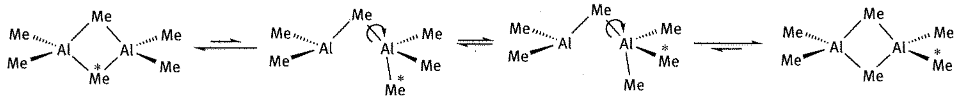


planar Al
propeller structure

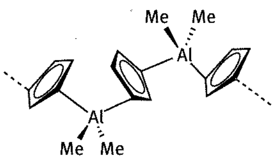


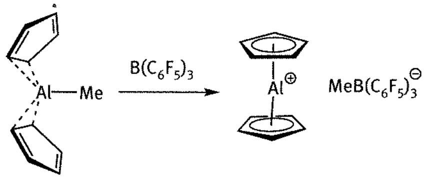
Fluxionality

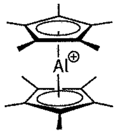
The degree of association of oligomeric aluminium alkyls changes with solvent and temperature. Al_2Me_6 is a dimer in the solid state and in solution, and a mixture of dimeric and monomeric structures in the gas phase. Me_2AlH is a trimer in solution but dimeric in the gas phase. All these processes indicate that **ligand exchange in aluminium complexes is facile.** The fluxional behaviour of Al alkyls explains why the ^1H NMR spectrum of Al_2Me_6 at room temperature shows only one single resonance for the six methyl ligands. The exchange between terminal and bridging methyls is rapid on the NMR time-scale, unless the solution is cooled to −70 °C:



Cyclopentadienyl complexes of aluminium show a variety of bonding modes, from η^1 to η^5, depending on the electron-deficient character of the metal centre. Me_2AlCp forms a zigzag chain with η^1-type interactions with neighbouring aluminium atoms, while $MeAl(\eta^2\text{-}Cp)_2$ is monomeric, as is the isocyanide adduct $(\eta^1\text{-}Cp)_3Al(C{\equiv}NBu^t)$. The reaction of $MeAl(\eta^2\text{-}Cp)_2$ with $B(C_6F_5)_3$ gives the aluminocenium cation, which is an initiator for the cationic polymerization of isobutene. The Cp* analogue has been structurally characterized.







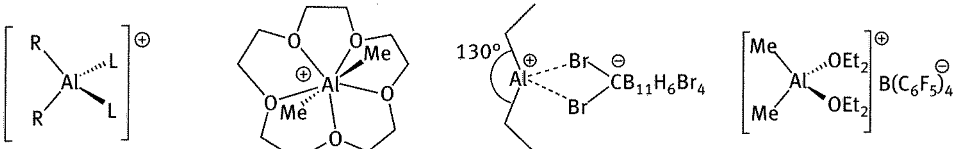
Box 1.5.2.1 ^{27}Al NMR spectroscopy

Although the ^{27}Al nucleus has a quadruple moment ($I = 5/2$) which leads usually to rather broad signals, ^{27}Al NMR spectroscopy can provide diagnostic information, particularly if the nucleus is in a highly symmetric environment. For example, on converting $MeAlCp_2$ into $AlCp_2^+$, the broad signal at $\delta(^{27}Al)$ 72.7 (half-width 250 Hz) is replaced by a much sharper one at δ −126.4 (half-width 30 Hz) [reference standard: $Al(acac)_3$].

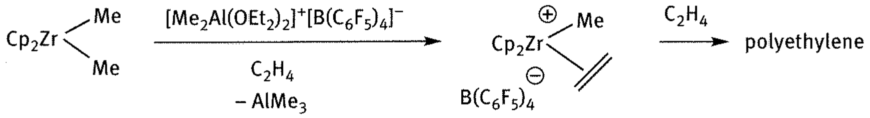
Cationic aluminium alkyls. The $[AlMe_2]^+$ cation is isoelectronic with $ZnMe_2$ but much more Lewis acidic, with a strong preference for forming tetrahedral adducts.

Since cationic Al alkyls can be expected to be strong electrophiles and good catalyst activators, several routes to their synthesis have been explored. Ligand-free $[AlMe_2]^+$ has been postulated as a transient species and attacks even extremely non-nucleophilic anions such as $[B(C_6F_5)_4]^-$. Stabilization by O- and N-donors has allowed the isolation of a number of cationic alkyls; these complexes are usually tetrahedral but higher coordination numbers are also possible. In the ion pair $[Et_2Al^+\cdots CB_{11}H_6Br_6^-]$ the Al cation is coordinated to two bromine atoms of the carborane anion to give a strongly distorted tetrahedral geometry; this compound is sufficiently electrophilic to initiate the carbocationic alkylation of benzene. The more stable complex $[Me_2Al(OEt_2)_2]^+$ can be made by protolysis of $AlMe_3$ with the strong Brønsted acid $[H(OEt_2)_2][B(C_6F_5)_4]$ and activates zirconium alkyls to give olefin polymerization catalysts.

$$AlMe_3 \xrightarrow[-\ Ph_3CMe]{[CPh_3][B(C_6F_5)_4]} \text{`}[AlMe_2]^+[B(C_6F_5)_4]^-\text{'} \longrightarrow Al(C_6F_5)_3 + BMe_3\uparrow$$

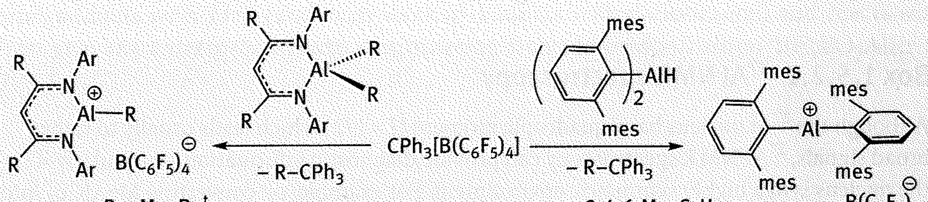


R = Me, Bu^t,
L = H_2NBut, Me_2NPh,
L_2 = TMEDA



Box 1.5.2.2 Low-coordinate organoaluminium cations

Low-coordinate organoaluminium cations are accessible provided sterically highly hindered ligands are employed—a general strategy for the synthesis of compounds with low coordination numbers and often unusual bonding patterns. The $[Al(aryl)_2]^+$ cation shown in the following schematic is almost linear; it initiates the oligomerization of 1-octene. The synthesis and stability of such ions depends on the use of non-coordinating perfluorophenylborates.

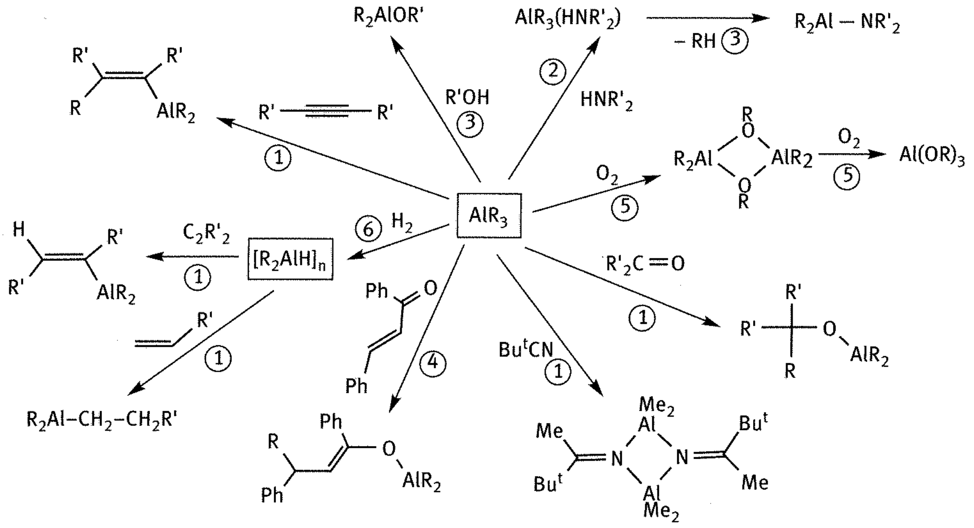


R = Me, Bu^t
Ar = 2,6-$Pr^i_2C_6H_3$

mes = 2,4,6-$Me_3C_6H_2$

1.5.2.3 Reactivity

Aluminium alkyls react rapidly with water and other protic reagents. Since there is a large energy difference between Al–O and Al–C bonds (ca. 350 vs. 255 kJ mol^{-1}), these reactions can be highly exothermic and violent, and need to be conducted under inert gas with suitable precautions. The same is true of the reactions with air and oxygen; most aluminium alkyls and alkyl hydrides are highly pyrophoric. As expected, sterically highly hindered alkyls are less reactive, as are compounds where one alkyl ligand is replaced by a heteroatom, as in R_2AlX ($X = OR, O_2CR, NR_2, Cl$, etc.). The reaction pattern is as expected for polar $M^{\delta+}$–$C^{\delta-}$ bonds; the first Al–alkyl bond reacts much faster than the second and third.

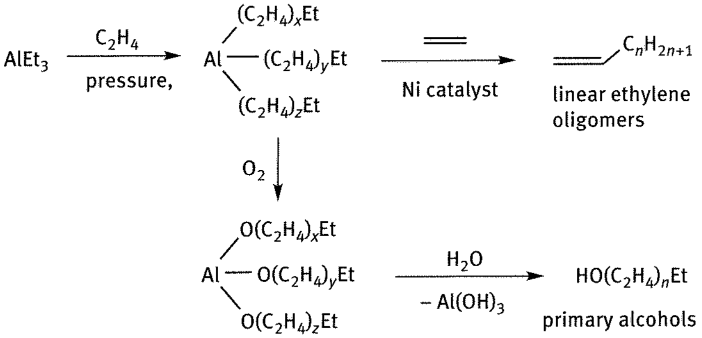


① 1,2-insertion; ② adduct formation; ③ protolysis; ④ 1,4-insertion; ⑤ oxidation; ⑥ hydrogenolysis

Of these reactions, two are remarkable and have led to industrial applications: the insertion of olefins into Al–C bonds ('**Aufbau reaction**', K. Ziegler), and the reaction with oxygen. Under pressure, ethylene inserts repeatedly into the Al–C bonds to give oligomers. Treatment with ethylene in the presence of a nickel catalyst releases oligomeric 1-alkenes, a valuable industrial starting material. Alternatively, the aluminium alkyl can be exposed to dry oxygen, which inserts into the Al–C bonds and converts the alkyls into aluminium alkoxides. Subsequent hydrolysis generates *primary* alcohols with 4–30 C atoms, i.e. within the range required for surfactants and washing powders, so-called **Ziegler alcohols**. It is important that the alcohols are primary and branch-free, since only linear alcohols are readily biodegradable.

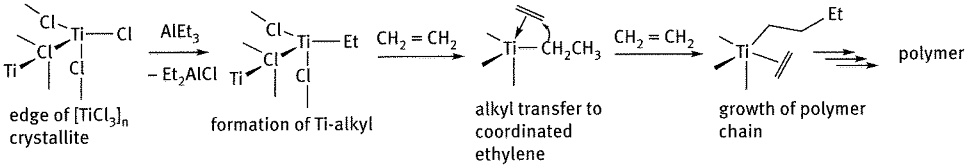
Aufbau reaction

For a time (1950–60s) surfactant alcohols made by the hydration of terminal alkenes were used; however since these were secondary (Markovnikov) products, their slow decay led to accumulation in waste water and persistent environmental problems.



Ziegler–Natta polymerization

Another reaction that is exploited in large scale industrial processes is the **alkylation** of transition metal chlorides by $AlEt_3$ or $AlEt_2Cl$. Treatment of $TiCl_4$ with $AlEt_3$ is the basis of highly effective catalysts for the polymerization of ethylene and propene (**Ziegler–Natta polymerization**, see Section 3.5.1). The key reaction is the replacement of a surface chloride ligand by ethyl, generating the Ti-alkyl groups necessary for the polymerization process:



A large proportion of the world's polyolefin production (of the order of 150 million tons annually, 2010 estimate) is based on Ziegler–Natta processes and requires the synthesis of $AlEt_3$ on a very substantial scale.

The hydrolysis of aluminium alkyls leads to so-called **aluminoxanes**. The simplest are oxo-bridged compounds $R_2Al–O–AlR_2$. As the hydrolysis proceeds further, compounds with one alkyl group per Al and more complex structures are obtained. The hydrolysis product of $AlMe_3$, **methylaluminoxane (MAO)**, is widely used in industry as a **catalyst activator** for certain types of olefin polymerization catalysts. It is an amorphous glassy substance of unknown structure and contains some associated $AlMe_3$. The reaction is usually given by the equation:

$$n\,\mathrm{AlMe_3} + n\,\mathrm{H_2O} \longrightarrow \left[\overset{\mathrm{Me}}{\overset{|}{\mathrm{Al}}}-\mathrm{O}\right]_n + 2n\,\mathrm{CH_4}$$

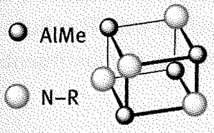
However, the product is methyl-rich, with a typical composition $[Al(CH_3)_{(1.4–1.5)}O_{(0.7–0.8)}]_n$, where $n \approx 6–30$. The main constituent is now thought to have the approximate composition $Al_{30}Me_{42}O_{21} \approx (MeAlO)_{21}(AlMe_3)_7$.

The Lewis acidity of aluminium alkyls and alkyl halides is the basis for another polymerization mechanism: the cationic polymerization of isoalkenes and vinyl ethers. Mixtures of AlR_3 or R_2AlX (R = Me, Et; X = Cl, Br, I) with Bu^tX or benzylic halides such as $PhCMe_2Cl$ generate equilibrium concentrations of *tert*-carbocations which initiate the industrially

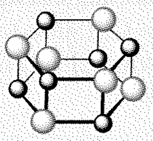
Box 1.5.2.3 The structure and function of MAO

As part of the catalyst formulation, MAO has several functions: (a) as an ***alkylating agent***, for the conversion of the catalyst precursor, a metal chloride, into a metal methyl complex; (b) as a ***Lewis acid*** for the activation of the catalyst precursor, by abstracting a halide or alkyl ligand and thus creating a vacant coordination site; (c) as an ***impurity scavenger***, to reduce catalyst poisoning. Since MAO must be used in large excess over the transition metal component in order to achieve adequate catalyst productivities, it may constitute over 50% of total catalyst costs. Numerous attempts have been made to elucidate its structure in order to improve its efficiency.

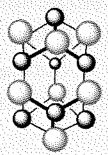
It is now thought that MAO forms a mixture of chains, rings, and cage structures. Methylaluminoxane itself has so far resisted all attempts to isolate and crystallize components; however, alkyl aluminium amides and the hydrolysis of higher Al alkyls, which give better defined products, serve as models for the structures that can be expected. The clusters are based on 4-, and 6-membered rings. The examples shown below are compounds where the solid state structures are known; in MAO there may be many larger structures and aggregates. The structural principles however are those found also in many silicate and aluminosilicate minerals.



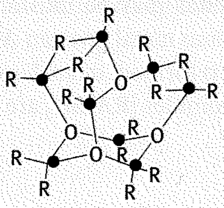
Al_4N_4



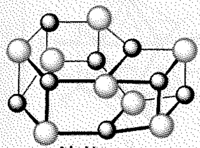
Al_6N_6



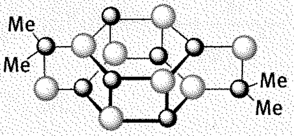
Al_7N_7



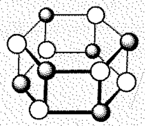
suggested tetrameric structure of $[Et_2Al–O–AlEt_2]_4$



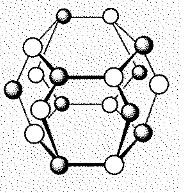
Al_8N_8



Al_8N_8

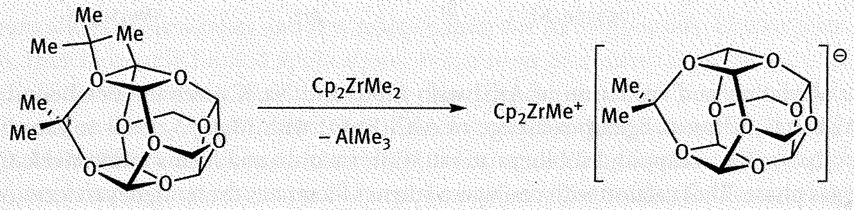


$Al_6O_6Bu^t_6$



$Al_9O_9Bu^t_6$

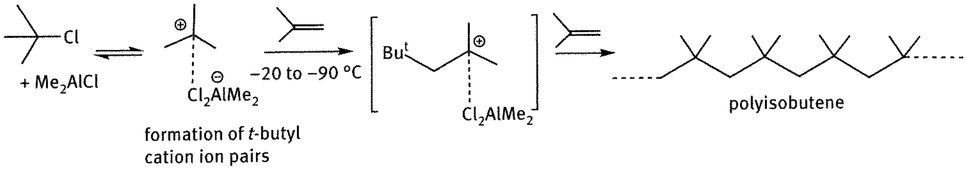
Calculations have shown that the clusters $(MeAlO)_8(AlMe_3)_2$ represent an energetically favourable model for some of the MAO structures involved in the activation of a metallocene catalyst, though in reality the MAO aggregates are likely to be more complex.



$(MeAlO)_8(AlMe_3)_2$ $[(MeAlO)_6(OAlMe_2)_3]^-$

important polymerization of isobutene. The reaction proceeds best at very low temperatures to suppress chain termination:

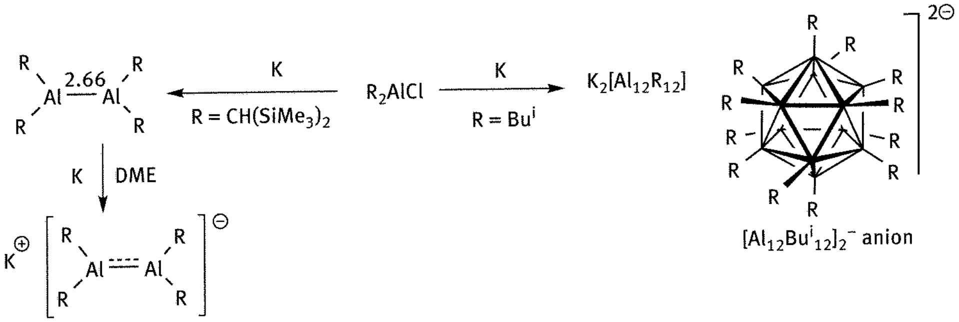
Isobutene–isoprene copolymers ('IIR butyl rubber') are impermeable to gases and mainly used as inner tubes of car tyres.

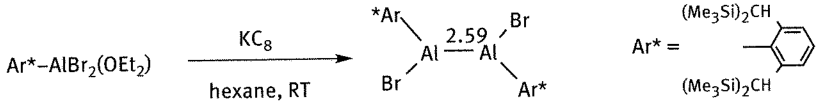


1.5.2.4 Aluminium Compounds in Low Oxidation States

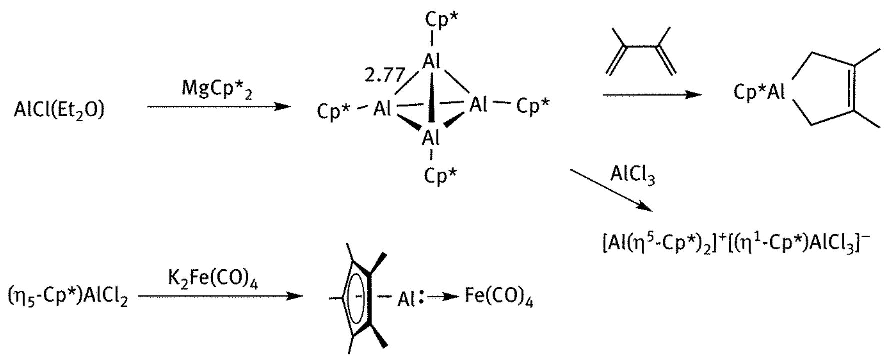
As a highly electropositive element, aluminium does not easily form compounds in low oxidation states. Halides of Al(I, II) are high temperature species that disproportionate under ambient conditions into Al(III) + Al(0), although toluene/NEt_3 or Et_2O solutions can be sufficiently stabilized to explore chemical reactions. Disproportionation is also prevented by sterically highly hindered ligands, i.e. the compounds are kinetically stabilized, even if oxidation to Al(III) is thermodynamically favoured. Al(I) compounds Al–R possess an electron pair and can act as 2-electron donors.

The chemical trends may be illustrated by the following examples. The reduction of R_2AlCl with potassium metal gives an Al(II) alkyl if $R = CH(SiMe_3)_2$, while with $R = Bu^i$ an icosahedral cluster is formed, in analogy to boranes. With suitably bulky aryl substituents, stable Al(II) aryl bromides $[RAlBr]_2$ are also accessible.





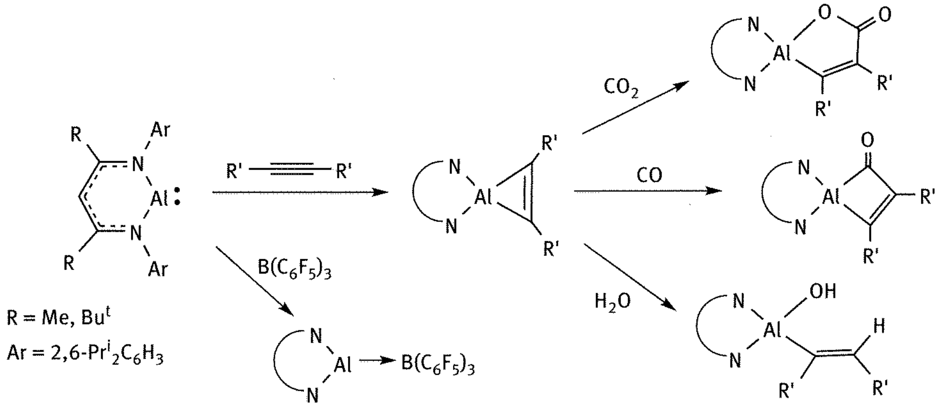
The alkylation and reduction of AlCl with $LiBu^t$ and Na/K gives the octahedral cluster $[Al_6Bu^t_6]^-$, whereas ligand exchange of $AlCl(Et_2O)$ with $MgCp^*_2$ leads to tetrahedral $Al_4(\eta^5\text{-}Cp^*)_4$. The compound sublimes at 140 °C in vacuum and forms **monomeric Cp*Al** in the gas phase. The reaction with conjugated dienes illustrates the tendency to form Al(III) products. Monomeric Cp*Al can also be generated in situ and trapped as a metal complex, e.g. with $Fe(CO)_4$:



Aluminium clusters

Depending on the reaction conditions and the bulky ligand, a series of nano-sized **clusters** could be characterized, such as $[Al_7R_6]^-$, $[Al_{12}R_6]^-$, $[Al_{69}R_{18}]^{3-}$, and $[Al_{77}R_{20}]^{2-}$ [$R = N(SiMe_3)_2$]. Their structures may be regarded as fragments of the crystal lattice of aluminium metal. Being aluminium and anionic, the clusters are highly sensitive and spontaneously combust on contact with air.

Bulky diketiminates ('nacnac' ligands) are also capable of stabilizing Al(I). The compounds oxidatively add acetylenes and form donor–acceptor complexes:



1.5.3 Gallium, Indium, and Thallium

Gallium alkyls are less polar and less reactive than the Al compounds. Unlike aluminium alkyls, they have only limited applications in synthesis or industrial processes, except for the use of $GaMe_3$ and $InMe_3$ in the vapour phase deposition of III–V semiconductor materials such as GaAs or InP in electronic devices (**metal–organic chemical vapour deposition, MOCVD**). GaAs is used in red light-emitting diodes. Organoindium compounds enjoy an increasing interest as part of organic synthesis protocols. Thallium trialkyls are unstable towards reduction. The stability of the +I and +II oxidation states increases down the group.

1.5.3.1 Compounds in the Oxidation State III

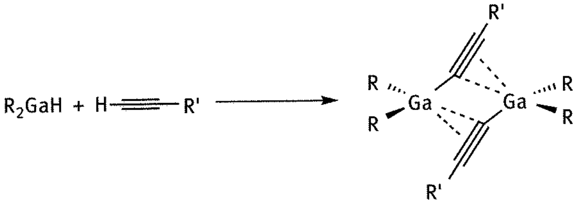
The metal trimethyls can be made from the halides by alkylation with Li or Mg reagents. $TlMe_3$ is also made from Tl(I) using MeI as oxidant. Iodomethane oxidizes TlMe to give Me_2TlI. Mixed-ligand compounds such as R_2Ga(alkynyl) are also accessible either by the salt method or from the hydrides R_2GaH and terminal acetylenes.

$$MCl_3 + 3\,LiR \xrightarrow{\text{hexane}} MMe_3 + 3\,LiCl$$

$$TlI + 2\,LiMe + MeI \longrightarrow TlMe_3 + 2\,LiI$$

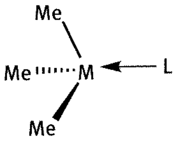
$$TlMe + MeI \longrightarrow Me_2TlI$$

$$TlX_3 + 2\,MeMgX \longrightarrow Me_2TlX + 2\,MgX_2$$



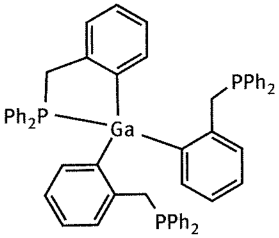
Unlike Al_2Me_6, $GaMe_3$, $InMe_3$, and $TlMe_3$ do not form dimers with 2e3c bonds; they are **monomeric** in solution and in the gas phase. In the crystal, too, they exist as **trigonal-planar** molecules, but each is weakly associated to a methyl group of a neighbouring molecule. The Tl–C bond is comparatively weak; $TlMe_3$ is light sensitive and decomposes, sometimes explosively, on heating to 90 °C. All three Ga, In, Tl trimethyls are considerably more sensitive to air and moisture than $HgMe_2$.

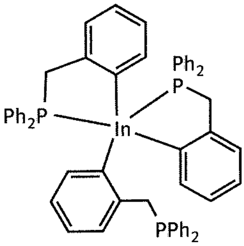
Gallium and indium dialkyl halides and pseudohalides Me_2MX form structures with bridging X, although there is a tendency towards higher coordination numbers, e.g. Me_2InCl is trigonal-bipyramidal via In···Cl···In associations. By contrast, Me_2TlI forms an ionic lattice with **linear** $[Me–Tl–Me]^+$ cations—the same geometry as isoelectronic $HgMe_2$.

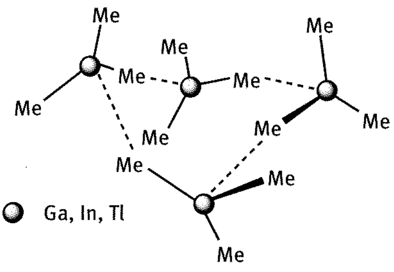


M = Ga,In,Tl

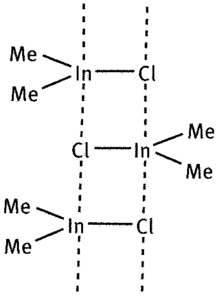
L = NMe_3, NCR, SR_2, PMe_3

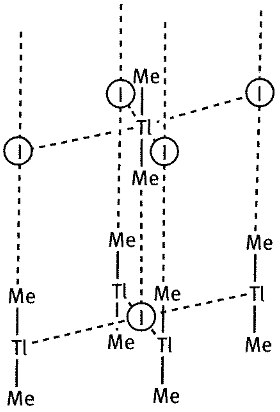






Me$_3$M in the solid state

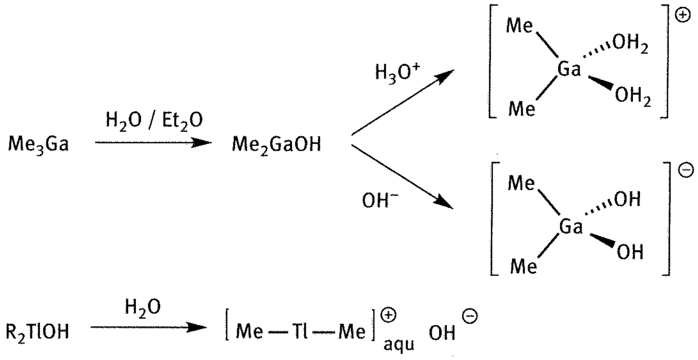




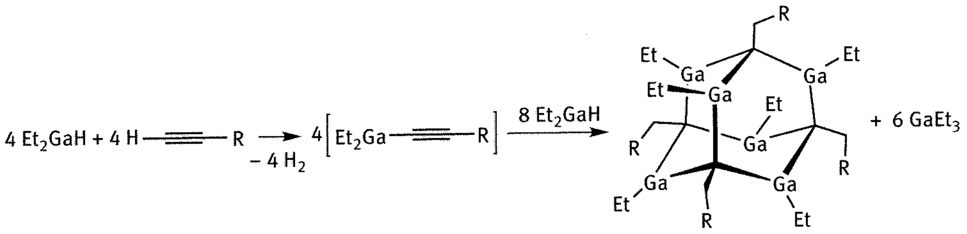
Me$_2$TlI in the solid state

The heavier elements form stronger adducts with soft donors such as phosphines and thioethers than does aluminium. The addition of LiR or other nucleophiles to Tl(III) alkyls gives the tetrahedral anions $[TlR_nX_{4-n}]^-$ (e.g. R = Me, Ph, C_6F_5; X = Cl, Br, I, NCS, etc.). While the Ga compounds are tetrahedral, indium shows a tendency to increase the coordination number due to its larger size, and five-coordinate complexes are formed.

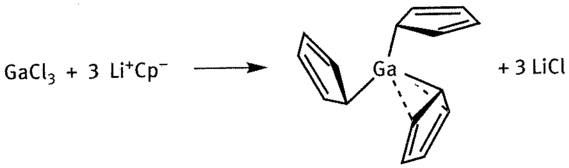
Whereas aluminium alkyls are pyrophoric and hydrolyse in a very exothermic reaction, the hydrolysis of $GaMe_3$ is much more controlled, and the tetrahedral aquo cation $[Me_2Ga(OH_2)_2]^+$, as well as the anion $[Me_2Ga(OH)_2]^-$ have been spectroscopically identified in solution. The thallium alkyl hydroxides R_2TlOH act as strong bases in aqueous solution.



The reaction of alkynes with an excess of alkylgallium hydrides leads not just to Ga–H addition to the C≡C triple bond but formation of a 'carba-gallane' with adamantane-type cage structure. This differs from analogous reactions of R_2AlH which form clusters with borane-like bonding.



Cyclopentadienyl compounds. $GaCp_3$ and $InCp_3$ are made from the halides by salt metathesis with LiCp or NaCp.

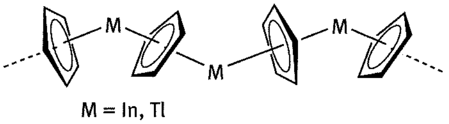


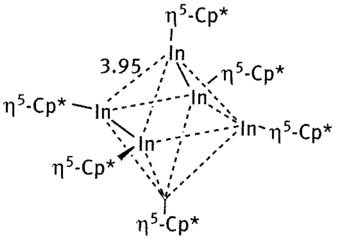
They contain η^1-bonded Cp ligands in a trigonal-planar molecule; there is a tendency towards π-interactions in the solid state. In the crystal, $CpGaMe_2$ has a Cp-bridged polymeric chain structure similar to $CpAlMe_2$.

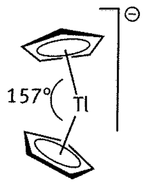
1.5.3.2 Ga, In, Tl Compounds in Low Oxidation States

Cyclopentadienyl compounds. The cyclopentadienyl complexes of Ga(I), In(I), and Tl(I) are synthetically more important than the M(III) Cp derivatives. TlCp is readily accessible from cyclopentadiene and a thallium(I) salt in the presence of a base, or from CpH and TlOH, as a yellowish-beige solid. Although in the crystal it is a coordination polymer with zigzag chain structure, it depolymerizes on heating in vacuum and can be purified by sublimation. Unlike most Cp^- salts, TlCp is stable to air and water. This makes it a convenient reagent for the transfer of Cp ligands to transition metal halides, particularly since the byproducts of these reactions, Tl(I) halides, are insoluble in water and easily removed. TlCp is a useful laboratory reagent for halide substitution from late transition metals (noble metal group), which themselves bind strongly to halide ligands.

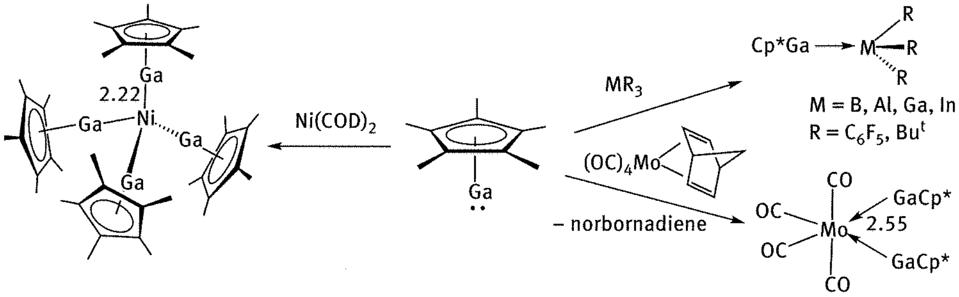
InCp has the same polymeric structure, with Cp–In–Cp angles of 128°; there are long In···In interactions (~4.0 Å) between the parallel chains. Unlike TlCp it is highly air-sensitive. In the gas phase, InCp is a monomer with η^5-bonded Cp. With increasing substitution of Cp the degree of association is reduced; for example, $In(C_5H_4Me)$ exists in solution as a monomer–dimer equilibrium. The pentamethyl-Cp derivatives GaCp* and InCp*, on the other hand, form a loose octahedral aggregate, $[MCp^*]_6$, with long M···M interactions of around 4 Å, whereas TlCp* is again an infinite polymer. The addition of $MgCp_2$ to TlCp gives salts of the $[TlCp_2]^-$ anion, a bent sandwich complex.



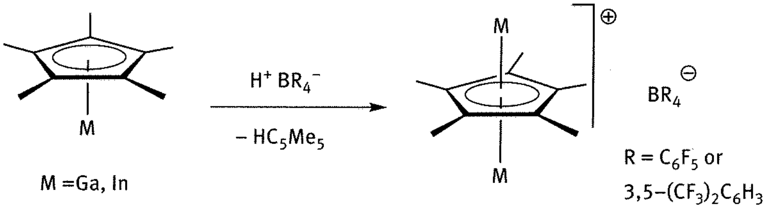




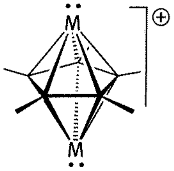
Ga(I) and In(I) Cp complexes have a pair of electrons which can act as a 2-electron donor towards Lewis acids and transition metals. Complexes with GaCp* ligands are known for a wide range of metals across the Periodic Table, including alkaline earth and lanthanide compounds. Some examples follow:



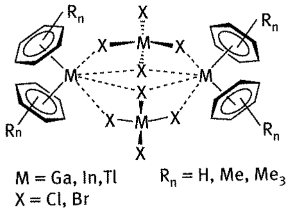
Careful protolysis of Cp*M gives bimetallic cations with an **inverse sandwich** structure:

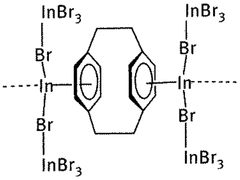


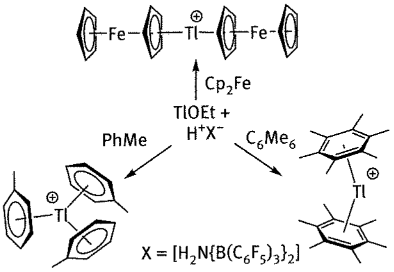
The structure can also be regarded as a *closo* cluster with *n* vertices and *n*+1 bonding electrons. Each M has a lone pair.



Arene complexes. Salts like $Ga^I[Ga^{III}X_4]$ are quite soluble in aromatic solvents, and a number of complexes of Ga^I, In^I, and Tl^I could be isolated where one or several arenes are η^6-coordinated to the M(I) ion. The arene bonding does not rely on donor–acceptor interactions, but is largely electrostatic. Calculations show that the metal ions impose no electronic geometric preferences and the sandwich structure can be distorted within wide limits. The number of coordinated arenes depends on their steric requirements as well as on the coordination power of the counter-anion (which competes for coordination sites). The stability of the complexes increases with increasing methyl substitution of the arene, in the order $C_6H_6 < C_6H_5Me < C_6H_3Me_3 < C_6Me_6$; i.e. electron-rich arenes coordinate more strongly and replace less electron donating ones. The stability of arene complexes decreases in the order $Ga^I > In^I > Tl^I$.



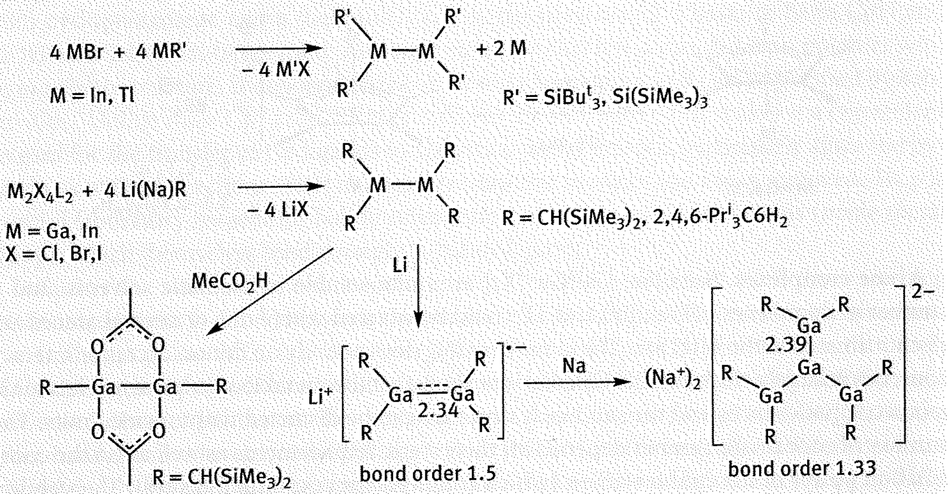




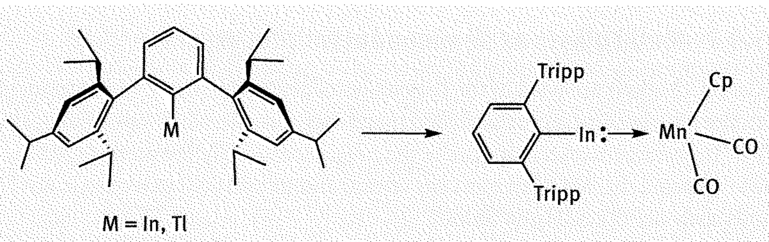
Box 1.5.3.1 Low-valent metal alkyls and aryls

The oxidation state II in Group 13 elements is thermodynamically unstable with regard to disproportionation into M(I) + M(III), and classical halides of the composition MX_2 are mixed-valence, $M^I[M^{III}X_4]$. However, the availability of relatively stable M(II) starting materials such as $Ga_2Br_4(dioxane)_2$ and $In_2Br_4(tmeda)_2$, has provided a route to a number of alkyls and aryls M_2R_4, where R is a very bulky ligand; these compounds are kinetically stabilized. These are the simplest examples of a large family of low-valent Ga, In, and Tl alkyls, many of which display unusual bonding patterns including varying degrees of π-bonding and **fractional bond orders**. For example, 1-electron reduction of M_2R_4 to the anion $[M_2R_4]^-$ shortens the M–M bond and increases the bond order to 1.5.

The reaction of TlCl with bulky LiR or NaR leads to disproportionation into $Tl^0 + Tl^{II}{}_2R_4$. It is one of many cases where the steric demand of the ligand seems to dictate the metal oxidation state. Low oxidation state Ga, In, and Tl complexes with very bulky R groups show a remarkable diversity of structures.

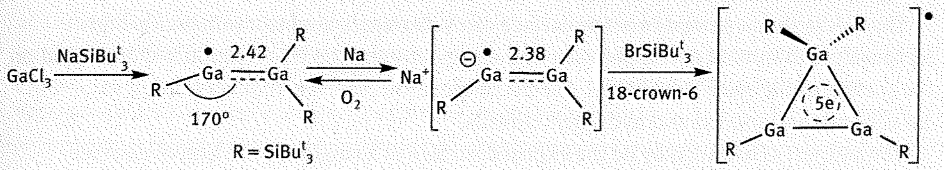


Indium(I) and thallium(I) compounds bearing the sterically extremely hindered 2,6-$(Tripp)_2C_6H_3$ ligand (Tripp = 2,4,6-tri-isopropylphenyl) are even monomeric in the solid state, an exceptional case of a metal with the **coordination number 1**. They act as 2-electron donors and form adducts with Lewis acids and transition metal complexes.

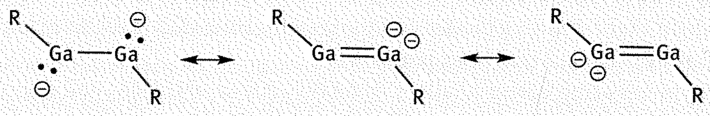


The reduction of Ga alkyls, aryls, and silyl derivatives is a route to a variety of **mixed-valence clusters**, from tetrahedral Ga_4R_4 to $Ga_{22}(SiBu^t_3)_8$ and $[Ga_{26}\{Si(SiMe_3)_3\}_8]^{2-}$ to the giant $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{3-}$. They can be understood as sections of the bulk metal lattice wrapped up and shielded by an envelope of hydrocarbon anions.

Low-valent gallium compounds with bulky ligands display bonding behaviour that challenges theoretical concepts. For example, the reaction of $GaCl_3$ with the 'super silyl' $NaSiBu^t_3$ gives the crystalline blue-black radical $Ga_2R_3^{\bullet}$, with a partial Ga–Ga π-bond. Further reduction with sodium metal leads to the deep red $[Ga_2R_3]^{\bullet-}$ radical anion, which undergoes 1-electron oxidation to the deep blue radical $Ga_3R_4^{\bullet}$, a ring with five delocalized electrons.



Reduction of the bulky aryl compound $RGaCl_2$ with sodium metal gives the dianion $[RGa–GaR]^{2-}$, with a very short Ga–Ga bond of only 2.32 Å [$R = 2,6\text{-}(Tripp)_2C_6H_3$]. The interpretation of the bonding in this compound has been controversial; it is probably best described by resonance structures with a strong Ga=Ga contribution:



III–V semiconductors

Box 1.5.3.2 Metal alkyls as semiconductor precursors

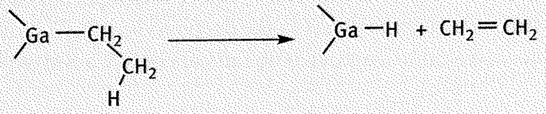
Volatile Group 13 alkyls are used in the deposition of crystalline III–V semiconductor films from the gas phase, in a process called metal-organic chemical vapour deposition = **MOCVD**. In these processes, vapours of the precursor, usually the methyls MMe_3, are carried into a heated reactor in an inert gas stream and mixed with gaseous Group 15 compounds such as PH_3, AsH_3, or $SbMe_3$.

$$GaMe_3 + AsH_3 \xrightarrow[400\text{–}800\ °C]{} GaAs + 3\,CH_4$$

$$GaR_3 + SbMe_3 \xrightarrow[500\text{–}600\ °C]{} GaSb + \text{hydrocarbons}$$

R = Me, Et

Metal ethyls decompose by β-H elimination:



The reactants are passed over the surface of a substrate heated to a sufficiently high temperature to initiate decomposition of the reagents, and the III–V product is deposited on the surface of the support material. The decomposition reaction involves homolysis of the M–C bonds and methyl and hydrogen radicals.

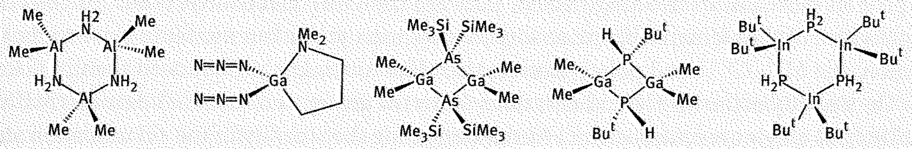
The support substrate may be the exposed surface of a single-crystal film of another semiconductor, and since silicon, III–V, and II–VI materials all crystallize as cubic phases with fairly similar lattice parameters, it is possible to continue the orientation of the supporting single crystal lattice into the newly deposited material, a process known as **epitaxial growth**. Different materials may thus be assembled, layer by layer, with varying thicknesses. In this way complex multi-sandwich structures of different semiconductors can be assembled, which are shaped into electronic devices. III–V materials convert electric energy into light (light-emitting diodes, LEDs): GaN for blue, GaP and GaAs (red), InGaN (green), or InGaP/AlGaInP (red **laser pointers**).

The same process using Group 12 alkyls, notably $ZnMe_2$ and $CdMe_2$, and chalcogenide precursors like H_2S, H_2Se, or Pr^i_2Te gives **II–VI** semiconductors (see Chapter 1.4).

The performance of semiconductors is strongly affected by impurities at sub-ppm levels; the incorporation of C, O, and N from the starting materials needs to be minimized to below-ppm levels, and ultra-high purity metal alkyls are required. Metal alkyls can be purified by formation of crystalline adducts with involatile phosphines or N-bases, followed by recrystallization to the required purity. Since adduct formation is reversible, the pure metal alkyls are released on heating.

Amine adducts of metal trimethyls are sometimes employed to improve their stability, even if these are less volatile. Internal chelates such as $R_2Ga(C_3H_6NMe_2)$ have been made for the same purpose. Compounds that incorporate both the Group 13 and 15 components in one molecule have the advantage of precisely controlled stoichiometry and greater stability (at the expense of lower volatility) and have been much studied. Some examples of M/E combinations that have been employed as single-source precursors for ME materials

(E = N, P, As, Sb) are shown in the following diagram. The same precursors can also be used for solution thermolysis in high boiling solvents for the preparation of nanoparticles and nanowires.



Key points

Group 13 elements are characterized by the dramatic differences between the lightest member, boron, a non-metal, and the heavier metallic elements. Boron compounds make strong, covalent B–C bonds and are important synthetic reagents. Trivalent Group 13 compounds are Lewis acids and are widely used in synthesis and catalysis. Aluminium alkyls have important large-scale applications in billion-dollar industrial processes. Al, Ga, and In alkyls are used in semiconductor production. The stability of the lower oxidation states increases down the group; monovalent organometallics MR have a lone electron pair and act as Lewis bases.

Exercises

1. Discuss the structures of (a) Al_2Me_6 and (b) $Al_2Cl_2Me_4$, and show which orbitals interact to form the bridges. What is the electron count per Al in each case?
2. Show the mechanism and reaction product of the hydroboration of 1-hexene with 9-BBN.
3. How does $AlMe_3$ react with $B(C_6F_5)_3$? Show the structures of the intermediates and the end product.
4. Show all reaction steps of the reaction of $GaMe_3$ with AsH_3.
5. What is meant by the 'Aufbau' reaction and how does it work? Show the steps.
6. Why does $Ph(Cl)B{-}NMe_2$ show two methyl signals in the ^1H NMR spectrum at room temperature?

1.6 Organometallic Compounds of the Carbon Group

Group 14 elements have four valence electrons and generally make four covalent bonds to give an octet electron configuration; they are therefore **electron-precise**. The electronegativities of the elements decrease slightly down the group but are fairly close to that of carbon; the $M^{\delta+}$–$C^{\delta-}$ bond polarization is therefore much less pronounced than in Group 13. The stability of the M–C bond decreases down the group, as does their heat of formation, and Pb(IV) alkyls are endothermic. At the same time the stability of the +II oxidation state increases.

The tetra-alkyls are non-Lewis acidic and stable to water and air; they are only weak alkylating agents. Lewis acidity increases if halide ligands are present. The elements from Si down the group are capable of increasing their coordination numbers to 5 and 6, and as the radii increase down the group, so does the tendency to undergo ligand exchange by extending the coordination sphere.

Coordination number	C	Si	Ge	Sn	Pb
4	0.15	0.26	0.39	0.55	0.65
6	0.16	0.4	0.53	0.69	0.78
Covalent radius	0.86	1.11	1.20	1.39	1.46

14
Si
28.086

1.6.1 Silicon Compounds

1.6.1.1 Synthetic Methods

Silicon alkyls are produced industrially by the direct oxidation of copper-activated elemental silicon (the *Rochow–Müller* process):

$$\mathrm{MeCl + Si/Cu \xrightarrow[300\ ^{\circ}C]{} Me_{\mathit{n}}SiCl_{4-\mathit{n}}}$$

The reaction proceeds by oxidative addition of Me–Cl to Si surface atoms. The resulting mixture of methylsilicon chlorides is separated by distillation. Me_2SiCl_2 is produced on a million ton/year scale.

More specialized alkyl- and arylsilanes can be made by salt metathesis. Specific alkyl silicon halides are also accessible by oxidative cleavage of Si–Si bonds with halogens:

$$\mathrm{R_{4-\mathit{n}}SiCl_{\mathit{n}} + \mathit{n}\ R'MgCl \xrightarrow[Et_2O]{} R_{4-\mathit{n}}SiR'_{\mathit{n}} + \mathit{n}\ MgCl_2}$$

$$\mathrm{R_3Si{-}SiR_3 + X_2 \xrightarrow{} 2\ R_3SiX \qquad X = Br, I}$$

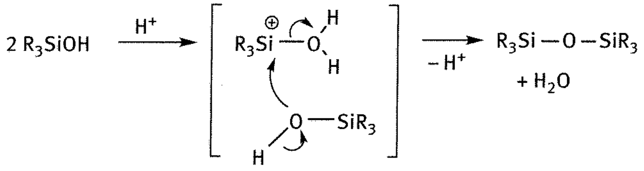
1.6.1.2 Reactivity

Alkylsilanes SiR_4 lack low-lying acceptor orbitals, which means they are unable to coordinate water and are therefore resistant to hydrolysis and chemical attack (very unlike $AlMe_3$, for example). Since the Me_3Si group is comparable in size to a *t*-butyl substituent, it is often introduced to provide steric bulk in compounds, as well as additional stability, and is often used as ligand substituent in organometallic complexes.

Alkyl silicon halides are susceptible to nucleophilic attack. Hydrolysis under basic conditions gives silanols R_3SiOH, which in the presence of H^+ will condense to give alkyl **siloxanes** (silyl ethers). The hydrolysis of R_2SiCl_2 gives silicon diols, which readily condense to polymers $[-R_2Si-O-]_x$, known as **polysiloxanes** or **silicones**.

Note differences in spelling: silicon the element, silicone the polymer

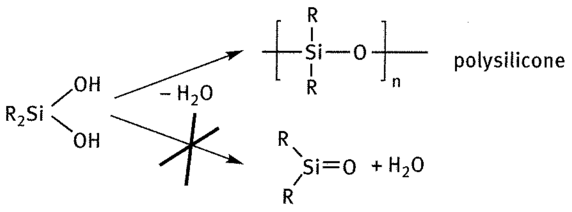
$$R_3SiCl + OH^- \longrightarrow R_3SiOH + Cl^-$$

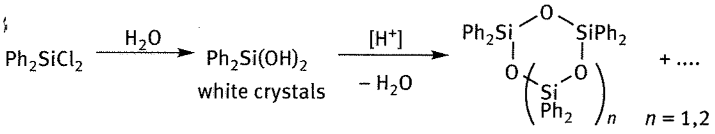


$\mathrm{Bu^tMe_2SiCl}$ is frequently used as protecting group precursor in organic synthesis. Removal of the silyl group by hydrolysis gives the silanol $\mathrm{Bu^tSiMe_2OH}$, which can be recycled and converted back to the chloride by reaction with thionyl chloride:

$$\mathrm{Bu^tSiMe_2OH} + Cl_2S{=}O \longrightarrow \mathrm{Bu^tSiMe_2Cl} + HCl + SO_2$$

Dialkylsilane diols $R_2Si(OH)_2$ condense very easily (unless the R groups are bulky, as in the fairly stable $\mathrm{Bu^t{}_2Si(OH)_2}$). The hydrolysis of Ph_2SiCl_2 gives $Ph_2Si(OH)_2$ as colourless crystals, which on heating condense to ring structures and/or polymers. Silicon **does not** form ketone-like Si=O bonds:





Box 1.6.1.2 Silicone polymers

Silicone polymers have a low barrier for conformational change and remain soft and flexible even at high molecular weights. They are water repellent, resistant to weathering and ultraviolet irradiation, and non-toxic. Combined with their chemically inert nature, this makes silicones suitable for medical applications (plastic surgery, **silicone implants**). Cross-linking silicone polymers can be achieved by heating with benzoyl peroxide or hydrosilylation, to give elastomers (**silicone rubbers**). They find applications as electrical insulators, gaskets, sleeves, tubing, and medical applications including heart valve implants. Silicones are also used as oils, lubricants, and as foam retardants (fermentation processes, sewage treatment). Phenyl-containing **silicone resins** are made by co-hydrolysis of $PhSiCl_3$ and $PhSiMeCl_2$, for applications as insulators in electrical equipment and machinery.

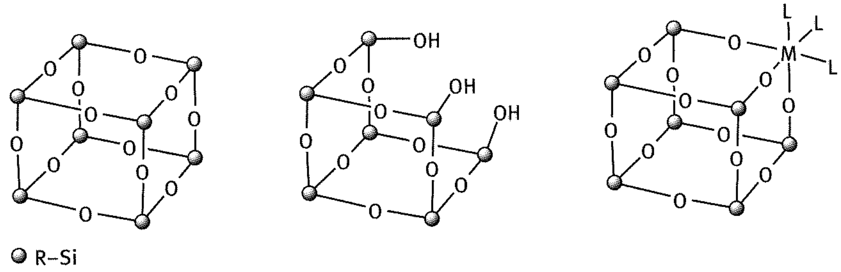
The condensation of acetate-terminated silicone oligomers leads to **silicone rubbers**. The compounds contain the hydrolytically labile triacetate $RSi(OAc)_3$ to provide a cross-linked polymer network which can no longer change shape when set (***bathroom sealant***).

The condensation of $Me_2Si(OH)_2$ leads to silicone polymers with chain and ring structures. In the presence of H^+ as catalyst, the formation of Si–O–Si linkages is **reversible**, so that cyclic or oligomeric siloxanes can easily be converted into high molecular weight polymers on treatment with catalytic amounts of strong acids. This method can be preferable to the hydrolysis of chlorosilanes, since the evolution of HCl is avoided. The molecular weight of silicone polymers can be controlled by adding chain terminating end groups, e.g. addition of $(Me_3Si)_2O$ leads to $-SiMe_3$ terminated polymers, and the molecular weight decreases with increasing $SiMe_3$ content of the polymerization mixture.

Silicones

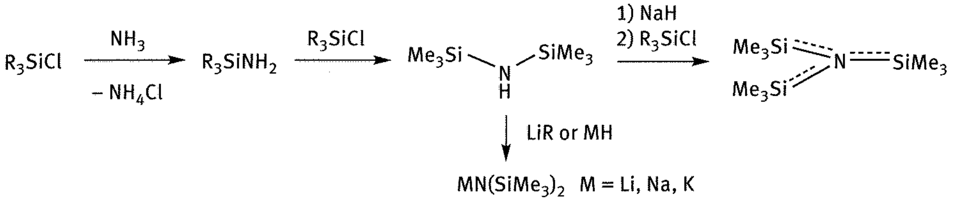
Silicones of lower molecular weight give **silicone oils**, widely used as heat transfer fluids. Some grades have low viscosity even at very low temperatures. Due to the very high thermodynamic stability of the Si–O bond, these compounds are thermally very stable and have a high flash point; they are therefore resistant to catching fire on heating, unlike paraffin oils.

The controlled hydrolysis of $RSiCl_3$ gives cage compounds, the so-called **silsesquioxanes** $R_8Si_8O_{12}$. Incompletely condensed compounds with remaining OH functionalities also exist; they can be used to incorporate transition metal complexes and have been studied, for example, as models for metal–O–Si interactions in silica-supported catalysts.

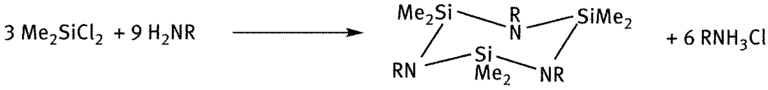


The reaction of silyl chlorides with ammonia leads to **silylamines** (silazanes), $H_{3-n}N(SiMe_3)_n$. Deprotonation of hexamethyldisilazane gives metal amides $MN(SiMe_3)_2$

(M = Li, Na, K) which are frequently used as sterically hindered, non-nucleophilic bases in synthesis, and since the M–N bond is readily protolysed, they are convenient starting materials for numerous metal complexes.



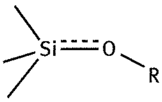
The aminolysis of R_2SiCl_2 leads to cyclosilazanes.

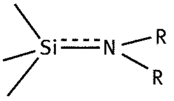


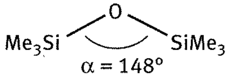
Si–E π-bonding

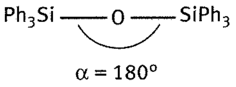
Si–O, Si–N bonding. Silicon bonded to O or N forms weak **π-interactions** with the lone pairs on the heteroatoms. This lowers the basicity of the heteroatoms and widens the Si–O–Si or Si–N–Si angles; for example, the angle in $(Me_3Si)_2O$ is 148°, substantially wider than the tetrahedral angle of 109°. Si–O–Si moieties have a **very low barrier of inversion**—a linear Si–O–Si arrangement ($\alpha = 180°$) is only slightly above the ground state. This flexibility is reflected in the mechanical properties of silicone rubber.

For the same reason, $HN(SiMe_3)_2$ and $N(SiMe_3)_3$ are **planar**, unlike alkyl amines such as $HNBu^t_2$ and NEt^t_3 which are pyramidal. Bis(silyl) amines and amides are therefore **poor nucleophiles**. Si–O π-interactions are also the reason why silanols are stronger acids that alcohols—the R_3SiO^- anion is better delocalized.







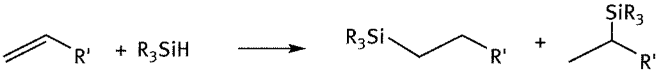


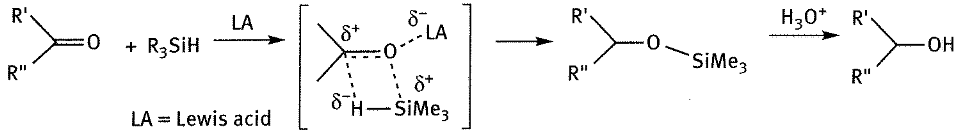
Silanes. The reduction of chlorosilanes with $LiAlH_4$ gives the corresponding silicon hydrides (**organosilanes**).

$$2\ R_2SiCl_2 + LiAlH_4 \longrightarrow 2\ R_2SiH_2 + LiAlCl_4$$

(R = alkyl, Ph)

Triorganosilanes R_3SiH are used for the **hydrosilylation** of alkenes, mediated by platinum catalysts. The hydrosilylation of C=O functions is thermodynamically favoured because it replaces weak Si–H by strong Si–O bonds; the reaction is facilitated by Lewis acids.

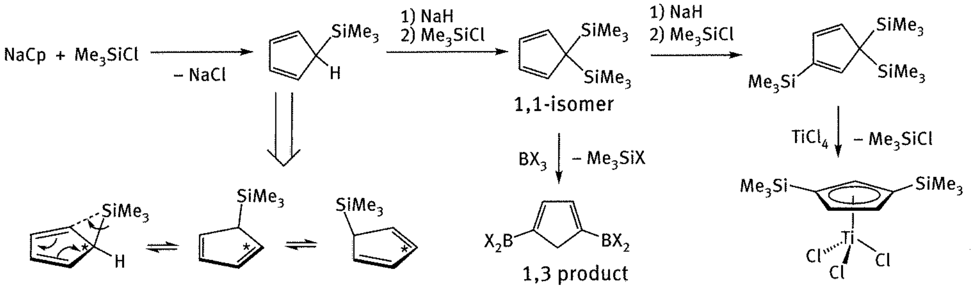




Cyclopentadienyl compounds. The reaction of NaCp with Me_3SiCl gives Me_3SiCp. In all these Si(IV) compounds Cp is η^1-bonded. Multiple deprotonation–silylation sequences lead to bis- and tris-silyl Cp derivatives. Formation of the 1,1-bis(silyl)Cp isomer is preferred. However, migration of the silyl substituent over the π-system is facile (**1,2-metallotropic shift**), and 1,1-bis(silyl)Cp leads to 1,3-substitution products. $SiMe_3$ substituents exert a strong +I effect and, apart from increasing the effective size of a Cp ligand, also enhance its electron donor character.

Whereas cyclopentadiene itself undergoes fast Diels–Alder dimerization, silyl–Cp compounds are slow to dimerize.

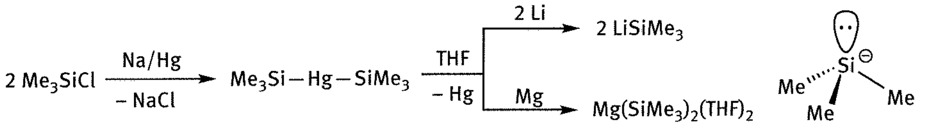
Cyclopentadienes with 1–4 $SiMe_3$ substituents are often used as sterically hindered Cp ligands in transition metal chemistry. The reaction with Lewis acidic transition metal chlorides proceeds with elimination of volatile Me_3SiCl and is a convenient salt-free method of complex preparation, since the by-product can simply be pumped off under vacuum.



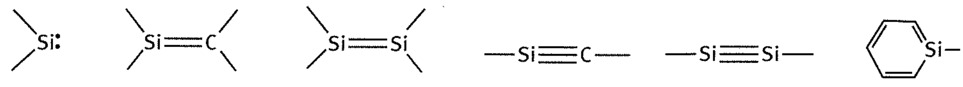
1.6.1.3 Compounds of Low-Valent Si

Si(II) Silyl anions R_3Si^- contain silicon in the oxidation state +II. These reagents are accessible by the reduction of alkyl silicon halides with sodium amalgam and can be used to make metal–Si bonds. Li and Mg silyl complexes can be made by transmetallation from $Hg(SiMe_3)_2$.

Silyl anions are **pyramidal** and have a **high barrier of inversion**.



There has been much interest in the silicon analogues of many of the compounds and intermediates familiar from the chemistry of carbon; notably alkenes, alkynes, carbocations, radicals, and carbenes. Whereas Period 2 elements like C, N, and O form multiple bonds readily through strong π-interactions of their p_z orbitals, the much higher energy difference between s- and p-orbitals and the larger size of the heavier elements makes π-bonds much weaker. Si=Si and Si=C double bonds can therefore only be generated under exceptional circumstances, and very bulky substituents have to be employed to provide the degree of kinetic stabilization necessary for their isolation under ambient conditions. Sterically unprotected species such as silylenes R_2Si, silenes $R_2Si{=}CH_2$, silynes $RSi{\equiv}CH$ (R = H, Me), and silabenzene C_5SiH_6 can be generated only at very low temperatures using matrix isolation techniques and characterized spectroscopically. They may also be inferred from their follow-on products, such as dimers or oligomers, or trapped with suitable reagents; for example, silylenes can form isolable transition metal silylene complexes $L_nM{=}SiR_2$.

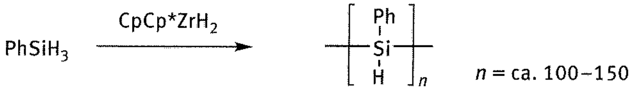


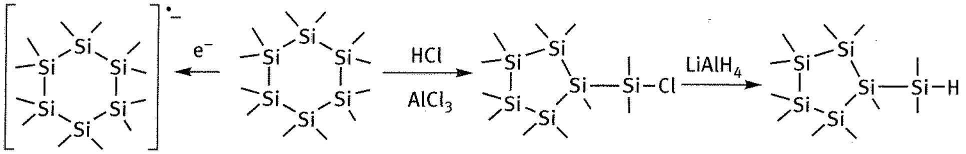
silylene silene di-silene silyne di-silyne silabenzene

$[R_2Si]_n$. The reduction of chlorosilanes $Cl(SiMe_2)_6Cl$ with sodium–potassium alloy gives oligosilanes. Cyclosilanes can be chlorinated and converted to Si–Cl and Si–H derivatives. The dehydrocoupling of silanes in the presence of Ti or Zr catalysts leads to polymeric silanes.

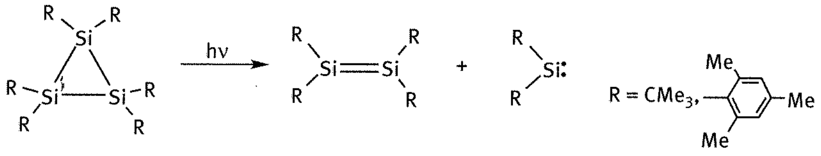
Reduction of dialkylcyclosilanes gives coloured radical anions, e.g. deep blue $[(SiMe_2)_5]^{\bullet-}$ or yellow $[(SiMe_2)_6]^{\bullet-}$.

$$Me_3SiCH_2Cl + Cl(SiMe_2)_6Cl \xrightarrow[\text{toluene}]{\text{Na/K}} Me(SiMe_2)_nMe \quad n = 10, 16, 22$$

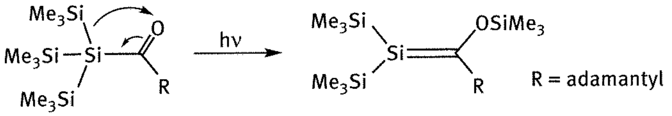

$$PhSiH_3 \xrightarrow{CpCp^*ZrH_2} \left[\begin{array}{c} Ph \\ | \\ -Si- \\ | \\ H \end{array} \right]_n \quad n = \text{ca. } 100\text{–}150$$



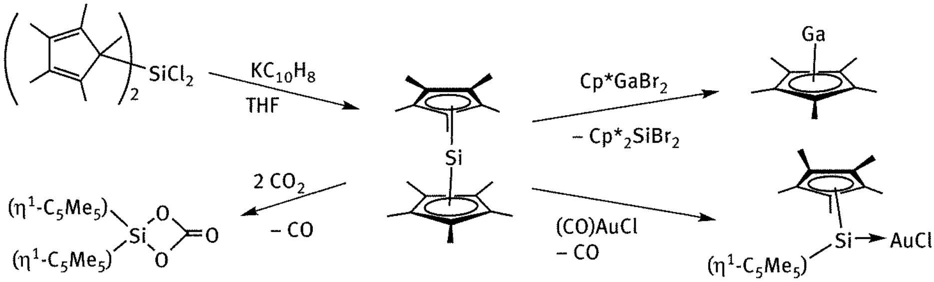
The photolysis of sterically hindered trisilanes Si_3R_6 gives disilenes plus silylene; the latter dimerizes to give more disilene. The reaction is fairly general and works for alkyl and aryl compounds.



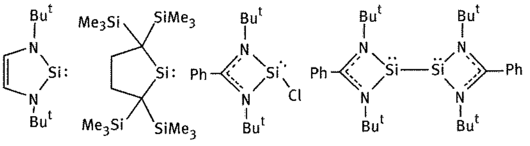
The first example of a silene was prepared by the photochemical rearrangement of an acylsilane. Again steric hindrance is the key to stability. The Si=C bond is short compared to Si–C (1.76 vs. 1.9 Å).

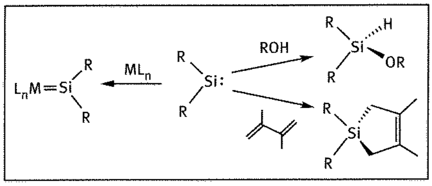


The reduction of $(\eta^1\text{-Cp}^*)_2SiCl_2$ with potassium naphthalide gives the **silicocene** $Si(\eta^5\text{-Cp}^*)_2$. As a monomeric Si(II) species the compound is highly air-sensitive, with a strong thermodynamic driving force towards oxidation to Si(IV). It acts as a 2-electron donor to metal complexes and is so oxophilic that it abstracts O from CO_2.



A number of different types of silylenes have now been isolated and structurally characterized; all undergo oxidative addition to form Si(IV) compounds. Silylenes act as 2-electron donors in transition metal complexes and may give either terminal ($L_nM{=}SiR_2$) or bridged complexes of the type $L_nM(\mu\text{-}SiR_2)_2ML_n$.





$[RSi]_n$. The reduction of alkyl silicon halides $RSiX_3$ with strong reducing agents (e.g. Na/naphthalene or Na/K alloy) leads to Si–Si bonded clusters Si_nR_n ($n = 4$–8). Larger substituents R favour smaller clusters. Si_4R_4 is analogous to the hydrocarbon, tetrahedrane C_4H_4.

Silyl radicals and silyl cations. Photolysis of R_3Si–H or $Hg(SiR_3)_2$ gives silyl radicals $R_3Si^\bullet$. These are **pyramidal**, unlike carbon radicals $R_3C^\bullet$ which are trigonal-planar.

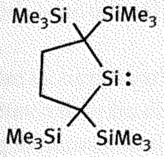
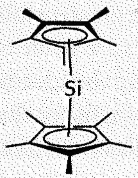
Silyl cations R_3Si^+ have attracted much interest as analogues of carbocations. However, they are much more difficult to generate and are extremely strong Lewis acids. The preferred method is the reaction of mono-silanes with CPh_3^+ salts of non-coordinating anions in arene solvents:

$$3\ Ar_2(Me)Si\text{–}H + 2\ CPh_3^+ \rightarrow 2\ Ph_3CH + Me_3SiH + 2\ Ar_3Si^+$$

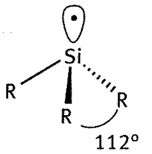
Silyl cations give adducts with solvents including toluene, interact with even extremely weakly coordinating anions, and tend to be **pyramidal** (unlike carbocations); a trigonal-planar geometry is only obtained with sterically highly hindered aryl substituents, as in $[Si(C_6H_2Me_3\text{-}2,4,6)_3]^+$. Halide- and hydride-bridged cations are also known. The reagent '$[Et_3Si]^+[B(C_6F_5)_4]^-$', often used as a very strong electrophile, contains the $[Et_3Si\text{–}H\text{–}SiEt_3]^+$ ion.

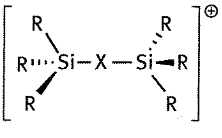
Box 1.6.1.3 ^{29}Si NMR spectroscopy

The ^{29}Si nucleus has a spin of ½. It covers a wide chemical shift range of nearly 1000 ppm and provides information about the electronic environment of the ^{29}Si nucleus. The two extremes are represented by Si(II) compounds with different degrees of donor interactions; see the following table. The chemical shifts of silylium cations SiR_3^+ are a diagnostic indicator of their planarity; in most compounds formulated as $[SiR_3]^+X^-$ the Si cations are four-coordinate and show less positive shifts.

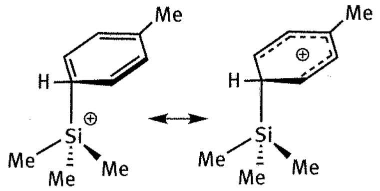
Compound	δ^{29}Si	Solvent	Compound	δ^{29}Si	Solvent
Me3SiOTf	43.7	CD_2Cl_2	$Et_3Si+[CB_{11}H_6Br_6]^-$	111.8	solid state
$Mes_3Si+[CB_{11}H_6Br_6]^-$	226.7	solid state	$MeR^*{}_2Si–Si+Bu^t2$ $[B(C6F5)4]^-$	303.0	CD_2Cl_2
	+567.4	C6D6		−423	solid state

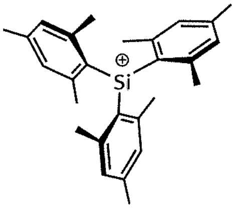
R = SiMeBu$^t{}_2$*





X = H, halide
R = Me, Et





1.6.2 **Germanium**

Organometallic compounds of Ge(IV) show a chemistry very similar to that of silicon. The main difference is the stability of the lower oxidation state: $Ge^{II}Cl_2$ is a stable starting material, whereas $SiCl_2$ is a high temperature species, so that Ge(II) compounds such as dialkyls R_2Ge are accessible. $Ge\{CH(SiMe_3)_2\}_2$ is stable and monomeric in solution, though it dimerizes to $R_2Ge{=}GeR_2$ in the crystal. The germanocenes $Ge(\eta^5\text{-}C_5R_5)_2$ (R = H, Me) can be made from $GeCl_2$; they have a tilted sandwich structure and are much less easily oxidized than $Si(\eta^5\text{-}Cp^*)_2$.

1.6.3 **Tin Compounds**

Organometallic compounds of tin resemble in principle the types of reagents and structures described for silicon. Key differences are however: (1) the much **larger radius** of tin, (2)

Applications

Box 1.6.3 Toxicity of tin(IV) reagents

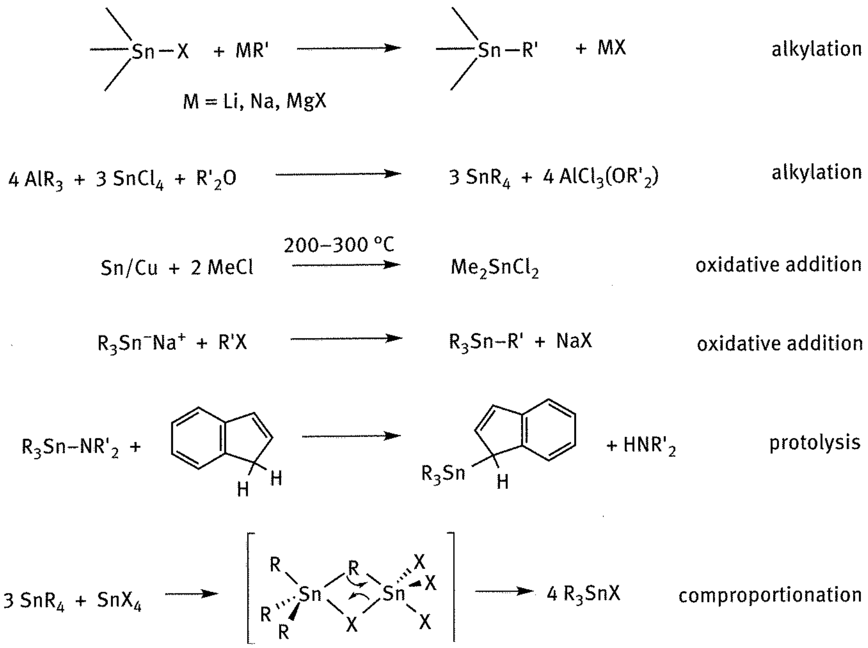
Some alkyl tin compounds are toxic, e.g. trimethyl and triethyl derivatives are toxic to mammals, while di-*n*-octyl tin compounds are not and have been used in food applications. The toxicity decreases with decreasing number of alkyl groups and increasing chain length. Tri-*n*-butyl tin compounds are toxic to fungi, shellfish, and crustaceans, and have been widely used in wood preservation and in anti-fouling paints for ocean-going boats and ships to prevent encrustation with marine organisms (which increase drag and hence increase fuel costs). Tin dialkyls are also used as stabilizers for PVC (polyvinyl chloride) plastics. Tin alkyl halides are therefore produced on an industrial scale. The release of tributyl tin compounds into the environment has however become problematic, and alternatives are being developed.

the consequently much **weaker Sn–element bonds**, (3) a tendency to adopt **coordination numbers 5–6**, and (4) the much greater **stability of the oxidation state +II**. The Sn–C bond is largely covalent, and tin alkyls are stable to air and water.

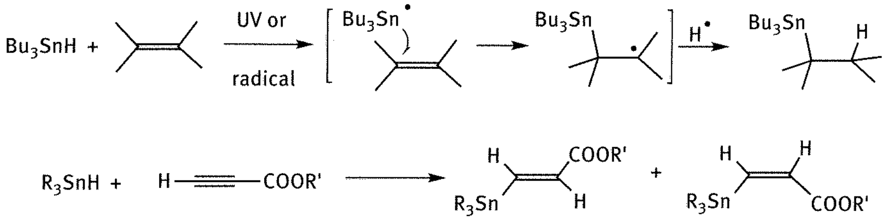
The weakness of the tin–carbon bond, combined with its resistance to hydrolysis, is being widely exploited in organic synthesis for the formation of C–C bonds. Tin alkyl derivatives do, however, have often an unpleasant odour and may irritate the skin, so that suitable precautions must be taken.

1.6.3.1 Synthesis of Tin Compounds

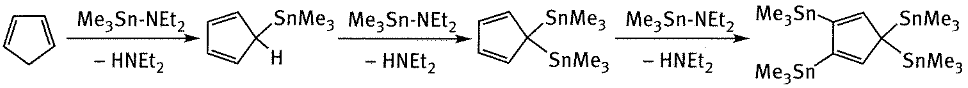
Tin alkyls and aryls can be prepared from $SnCl_4$ by: (1) standard **alkylation** methods, (2) directly from tin metal by **oxidative addition**, (3) by alkylation of the **SnR_3^-** anion, and (4) by **protolysis** of tin amides. Alkyl tin halides can also be made by (5) **comproportionation** of SnR_4 with SnX_4. These alkyl exchange reactions are facilitated by the Lewis acidity of Sn(IV) and its ability to form five-coordinate intermediates.



Another method for forming Sn–C bonds is the **hydrostannation** of alkenes. The Sn–H bond is weak and prone to homolysis; the relatively stable trialkyltin radical can be generated either by UV irradiation or adding a radical source such as AIBN. The method can be used for the preparation of alkyls with functional groups. The hydrostannation of alkynes gives vinyl tin compounds, usually as a mixture of *E* and *Z* isomers. As this is a radical reaction, functional groups such as OH are tolerated.



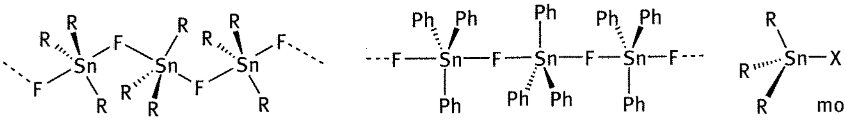
Sn(IV) cyclopentadienyl compounds can be made either from R_3SnCl and Na^+Cp^-, or from cyclopentadiene and tin amides, such as $R_3Sn–NEt_2$. The Cp rings in Sn(IV) compounds are η^1-bonded. Like the $SiMe_3$ analogues, Cp–Sn compounds are **fluxional**, and 1,2-metallotropic shifts of the SnR_3 group render all cyclopentadienyl-H atoms equivalent on the NMR time scale, resulting in a single resonance. $CpSnR_3$ compounds are more reactive Cp transfer agents than their Si analogues and are used to make transition metal Cp complexes.



1.6.3.2 Structures of Sn(IV) Compounds

Tin tetra-alkyls and aryls SnR_4 are tetrahedral, electron-precise, non-Lewis acidic, and dissolve readily in non-polar solvents. Tin organometallics $R_{4-n}SnX_n$ with more electron-withdrawing substituents X such as halide or oxide tend to form five- or six-coordinate adducts, either with themselves or with donor ligands L, depending on the steric requirements of the R and L ligands. They differ in this respect significantly from the Si analogues which tend to be monomeric and are much more volatile; this difference has consequences for synthetic workup procedures. Tri-alkyl tin fluorides with small R groups are **coordination polymers**; they may adopt zigzag or linear structures, depending on the size of R, and are poorly soluble, which allows their facile removal from organic reaction mixtures. They can be converted into more soluble and reusable R_3SnX (X = Cl, Br) by refluxing with NaX in THF. Bulkier ligands lead to monomeric compounds, including some fluorides. Whereas Me_3Si esters are volatile, Me_3Sn carboxylates form associated structures.

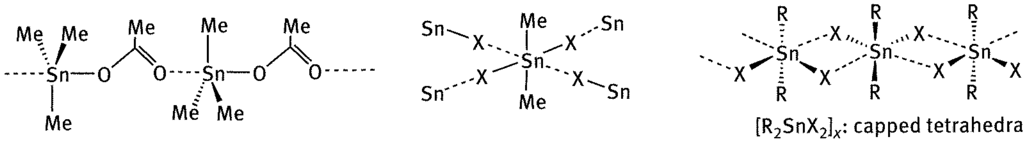
The carboxylate bonding is asymmetric, with a strong and a weak Sn–O interaction. The structural diversity for various classes of tin compounds is illustrated in the following diagram:



$[Me_3SnF]_x$: zigzag

$[Ph_3SnF_x$: linear polymer

monomeric:
R = Ph, X = Cl
R = Cy, X = F

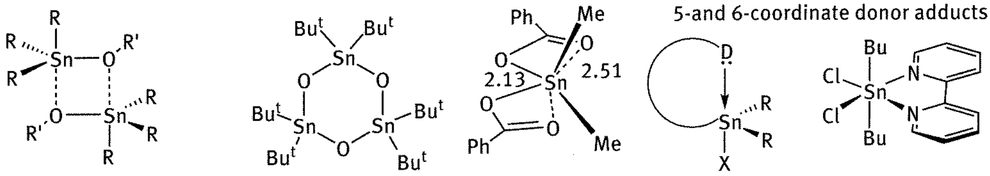


$[Me_3Sn(OAc)]_x$

$[Me_2SnF_2]_x$: sheet structure

$[R_2SnX_2]_x$: capped tetrahedra or 'distorted octahedra'

5-and 6-coordinate donor adducts:



alkyl tin hydroxides and alkoxides (R' = H, Me)

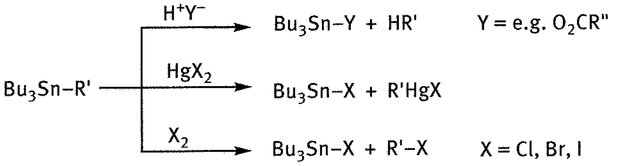
alkyl tin oxide

alkyl tin dicarboxylate; bi-capped tetrahedron

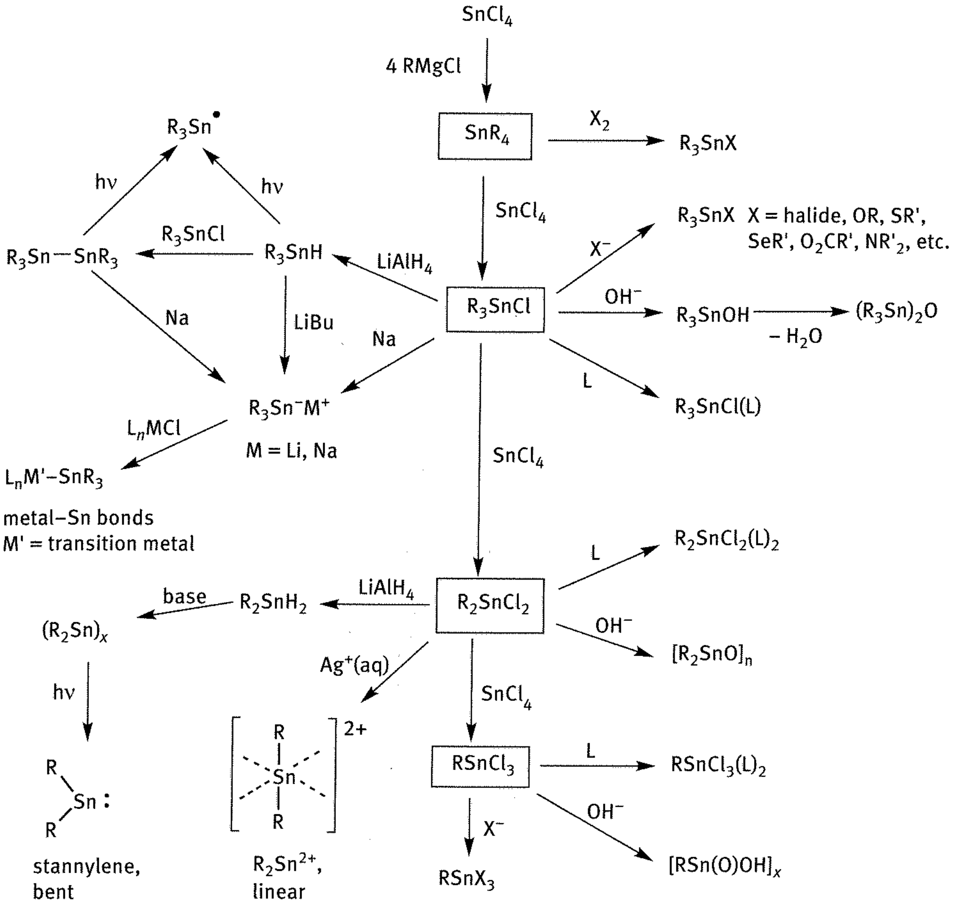
D trans to X = halide

1.6.3.3 Reactivity of Tin Compounds

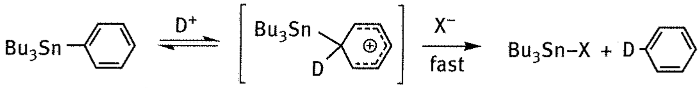
Organometallic tin reagents $R_{4-n}SnX_n$ display the range of reactions typical of metal halides: ligand substitution, reduction, hydrolysis, and the formation of coordination complexes. The ligand exchange reactions are facilitated by the ready formation of five- and six-coordinate intermediates. Characteristic differences between Sn and Si are: (1) the facile reduction to thermally stable stannyl anions $[R_3Sn]^-$ (Sn^{II}) which are strong nucleophiles, and (2) the tendency to form $R_3Sn^\bullet$ radicals (see general reaction scheme).



The main classes of tin compounds are interlinked, as shown in the following reaction scheme:



The Sn–C bond is cleaved by electrophiles, such as H^+, metal ions, or halogens. Bonds to sp^2-hybridized carbon react more readily than sp^3-C, since attack at sp^2-C can lead to a delocalized cationic intermediate. The order of reactivity is Ph > $PhCH_2$ > CH_2=CH > Me > higher alkyl.

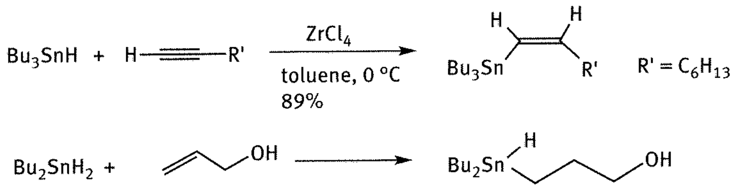


Allyltin compounds are more reactive than alkyls; e.g. $Sn(CH_2CH{=}CH_2)_4$ reacts with carboxylic acids under substitution of all four allyl groups, and the reaction with LiMe is a good way of producing salt-free allyl lithium reagents:

$$Sn(CH_2CH{=}CH_2)_4 + 4\ LiR \rightarrow SnR_4 + 4\ LiCH_2CH{=}CH_2$$

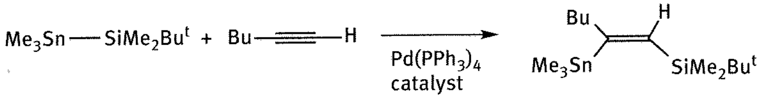
Sn–H + C=C

Hydrostannation. The addition of Sn–H across C–C multiple bonds proceeds most readily with alkynes. R_3SnH can be generated in situ from R_3SnCl and Et_3SiH. Hydrostannations benefit from catalysis by a Lewis acid such as $ZrCl_4$ or $B(C_6F_5)_3$. A mixture of vinyl tin isomers is usually obtained.

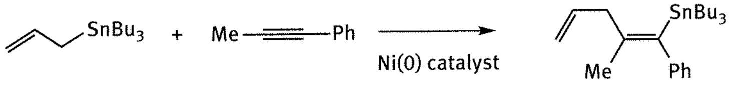


Sn–M + C≡C

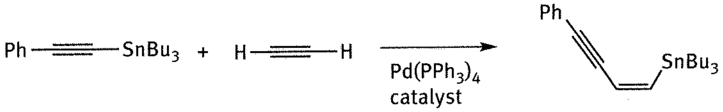
Metallastannation. This method enables the simultaneous addition of tin as well as another metalloid element to a C≡C bond. The reaction is catalysed by palladium complexes and presumably involves Sn–Pd–Si intermediates.



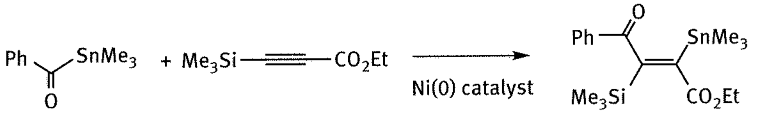
Carbostannation. The simultaneous addition of Sn and C substituents to triple bonds is a widely used method in organic synthesis. The reaction is catalysed by nickel or palladium complexes and yields synthetically useful functionalized tin vinyl species, for example:



cis-addition, regiospecific



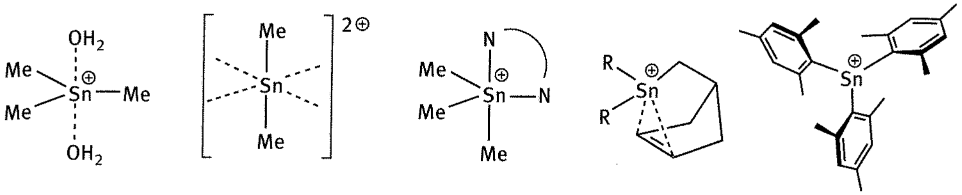
enyne formation



formation of conjugated ketones

SnR_3^+

Cationic complexes. The hydrolysis of Me_3SnCl in the presence of $Na[BPh_4]$ gives the stannylium ion as a trigonal-bipyramidal, bis-aquo cation. The hydrolysis of Me_2SnCl_2 generates the hydrated $[SnMe_2]^{2+}$ ion, which is **isoelectronic** with $[TlMe_2]^+$ and $HgMe_2$; all these compounds are **linear**. $[SnMe_3]^+$ forms a variety of five-coordinated donor adducts, e.g. with 2,2′-bipyridyl. Tin, like other Group 14 elements other than C, has a large separation between s- and p-levels and does not readily form sp^2-type planar structures. A planar geometry can however be enforced by high steric hindrance, as in trigonal-planar $[Sn(mes)_3]^+$ (see also Si analogue).

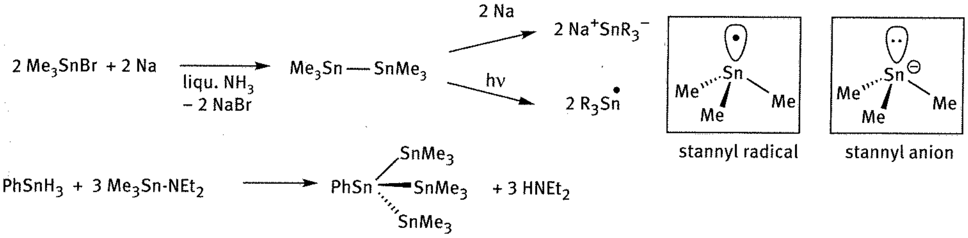


1.6.3.4 Tin in Oxidation States +III and +II: Sn–Sn Bonds, Tin Radicals, and Stannylenes

Tin forms numerous compounds with Sn–Sn bonds. The reduction of trialkyl tin halides leads to distannanes $R_3Sn–SnR_3$. The condensation reaction of tin hydrides with tin amides also leads to products with metal–metal single bonds.

Photolysis of distannanes leads to the formation of stannyl radicals $R_3Sn^{\bullet}$, while the reduction with excess alkali metals gives salts of **stannyl anions**. Whereas carbon radicals have a low barrier of inversion and are planar, stannyl radicals are **pyramidal**, as is the stannyl anion.

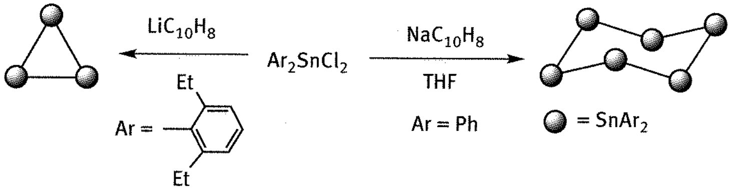
Sn(III)



stannyl radical

stannyl anion

The reduction of dialkyl tin dihalides leads to **cyclostannanes** $(R_2Sn)_x$ ('poly-stannylenes') ($x = 3–9$), which are structurally similar to cycloalkanes. Another route to such species is the H_2 elimination from R_2SnH_2, catalysed by organic bases like pyridine.

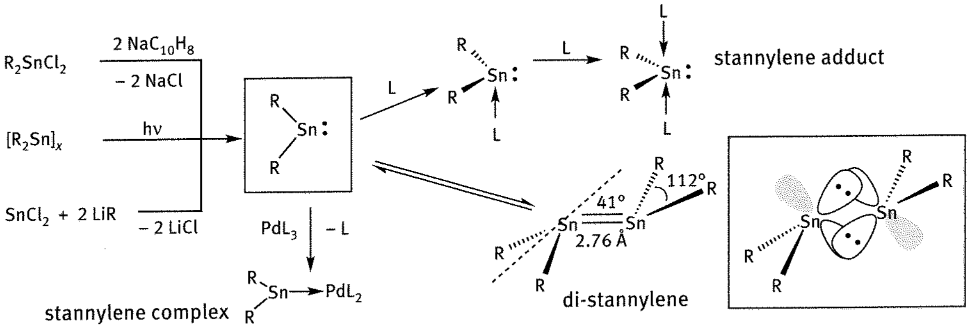


The photolysis of cyclostannanes gives **stannylenes**, the tin analogues of carbenes. Since Sn(II) starting materials like $SnCl_2$ are readily available and stable (very unlike CCl_2!), stannylenes can also be made by alkylation of $SnCl_2$. Stannylenes can form adducts with Lewis bases; they also act as 2-electron donors towards transition metals.

Sterically highly hindered stannylenes are in equilibrium with **di-stannylenes**, with a *nominal* **Sn=Sn** double bond. However, in contrast to alkenes, di-stannylenes are **not planar**, and the Sn–Sn bond is quite long. A weak π-bond has been suggested.

Box 1.6.3.1 Tin(II) and lone electron pairs

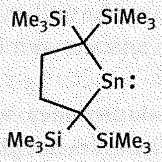
Stannylenes have a lone pair of electrons, and it is often argued that the structures are the result of the Coulomb repulsion of a 'stereochemically active lone pair'. However, the lone pair resides largely in an s-orbital, which has spherical symmetry, while the Sn–C bonds in these compounds have strong p-character. Since p-orbitals form angles of 90° with one another, the bent structures of R_2Sn, of adducts $R_2Sn(L)$ and of the stannyl anion R_3Sn^- can be explained without assuming a stereochemically active lone pair. This applies generally for the pyramidal structures of Sn(II) including $[SnCl_2]_x$ and the $[SnCl_3]^-$ anion.



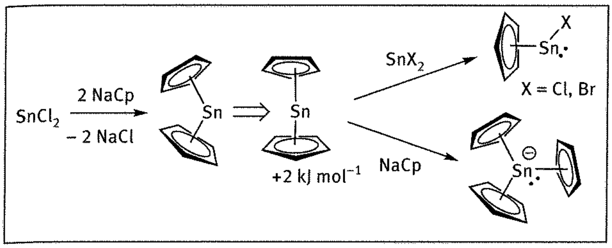
Sn(II) cyclopentadienyl compounds are much more stable and accessible than their Si(II) analogues. The Cp rings may be co-planar or tilted, depending on their substituents. Calculations have shown a very shallow conformational potential energy well, with only very small energy differences between tilted and co-planar sandwich structures.

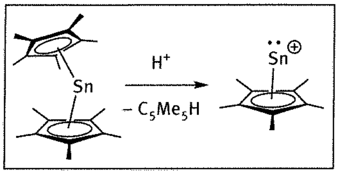
Box 1.6.3.2 ^{119}Sn NMR spectroscopy

The ^{119}Sn nucleus is the most abundant of the tin isotopes with a spin of ½. It has a very wide chemical shift range of ca. 5200 ppm. Sn(II) compounds are more highly shielded than Sn(IV) compounds and show a wider range of shifts. Structural information can be deduced from the chemical shifts as well as the Sn–H and Sn–C coupling constants, and have been used, for example, as a measure of the planarity of SnR_3^+ cations. (Reference standard: $SnMe_4$, $\delta = 0$ ppm.)

Compound	δ^{119}Sn	Compound	δ^{119}Sn	Comment
$MeSnCl_3$	+20	$Bu_2Sn(OBu^t)_2$	−34	monomer, 4-coord.
Me_2SnCl_2	+141	$[Bu_2Sn(OMe)_2]_2$	−165	dimer, 5-coord.
Me_3SnCl	+164	$[(mes)_3Sn]^+[B(C_6F_5)_4]^-$	+806	Sn(IV) cation, 3-coord.
	+2323	$[(C_5Me_5)Sn]^+BF_4^-$	−2247	Sn(II) cation

Mono-Cp compounds can be made from SnX_2 and Cp_2Sn by ligand redistribution. Protonation of $Sn(\eta^5\text{-}Cp^*)_2$ gives the $[SnCp^*]^+$ cation, which is isoelectronic and isostructural to MCp^* (M = Al, Ga, In).





1.6.4 Lead Compounds

82
Pb
207.2

The organometallic chemistry of lead follows the general pattern described for tin. There are however a number of differences:

(1) Lead has a **larger radius** and a tendency towards higher coordination numbers.

(2) The **lower oxidation** state, Pb(II), is now dominant for all inorganic compounds. $Pb(OAc)_4$ is an oxidizing agent.

(3) The Pb–element bond is significantly weaker than the Sn–E bond.

Similarly, the Pb–Pb bond is comparatively weak. Consequently, metal–metal bonded compounds, which were a prominent feature in tin chemistry, are more labile and **thermally less stable**. Although hydrides R_3PbH exist, they are thermally labile (e.g. Me_3PbH decomposes > –40 °C). The $[R_3Pb]^-$ anion has the lowest H^+ affinity of all the anions $[R_3M]^-$ (M = Si > Ge > Sn > Pb).

PbEt₄ uses

The main application of organometallic lead compounds was the use of tetraethyl lead as a fuel additive to prevent premature ignition of petrol engines (anti-knock agent). $PbEt_4$ is endothermic but kinetically stable; it decomposes on heating by Pb–C bond homolysis and is a source of ethyl radicals. As a heavy metal, lead is toxic, and the use of $PbEt_4$ has now been phased out. Compared to Si and Sn, lead compounds have found only limited applications in organic synthesis.

Synthesis. Unlike Sn compounds, lead tetra-alkyls are rarely made metal(IV) precursors but are accessible from Pb(0) by oxidative addition, or from $Pb(II)Cl_2$ by disproportionation:

$$6\,PbCl_2 + 12\,MeMgBr \xrightarrow[Et_2O]{} 6\,\text{'}PbMe_2\text{'} + 12\,MgClBr$$

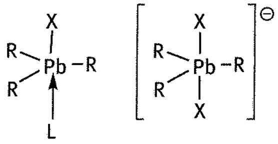
$$\downarrow$$

$$3\,PbMe_4 + 3\,Pb \qquad \text{disproportionation}$$

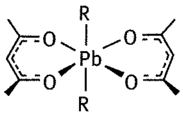
$$Pb(OAc)_4 + 4\,RMgX \xrightarrow[Et_2O]{} PbR_4 + 4\,MgX(OAc)$$

$$Pb + 4\,MeI \xrightarrow[Et_2O]{} Me_2PbI_2 \qquad \text{direct method}$$

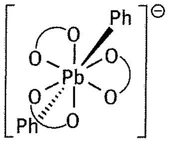
Structures. Lead(IV) alkyl halides readily coordinate halide or carboxylate anions to give complex anions with coordination numbers up to 8. $[Me_3Pb(O_2CR)]_n$ is a polymer chain with five-coordinate Pb, similar to the tin analogue.



CN 5; X = halide

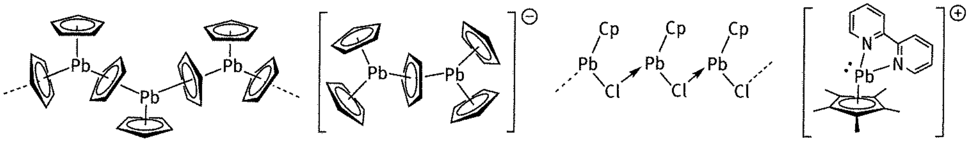


CN 6; $PbR_2(acac)_2$



CN 8; $[PbPh_2(OAc)_3]^-$

Lead(II) forms a number of cyclopentadienyl derivatives. $Pb(\eta^5\text{-}Cp)_2$ is monomeric in the gas phase, with a bent sandwich structure, but forms a number of polymeric crystalline phases in the solid state. The $[Pb_2Cp_5]^-$ anion can be regarded as a fragment of these polymer structures. $[CpPbCl]_x$ and $[Cp_2Pb(BF_3)]_x$ form insoluble polymers, in which the metal is thought to act as both donor and acceptor, i.e. as Lewis acid and Lewis base. The $[PbCp]^+$ cations also have a lone pair but act as Lewis acids and form complexes with donor ligands.



Key points

As a rule, Group 14 elements form electron-precise compounds, with few exceptions. The M–C bonds are highly covalent. The bond strength decreases down the group, and the ability to act as an alkylating agent increases. Silicon alkyls are the basis of large-scale industrial applications. The high stability of the Si–O bond allows polysiloxanes to be used for high temperature baths, as insulators, and as medical implants. Tin alkyls are extensively used in C–C bond formations. The stability of the lower oxidation states increases down the group.

Exercises

1. Show two routes for the synthesis of Me_3SiCl.
2. The ^1H NMR spectrum of Me_3SiCp at −10 °C shows four signals in the ratio 1:2:2:9. On warming to 130 °C the spectrum is simplified and shows only two signals in the ratio 5:9. Explain this observation.
3. Ph_3SnBr reacts with sodium metal in a 1:1 molar ratio to give **A**. Product **A** reacts with two further equivalents of Na to give **B**. Show the chemical equations and products.
4. Al_2Me_6 reacts readily with water and oxygen but $SiMe_4$ and $SnMe_4$ do not. Explain this observation.
5. Show why and how stannylenes R_2Sn can act as both Lewis acid and Lewis base.
6. What is a polysiloxane, what is its structure, and what are its applications?
7. An industrial method for the synthesis of $PbEt_4$ is the alkylation of $PbCl_2$ with $LiAlEt_4$. Only three of the four Et ligands of the aluminate are exchanged, and one of the products is $LiAlEtCl_3$. Give the balanced equation for this process.

2

Organometallic Compounds of Transition Metals

As was shown in Part 1, the Main Group elements are divided into the s-block (alkali and alkaline earth elements) and the p-block (from the boron group to noble gases) which, as this classification signifies, use s- and p-orbitals for chemical bonding. Inserted between these element blocks are the so-called *transition metals*. Going from left to right across the Periodic Table, from Period 4 (main quantum number 4) onwards, d-orbitals begin to be filled. The elements arising from the filling of the 3d, 4d, and 5d shells are commonly referred to as first row, second row, and third row transition metals, respectively, and each group of elements with identical d-electron count forms a triad. As shown in the following table, the group number is conveniently identical to the number of d-electrons of each element in its zero-valent state.

Structure of the transition block

The five d-orbitals are aligned along, as well as in between, the *x*, *y*, and *z* axes: d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{z^2}, so that orbitals with appropriate symmetry are available for bonding in many directions. From Group 4 onwards the chemical differences between transition and Main Group elements become very pronounced, and the term 'transition metals' is therefore usually applied to the elements in Groups 4–10. These elements show a particularly rich chemistry of varying oxidation states and the most unusual bonding and reactivity patterns in organometallic chemistry, which is the reason for their importance in industrial processes and a multitude of catalytic applications.

Starting with scandium (Sc) **the 3d energy level sinks below the 4s level**, so that the chemistry of scandium and the following elements is dictated by the **occupancy of these d-levels**.

Group	3	4	5	6	7	8	9	10	11	12
N	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$	$d^{10}s^2$
4	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
5	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
6	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
7	Ac									

f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Box 2.0 Electron configuration and d-electron count

The electron configuration of transition metal atoms is often quoted as [noble gas]$nd^x(n+1)s^y$ (i.e. [Ar]$3d^24s^2$ for titanium, for example). However, as stated above, from scandium onwards the d level of transition elements sinks below the s level. Also for the metal ***ions,*** d is always below s. In a chemical environment the ***effective electron configuration of transition metals is therefore*** $d^4, d^5, d^6, \dots d^{10}$:

Electron configuration: d^{x+y} NOT d^xs^y

The number of d-electrons of the element is identical to the group number.

The table on the preceding page gives the d-electron configuration for each transition metal triad (oxidation state 0). This will be important for understanding electron counting and the magnetism of transition metal complexes.

Up to Group 7 the number of d-electrons gives the maximum obtainable oxidation state.

The elements in Group 3 (Sc, Y, and La) exist mainly as M^{3+} ions; their chemistry is not unlike that of aluminium, and they are referred to as '**rare earth**' metals.

Lanthanides

The element lanthanum is followed by 14 elements which arise by filling the seven 4f orbitals. The elements from cerium (Ce) to lutetium (Lu) are called the '**lanthanides**'. f-Orbitals are not significantly involved in covalent bonding, and these elements form mainly compounds based on M^{3+} ions which are chemically generally similar. They do however provide some interesting magnetic and electrophilic organometallic compounds.

Actinides

In analogous fashion, the elements following actinium (Ac) are referred to as the '**actinides**'. Of these, only thorium and uranium have a significant organometallic chemistry.

Lanthanide contraction

Since 14 elements are inserted between lanthanum and the next transition element, hafnium, the increased nuclear charge leads to a significant contraction of the atomic and ionic radii: the so-called '**lanthanide contraction**'. This has important structural and bonding consequences: the radii of Row 6 transition metals tend to be smaller than those of Row 5 metals, while the metal–carbon bonds become stronger, for example.

Coinage metals

Group 11 elements (Cu, Ag, Au), the **coinage metals**, behave in their higher oxidation states like transition metals, while their M^+ ions have a d^{10} electron configuration, i.e. a completely filled d-shell, and therefore have Main Group characteristics. The Group 12 elements, finally, are best regarded as Main Group elements; they have therefore been included in Part 1.

General Trends: Electronegativity and Bond Strength

The following table lists the Pauling electronegativities (EN) of transition metals. For comparison, the electronegativities of C and H are 2.5 and 2.2, respectively.

Ti	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9
Zr	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**
1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9
Hf	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**
1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4

⇓ increasing stability of higher oxidation states

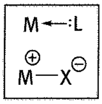
⇓ increasing M–C bond strength

more polar M–C σ-bonds ⟺ more covalent M–C σ-bond

Metals are more electropositive than carbon and hydrogen, and in M–X bonds the metals M are positively polarized. However, the Row 5 and 6 elements in Groups 8–11 from ruthenium to gold are collectively referred to as the **noble metals** (shaded), and they are characterized by high electronegativities and covalent bonding to carbon, such that an Au–C σ-bond, for example, is non-polar and generally stable to air and moisture.

The metal–carbon bond strength in the transition metal block increases as one goes down a given triad from Rows 1 to 3. This is opposite to the bond energy trend described for Main Group elements and reflects the involvement of d-orbitals in M–C bonding. Third row metals tend to make the most thermodynamically stable complexes, and are usually less reactive and less involved in catalysis than second row metals (with some exceptions).

2.1 Ligand Types

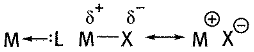


$\mathrm{M} \leftarrow :\mathrm{L}$ $\overset{\oplus}{\mathrm{M}}-\mathrm{X}^{\ominus}$

Whereas the organometallic chemistry of Main Group elements is dominated by compounds with metal–carbon σ-bonds, transition metals are capable of binding to a much greater variety of ligands, including those that interact with the metal through their π-electron systems. As a very general classification, ligands come in two types:

(1) **L-type ligands** donate an electron pair to the metal, and

(2) **X-type ligands**, where X is an electronegative element that forms M–X σ-bonds; these may be polar or covalent and can be expressed by a resonance form that accumulates negative charge on X:



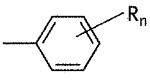
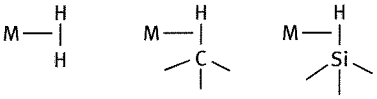
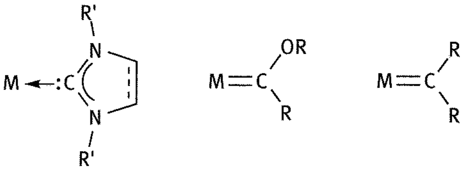
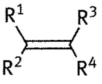
$$\mathrm{M} \leftarrow :\mathrm{L} \quad \overset{\delta^+}{\mathrm{M}}-\overset{\delta^-}{\mathrm{X}} \longleftrightarrow \overset{\oplus}{\mathrm{M}}\ \mathrm{X}^{\ominus}$$

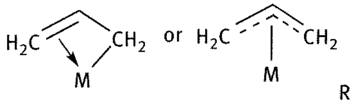
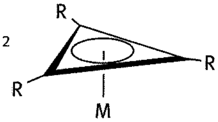
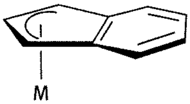
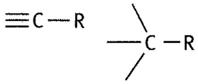
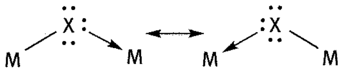
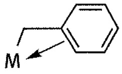
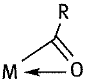
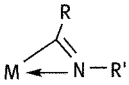
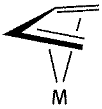
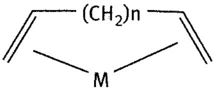
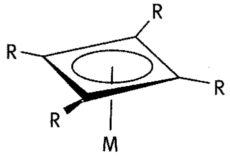
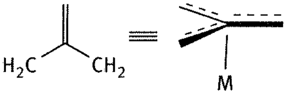
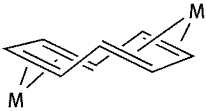
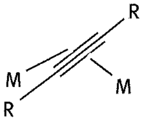
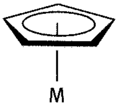
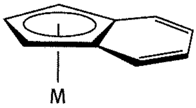
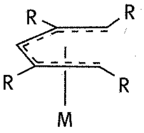
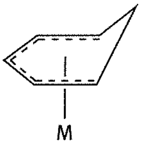
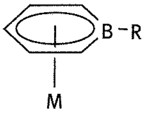
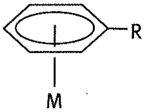
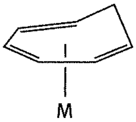
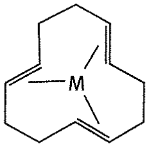
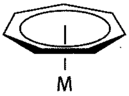
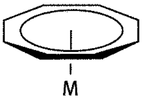
There are also more complex forms of interaction where a ligand has both L- and X-characteristics, **LX** and **L_2X**. Ligand types are indicated in the following table.

Ligands contribute electrons to the metal centre, and the stability and reactivity of such complexes depend strongly on the total electron count:

total number of electrons per metal centre = number of d-electrons
+ sum of ligand electrons − overall charge.

There are various ways of determining the electron count and the number of electrons provided by a given ligand. Here, we will use the 'neutral ligand' approach and consider each ligand as a neutral entity. This implies that ***for the purpose of electron counting only*** the metal is considered as zero-valent, so that there is no need to worry about its oxidation state at this stage.

Ligand type	**Type**	**Examples**
1-electron ligands: *X-type*	σ-ligands:	–H, alkyls: $-CH_3$, $-CH_2R$, –CH=CHR (vinyl, alkenyl), –C≡CR (alkynyl), $-SiR_3$ silyl  aryl terminal halides, alkoxides, amides: –Cl, –Br, –I, –OR, $-NR_2$
	σ-donor	 dihydrogen, alkane and silane complexes
2-electron ligands: *L-type*	n-donor, π-acceptor ligands:	C≡O, C≡NR isonitriles, PR_3 phosphines  carbenes, alkylidenes
	π-donor / acceptor ligands	$CH_2=CH_2$ ethylene,  alkenes

Ligand type	Type	Examples
3-electron ligands: *LX-type*		 η^3-allyl, η^3-enyl  cyclopropenyl  η^3-indenyl  terminal and bridging carbyne (alkylidyne)  bridging halide, alkoxide, amide  η^3-benzyl  η^3-acyl  η^3-iminoacyl
4-electron ligands: *L_2 and LX_2 type*		 η^4-diene, conjugated  η^2, η^2-diene, nonconjugated  η^4-cyclobutadienyl  η^4-trimethylenemethane  η^4, η^4-cyclooctadiene  bridging alkyne
5-electron ligands: *L_2X type*		 η^5-cyclopentadienyl  η^5-indenyl  η^5-pentadienyl  η^5-cyclohexadienyl  boratabenzene complex
6-electron ligands		 η^6-arene  η^6-cycloheptatriene  η^6-cyclododecatriene
7-electron ligands		 η^7-cycloheptatrienyl
8-electron ligands		 η^8-cyclooctatetraenyl

2.2 Common Types of Organometallic Complexes

The ligands classified in the previous section form various types of complexes with transition metals, as well as the lanthanides and actinides. Their structures, thermal stability, and reactivity depend on the electronic characteristics of the metal centre on the one hand, and on the steric requirement of the ligands on the other. Complexes that contain only one type of ligand are called homoleptic; compounds containing only two types of atoms are called binary.

Ligands may occupy one, two, three, or more coordination sites and are correspondingly termed mono-, bi-, tri-, and polydentate ligands. Ligands attached with more than one atom to the same metal tend to form significantly more stable complexes than monodentate ligands (the 'chelate effect').

While the most common coordination number is 6 (octahedron or trigonal prism) and 7-, 8-, and 9-coordinate complexes are found, steric or electronic reasons may impose alternative and lower coordination numbers. Complexes of metal centres with a d^8 electron configuration are predominantly *square-planar*; this holds true particularly for second and third row metals and if the ligands are strong donors. Where steric factors prevail, the complexes will be tetrahedral since in this geometry steric repulsion is minimized. Metal centres in positively charged complexes are more Lewis acidic than their neutral counterparts and often have a higher coordination number.

Representative types of complexes with monodentate ligands are the examples of halide, alkyl, CO, and phosphine complexes shown in Table 2.2.1.

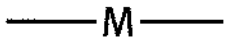
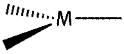
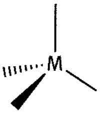
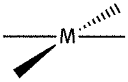
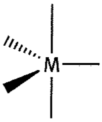
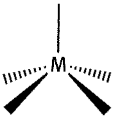
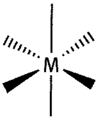
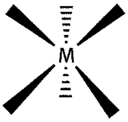
For coordination numbers of 5 and 6, two alternative geometries are possible. For CN 5, trigonal-bipyramidal (tbp) and square-pyramidal geometries are usually separated by only a rather small energy difference, which provides a pathway for ligand scrambling. π-Donor and electronegative ligands favour tbp (as in $NbCl_2Me_3$), whereas the σ-only complex $TaMe_5$ is square-pyramidal in the gas phase. For CN 6 and d^0–d^2 electron configurations supported by strong σ-donors (methyl ligands), a trigonal-prismatic geometry is favoured over the conventional octahedron. However, in most other cases, and certainly with π-acceptor ligands, the octahedral geometry is more stable.

The importance of steric hindrance. Complexes with coordination number 3 are rare. As can be seen from the examples in Table 2.2.1, in order to be able to isolate complexes of low coordination number (as opposed to generating them at low temperatures for spectroscopic analysis), ligands of high steric hindrance are required. These provide kinetic shielding. For example, whereas $TiMe_4$ is thermally unstable, the bulkier $Ti(CH_2SiMe_3)_4$ is stable at room temperature.

The bulk of the ligand often dictates the coordination number and the metal oxidation state; for example, alkylation of $CrCl_3$ gives three-coordinate Cr(III) products CrR_3 if $R = CH(SiMe_3)_2$ but Cr(IV) alkyls if $R = CH_2SiMe_3$.

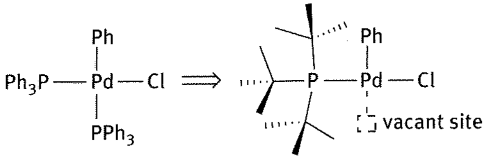
Steric hindrance is often used to control coordination number, particularly for metals that act as precursors for catalysts. For Pd(0) complexes, which generally form coordinatively and electronically saturated, 18 VE phosphine complexes PdL_4, it is often useful to employ bulky phosphines to facilitate dissociation of L (to give PdL_3 or PdL_2) or to prevent

Table 2.2.1 Common coordination geometries for organometallic transition metal complexes

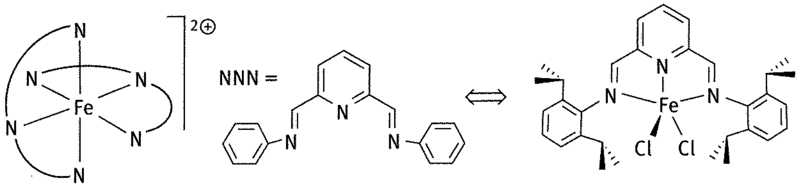
MX_n, ML_n	$n = 2$	$n = 3$	$n = 4$	$n = 4$
Geometry				
	linear	trigonal-planar	tetrahedral	square-planar (sqp)
Halide	$HgCl_2$		$TiCl_4$, $[CoCl_4]^{2-}$	$[PdCl_4]^{2-}$
Metal alkyls	$R_3C{-}Mn{-}CR_3$ R =$SiMe_3$	$Cr(CHR_2)_3$ R =$SiMe_3$	$TiMe_4$ $Ti(CH_2SiMe_3)_4$	$[Pt(C{\equiv}CR)_4]^{2-}$
Metal carbonyl	$[Au(CO)_2]^+$ d^{10}, 14 VE	$[Cu(CO)_3]^+$ d^{10}, 16 VE	$Ni(CO)_4$ d^{10}, 18 VE	$[Rh(CO)_4]^+$ d^8, 16 VE
Phosphine complex	$Pd(PBu^t{}_2Ph)_2$, $(R_3P)AuCl$	$Ni(PEt_3)_3$	$Ni(PMe_3)_4$, $NiCl_2(PPh_3)_2$	$[Rh(PMe_3)_4]^+$, $NiCl_2(PMe_3)_2$
MX_n, ML_n	$n = 5$	$n = 5$	$n = 6$	$n = 6$
				
	trigonal-bipyramidal (tbp)	square-pyramidal	octahedral	trigonal-prismatic
Halide	$MoCl_5$		$[TiCl_6]^{2-}$, WCl_6	
Alkyl	$NbCl_2Me_3$	$TaMe_5$	$[RhMe_6]^{3-}$	$[ZrMe_6]^{2-}$, WMe_6
Carbonyl	$Fe(CO)_5$ d^8,18 VE		$Cr(CO)_6$ d^6,18 VE	
Phosphine complex	$Fe(PMe_3)(Me_2PCH_2{-}CH_2PMe_2)_2$ $Rh(H)(CO)(PPh_3)_3$	$R_2C{=}RuCl_2(PR_3)_2$	$[Fe(Me_2PCH_2{-}CH_2PMe_2)_3]^{2+}$ $WCl_3(PMe_2Ph)_3$	

higher coordination altogether, as in the two-coordinate $Pd(PBu^t{}_2Ph)_2$. Three-coordinate complexes of d^8 metals retain a square geometry but with one site unoccupied, which results in a T-shaped structure.

Steric hindrance can also be used to suppress certain reaction pathways or enable completely different reactivity. For example, iron complexes of bis(imino)pyridines with small phenyl substituents on N give bis(ligand) complexes $[Fe(NNN)_2]^{2+}$ which have long been studied for their redox behaviour. However, bulky imine- substituents allow the coordination of only one ligand per metal, and the complexes become highly active ethylene polymerization catalysts.



less active more active

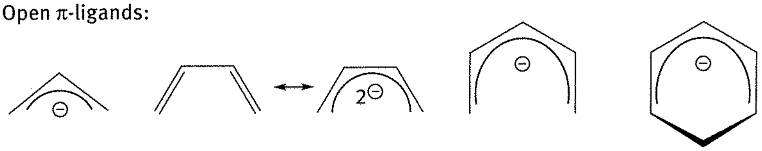


inactive as catalyst highly active

π-Ligands. Organometallic complexes often contain neutral, anionic, or formally cationic open or closed unsaturated ligands which bind to the metal through their π-electron systems. Their structure can usually be derived from an octahedron where two or three coordination sites are occupied by π-ligands. Ligands with negative charge are classed as **LX** (3-electron donor) or **L$_2$X** (5-electron donor) types. The most important of these, the cyclopentadienyl anion $C_5H_5^-$ (Cp^-), falls into the L_2X category.

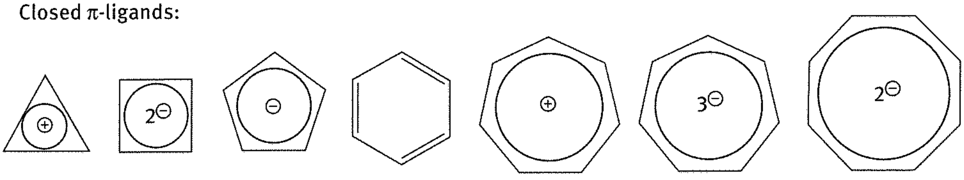
Complexes where the metal is enclosed between two such planar cyclic π-ligands are referred to as **sandwich complexes**, while those containing a cyclic π-ligand as well as one or more monodentate ligands are described as **half-sandwich complexes**, or as complexes with 'piano stool' geometry. There are systematic series of open and closed π-systems:

Open π-ligands:



η^3-allyl η^4-diene, enediyl η^5-pentadienyl η^5-cyclohexadienyl

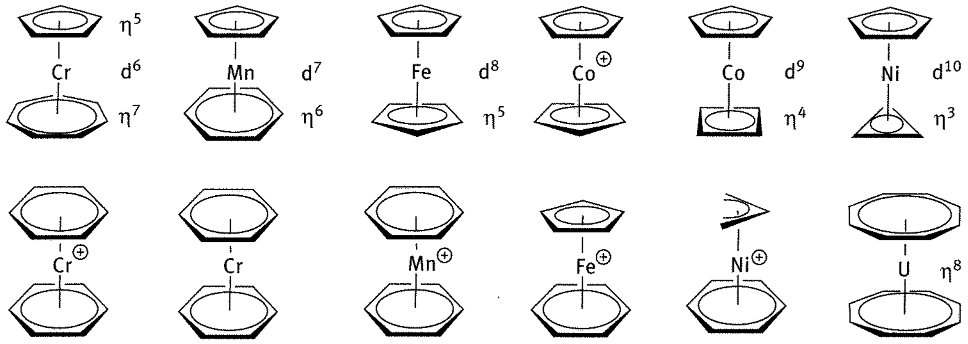
Closed π-ligands:



2π 6π 6π 6π 6π 10π 10π

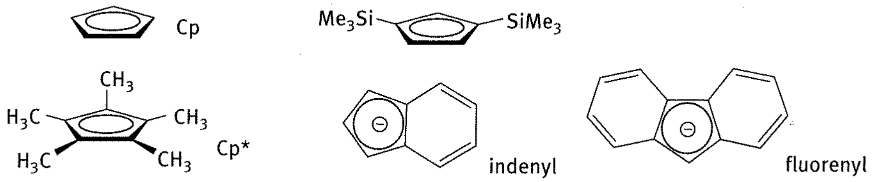
There are isoelectronic series of sandwich and half-sandwich complexes, in various ligand combinations, depending on the electron count of the metal centre and the number of π-electrons supplied by the ring ligands. Large ions like U^{4+} and Th^{4+}can also form sandwich complexes with the large $C_8H_8^{2-}$ ring, a 10π Hückel aromatic system.

Sandwich complexes:



The Cp ligands can be substituted as required. In order to achieve steric stabilization of otherwise very labile species, bulky substituents on the Cp ring are frequently used. One of the most important bulky Cp ligands is pentamethyl-Cp, $C_5Me_5^-$ (usually abbreviated Cp*). The introduction of five methyl substituents doubles the effective diameter of the ligand and its thickness; each Me substituent also shifts the redox potential by an incremental amount, so that MCp^*_2 complexes are easier to reduce than their MCp_2 congeners.

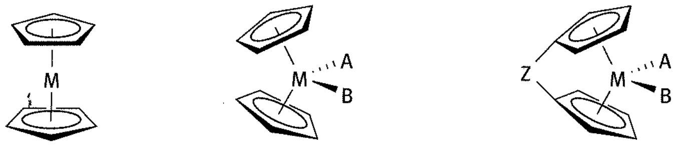
Commonly used Cp ligands:



A particularly widely-used class of sandwich complexes are those with two Cp rings (MCp_2, 'metallocenes'), especially those carrying additional ligands, $Cp_2M(X)(Y)$. To accommodate these, the two Cp rings must be tilted, which affects the energies of the frontier orbitals. Complexes with a wide variety of ligands, Cp_2ML_2, Cp_2MXL, and Cp_2MX_2, exist and are used for a myriad of functionalizations, and in synthetic and catalytic applications.

Connecting the two Cp ligands via a linker prevents Cp rotation and controls the coordination gap aperture, for enhanced reactivity.

Types of metallocene complexes:



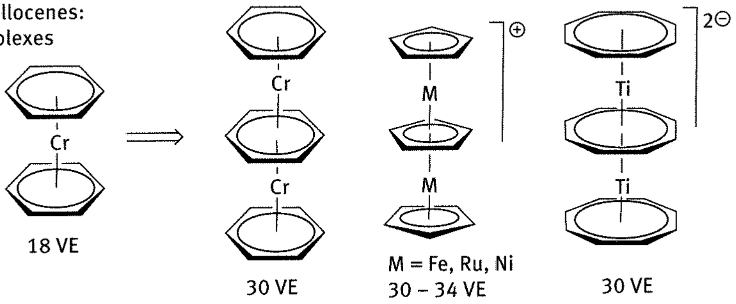
bent metallocene
A, B = X- or L-type ligand

ansa-metallocene
ansa (Latin) = handle
Z = bridging group

As is explained in Chapter 2.3, sandwich complexes are most stable if they attain an electron count of 18. This 'magic number' is one of a series: capping a sandwich like Cr(benzene)$_2$ with another [Cr(benzene)] unit gives a so-called triple-decker complex, Cr$_2$(benzene)$_3$; here the electron count is extended from **18 to 30 valence electrons (VE)**. Other triple-decker structures also exist, with up to 34 VE.

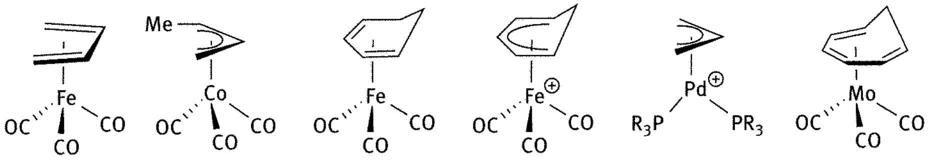
Extending the 18-electron rule: see Section 2.5.2.

Higher-order metallocenes: triple-decker complexes

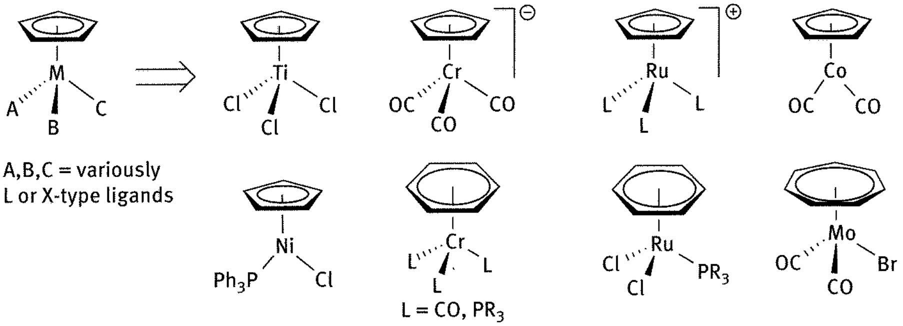


Half-sandwich complexes. Transition metal fragments bearing donor or anionic ligands, such as CO, phosphines, halides, hydride, etc., form half-sandwich complexes with π-donor ligands. Coordination enhances the reactivity, and half-sandwich complexes probably constitute the largest and most diverse class of complexes with extended π-systems. Some representative examples of neutral and charged half-sandwich complexes with π-ligands ranging from η^3-allyl to aromatic ring systems are shown in the following diagram.

Open-ligand half-sandwich complexes:



Representative examples of half-sandwich complexes:



A,B,C = variously L or X-type ligands

2.3 Electron Counting and the 16/18-Electron Rule

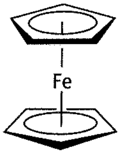
2.3.1 Counting Conventions

As was illustrated in Part 1, for compounds of Main Group elements the octet rule indicates particular stability: the available s- and p-orbitals are fully occupied and form four 2-electron-2-centre bonds, which together give an electron octet. The equivalent for transition metals is the **18-electron rule**: it, too, predicts a particular stability whenever the sum of d-electrons, ligands, and positive or negative charges reaches the 'magic number' of 18 valence electrons (VE). It is sometimes also referred to as the 16/18-electron rule because some metals, for well-understood electronic reasons, prefer an electron count of 16.

The 18-electron rule is best considered as a rule-of-thumb and a useful guide. It is most consistently followed by complexes with ligands like CO, which bind strongly through donor and acceptor interactions and exert strong ligand fields. A common explanation for the particular stability associated with an electron count of 18 is that 18 electrons are required to fill one s-, three p-, and five d-orbitals in a metal's valence shell, so that a noble gas configuration can be reached. More recent theoretical considerations have cast doubt on the involvement of p-orbitals in ligand bonding and suggest that the metal–ligand σ^*-orbitals are populated instead; however, the result is the same.

Electron counting can follow two conventions. In the list of ligands in Chapter 2.1 we have considered each ligand as a neutral entity, so that a methyl or a chloride is considered as a neutral radical delivering one electron to the metal. In this way there is no need to assign oxidation states.

Alternatively, one can consider all ligands that are known to form stable anions as negatively charged, and compensate for the charges by applying the appropriate oxidation state to the metal. While this does not change the outcome, the assignment of oxidation states is not always straightforward, so it is usually simpler not to worry about the electronic structure of complexes for electron counting purposes.

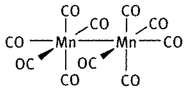


Ferrocene =
bis(η^5-cyclopentadienyl)iron

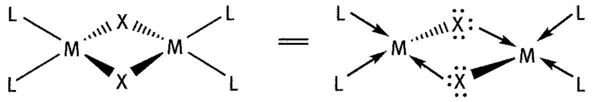
Covalent counting convention		Ionic counting convention	
C_5H_5	$5e^-$	$C_5H_5^-$	$6e^-$
Fe(0)	d^8	Fe^{2+}	d^6
C_5H_5	$5e^-$	$C_5H_5^-$	$6e^-$
	18 VE		18 VE

In compounds with **metal–metal bonds**, the electrons donated from one metal to another are taken into account. For example, manganese carbonyl has the structure $(OC)_5Mn–Mn(CO)_5$. With a d-electron configuration of d^7 and two electrons donated by each CO ligand, the electron count of each $Mn(CO)_5$ fragment is $d^7 + 5 \times 2 = 17$ electrons; the additional electron from the second manganese atom makes this 18 VE for each metal centre.

metal–metal bonds

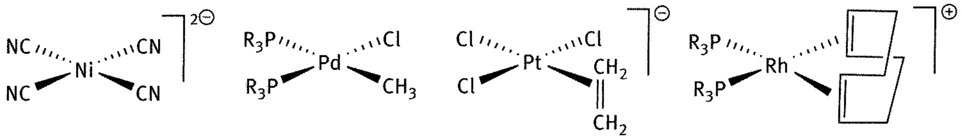


As was discussed in Chapter 1.1, a bridging halide (or another heteroatom with at least one lone electron pair) contributes a total of three electrons (X = halide, OR, SR, NR_2, etc., L = general neutral donor ligand):



d^8, square-planar: 16 VE

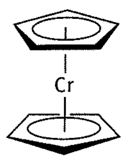
Complexes of metal centres with a $\mathbf{d^8}$ electron configuration adopt mostly a **square-planar** geometry with an **electron count of 16.** This is particularly true for second and third row transition metals, such as Rh(I), Ir(I), Pd(II), Pt(II), and Au(III), and for complexes of strong-field ligands, such as cyanide CN^-, and strong donor ligands like PR_3. The reason is the increased stabilization of the d-shell as the atomic number increases, so that the occupied d_{z^2} orbital no longer participates in ligand bonding. Some examples:



Note that square-planar geometry is preferred for *electronic* reasons, whereas the *sterically* most favourable geometry in complexes with four ligands is tetrahedral. Therefore complexes of Ni^{II}–Pt^{II} are mostly square-planar, whereas Ni^0–Pt^0 complexes (d^{10}) are tetrahedral.

2.3.2 **Electron Counting and Oxidation States**

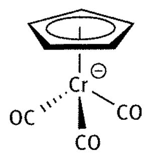
For the purpose of oxidation state assignment, ligands that exist as free molecules are considered neutral, for example CO, ethylene, phosphines, or benzene, while those that are typically present in salts and are more electronegative than the metal are treated as negatively charged, such as Cl^- or the cyclopentadienyl anion, $C_5H_5^-$ (Cp^-). On occasions, ligands can also be considered as carrying a positive change, as in linearly bonded NO^+, a 2-electron ligand which is isoelectronic with CO. The oxidation state of the metal is given by the charge necessary to compensate the negative charges, taking also account of any overall negative or positive charge of the complex. Oxidation states are useful for determining the d-electron count of a metal centre; for example, knowing that an ion is d^6 (Fe^{II}, Co^{III}), d^8 (Rh^I, Pt^{II}), or d^{10} (Ni^0) will suggest adherence to octahedral, square-planar, or tetrahedral coordination geometry, respectively. The following examples illustrate these principles and also introduce different structural types of organometallic compounds. It must be kept in mind, however, that ***oxidation states are a formalism, not a physical property: they cannot be measured.***



Sandwich complex
Chromocene

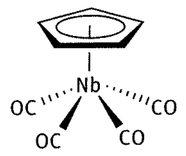
Electron count: Cr d^6
Cp: $2 \times 5 = \underline{10\ e^-}$
16 VE

Oxidation state:
2 Cp^- anions per Cr,
overall no charge: Cr(II)



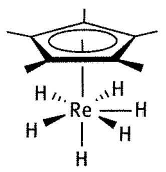
Half-sandwich complex
('Piano stool complex')
Electron count: Cr d^6
Cp: $5\ e^-$
3 CO: $3 \times 2 = \underline{6\ e^-}$
Charge $\underline{1\ e^-}$
18 VE

Oxidation state: one Cp^-
overall 1– charge: Cr(0)



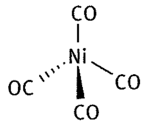
Half-sandwich complex
(7-coordinate)
Electron count: Nb d^5
Cp: $5\ e^-$
4 CO: $4 \times 2 = \underline{8\ e^-}$
18 VE

Oxidation state: one Cp^-
anion no overall charge:
Nb(I)



Half-sandwich complex
(9-coordinate)
Electron count: Re d^7
Cp: $5\ e^-$
6 H: $6 \times 1 = \underline{6\ e^-}$
18 VE

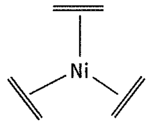
Oxidation state: Cp^-
plus 6 H^-, no overall
charge: Re(VII)



Nickel tetracarbonyl
tetrahedral
Electron count: Ni d^{10}

4 CO = + $4 \times 2 = \underline{8\ e^-}$
18 VE

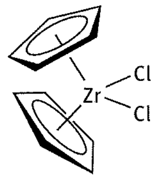
Oxidation state:
neutral ligands,
no overall charge: **Ni(0)**



Tris(ethylene)nickel
trigonal-planar
Electron count: Ni d^{10}

3 C_2H_4: $3 \times 2 = \underline{6\ e^-}$
16 VE

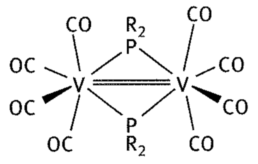
Oxidation state:
neutral ligands,
no overall charge: **Ni(0)**



Bent metallocene
Electron count:

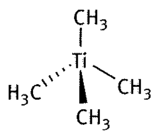
Zr d^4
2 Cl: $2\ e^-$
Cp: $2 \times 5 = \underline{10\ e^-}$
16 VE

Oxidation state:
2 Cp^- anions, 2 Cl^-
anions, overall no
charge: Zr(IV)



Electron count: V d^5
shared electrons
from V=V bond: $2\ e^-$
4 CO = $4 \times 2 = 8\ e^-$
bridging PR_2: $\underline{3\ e^-}$
18 VE

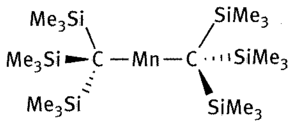
Oxidation state: 2 PR_2^-,
no overall charge: **V(I)**



Tetramethyltitanium
tetrahedral

Electron count: Ti d^4
4 CH_3 radicals = $\underline{4\ e^-}$
8 VE

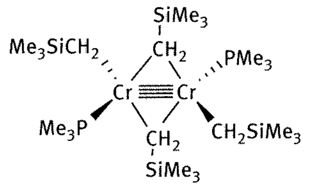
Oxidation state:
4 alkyl anions CH_3^-
no overall charge:
Ti(IV)



A manganese dialkyl,
very high steric hindrance,
monomeric, linear
Electron count: Mn d^7

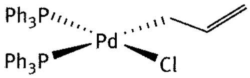
2 alkyl radicals = $\underline{2\ e^-}$
9 VE

Oxidation state:
2 anionic alkyl ligands,
no overall charge: **Mn(II)**



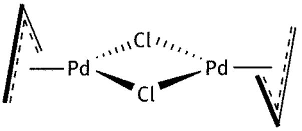
M–M bonded dimer Cr d^6
shared electrons from Cr–Cr bond: $4\ e^-$
shared electrons from bridging alkyls: 2 x 0.5 = $1\ e^-$
terminal alkyl: $1\ e^-$
1 phosphine per Cr: $\underline{2\ e^-}$
14 VE

Oxidation state:
PMe_3 neutral,
2 alkyl anions R^- per Cr,
no overall charge: **Cr(II)**



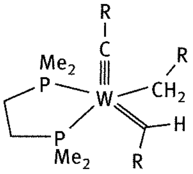
Square-planar,
σ-allyl complex
Electron count: Pd d^{10}
2 PPh3 = 2 x 2 = 4 e$^-$
σ-allyl = 1 e$^-$
Cl 1 e$^-$
16 e$^-$

Oxidation state:
PPh3 neutral
2 anionic ligands,
no overall charge: **Pd(II)**,
typical structure for d^8 configuration



π-Allyl complex, dimer
square-planar
Electron count: Pd d^{10}
η^3-allyl = 3 e$^-$
σ-bonded Cl = 1 e$^-$
n-donor Cl = 2 e$^-$
16 e$^-$

Oxidation state:
1 allyl anion per Pd,
1 chloride per Pd
no overall charge: **Pd(II)**,
typical structure for d^8 configuration

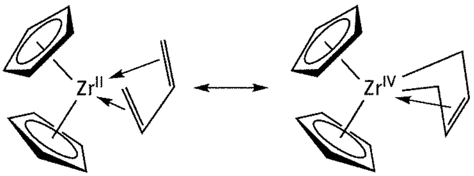


Complex with alkyl, carbene and carbyne ligands
Electron count: W d^6
carbyne = 3 e$^-$
carbene = 2 e$^-$
alkyl = 1 e$^-$
2 phosphines = 4 e$^-$
16 e$^-$

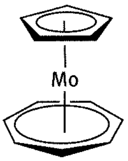
Oxidation state:
if carbene is considered neutral,
carbyne + alkyl suggest W(IV);
if all C ligands are considered anionic, W(VI).

Whereas in most cases oxidation states can be assigned unambiguously, there are incidents where there is room for debate. For example, 1,3-butadiene is a neutral π-donor ligand. However, it is able to accept electron density from the metal into its π* orbitals ('back-bonding'), and in the case of early transition metals like zirconium, with energetically high-lying d-orbitals, this back-donation of electron density can be so extensive that the butadiene takes on the characteristics of a butenediyl dianion $C_4H_6^{2-}$, with two σ-bonds to the metal. Zirconocene butadiene complexes can therefore be described as either Zr^{II} or Zr^{IV}; the bond length distribution suggests that the Zr^{IV} resonance form makes a major contribution.

Such ambiguities are not uncommon. Whereas in the Zr diene case, the bond length distribution is an indicator, other cases are less obvious. Take for example mixed sandwich compounds of the cycloheptatrienyl ligand, such as (η^5-Cp)Mo(η^7-C_7H_7). Here Cp may be regarded as Cp$^-$ and the seven-membered ring as $C_7H_7^+$ (the well-known, isolable tropylium cation); both are familiar planar 6π Hückel aromatic systems, isoelectronic with benzene. This assignment would leave the metal in the oxidation state 0. On the other hand, spectroscopic and computational studies have shown that the 7-ring carries considerable negative charge and is better described as $C_7H_7^{3-}$, a 10π Hückel aromatic system, which would leave the metal in the oxidation state +IV. The real situation is somewhere between these two extremes.



Zr(II) diene complex Zr(IV) butenediyl complex



$C_5H_5^-$ 6π C_5H_5- 6π
Mo(0) d^6 $\Longleftrightarrow$ Mo(IV) d^2
$C_7H_7^+$ 6π $C_7H_7^{3-}$ 10π

Fortunately, in most cases metal oxidation states can be assigned more straightforwardly. However, oxidation states are a formalism and not necessarily a good guide to reactivity. Whether a metal centre will undergo a given reaction will be strongly modulated by all the ligands present, and formally similar complexes can display widely differing reactivities. For example, there are numerous thermally stable Ni(0) phosphine complexes $Ni(PR_3)_4$. However, whereas $Ni(PMe_3)_4$ is highly pyrophoric and very easily oxidized, $Ni\{P(OPh)_3\}_4$ is stable to air and moisture. Both have a d^{10} configuration, but the strongly donating PMe_3 ligands push the d-orbital levels of the first to much higher energy, so that the energy gain by oxidation is far greater.

Key points

Ligands are classified according to the number of electrons they donate to the metal centre.

For electron counting purposes only, it is convenient to consider all ligands as neutral and the metal centre as zero-valent. Mononuclear complexes tend towards an electron count of 18. Steric hindrance may reduce this.

Complexes with strong π-acceptor ligands (CO, NO) usually obey the 18-electron rule.

Metals with d^8 configuration form square-planar 16-electron complexes.

For the assignment of the metal oxidation state, ligands that exist as free molecules are considered neutral, and ligands that form typical anions are considered negative: Cl^-, O^{2-}, etc. The oxidation state is then equal to the balancing charge.

Exercises

1. Give examples of
   - (i) a metallocene complex;
   - (ii) a half-sandwich complex;
   - (iii) an arene complex.
2. Assign the number of electrons donated to metal centres by the following ligands:
   - (i) hydride;
   - (ii) bridging chloride;
   - (iii) CO;
   - (iv) a phosphine PR_3;
   - (v) ethylene;
   - (vi) 1,3-butadiene;
   - (vii) cycloheptatriene;
   - (viii) cyclopentadienyl.
3. What is the electron count of the metal centre in the following complexes:
   - (i) Cp_2Co;
   - (ii) $[Cp_2Co]^+$;
   - (iii) Cp_2Ni;
   - (iv) $CpMn(CO)_3$;
   - (v) $Fe(CO)(1,3\text{-butadiene})_2$;
   - (vi) $Co(NO)(CO)_3$;
   - (vii) $CpNi(\eta_3\text{-allyl})$;
   - (viii) $Ni(C_2H_4)2(PPh_3)$.
4. What are the formal metal oxidation states in the complexes in question 3?

2.4 Ligand Properties and Metal–Ligand Bonding

The previous chapter has introduced a number of ligands that bind to transition metals and are the basis for a number of key compound classes. Some of these ligands would not give stable compounds with Main Group elements, most notably carbon monoxide, alkenes, and alkynes. This section will describe fundamental aspects of ligand bonding to transition metals.

According to the predominance of certain ligand types, organometallic compounds can be subdivided into different ligand classes, and more detailed aspects of their chemistry will be explored in subsequent chapters. Most metal complexes contain more than one type of ligand. Some of these occupy a 'spectator' role, while others are the focus of chemical reactivity. It will therefore also be important to learn which ligands undergo specific reactions, while others act more like bystanders or protecting groups. Knowledge of the electronic and steric characteristics of ligands will help with this.

2.4.1 Carbon Monoxide

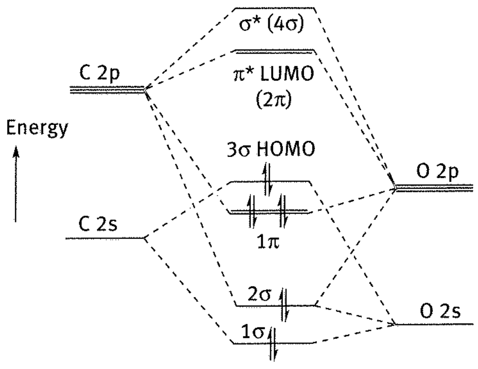
C≡O

One of the most ubiquitous ligands in transition metal organometallic chemistry is carbon monoxide, C≡O. It also illustrates key features of ligand bonding to d-block elements.

Carbon monoxide is a very weak base. Its protonated form, the formyl cation HCO^+, is very unstable and requires super-acidic conditions for its formation, and there are very labile adducts of CO with Lewis acids such as BH_3. It contrasts in this respect with donor ligands known from classical coordination chemistry, such as NH_3 or pyridine, both of which bind readily to BH_3 as well as Lewis acidic metal centres like Ni^{2+}. On the other hand, NH_3 does not form isolable complexes with Ni^0, whereas CO does. Why?

CO bonding

The C≡O molecule shows the presence of a C-centred lone pair (HOMO), a σ-bond generated from the p_z orbitals of C and O, and two orthogonal π-bonds, which together give the C–O triple bond. The HOMO is weakly C–O antibonding in character. There are also two C–O antibonding π* orbitals, which could accept electron density from sufficiently high-lying orbitals such as the occupied 3d (or 4d, 5d) levels of transition metals. It is this combination of σ, π, and π* orbitals which is responsible for the reactivity of CO, and which is lacking in simple donors like NH_3. A simplified MO diagram illustrates this bonding pattern:

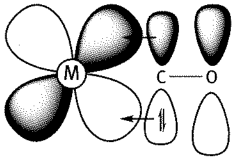


CO can interact with a transition metal in three ways: as σ-donor, as π-donor, and as π-acceptor. Of these, the σ-donor and π-acceptor contributions are the most important; in particular, the π-acceptor capacity of CO is responsible for its ability to bind to electron-rich metal centres. The π-donor interaction is weak (and often neglected).

$M(\sigma) \longleftarrow :C{=}O$

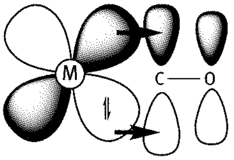
σ-donor interaction

(shading indicates the orbital phases)



$M(\pi) \longleftarrow C{=}O$

π-donor interaction



$M(\pi) \longrightarrow C{=}O\ (\pi^*)$

π-acceptor interaction

These interactions are responsible for a strengthening of the M–C bond. Although the donation of the 3σ lone pair to the metal strengthens the C–O bond, this is (usually) more than compensated by the back-donation from the metal into the CO π* orbital, which weakens the C–O bond. Overall, a metal–CO interaction can be described by two resonance forms, where the formulation with a C–O bond order of less than three makes an important contribution:

$$\overset{\ominus}{\ddot{M}}{-}C{\equiv}\overset{\oplus}{O}: \longleftrightarrow M{=}C{=}\ddot{O}:$$

The most sensitive method of observing the bonding interactions in CO complexes is **infrared spectroscopy**. CO stretching vibrations involve substantial changes in dipole moment and therefore give rise to intense bands in the infrared spectrum. This gives diagnostic information about the electronic characteristics of a carbonyl complex.

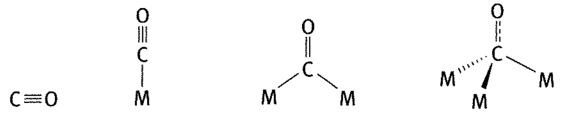
The number of IR bands can be used for structure determination; see Appendix 2

Gaseous CO has a stretching frequency $\nu_{CO} = 2143\ cm^{-1}$. Reduction of the antibonding character of the lone pair by protonation (to give $HC{\equiv}O^+$) leads to an increase to $2184\ cm^{-1}$, and coordination to a Main Group Lewis acid like BH_3 gives $OC{-}BH_3$ with $\nu_{CO} = 2164\ cm^{-1}$. However, in most metal complexes, the C–O stretching frequency is well below these value, typically 2100–1900 cm^{-1} but may fall below 1700 cm^{-1}, depending on the degree of back-bonding.

Back-bonding					
	ν_{CO}		decreases		ν_{CO}
$Ni(CO)_4$	2060	↓	↑	$[Mn(CO)_6]^+$	2098
$[Co(CO)_4]^-$	1890			$Cr(CO)_6$	2000
$[Fe(CO)_4]^{2-}$	1790			$[V(CO)_6]^-$	1860
		increases			

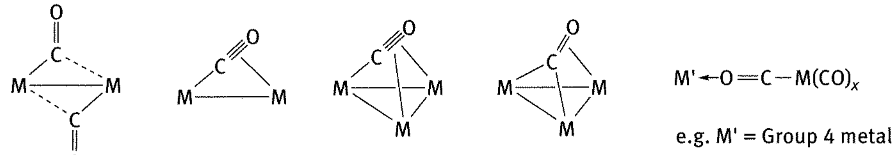
Bridging CO

CO acts in most cases as a terminal ligand but it can also bridge two or three metal atoms. In bridging situations, back-bonding is increased, with a corresponding strong decrease of the ν_{CO} value.



	C≡O	terminal	μ_2-CO	μ_3-CO
ν_{CO}(cm^{-1})	2143	2100–1850	1850–1750	1730–1620

In di- and polymetallic compounds and metal carbonyl clusters, CO may also be found in a variety of non-symmetric bridging situations. Metal carbonyl complexes may act as ligands themselves: since electropositive metals, like alkali cations or Group 3 and 4 compounds, are highly oxophilic, they may bind to the O of a carbonyl ligand to give 'isocarbonyl' bonding. This interaction lowers the C–O stretching frequency of the bridging CO.



$M'\leftarrow O{=}C{-}M(CO)_x$

e.g. M' = Group 4 metal

semibridging

α,π-bridging CO 4-el. donor

μ_3-η^2:η^2-bridging CO

isocarbonyl bonding

CN⁻, NO⁺, CS, N₂, CNR

There are numerous isoelectronic analogues of CO: the cyanide anion $C{\equiv}N^-$, isocyanides $C{\equiv}N{-}R$, thiocarbonyl CS, and dinitrogen N_2. The nitrosyl cation NO^+ is an even stronger π-acceptor than CO; the neutral nitric oxide $NO^\bullet$ is a radical and can act as 3-electron donor.

$$\overset{\oplus}{N}{\equiv}O > C{\equiv}O > C{\equiv}\overset{\ominus}{N} > C{\equiv}N{-}R > C{\equiv}S > N{\equiv}N$$

isoelectronic n-donor/π-acceptor ligands in order of decreasing π-acceptor capacity

Whereas N_2 is non-polar and, as a poor π-acceptor, forms labile complexes, the strong donor–acceptor interaction of cyanide and CO gives stable complexes with metal-containing enzymes and is responsible for their high toxicity if ingested. CO displaces O_2 in haemoglobin, while cyanide binds to the iron sites of cytochrome c oxidase, an important enzyme in the electron transport chain. Isocyanides are similarly toxic.

2.4.2 Alkene and Alkyne Ligands

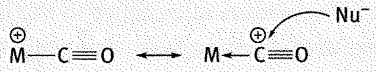
Alkene–metal bonding

The bonding pattern of **alkenes** (= olefins) to transition metals resembles that described for CO, except that in this case it is the π-molecular orbital of the alkene that acts as electron donor. Ethylene coordination is the simplest example of a π-complex. Whereas π-donation is typically weak, metal–ligand bonding is strengthened by back-donation. This synergistic

Box 2.4.1 CO reactivity

Free CO is not susceptible to nucleophilic attack. Bonded to metals, however, the reaction of CO with nucleophiles such as OH^- or CH_3^- is frequently observed and forms the basis of many catalytic processes. Reaction occurs by attack of a lone electron pair of the nucleophile on a LUMO of the substrate, which in this case is the π* orbital of CO. However, as shown in the preceding section, this is partially occupied by back-bonding, which should make nucleophilic reactions more difficult. The opposite is the case. So how can this be explained?

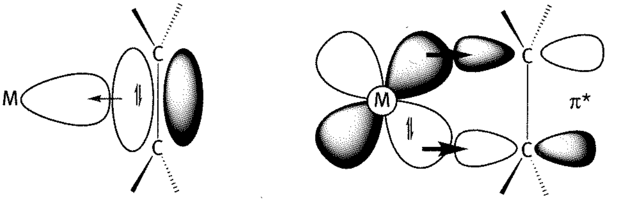
It was found that in super-acidic media, i.e. in the absence of nucleophilic anions or ligands, CO coordinates to metal ions such as Pt^{2+} and Ir^{3+} to give carbonyls with an unusually high ν_{CO} frequency, significantly higher than that of free CO; for example, $[Pt(CO)_4]^{2+}[Sb_2F_{11}^-]_2$ shows $\nu_{CO} = 2261\ cm^{-1}$. Such complexes are characterized by an absence of back-bonding and are described as *'non-classical'* CO complexes. As a result they are highly susceptible to nucleophilic attack:



The same situation arises in excited 'normal' CO complexes. Since the bonds in complexes are not static but elongate with every vibration, as a vibrationally excited M–C bond is stretched, back-bonding is reduced while C–O polarization is increased, which provides a pathway for the nucleophile to take advantage of the electron deficiency and accumulation of positive charge on the coordinated C atom. Such a polarization is not possible in free CO, and hence there is no nucleophilic attack.

The increase in ligand polarization in vibrationally excited complexes is quite general: otherwise unreactive ligands, e.g. alkenes and alkynes, become highly susceptible to nucleophilic attack whenever coordination and ligand vibrations in a complex lead to a polarization of the C–C bond.

description of alkene bonding has become known as the ***Dewar–Chatt–Duncanson model*** (Dewar 1951, Chatt & Duncanson, 1953).



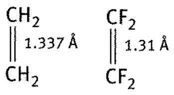
π-donation π-acceptor interaction

Alkenes are weaker π-acceptors than CO, although this varies depending on the metal and other ligands present. Similar to CO, back-donation strengthens the metal–alkene bond and weakens the C–C bond, as can be seen from the elongation of the C–C distance. In extreme cases, the C–C bond of the coordinated alkene can reach the value of a C–C single bond.

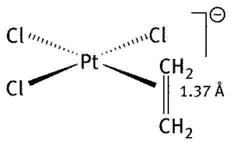
In principle the effect of back-donation on the strength of the C=C bond should be detectable by IR spectroscopy. Free ethylene has $\nu_{C=C} = 1623\ cm^{-1}$. In metal complexes this band is usually found at around 1490–1580 cm^{-1}, but since this range frequently overlaps with other ligand vibrations, assignments are difficult, and this method is of little diagnostic value.

The π-acceptor capacity of alkenes depends, on the one hand, on the metal and its oxidation state, and on the other on the alkene substituents. Early transition metals have high-lying d-orbitals which, if filled, provide very strong back-donation. Group 8–10 metal ions (Fe^{2+}, Ni^{2+}, Pt^{2+}, etc.) form either no alkene complexes or show little evidence of back-donation, while in zero-valent compounds of the same metals (d^8–d^{10}) back-donation is important. In such compounds the alkene is oriented in such a way as to maximize back-donation. This is why in Zeise's salt the C_2H_4 ligand is perpendicular to the molecular plane, so that steric repulsion is minimized, while in zero-valent compounds like $Pt(C_2H_4)_3$ or the $Fe(CO)_4(C_2H_4)$ complex shown in the following diagram, the ethylene is oriented in-plane, for optimal overlap with the π* orbitals.

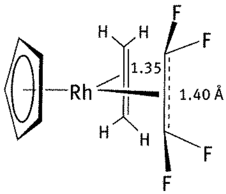
Electron-withdrawing substituents like F or CN increase the π-acceptor strength of the alkene and lead to significant elongation of the C–C bond, illustrated for nickel in the following diagram. The back-donation process leads to a change in the hybridization of the olefinic C atoms, from sp^2 towards sp^3. This is indicated by changes in the angles around C, which are reduced by back-bonding from 120° towards values more characteristic of tetrahedral carbon: in Pt^{II} complexes the alkene substituents are bent away from the metal by ca. 15°, in Pt^0 complexes by ~35°. In some ethylene adducts of osmium carbonyls, the tendency of the 5d element to achieve a higher oxidation state leads to extreme back-bonding, with the C–C bond length approaching single bond values. Some examples:



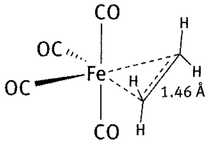
free alkenes



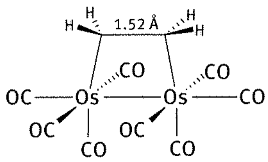
Zeise's salt, Pt(II), d^8
very weak back-bonding



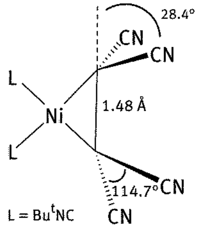
Rh(I), d^8
back-bonding to $C_2F_4 > C_2H_4$



Strong back-bonding from Fe:
Fe(0) of Fe(II)?

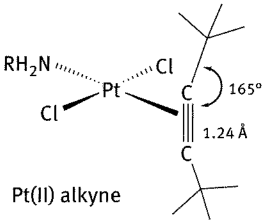


Os_2 complex:
$C_2H_4^{2-}$ rather than alkene bonding

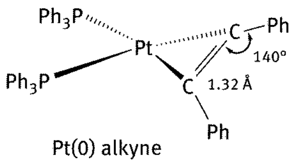


Alkyne–metal bonding

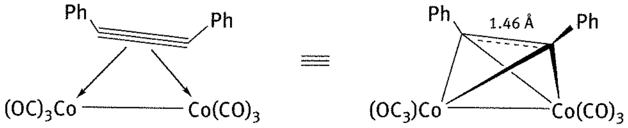
Alkynes (= acetylenes) bond to metals in very similar ways but are stronger π-acceptors than alkenes. This is expressed most clearly in the reduction of the C–C–R angles, from 180° to about 140°. Here, too, back-donation depends on the oxidation state of the metal. Since alkynes have two orthogonal π-systems, they can bridge two metal centres and, with extensive back-bonding, may form compounds best described as dimetalla-tetrahedranes, with C–C bond orders approaching 1.5 or less.



Pt(II) alkyne



Pt(0) alkyne



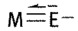
Box 2.4.2 ^{13}C NMR spectroscopy

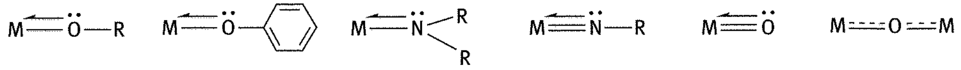
Apart from X-ray crystallography, one of the most informative structural tools for evaluating the bonding mode of alkenes and alkynes is ^{13}C NMR spectroscopy. Back-bonding induces a chemical shift change to higher field. It also alters the C–H spin–spin coupling constant, $^1J_{CH}$. This varies linearly with the s-character of the C–H bond, and coordination leads to diagnostic changes. Unfortunately due to the limited sensitivity of the ^{13}C nucleus, J_{CH} values are rarely reported.

Compound	δ^{13}C (alkene/alkyne C)	Δδ (bound – free)	$^1J_{C-H}$[Hz]
Free C_2H_4	122.8		156
Free Me–C≡C–Me	73.9		–
$(Ph_3P)_2Pt(C_2H_4)$	39.6	−83.2	146.5
$(Ph_3P)_2Pt(C_2Me_2)$	112.8	38.9	
$(Me_3SiCp)_2NbH(C_2H_4)$	10.3, 14.7	−112.5, −108.1	

2.4.3 π-Donor Ligands

Inorganic and organometallic complexes are often ligated to heteroatoms with one or more lone pairs of electrons, for example M–NR_2 (amido), M=NR (imido), M–OR (alkoxo), and M=O (oxo) ligands. Although these act primarily as anionic σ-donor ligands, in cases where the metal has an energetically accessible vacant d-orbital, the lone pair can act as a π-donor and increase the effective electron count of the metal centre. This is particularly pronounced in early transition metal and lanthanide alkoxides, amides, and imides, so that an imido ligand is usually regarded as a linear 4-electron ligand. As was discussed in Section 1.6.1.2 for Si–N and Si–O compounds, this π-donation to an electron-deficient metal centre reduces the basicity of the O or N ligands and leads to trigonal-planar –NR_2 geometries. Similarly, π-donation is responsible for the typically linear M–O–M geometries of bridging oxide ligands of less electron-rich metals.





2.4.4 Phosphines, Carbenes: Electronic and Steric Parameters

Donor/acceptor ligands play an essential role in modifying the electronic and steric characteristics of metal centres. They are therefore essential for catalysis. By far the most important class of ligands are the phosphines.

Phosphines bind to transition metals firstly by donating a lone pair of electrons. However, unlike amines, they are also capable of accepting electron density from the metal. Although P, as a third row element, possesses unoccupied d-orbitals, the P–C antibonding σ^* orbitals have been found to act as acceptors. The expected lengthening of the P–C bond through populating σ^* levels is counteracted by the effect of reducing the lone pair density on P.

The substituents of a phosphine can be varied widely and independently from one another, which provides a huge possible range of phosphines $PR^1R^2R^3$, where $R^{1,2,3}$ = alkyl, aryl, alkoxide, aryloxide, amide, halide, etc. Alkyl substituents exert a positive inductive effect (+I), which raises the lone pair energy and consequently the d-orbital energy of the metal centre. This increases the reactivity of the metal centre and its susceptibility to oxidation. Electron-withdrawing R groups have the opposite effect. In addition, bulky substituents like *tert*-butyl or *ortho*-tolyl provide steric hindrance and shield the metal kinetically. This may retard the reaction rate but often improves selectivity, and prevents side reactions and decomposition; bulky substituents also restrict the maximum number of phosphines that can bind to a metal centre and therefore enhance coordinative unsaturation, which is often a precondition for generating a catalytically active species. The characterization of phosphines therefore requires knowledge of two parameters: the electronic effect, and the steric influence.

The Tolman electronic parameter. Since the ν_{CO} frequency in metal carbonyl complexes is highly sensitive to changes in back-bonding, and since this back-bonding depends on the other ligands in the complex, measurement of the CO stretching frequency can be used as a tool for quantifying the electronic influence of a phosphine (Tolman, 1973). Mono-substituted nickel carbonyl complexes L–Ni(CO)$_3$ are ideal since here steric interactions are not important. A tetrahedral complex LM(CO)$_3$ has two IR-active bands, A_1 and E (Appendix 2), of which the A_1 mode is the higher and is sufficiently well resolved to allow precise determinations. The most strongly donating phosphine leads to the highest back-bonding and therefore the lowest ν_{CO} value in the series:

L in L–Ni(CO)$_3$	ν_{CO} [cm^{-1}]	L in L–Ni(CO)$_3$	ν_{CO} [cm^{-1}]
PBu^t_3	2056.1	$PMePh_2$	2067.0
PCy_3	2056.4	PPh_3	2068.9
PPr^i_3	2059.2	$P(OMe)_3$	2079.5
PEt_3	2061.7	$P(OPh)_3$	2085.0
PMe_3	2064.1	PCl_2Ph	2092.1
PMe_2Ph	2065.3	PCl_3	2097.0
P(*o*-$C_6H_4Me)_3$	2066.6	PF_3	2110.8

Electronic parameter ν

Each substituent R^1, R^2, R^3 contributes to the frequency shift by an increment χ, from $\chi = 0.0\ \mathrm{cm^{-1}}$ for $R = Bu^t$ (strongest +I effect, reference standard) to $\chi = 19.6\ \mathrm{cm^{-1}}$ for $R = CF_3$. The frequency shifts induced by the substituents are approximately additive:

$$\boxed{\nu = 2056.1 + \sum_{i=1}^{3} \chi_i}$$

This makes it possible to predict the electronic parameters for new phosphine ligands that have not yet been measured.

The π-acceptor strength of ligands, also referred to as **π-acidity**, increases in the order:

$$PBu^t_3 < PMe_3 < P(OMe)_3 < P(OAr)_3 < PCl_3 < CO \approx PF_3$$

and more generally:

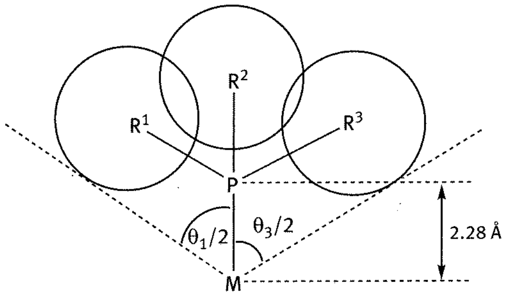
$$NH_3 < N{\equiv}CR < PR_3 < P(OR)_3 < PCl_3 < CO < NO$$

An alternative scale has been developed using molybdenum carbonyl complexes as IR probes. These allow the assessment of both monodentate [L–Mo(CO)$_5$] and bidentate phosphines [(L–L)Mo(CO)$_4$]. The ligand trends are equivalent to the nickel scale shown in the previous table.

Steric parameter Θ

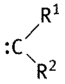
The steric parameter Θ. Bulky substituents on phosphorus exert a powerful steric influence and control reactivity and coordination numbers. Tolman defined the steric requirements of a phosphine ligand by measuring the cone angle of its complex to a metal centre, using the typical Ni–P distance of 2.28 Å as the baseline and drawing the tangent on the van der Waals envelope of the ligand. This angle θ (rather than the C–P–C angles, which do not vary much for different phosphines) reflects the special requirement of a given ligand as experienced by the metal centre.

The steric parameter is quite independent from the electronic increments. Ligands like PBu^t_3 envelop the metal and enclose almost a hemisphere of the coordination shell. Ligands with projecting substituents, like P(o-tolyl)$_3$, occupy even more space on average, although since there is rotation about the P–C bonds, different conformational isomers are possible. For different substituents R^1, R^2, R^3, Θ is the sum of the individual angles.

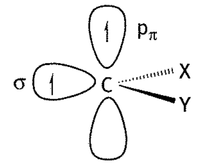


$$\Theta = 2/3 \sum_{i=1}^{3} \theta_i/2$$

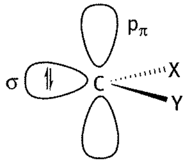
L	θ [°]	L	θ [°]
PH_3	87	$PMePh_2$	136
PF_3	104	PPh_3	145
$P(OMe)_3$	107	PPr^i_3	160
PMe_3	118	PCy_3, PBu^t_2Ph	170
PMe_2Ph	122	PBu^t_3	182
$P(OPh)_3$	128	P(*o*-tolyl)$_3$	194
PR_3, R = Et, Pr^n, Bu^n	132	$P(mes)_3$	212



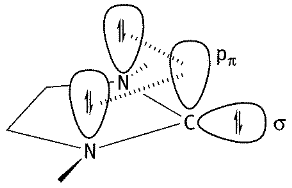
Carbenes. Carbenes, CR_2, are 2-electron donors with a bent R–C–R geometry and sp^2-hybridized C. They possess an sp^2-orbital (referred to as σ) in the plane and a p_π orbital perpendicular to it. Carbenes can in principle form either singlet or triplet ground states. The singlet state is favoured if the energy gap between these two orbitals is large. This is the case if the p_π orbital interacts with a lone pair of a heteroelement substituent (e.g. X and/or Y = N or O). Carbenes that are stable at ambient temperature and exist as isolable molecules are of the heteroatom-stabilized type. Other carbenes have to be generated in the metal coordination sphere.



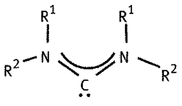
triplet carbene



singlet carbene
π-acceptor

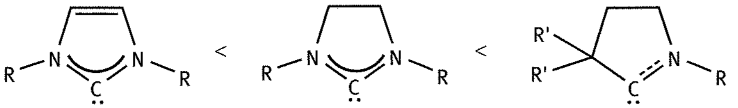


orbital interactions in an
N-heterocyclic carbene



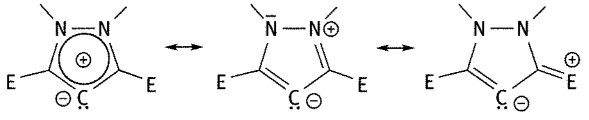
ADC

Nitrogen-substituted carbenes have become increasingly important ligands in organometallic chemistry and catalysis. These are mostly based on the imidazole skeleton and generally referred to as '***N-heterocyclic carbenes***', or **NHCs**. They are stabilized on the one hand by the π-donor interactions of the N atoms, and on the other by bulky substituents on nitrogen. There are also open, acyclic N-stabilized carbenes, $C(NR^1R^2)_2$, so-called ***acyclic diamino carbenes*** (**ADCs**); these are usually generated within the metal coordination sphere by adding amines to metal isocyanide complexes. N-heterocyclic carbenes are even more strongly electron donating than trialkylphosphines, and poorer π-acceptors. The basicity increases with the degree of saturation of the ring. There are also 6- and 7-membered NHCs, although those based on 5-rings are by far the most widely applied. Some representative examples:

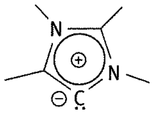


NHCs in order of increasing donor strength

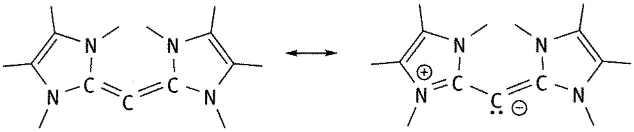
More recently a number of 'abnormal' carbenes have been isolated with very strong donor properties. Their description in canonical terms requires several resonance forms, and the compounds are best understood as internal zwitterions, or 'mesoionic' structures. The carbene-C has vinyl anion character, which explains the strongly donating character of these ligands. Abnormal carbenes are on occasions formed by rearrangement of 'normal' NHCs.



E = OR, NR_2

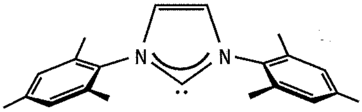
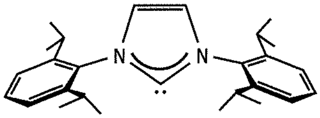
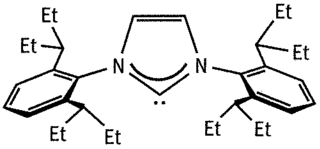


'abnormal' carbene

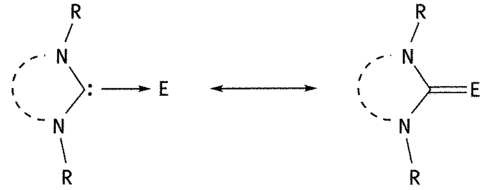


bent-allene-type carbenes

The electronic characteristics of NHC ligands can be assessed by the Tolman method. The data indicate the greater donor strength compared even to PBu^t_3.

L in L–Ni(CO)$_3$	Abbreviation	ν_{CO} [cm^{-1}] (in CH_2Cl_2)	%V_{bur}
	IMes	2050.7	34.0
	IPr	2051.5	38.1
	IPent	2049.3	39.4

Although the Tolman electronic parameter (TEP) suggests that N-heterocyclic carbenes act on the metal centre primarily as very strong σ-donors, depending on the bonding situation carbenes can also function as π-acceptors:

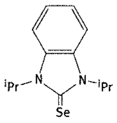
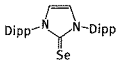
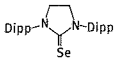
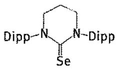
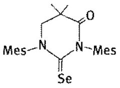
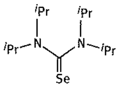
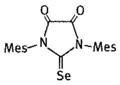


E = metal, PPh or Se

Electronic parameter
E_L: $E(\text{obs}) = 1.11(\Sigma E_L) - 0.43$ (V)
$E_L(\text{NHC}) = +0.29$
$E_L(\text{py}) = +0.25$

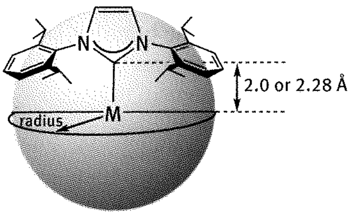
Various attempts have been made to assess the donor and acceptor strength of NHC ligands by more straightforward means than formation of $Ni(CO)_3$ complexes. One such method is to use electrochemical methods to provide information about ligand properties. The redox potentials of Fe(II) half-sandwich complexes $[CpFe(CO)(carbene)(L)]^+$ show that imidazole-type carbene ligands are stronger donors than most phosphines but also have some π-acceptor capacity; Lever's electrochemical parameter E_L, which measures the contribution of each ligand to the observed potential E_{obs}, is almost identical for NHCs and pyridine.

Another method is the comparison of the NMR chemical shifts of NHC derivatives, such as the ^{77}Se NMR resonances of the synthetically readily accessible carbene selenides. This is a highly sensitive method, given the very wide ^{77}Se chemical shift range. This method seems to correlate with π-acceptor strength but less well with the ν_{CO} Tolman parameters of the corresponding NHC complexes.

Carbene							
δ ^{77}Se	67	87	181	271	472	593	856
Tolman [cm^{-1}]	2054	2051.5	2052	2044	2050		2068

% buried volume

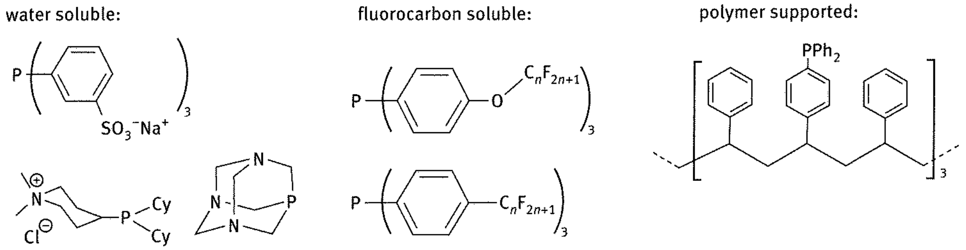
The determination of the steric influence of NHC ligands is more difficult, since these ligands are not approximately circular—they extend far more in the plane of the ring than perpendicular to it. This is particularly important for NHCs since in most cases large R groups are used to achieve stabilization, such as cyclohexyl, 2,4,6-Me_3 C_6H_2, or 2,6-$Pr^i_2C_6H_3$. The steric impact of these ligands can be estimated by calculating the percentage of a sphere around a metal centre that is occupied by the ligands, the ***percent of 'buried volume'***, $\%V_{bur}$. These calculations are based on ligand parameters taken from crystal structures and naturally depend on the assumed metal–ligand distance (usually 2.0 or 2.28 Å). The radius of the sphere is set to 3.5 Å.



This method depends naturally on the metal concerned and would give slightly lower values for large metals with larger M–C distance. Most bulky ligands cover about 30–40% of the sphere volume, with less prominent variations than the cone angle model. However, both methods for assessing the steric requirements of ligands show very similar trends, e.g. phosphines with very large cone angles also lead to the largest $\%V_{\mathrm{bur}}$ values [e.g. $P(mes)_3$, $\%V_{\mathrm{bur}} = 53.1$].

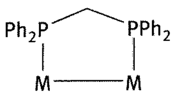
2.4.5 **Common Co-Ligands**

Organometallic complexes and catalysts depend for stability and reactivity on co-ligands, which are mostly P, N, and O-donors. Phosphines are particularly widely used. The properties of monodentate ligands have been discussed in the previous section. Modification of the organic substituents is used to achieve solubility in solvents as polar as water or as non-polar as fluorocarbons; both techniques are used to facilitate the separation of phosphine-stabilized homogeneous catalysts from the reaction mixture. The attachment of phosphine substituents to polymers such as polystyrene generates heterogenized phosphines and catalysts that can simply be filtered off at the end of a reaction.

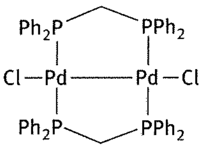


Bidentate phosphines

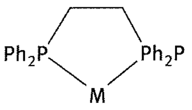
Apart from varying the donor capacity of the P atom, connecting two or more P donors by a bridge opens up new possibilities. Bi- and polydentate ligands offer additional stabilization by the chelate effect: the formation constant of a bidentate ligand is substantially higher than that of a monodentate ligand. In addition, the length and rigidity of the backbone vary the bite angle of the diphosphine, and the conformation and fluxionality of the chelate ring can greatly affect reactivity. Some examples of common chelating phosphines and the size of chelate rings they produce are shown in the following diagram. For catalytic applications such as C–C coupling reactions (cf. Chapter 3.6), choice of a suitable chelate size can mean the difference between a poor and a highly active system. It is often a 'Goldilocks' situation: too much or too little rigidity or flexibility in the chelate ring can be equally disadvantageous; the size has to be just right.



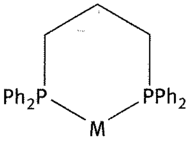
diphenylphosphinomethane, dppm
small bite angle: prefers to bridge two metals



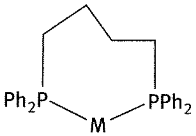
'A-frame' complex



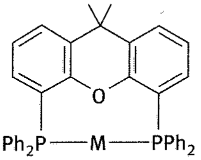
dppe
5-ring, rigid, stable



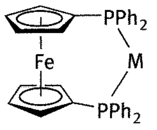
dppp
6-ring, moderately stable



dppb
flexible 7-ring



Xantphos
rigid, trans

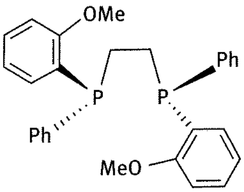


diphosphinoferrocene, dppf

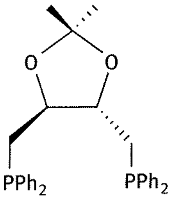
For ligand effects in asymmetric hydrogenation, see Section 3.3.1.3

In addition, the bridge in a chelating phosphine gives considerable scope for further development. In particular the bridge can be made chiral, for the induction of asymmetry in a catalytically active centre.

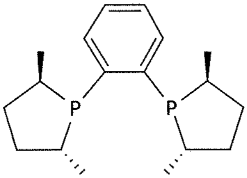
Phosphorus has a substantially higher inversion barrier than nitrogen (PH_3: 155 kJ mol^{-1}, compared to 25 kJ mol^{-1} for NH_3), which means that phosphines can be prepared where P is the centre of chirality. These were indeed the first attempts to generate chiral P ligands for asymmetric catalytic applications. More common and easier to prepare are phosphines with chirality built into the substituents or the backbone. These types of ligands are extensively used in chiral catalysis, particularly in asymmetric hydrogenation where they often give well over 95% enantiomeric excess. Some examples are:



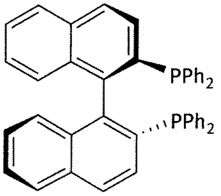
DIPAMP



DIOP



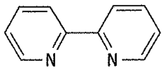
DuPhos



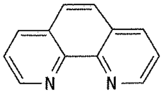
BINAP

Chiral phosphines

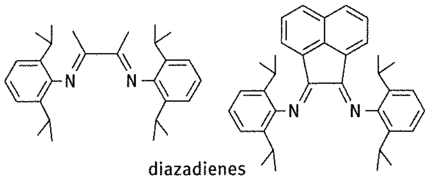
Nitrogen ligands. Neutral and anionic bi- and tridentate nitrogen ligands are commonly used to provide steric hindrance and stabilization. Diazadienes are excellent N-donors as well as good π-acceptors which, when bonded to electropositive metals, may act as non-innocent ligands and take up an electron to give a radical anion. The acetylacetonato anion (acac, pentanedionato) has long had a prominent role in coordination chemistry; its imido derivative nacnac has the advantage of introducing bulky substituents on the N atoms. Pyrazolylborates can act as bi- and tridentate anionic ligands.



bipy (2,2′-bipyridyl)

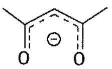


phen (1,10-phenanthroline)

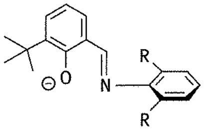


diazadienes

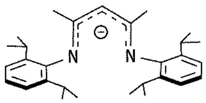
diazadiene radical anion



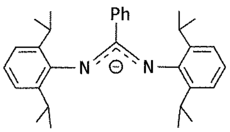
acac anion



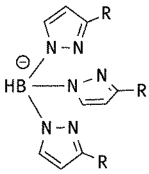
iminophenolate



nacnac anion



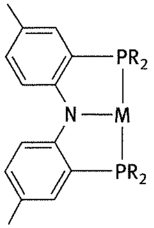
benzamidinate



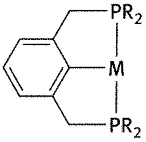
$HB(pz^R)_3^-$

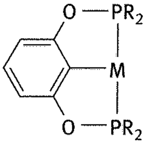
Particular stability is often provided by tridentate ligands that stabilize square-planar coordination environments. These can be neutral or anionic chelates. In view of the tight bonding they provide, they are frequently referred to as ***'pincer ligands'***.

Pincer ligands

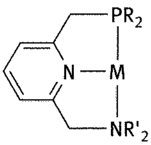


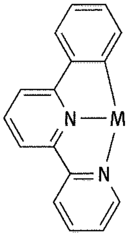
PNP⁻



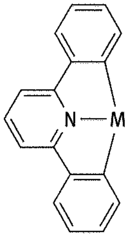


POCOP



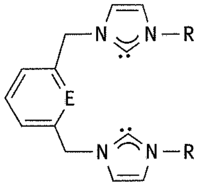


N^N^C

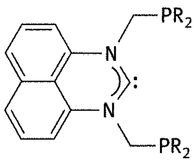


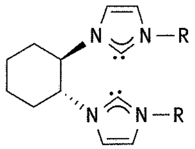
C^N^C

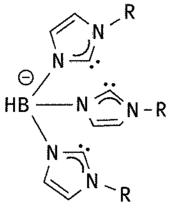
Polydentate and pincer carbene ligands:



E = N, C⁻







Key points

Unsaturated carbon compounds like CO, alkenes, and alkynes interact with metals in two ways: σ-donor interaction, where electron density from the π-bonds is shared with unoccupied metal orbitals, and π-acceptor interaction from the metal to the ligand. This is known as ***donation*** and ***back-donation*** (or ***back-bonding***). The latter is a major contributor to metal–ligand bonding.

The electronic and the steric characteristics of ligands determine the reactivity of a metal centre. These effects can be quantified. Most important of these scales are the Tolman steric and electronic parameters of phosphine ligands.

Back-donation often controls the orientation of the ligands and changes the bond order of π-ligands.

Exercises

1. Order in sequence of increasing π-acceptor strength: NO^+, $P(OMe)_3$, N≡CR, PBu^t_3, PCl_3, PPh_3, CO, NH_3.
2. Why are Tolman cone angles calculated using Ni–PR_3 complexes and not just for the free phosphines PR_3?
3. Why can both alkynes and imido ligands be said to act as 4-electron donors? Describe the structural indicators that justify this description.
4. Explain why the stretching frequency of CO coordinated to strongly electrophilic metal cations is often higher than that of free CO.

2.5 L-Type π-Acceptor Ligands: Metal Carbonyl Complexes

M−C≡O

Transition metal carbonyl complexes are a very diverse key class of compounds and exist for almost every metal in question, in a range of oxidation states. Not only do metal carbonyls illustrate the most important aspects of structure and bonding, they also exemplify key reaction steps and fundamental pathways of ligand reactivity that underlie most of catalysis. These reaction steps will therefore be introduced here and referred to again in later sections.

Discovery of $Ni(CO)_4$, $Fe(CO)_5$

Metal carbonyls were among the first organometallic compounds to be made. When the scientist and industrialist Ludwig Mond discovered nickel tetracarbonyl, $Ni(CO)_4$, in 1888, he recognized that this was a metal compound unlike any other previously encountered: in particular, this compound was not a salt but a volatile liquid and decomposed thermally to deposit metallic nickel. These properties were quickly turned into a process for the production of pure, iron-free nickel (the so-called Mond process), which is still in operation today. Iron carbonyl, $Fe(CO)_5$, was discovered independently a year later by Mond and M. Berthelot. The chemistry of metal carbonyls has remained closely linked with industrial developments and catalytic processes.

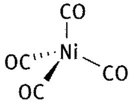
2.5.1 Synthesis of Metal Carbonyls

CAUTION: Volatile CO complexes are highly toxic. $Ni(CO)_4$: EU Category 3 possible carcinogen.

From the metal. The simple carbonyls of iron and nickel can be made by reaction of CO with finely divided metal. Both are liquids and can combust on contact with air. The stoichiometry is dictated by the 18-electron rule.

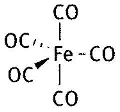
$$\mathrm{Ni + 4\,CO \xrightarrow{1\ bar,\ 25\ ^{\circ}C} Ni(CO)_4}$$

colourless liquid, dec. >35 °C
bp. (estimate) 42 °C



$$\mathrm{Fe + 5\,CO \xrightarrow[CO\ pressure]{100\ ^{\circ}C} Fe(CO)_5}$$

straw-coloured liquid, bp. 103 °C



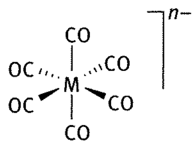
By reduction of metal salts. This is the most generally applicable method.

$$\mathrm{TiCl_4(DME) + 6\,KC_{10}H_8 \xrightarrow[15\text{-}crown\text{-}5]{1\ bar\ CO} [K(15\text{-}c\text{-}5)^+]_2[Ti(CO)_6]^{2-} + 4\,KCl + 6\,C_{10}H_8}$$

18 VE

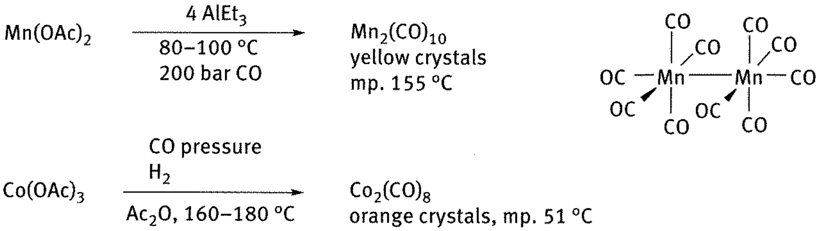
$$\mathrm{VCl_3 + 4\,Na \xrightarrow[diglyme,\ 150\ ^{\circ}C,\ -3\,NaCl]{CO\ (200\ bar)} \underset{18\ VE}{Na[V(CO)_6]^-} \xrightarrow[-\,H_2]{H_3PO_4} \underset{17\ VE}{V(CO)_6}}$$

$$\mathrm{CrCl_3 + Al \xrightarrow[AlCl_3,\ C_6H_6]{CO\ (300\ bar)} \underset{18\ VE}{Cr(CO)_6} + AlCl_3}$$



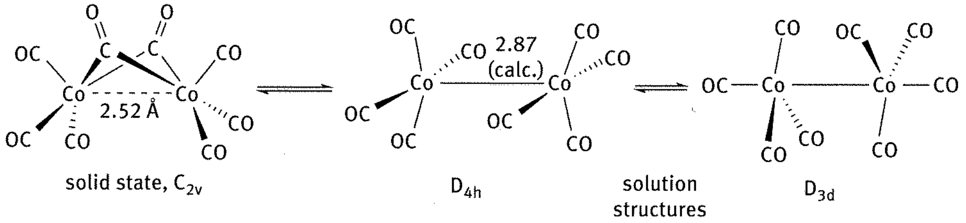
M	*n*
Ti	2
V	1, 0
Cr	0

$[V(CO)_6]^-$ is an 18 VE species. Protonation would be expected to give $HV(CO)_6$; however, this seven-coordinate product is unstable and eliminates H_2 to give the 17 VE radical $V(CO)_6$, which is sterically too congested to allow dimerization to a higher-coordinate dimer. By contrast, the mononuclear 17 VE carbonyls of Mn and Co, $Mn(CO)_5$ and $Co(CO)_4$, are coordinatively unsaturated (CN less than 6) and can form metal–metal bonded dimers with an 18-electron count. Whereas $Mn_2(CO)_{10}$, with its octahedral coordinatively saturated metal centres, is comparatively unreactive, $Co_2(CO)_8$ has a rich organic chemistry (e.g. *Pauson–Khand reaction*, Box 2.6.3) and is an important catalyst precursor (see Chapter 3.4: Carbonylations).



$Co_2(CO)_8$ exists in the solid state as the CO-bridged dimer $[(CO)_3Co(\mu\text{-}CO)]_2$, but in solution it forms at least two other isomers without CO bridges, with D_{4h} and D_{3d} symmetry. It is thermally unstable towards CO dissociation and readily gives the black cluster $Co_4(CO)_{12}$. Although the 18-electron rule would suggest the existence of a metal–metal bond in the bridged form of $Co_2(CO)_8$, electron delocalization via the μ-CO ligands takes place instead.

Bonding in metal carbonyls: see Section 2.4.2.



Second and third row transition metals give a large variety of polynuclear metal carbonyl clusters. Whereas $RhCl_3$ reacts with CO under mild conditions (ethanol as solvent and reducing agent) to give the 16 VE carbonyl halide $[RhCl(CO)_2]_2$, carbonylation of $RhCl_3$ under forcing conditions produces the cluster $Rh_4(CO)_{12}$; the Rh analogue of $Co_2(CO)_8$ is also known but is only stable under CO pressure. The trend towards cluster formation that is observed for Rh, Ir, Pd, and Pt carbonyls reflects the stronger M–M bonds in second and third row transition metals, compared to their first row congeners.

$$\mathrm{RhCl_3} \xrightarrow[\text{high temperature}]{\text{CO pressure}} \mathrm{Rh_4(CO)_{12}} \qquad \text{tetrahedral cluster}$$

Metal carbonyl complexes play an important role in biology and medicine (Box 2.5.1).

Higher nuclearity metal carbonyls and metal carbonyl clusters. Shortly after $Fe(CO)_5$ had been discovered, it was also found that exposure to light gave compounds with a lower CO/Fe ratio. This is a general reactivity pattern of metal carbonyls: CO ligands can dissociate on heating or irradiation, and photolytic CO dissociation remains a mild and much-used

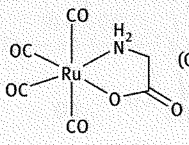
Metal carbonyl clusters

Box 2.5.1 Metal carbonyl complexes in biology and medicine

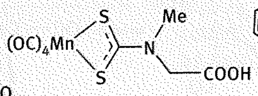
The discovery that metals such as iron are capable of forming stable complexes with CO was entirely unexpected—nothing like this had ever been seen in nature. After all, under aerobic, aqueous conditions iron is oxidized to Fe^{2+} and Fe^{3+} ions which prefer O and N ligands. However, it is now evident that CO complexes are important in biochemical processes as well as medicine.

CORMs. CO gas in large doses is toxic due to its high binding affinity for haemoglobin. However, CO is constantly produced in the body during the oxidative degradation of haeme to biliverdin. In the body, CO has an anti-inflammatory, vasodilatory, and anti-proliferative effect; it reduces cell death, protects tissues against the effects of oxygen deficiency and plays a valuable role in the treatment of cardiovascular disease and inflammatory disorders, as well as organ transplantation.

The key is to release CO in a controlled manner. Whereas the application of CO gas is highly hazardous, metal carbonyl complexes of sufficient stability under physiological conditions can provide controlled CO release. The necessary water solubility is achieved by suitable co-ligands and by making charged complexes. These compounds are known as *'CO-Releasing Molecules'* or **CORMs**. Fe, Ru, Mn, Mo, and Re carbonyl complexes are being developed. Some types are shown in the following diagram. The ruthenium glycinato complex (**1**) was one of the first examples. The manganese carbonyl (**2**) has low toxicity and reacts with N-donors such a histidine to release CO. On irradiation with visible light the precursor complex (**3**) releases CO for photo-induced cytotoxicity towards colon cancer cells. (**4**) and (**5**) are stable compounds that only become active after entering a cell, where esterases cleave the ester function and produce labile CO-releasing complexes.



1



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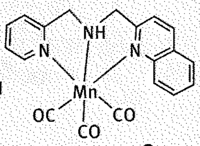
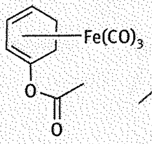


3



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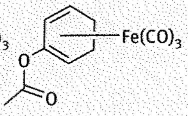
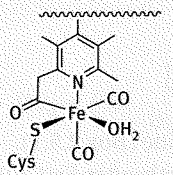
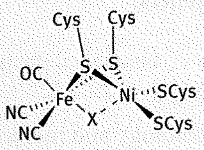


5

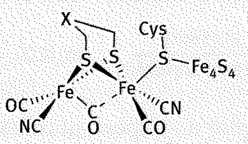
Metal-CO enzymes: [FeFe]-hydrogenase. Many microorganisms use iron carbonyls to catalyse redox reactions of molecular hydrogen, the so-called [FeFe]-hydogenases. These contain a cuboidal Fe_4S_4 cluster (the so-called H-cluster) linked through a cysteine S atom to an Fe_2S_2 unit, which contains both CO and CN ligands as well as a dithiolate bridge. The remarkable ability of these di-iron hydrogenases to catalyse the reduction of H^+ to hydrogen may offer a route to H_2 generation under mild conditions with possible applications in fuel cells. Another class are the mono-iron hydrogenases.



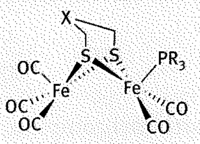
Proposed Fe site in [Fe]-hydrogenase



[NiFe]-hydrogenase

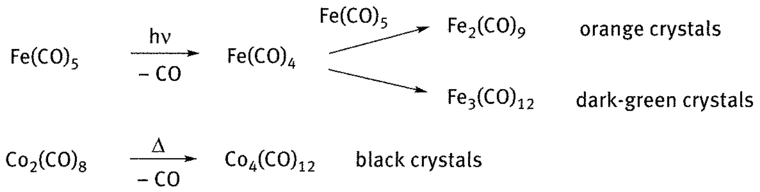


Active centre in [FeFe]⁻ hydrogenase. X = CH_2, NH, or O



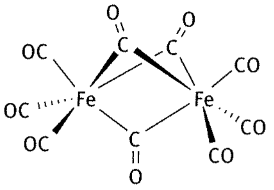
Example of a hydrogenase model

method for ligand substitution. $Fe(CO)_5$ forms two products, $Fe_2(CO)_9$ (involatile and insoluble) and $Fe_3(CO)_{12}$ (green crystals, soluble). Similarly, CO loss from $Co_2(CO)_8$ (orange-brown crystals) on heating gives the cluster $Co_4(CO)_{12}$.

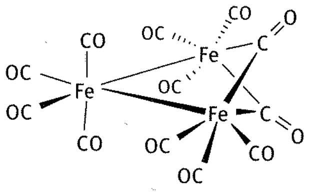


The only metal carbonyls of second and third row metals that are stable under ambient conditions are metal–metal bonded clusters. The simplest representatives are shown in the following diagram. Whereas Fe and Co clusters contain bridging CO, the larger atomic radii of the heavier elements generally disfavour CO bridges (but certainly do not rule them out).

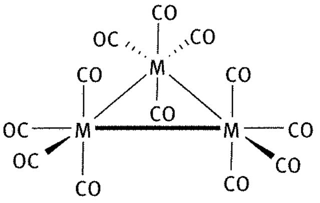
Numerous higher nuclearity clusters including mixed-metal and mixed-ligand species have been prepared. Many can be understood as fragments of the metallic crystal lattice. A detailed discussion is beyond the scope of this text. Some clusters incorporate C or CR fragments. These are relevant in the context of CO reduction to hydrocarbons in the Fischer–Tropsch process (see Box 2.5.7).



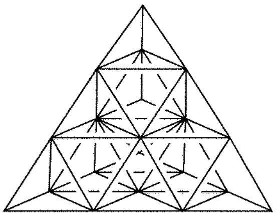
$Fe_2(CO)_9$



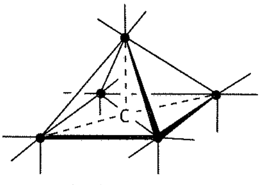
$Fe_3(CO)_{12}$



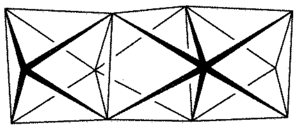
$M_3(CO)_{12}$ (M = Ru, Os)



$[PBu_4]_2[Os_{20}(CO)_{40}]$ (242 VE)



$M_5C(CO)_{15}$ M = Ru, Os
carbido cluster



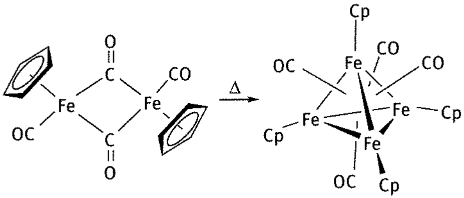
$[PPh_4]_2[Ir_{12}(CO)_{26}]$

2.5.2 Bonding in Binuclear and Cluster Complexes

The bonding concepts in binuclear metal carbonyls (and non-carbonyls) and the relationship with the 18-electron rule have been a matter of debate. Probably the best-known example is $Fe_2(CO)_9$: this molecule consists of two $Fe(CO)_3$ fragments bridged by three CO ligands, each of which formally donates one electron to each metal centre, giving an electron count of 17 per Fe. To achieve 18 VE, and to account for the diamagnetic ground state of $Fe_2(CO)_9$, a metal–metal bond has customarily been postulated. However, it is also well known from structural and theoretical studies that there is no electron density along the Fe–Fe vector, and in fact the relevant orbitals are antibonding. Similarly, while it is intuitively suggestive that semi-bridged complexes like $[Cp_2Cr(\mu\text{-}CO)_2]_2$ achieve an 18-electron count per Cr via a Cr–Cr triple bond (for which there is precedent in other types of compounds), there are cogent theoretical arguments that a **M–M bond is absent** and electron delocalization takes place via the bridging carbonyl ligands.

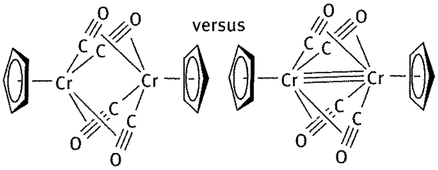
When is an M–M bond not an M–M bond?

Assuming metal–metal bonds in bimetallic organometallic complexes is an intuitive and useful way to rationalize their structures and diamagnetism, and it facilitates the visualization of polyhedral geometries. However, the physical reality is often different. *Even crystallographically determined M–M distances are not a good guide for assigning or proving the existence of metal–metal bonds.*



$[CpFeCO(\mu_2\text{-}CO)]_2$

$[CpFe(\mu_3\text{-}CO)]_4$



Metal cluster formation is an expression of electron deficiency: in a cluster there are more orbitals available than there are electrons to occupy them in a simple 2e2c bonding pattern. The situation with metal clusters is therefore similar to boranes and carboranes, for which electron-deficient bonding is well established.

Like borane clusters, it is useful to regard metal clusters as being composed of building blocks for each corner, each of which contributes a given number of electrons to cluster bonding. The number of electrons z per Main Group building block E–R is given by the number of valence electrons of E plus those added by the substituents R, minus those involved in E–R bonding. Boron has three valence electrons, one of which is engaged in bonding to one H, which leaves two electrons per B–H unit for cluster bonding. Likewise, a C–H unit contributes three electrons.

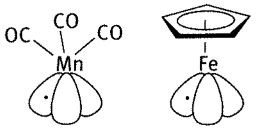
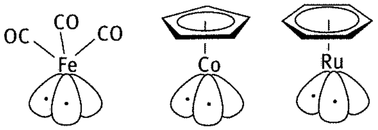
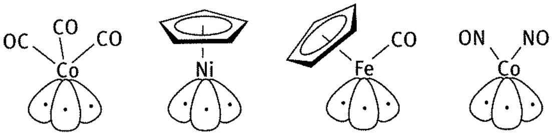
For transition metals this calculation is extended to account for d-electrons. The number z of electrons available per building block for cluster bonding is:

$$z = d + yL - 12$$

where d = number of valence shell d-electrons, y = number of attached ligands, L = number of electrons contributed by each ligand.

Therefore, an $Fe(CO)_3$ fragment (d^8) contributes $z = 8 + 3 \times 2 - 12 = 2$ electrons, a $Co(CO)_3$ fragment $9 + 6 - 12 = 3$ electrons (Table 2.5.2.1). These electrons are located in orbitals pointing towards the cluster. Those fragments with identical electron number z are in principle interchangeable, and substituting one for another does not alter the electron count of the cluster or complex. Ignoring differences in total electron count between first, second, and third row metals, these fragments are ***isoelectronic***.

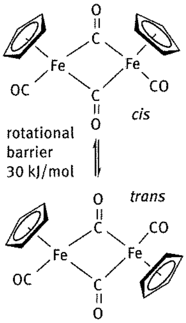
Table 2.5.2.1 Metal–ligand fragments and their electron contributions to cluster bonding

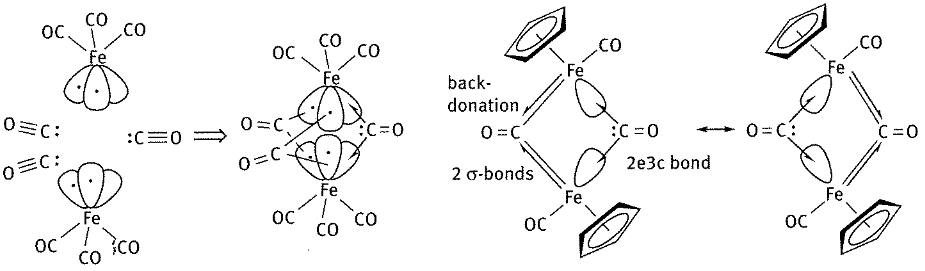
Fragment	z	Fragment	z	Fragment structures
$Mn(CO)_3$	7 + (3 × 2) − 12 = **1**	$(\eta\text{-}C_5H_5)Fe$	8 + 5 − 12 = **1**	
$Fe(CO)_3$	8 + (3 × 2) − 12 = **2**	$(\eta\text{-}C_5H_5)$ Co	9 + 5 − 12 = **2**	
$Co(CO)_3$	9 + (3 x 2) − 12 = **3**	$(\eta\text{-}C_5H_5)Ni$	10 + 5 −12 = **3**	

Returning now to the structure of oligonuclear metal carbonyls, electron-deficient bonding can be expected *in cases where there are π-orbitals of suitable symmetry and energy available for charge delocalization.* The structure of $Fe_2(CO)_9$ may be decomposed into two $Fe(CO)_3$ fragments, each equipped with two electrons for delocalized bonding, which interact with three bridging CO ligands. The two half-occupied orbitals can form ketone-type 2e2c bonds with two of the CO ligands. The lone pair of the third CO can then interact with the two vacant Fe orbitals, giving overall a delocalized CO-bridged structure ***without*** a direct Fe–Fe bond.

The bonding in $[CpFe(CO)(\mu\text{-}CO)]_2$ is analogous, the difference being that since here each Fe fragment contributes one electron more than in $Fe_2(CO)_9$, the number of bridging CO ligands is reduced to two to achieve the same electron configuration. The additional electron density per Fe contributes to the π-bonding in the planar Fe_2C_2 core. The $(\mu\text{-}CO)_n$ bonding can be described by several resonance structures; all bridging CO ligands are equivalent.

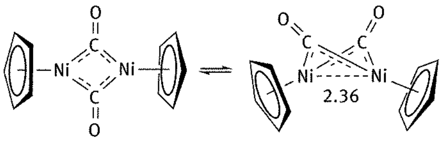
CO bridge formation is reversible: *cis*/*trans* isomerization





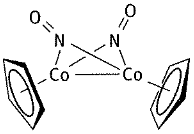
Generally, ***where strong π-acceptor ligands such as CO are present in bridging positions, π-delocalization is preferred over M–M bond formation.*** The assumption of M–M bonds is useful for deriving the shape of a molecule and accounting for its magnetism, but its physical reality needs to be checked in each case. Thus, there is no metal–metal bond in the CO-bridged edge of $Fe_3(CO)_{12}$, or in the Ni(I) dimer $[CpNi(\mu\text{-}CO)]_2$. An M–M bond is present in $Mn_2(CO)_{12}$ and $Cp(CO)_3Cr\text{–}Cr(CO)_3Cp$, both of which contain coordinatively saturated metal centres and lack bridging CO ligands. On the other hand, the postulated Cr≡Cr triple bond in $[CpCr(\mu\text{-}CO)_2]_2$ is absent; instead there is electron-deficient delocalized bonding.

Very strong π-acceptor ligands can, on the other hand, on occasions withdraw electron density from M–M antibonding orbitals and thereby make M–M bonding possible. According to photoelectron spectroscopic studies, this is the reason for the different gas phase structures of the isoelectronic compound pair $[CpNi(\mu\text{-}CO)]_2$ and $[CpCo(\mu\text{-}NO)]_2$: the former has a delocalized planar structure without an M–M bond, the latter is an M–M bonded non-planar molecule. Planar and folded structures are easily interconverted: in the crystal, $[CpNi(\mu\text{-}CO)]_2$ is folded but its C_5H_4Me analogue is strictly planar, while $[CpCo(\mu\text{-}NO)]_2$ is planar in the solid (Co–Co 2.37 Å) but bent in solution and the gas phase.



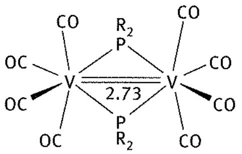
gas phase

solution, solid



solution, gas phase

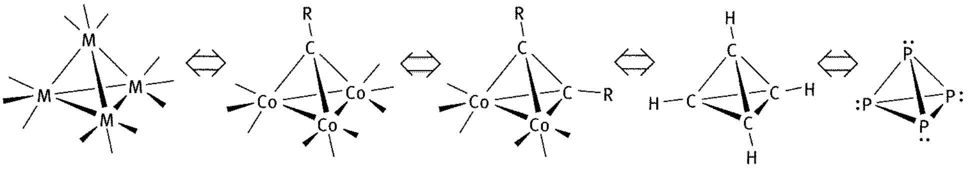
ν_{NO} 1585, 1525 cm^{-1}



In the *absence* of strong π-acceptor ligands, M–M bonds prevail; for example, the phosphide-bridged complexes $(CO)_4M(\mu\text{-}PEt_2)_2M(CO)_4$ are binuclear compounds with M–M bond orders of 2 (M = V), 1 (M = Cr), and 0 (M = Mn), with an 18 VE count per M.

Although clusters are normally drawn as shown, electron density measurements have suggested that direct M–M bonds are absent where a bond is bridged by CO.

The isolobality approach also simplifies the understanding of higher nuclearity clusters, such as $M_4(CO)_{12}$, where one or several vertices can be replaced with CR moieties, for example. All these structures are tetrahedral and follow the same structural principles as the hydrocarbon tetrahedrane (C_4H_4) or the P_4 molecule.



$M_4(CO)_{12}$, M = d^9 metal

carbido cluster

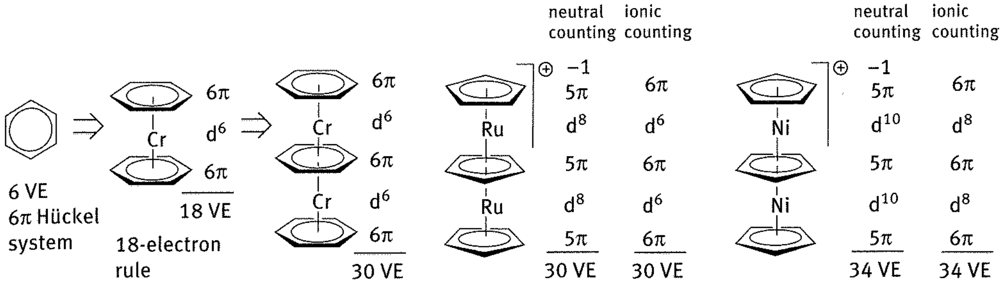
tetrahedrane

P_4 molecule

18 VE
↓
30/34 VE

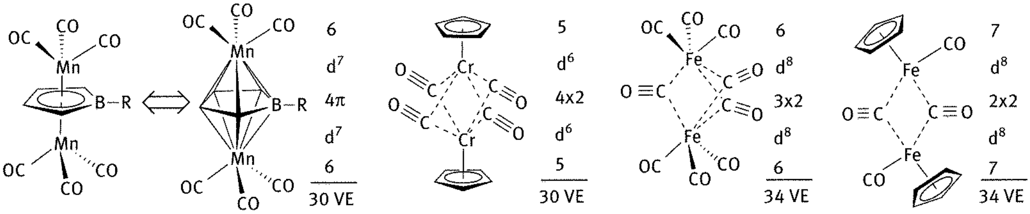
Extending the 18-electron rule. Particularly stable electron configurations, often called 'magic numbers', progress with structural complexity from planar 6π (Hückel aromatic) to '3D aromatic' 18-electron complexes, and beyond. This is best illustrated by the example of sandwich complexes of arenes: adding a (benzene)Cr fragment to benzene itself represents the transition from a 6 to an 18 VE system. Similarly, continuing this stacking, the next 'magic number' will be 30, to give a triple-decker structure. [Note that in $Cr_2(C_6H_6)_3$ the six π-electrons on the central benzene ligand are shared between both Cr atoms. This delocalization satisfies the electron demand of each metal centre. Although formally each Cr has an electron count of 15, there is no Cr–Cr bond, which would have to pass through the central ring.]

The energy differences between the optimum and slightly higher electron counts are smaller in triple-decker than in simple sandwich structures, and there are triple-deckers with up to 34 electrons. The additional four electrons elongate the M–M distance in such clusters and weaken rather than strengthen cluster bonding. As it turns out, most of the binuclear compounds discussed in the previous section, and many others, belong to the 30–34 VE family.

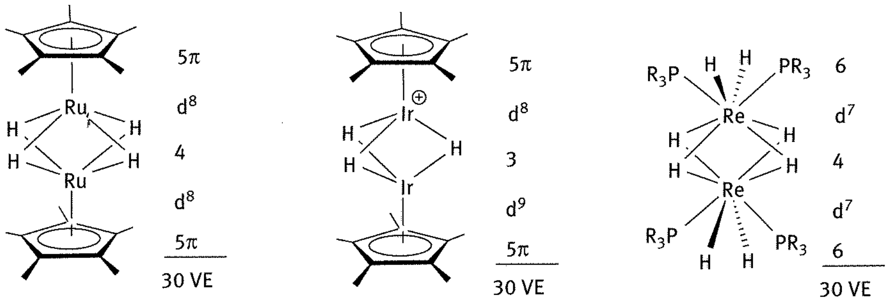


The relationship of this formalism to metal clusters becomes clearer when another example of a triple-decker-type complex, the borole complex $(CO)_3Mn(\mu,\eta^5\text{-}C_4H_4BR)Mn(CO)_3$ is examined. Borole (C_4H_4BR) is a 4π ring and requires two electrons to become a 6π aromatic system; these are supplied by the two $Mn(CO)_3$ 1-electron donor fragments. An equivalent description is that of a metallacarborane cluster. Clearly, the cluster formulation requires no metal–metal bond. Other binuclear compounds can be similarly considered as delocalized clusters, with either 30 or 34 VE count. Most metal carbonyl dimers fall into the 34 VE category, including $Fe_2(CO)_9$.

The same considerations apply to hydride-bridged binuclear compounds; here, too, cluster-type electron-deficient bonding makes the assumption of M–M bonds unnecessary.



sandwich and cluster formulation



Key points

CO binds to metals in low oxidation states. The stability of these complexes is due to the strong back-bonding contribution.

Mononuclear CO complexes and their derivatives tend to obey the 18-electron rule.

CO dissociation leads to binuclear metal carbonyls and/or metal carbonyl clusters. Tendency to cluster formation increases from the first to third row metals.

Binuclear carbonyls with bridging CO ligands display cluster-type electron-deficient bonding, without M–M bonds. They belong to 30/34 VE compound classes.

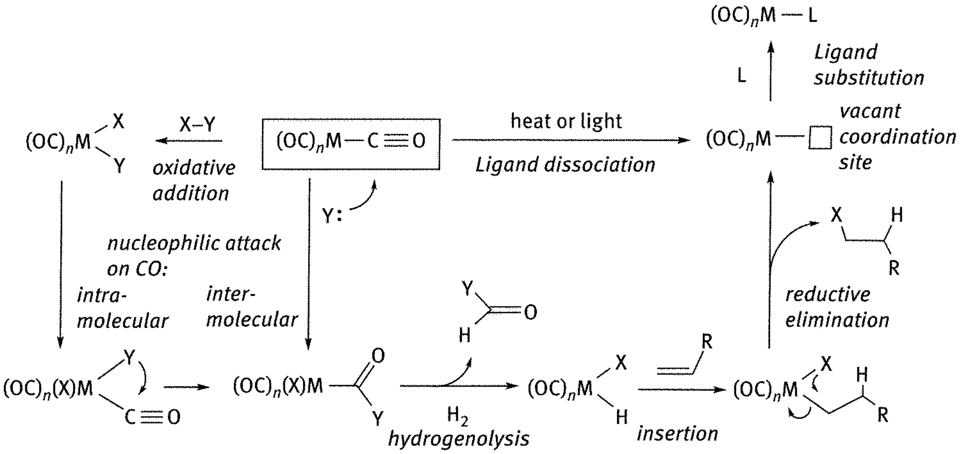
Binuclear metal carbonyls without bridging CO are M–M bonded.

Exercises

1. Account for the absence of a Co–Co bond in solid $Co_2(CO)_8 = [(OC)_3Co(\mu\text{-}CO)]_2$. Does this compound obey the 30/34 VE rule?
2. Describe the bonding in $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$.
3. Discuss the electron count and bonding in $(Cp^*Re)_2(\mu\text{-}CO)_3$.
4. How many electrons are contributed to cluster bonding by the following fragments: $Fe(CO)_3$, $Mn(CO)_3$, μ-CO, μ-C_4H_4BR, μ-C_6H_6, μ-CR, μ-CH_2?

2.5.3 Reaction Mechanisms of Metal Carbonyls

Metal carbonyls display a number of key reaction patterns that will recur for other ligand classes as well and which form the basis of most catalytic cycles: *Ligand dissociation; ligand substitution; oxidative addition; reductive elimination; intra- or intermolecular nucleophilic attack:*



2.5.3.1 Ligand Substitution: Principles and Mechanisms

Most stoichiometric and catalytic reactions begin with a ligand substitution step to allow the substrate to bind to the metal centre. Different reaction mechanisms can be distinguished based on their kinetic behaviour and can generally be divided into ***dissociative*** and ***associative*** pathways.

Which reaction pathway is followed depends not least on the electron count of the complex concerned and can have a profound effect on reaction rates. For example, the square-planar 16 VE compound Rh(acac)$(C_2H_4)_2$ and its 18 VE relative CpRh$(C_2H_4)_2$ undergo exchange with excess ethylene via associative and dissociative pathways, respectively; however, Rh(acac)$(C_2H_4)_2$ reacts about 10^{14} times faster!

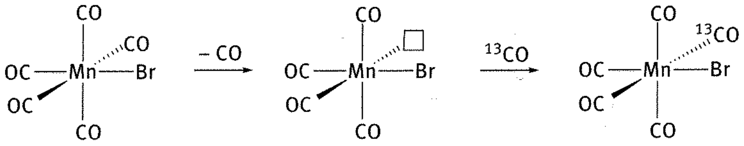
Dissociative substitution. Ligand dissociation from the starting complex is rate determining; the rate does not depend on the concentration of the incoming ligand. The entropy of activation $\Delta S^{\ddagger}$ is small and positive.

$$L_nM{-}X \xrightarrow[k_1]{} \underset{\text{coordinatively unsaturated intermediate}}{L_nM} + X \xrightarrow[k_2]{Y} L_nM{-}Y \qquad \text{Rate} = -\frac{d[L_nMX]}{dt} = k_1[L_nMX]$$

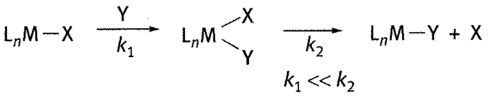
$$k_1 \gg k_2$$

Since most reactions are carried out in solution, it is important to keep in mind that ***truly coordinatively unsaturated intermediates are rarely if ever present*** since the solvent acts as a weakly coordinating ligand and takes the place of X. Since the concentration of the solvent by definition is 1, it does not enter into the rate equation. However, coordination of solvents to intermediates can greatly influence the reaction rate by stabilizing the transition state.

Dissociative ligand substitution occurs for 18 VE complexes. It is frequently (but not exclusively) stereospecific: the coordinatively unsaturated intermediate retains the geometry of the starting complex, for example in the *cis*-substitution in Mn(I) carbonyls:



Associative substitution. Here the incoming ligand binds to the starting metal complex, thus increasing the coordination number. This is followed by ligand dissociation in a second step. Since binding another ligand involves a reduction in the degrees of translational and rotational freedom, the entropy of activation $\Delta S^{\ddagger}$ is large and negative.

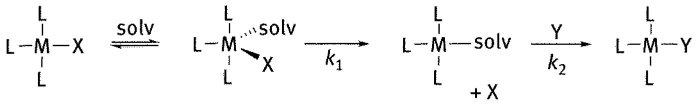


$$L_nM{-}X \xrightarrow[k_1]{Y} L_nM\begin{smallmatrix}X\\Y\end{smallmatrix} \xrightarrow[k_2]{} L_nM{-}Y + X \qquad k_1 \ll k_2$$

Second-order rate law:
Rate = $k_1[L_nMX][Y]$

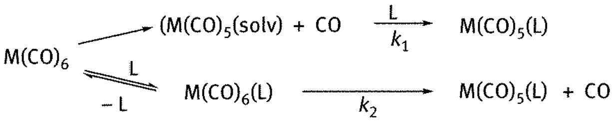
Associative ligand exchange requires that the metal complex has a sufficiently low coordination number to allow another ligand to enter the coordination sphere. This mechanism is therefore typically found for 16 VE square-planar complexes of metals with d^8 configuration.

If the reaction is conducted in a coordinating solvent, it may follow a solvent-assisted associative substitution, which involves a solvent-association equilibrium before the reaction with Y:



Rate = $k_1[L_nMX] + k_2[L_nMX][Y]$

For example, this type of rate law is observed in the substitution of $M(CO)_6$ (M = Cr, Mo, W) by PPh_3 or PBu_3, where an associative and solvent-assisted pathways compete to give the same product.



independent of [L]

1st order in [L]

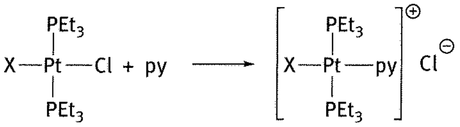
The rates of associative substitution will obviously depend primarily on the incoming nucleophile Y and the nature of the metal M. However, in square-planar complexes and for a given M and Y there can also be great variations in rate as a function of the ligand *trans* to the leaving group X. This is a kinetic phenomenon known as the ***trans* effect**. Platinum(II) complexes in particular show a strong *trans* effect and have been studied in much detail.

Trans effect: kinetics

The strongest *trans* effect is observed for strong donor ligands, such as hydride or alkyl, and strong π-acceptor ligands like CN^-, CO, and phosphines. The reason is on the one hand a labilization of the bond in *trans* position by strong donors, i.e. labilization of the square-planar ground state, whereas the effect of π-acceptors is thought to be the result of stabilization of the five-coordinate transition state. Either way this can affect the rate of substitution by many orders of magnitude.

The *trans* effect decreases in approximately the following sequence (which follows the trend in the spectrochemical series from typical strong-field to weak-field ligands):

$$H^- > CH_3^- \geq CN^- \approx CO > PR_3 > Cl > NH_3 > OH^- > NO_3^- \approx H_2O$$



Relative rates:

X = Cl	CH_3	H
1	170	13,000

By contrast, the analogous *cis* isomer of square-planar complexes shows hardly any influence of X on rate (there is what is termed a *cis*-effect, but this is small, with only a factor of 2–3 between rates).

Trans effect versus trans influence

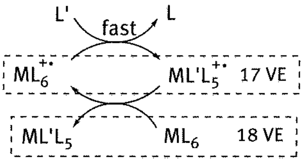
The *trans* effect concerns the structure of the transition state and is a *kinetic* phenomenon. This is to be distinguished from the ***trans* influence**, which describes the lengthening of a metal–ligand bond in the *ground state* due to the influence exerted by a ligand *trans* to this bond. The *trans* influence is often used to explain variations in crystallographically determined M–L bond distances.

17-electron complexes. Metal complexes with an electron count of less than 18 undergo ligand substitutions many orders of magnitude faster than their 18 VE analogues. Irradiation can drastically accelerate substitution by generating 17 VE radical intermediates, e.g. photolysis of $Mn_2(CO)_{10}$ generates $Mn(CO)_5^{\bullet}$ which reacts rapidly with PPh_3. The 17 VE species reacts with L to give a 19 VE adduct with a half-order M–L bond. For example, whereas $[V(CO)_6]^-$ (18 VE) is inert to PPh_3 even under forcing conditions, the radical $V(CO)_6^{\bullet}$ (17 VE) reacts rapidly even at –70 °C. These substitutions follow an associative mechanism.

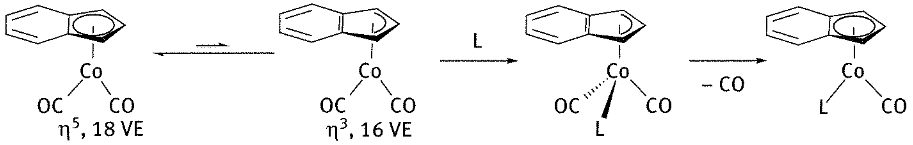
$$\underset{17\ \text{VE}}{\dot{V}(CO)_6 + L} \longrightarrow \underset{19\ \text{VE}}{L{-}\dot{V}(CO)_6} \xrightarrow{\text{fast}} \underset{17\ \text{VE}}{L{-}\dot{V}(CO)_5} + CO$$

Redox catalysis

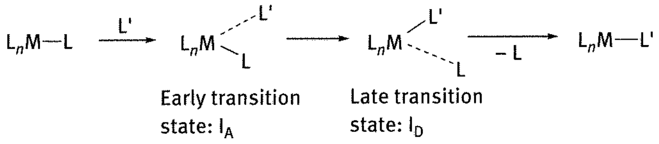
The same principle operates in redox-catalysed substitution reactions: a small fraction of an 18 VE complex is oxidized to a 17 VE species which undergoes rapid substitution. This is followed by electron transfer from another 18 VE species, so that only catalytic concentrations of 17 VE species are required.



Associative substitution and ring slippage. Changes in the hapticity of cyclopentadienyl ligands from η^5 to η^3 are sometimes a pathway for generating a coordination site in 18 VE complexes that facilitates ligand association and substitution. This is mainly observed for electron-rich 18 VE complexes with indenyl ligands. For example, the indenyl complex $(Ind)Co(CO)_2$ reacts 10^8 times faster than $CpCo(CO)_2$.



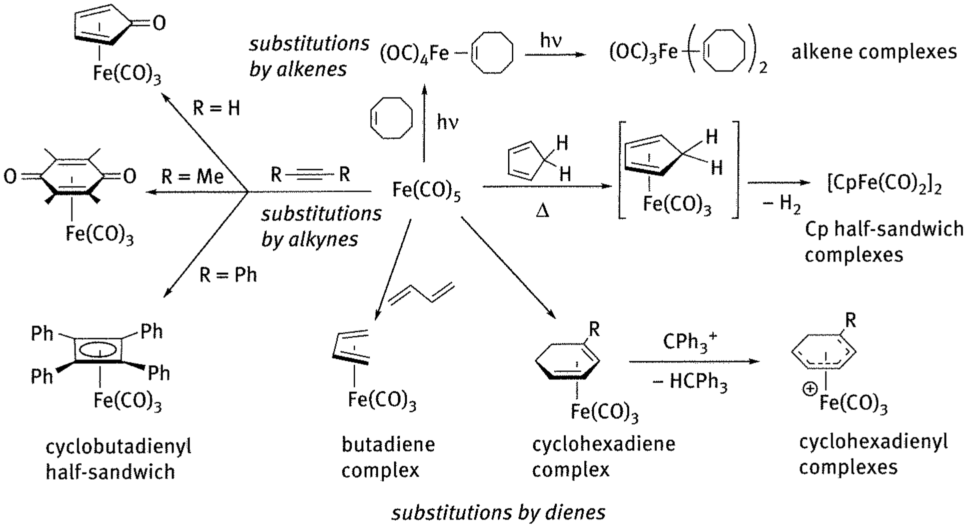
Interchange mechanism. There are many instances where the rate-limiting step of a substitution reaction contains a bonding contribution from both the incoming and the outgoing ligand. This is particularly the case where the complex in question is cationic, so that the substitution is preceded by ion association. Depending on the position of the transition state along the reaction coordinate, i.e. depending on the strength of the bonding interactions of L and L′, one differentiates between ***associative*** and ***dissociative interchange***, I_A and I_D. For example, the olefin polymerization catalysis with metallocene borate ion pair catalysts (Section 3.7.2) follows an I_A mechanism.



2.5.3.2 CO Ligand Substitution: Overview and Methods

Substitution reactions of metal carbonyls provide a convenient route to a large variety of compound classes, each of which have themselves become important starting materials.

Photochemical substitutions can be carried out at room temperature or below, and allow the isolation of thermally sensitive products like mono- and bis-alkene compounds. The parent ethylene complexes, $Fe(C_2H_4)(CO)_4$ and $Fe(C_2H_4)_2(CO)_3$, are thermally unstable. The reaction with butadiene proceeds stepwise via $(OC)_4Fe(\eta^2$-butadiene). The reactions with acetylenes involve C–C coupling and can on occasions include incorporation of CO. Substitutions with alkynes and cyclopentadiene give rise to cyclopentadienyl and cyclobutadienyl half-sandwich complexes, respectively.

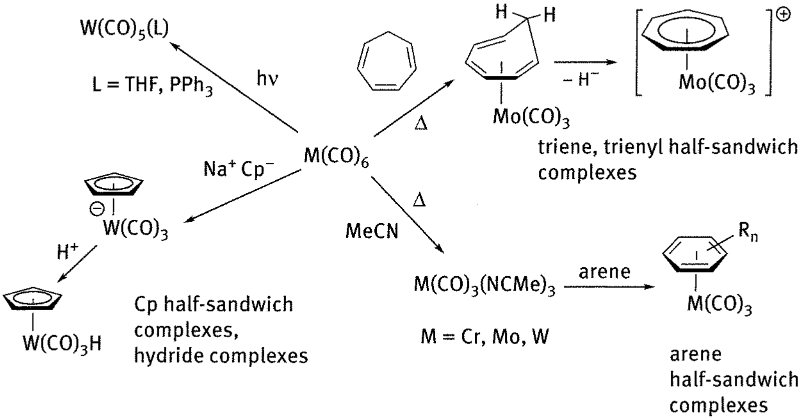


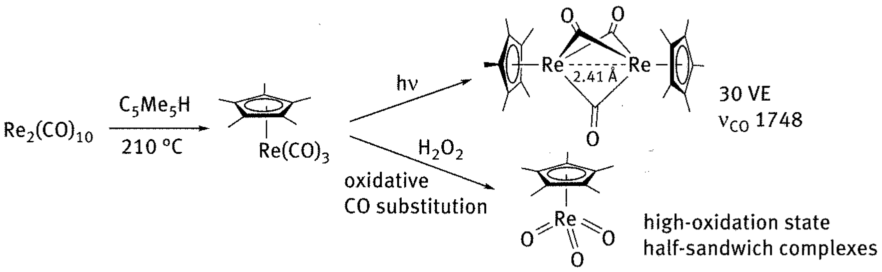
Since $Fe(CO)_5$ is thermally stable and toxic, it is usually preferable to employ the involatile $Fe_2(CO)_9$ as starting material. This dissociates into $Fe(CO)_5$ and the reactive $Fe(CO)_4$ fragment. $Ru_3(CO)_{12}$ can similarly be used as source of $Ru(CO)_4$.

Another way of facilitating CO substitution is the selective oxidation to CO_2, using amine oxides:

$$M(CO)_n + Me_3N\text{-}O \xrightarrow{L} M(CO)_{n-1}(L) + CO_2 + Me_3N$$

Metals with d^6 electron configuration, such as M^0 (M = Cr, Mo, W) and M^I (M = Mn, Re), are known as kinetically inert, and substitutions require more forcing conditions. One way to overcome this lack of reactivity is to generate complexes of coordinating (but labile) solvents, such as THF or MeCN (acetonitrile). For example, refluxing $W(CO)_6$ in MeCN gives $W(CO)_3(MeCN)_3$. Acetonitrile ligands bind sufficiently strongly to give isolable adducts but are labile enough for facile substitution, e.g. by arenes. Some reactions of d^6 metal carbonyls are summarized in the following schematic.





By contrast, substitution reactions of $Co_2(CO)_8$ are very facile, on the one hand because the compound has a d^9 configuration and is not coordinatively saturated, and on the other since it dissociates readily to give the 17 VE $Co(CO)_4^{\bullet}$ radical which, as shown in the previous schematic for $V(CO)_6^{\bullet}$, undergoes CO substitution reactions very much faster than even-electron compounds or intermediates.

The ease with which CO ligands can be substituted decreases with increasing degree of substitution, and removal of the last one or two CO ligands is usually very difficult. Since most ligands are better electron donors than CO, substitution increases the electron density on the metal centre and therefore strengthens back-donation, so that with each CO substitution step the M–C bond strength to the remaining CO ligands increases (as reflected in the decrease in the ν_{CO} frequencies). This also reduces the susceptibility of CO ligands to nucleophilic attack.

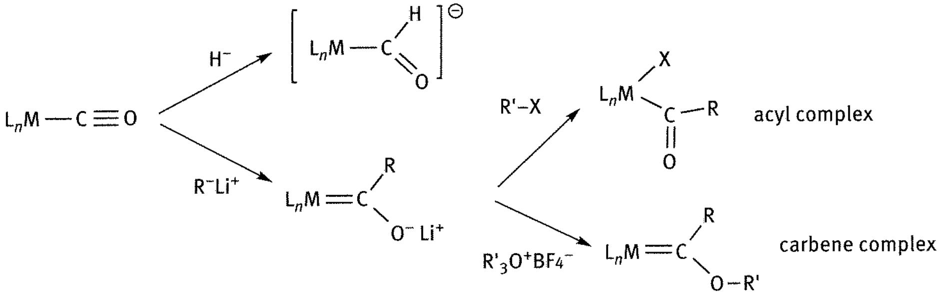
Rate of CO substitution:

$$M(CO)_n > (L)M(CO)_{n-1} > (L)_2M(CO)_{n-2} > (L)_3M(CO)_{n-3} > \text{etc.}$$

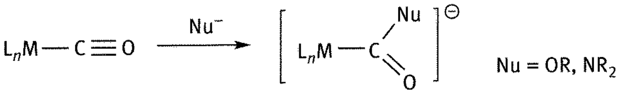
2.5.3.3 Nucleophilic Attack on CO

Nucleophilic attack on a coordinated CO ligand is a common step in catalytic and stoichiometric reactions. With weak back-bonding and strong polarization, CO ligands in cationic carbonyl complexes are highly reactive and may be attacked even by weak nucleophiles such as water, whereas neutral complexes require stronger nucleophiles (OH^-, amines). Electron-rich metal carbonyls ($\nu_{CO} \leq 2000\ cm^{-1}$) are less reactive. The rate of nucleophilic attack decreases as CO is substituted by more electron-rich ligands such as phosphines.

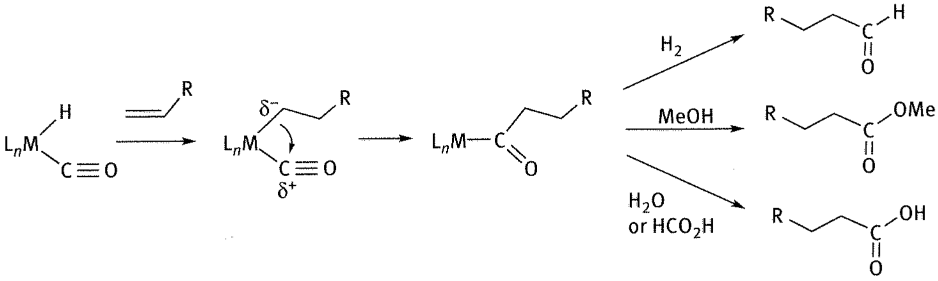
Nucleophilic attack by hydride gives formyl complexes which in some cases (M = Cr, Mo, Fe) are isolable. Lithium alkyls lead to O-stabilized carbenes which can be stabilized by a subsequent alkylation step with Me^+. This is a route to carbene complexes ('Fischer carbenes', Chapter 2.12).



Attack by alkoxides or amides leads to alkoxycarbonyl and carbamoyl (aminocarbonyl) compounds.



Intramolecular nucleophilic attack on CO is a key step in catalytic alkene functionalization reactions. Alkene insertion into a M–H bond generates an alkyl which is transferred to a CO ligand in the *cis* position. The M–acyl bond can then be cleaved with various reagents to give hydroformylation or carbonylation products (cf. Section 3.4.2):



Box 2.5.3 Nucleophilic attack on CO for hydrogen production

Of particular importance is attack by OH^- on metal carbonyls. This reaction models the processes that occur on the surface of heterogeneous metal catalysts (usually Cr-promoted iron or ruthenium, or Cu/ZnO) in the so-called **water-gas shift (WGS) reaction**. This is a large technical process for the production of hydrogen from CO and steam. It is usually coupled with **steam reforming**, also a large heterogeneously catalysed process that converts hydrocarbons (mostly methane) into CO and hydrogen. Together, these processes generate the hydrogen required for the ammonia process and other industrial scale hydrogenations.

The cycles also show that H_2 production is inextricably linked to CO_2 production *(unless produced by electrolysis using hydroelectric, nuclear, or wind power). Using H_2 as a fuel does not, therefore, eliminate greenhouse gas emissions.*

How 'clean' is H_2 as fuel?

Steam reforming:

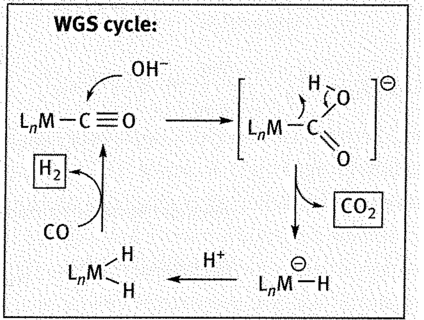
$$CH_4 + H_2O \overset{\substack{\text{Ni catalyst} \\ 700\text{–}1100\ °C}}{\rightleftharpoons} CO + 3\,H_2$$

Water-gas shift:

$$CO + H_2O \overset{\substack{\text{Fe or Ru catalyst} \\ 200\text{–}350\ °C}}{\rightleftharpoons} CO_2 + H_2$$

Overall process:

$$CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$$



2.5.4 Metal Carbonyl Anions

$\overset{\ominus}{M}{\equiv}C{=}O$

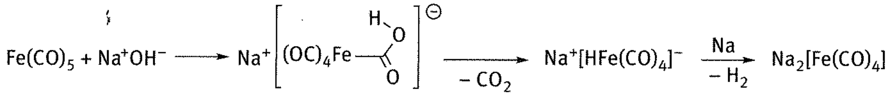
In some cases, the reduction of a metal salt with a powerful reducing agent such as an alkali metal under CO pressure generates anionic carbonyl complexes, provided this reduction results in an 18-electron configuration. Similarly, pre-formed metal carbonyl complexes can be reduced to give anionic products. The addition of two electrons is accompanied by the loss of one CO ligand. Metal carbonyl hydrides may be deprotonated to give anionic compounds.

Overview of synthetic methods:

By disproportionation:

$$3\,Mn_2(CO)_{10} \xrightarrow[120\ °C]{\text{pyridine}} 2\,[Mn(py)_6]^{2+}\,[Mn(CO)_5{}^-]_2$$

By nucleophilic attack on CO:

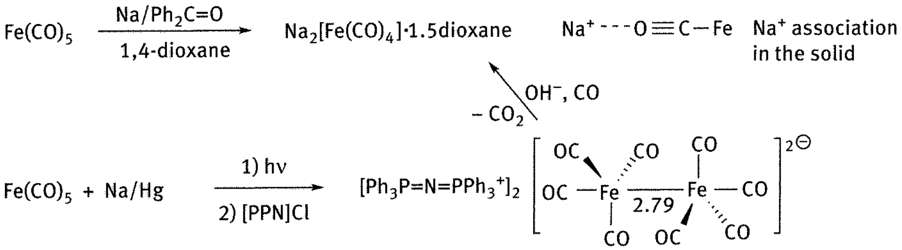


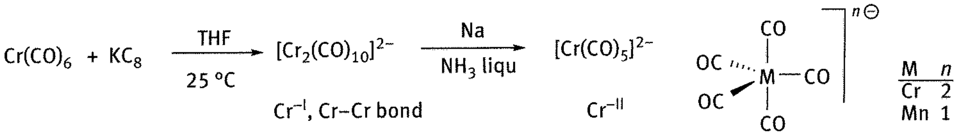
(see *water-gas shift* reaction for the generation of H_2 from CO and $H_2O \rightarrow H_2 + CO_2$, Box 2.5.3).

Bulky cations like PPN⁺ often facilitate the isolation of large complex anions.

By reduction:

$$\mathrm{ZrCl_4(THF)_2 + 6\,KC_{10}H_8 \xrightarrow[\text{15-crown-5, }-4\,KCl]{THF} [K(15\text{-}crown\text{-}5)]_2[Zr(CO)_6]}$$

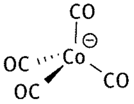




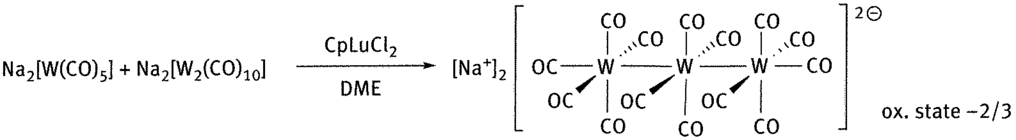
reductive M–M bond cleavage:

$$\mathrm{Mn_2(CO)_{10} + 2\,Na \xrightarrow[THF]{} Na[Mn(CO)_5]}$$

$$\mathrm{Co_2(CO)_8 + 2\,Na \xrightarrow[THF]{} Na[Co(CO)_4]}$$

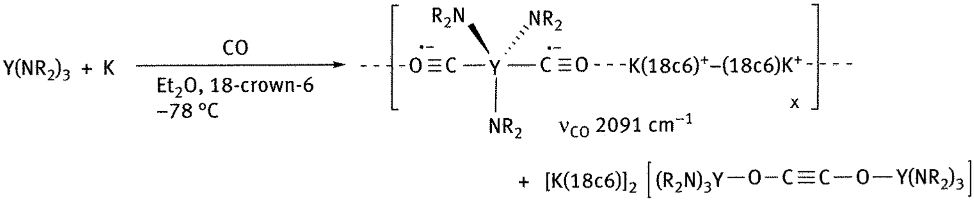


By oxidation of carbonyl anions:

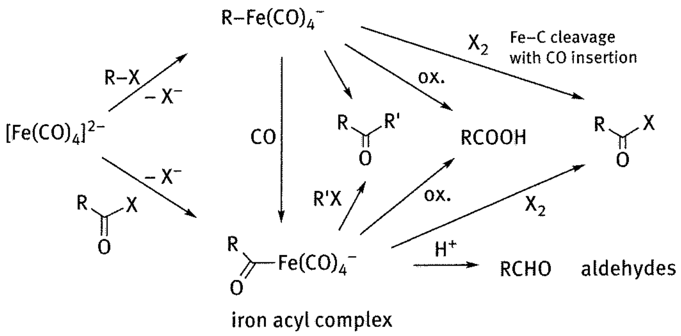


The anions $[M(CO)_6]^{2-}$ (M = Ti, Zr, Hf) are the only binary carbonyl complexes of Group 4 metals. The analogous Group 5 complexes $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ are prepared similarly. Although thermally stable, these and other anionic carbonyl complexes are highly sensitive to oxidation.

An unusual case of a CO complex of a lanthanide is obtained by treating mixtures of $Y[N(SiMe_3)_2]_3$ and potassium metal (to reduce Y^{III} to Y^{II}) with CO. This generates the $[(R_2N)_3Y(CO)_2]^{2-}$ anion, which contains CO^{1-} radical anions. The reaction is accompanied by CO coupling.



Reactions. Carbonyl metallate anions oxidatively add alkyl and acyl halides to generate M-alkyl bonds which, due to the negative charge of the complexes, possess Grignard-like reactivity. The iron carbonyl salt $Na_2Fe(CO)_4$ (*Collman's reagent*) has extensive synthetic applications:



Super-reduced metal carbonyl anions. While the reduction of metal carbonyls with common reducing agents such as sodium amalgam in THF stops at the stage of mono- or dianions, more forcing reducing conditions (typically reduction by solvated electrons: Na in liquid ammonia, lithium-naphthalene, alkali metals and crown ethers, or sodium in hexamethylphosphoramide) generate highly reduced carbonyl metallates in which the formal oxidation state of the metal centre may be as low as –IV. Examples are the tri-anions $[M(CO)_5]^{3-}$ (M = V, Nb, Ta), $[M(CO)_4]^{3-}$ (M = Mn, Re) and the tetra-anions $[M(CO)_4]^{4-}$ (M = Cr, Mo, W):

$$Na[V(CO)_6] + 3\ Na \xrightarrow{NH_3\ liq.} Na_3[V(CO)_5] + 0.5\ Na_2C_2O_2$$

$$Na[Mn(CO)_5] + 3\ Na \xrightarrow{HMPA} Na_3[Mn(CO)_4] + 0.5\ Na_2C_2O_2$$

$$K[Co(CO)_4] + 3\ K \xrightarrow{NH_3\ liq.} K_3[Co(CO)_3] + 0.5\ K_2C_2O_2$$

During these reactions the liberated CO is reduced to a coupling product, acetylenediolate, $^{-}OC{\equiv}CO^{-}$.

Naturally, metal carbonyl anions are extremely strong bases and the metal centre is very electron rich. Consequently these compounds show extensive back-bonding, as shown by the exceptionally low ν_{CO} frequencies, which are as low as 1462 cm^{-1} for the most highly reduced species (Table 2.5.4.1).

This extensive acceptance of electron density from the metal is a reminder that **oxidation states are purely formal assignments**—the CO ligands become highly negatively polarized, so that the electron density on the metal centre, and hence the d-orbital energy, increases much less than negative oxidation states of –III or –IV would imply.

Table 2.5.4.1 IR frequencies of metal carbonyl anions.

Carbonyl anion	ν_{CO} [cm^{-1}]	Super-reduced anion	ν_{CO} [cm^{-1}]
$[V(CO)_6]^-$	1860	$[V(CO)_5]^{3-}$	1807(w), 1630(s), 1580(s)
$[Cr(CO)_5]^{2-}$	1750	$[Cr(CO)_4]^{4-}$	1462(s)
$[Mn(CO)_5]^-$	1893, 1860	$[Mn(CO)_4]^{3-}$	1790(w), 1600(s)
$[Fe(CO)_4]^{2-}$	1790		
$[Co(CO)_4]^-$	1890 ($AsPh_4^+$)	$[Co(CO)_3]^{3-}$	1740, 1610(vs)

2.5.5 **Metal Carbonyl Cations**

$\overset{\oplus}{M}-C\equiv O$

Placing a positive charge on the metal centre contracts the d-shell and reduces the tendency towards back-bonding. This weakens the M–CO bond and facilitates the displacement of CO by more nucleophilic ligands such as halide or water. Cationic metal carbonyl complexes are therefore formed only if paired with anions of low nucleophilicity.

Preparation:

By halide abstraction with Lewis acids:

$$Mn(CO)_5Cl + AlCl_3 \xrightarrow[300\ \text{bar CO}]{100\ °C} [Mn(CO)_6]^+AlCl_4^-$$

By oxidation:

$$Mn_2(CO)_{10} + 2\,HF + 2\,BF_3 \xrightarrow[RT]{0.6\ \text{bar CO}} 2\,[Mn(CO)_6]^+BF_4^- + H_2$$

$$Co_2(CO)_8 + 2\,(CF_3)_3B\text{-}CO + 2\,HF \xrightarrow[HF_{\text{anhydr.}}]{CO} 2\,[Co(CO_5]^+[FB(CF_3)_3]^- + H_2$$

A particular successful strategy are reactions in super-acidic media such as HF/SbF_5, which generate the extremely non-nucleophilic anions SbF_6^- and $Sb_2F_{11}^-$, for example:

$$Fe(CO)_5 + XeF_2 + CO + 4SbF_5 \xrightarrow[HF/SbF_5,\ 2d]{50\ °C,\ 1\ \text{bar}} [Fe(CO)_6]^{2+}[Sb_2F_{11}^-]_2 + Xe$$

$$2\,IrF_6 + 15\,CO + 12\,SbF_5 \xrightarrow[SbF_5,\ 50\ °C]{1\ \text{bar CO}} 2\,[Ir(CO)_6][Sb_2F_{11}]_3 + 3\,COF_2$$

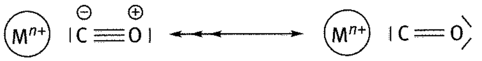
Under these conditions highly electrophilic carbonyl complexes of metals in oxidation states +II and +III can be isolated, as well as the linear dicarbonyl cations $[Au(CO)_2]^+$ and even $[Hg(CO)_2]^{2+}$, the only example of an isolable Main Group carbonyl (Table 2.5.5.1).

These so-called 'non-classical' metal carbonyls demonstrate interesting bonding concepts. The near absence of a back-bonding contribution is evident from the very long M–C

Table 2.5.5.1 IR frequencies of homoleptic metal carbonyl cations.

d^6	ν_{CO} [cm^{-1}]	d^8	ν_{CO} [cm^{-1}]	d^{10}	ν_{CO} [cm^{-1}]
$[Fe(CO)_6]^{2+}$	2215	$[Pd(CO)_4]^{2+}$	2259	$[Au(CO)_2]^+$	2235
$[Ru(CO)_6]^{2+}$	2214	$[Pt(CO)_4]^{2+}$	2261	$[Hg(CO)_2]^{2+}$	2280
$[Os(CO)_6]^{2+}$	2209				
$[Ir(CO)_6]^{3+}$	2268				

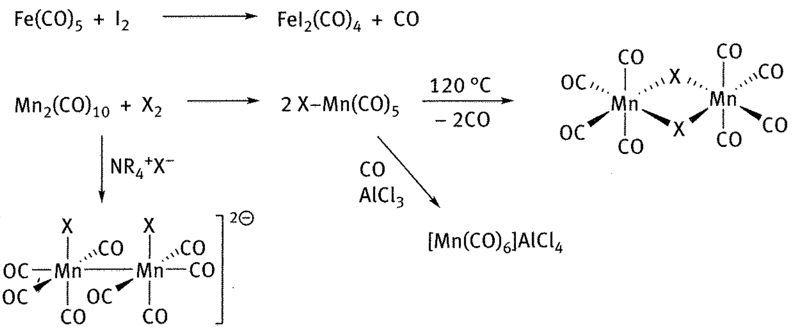
distances in these cations (ca. 2.0 Å). However, this alone cannot explain IR frequencies that are substantially higher than that of free CO. Calculations have shown that placing a positive point charge at the C-end of CO increases the polarization and increases the Coulomb contribution to C≡O bonding. Conversely, placing a point charge at the O-end favours the ketone-like resonance form and lowers the CO vibration (as in isocarbonyl bonding).



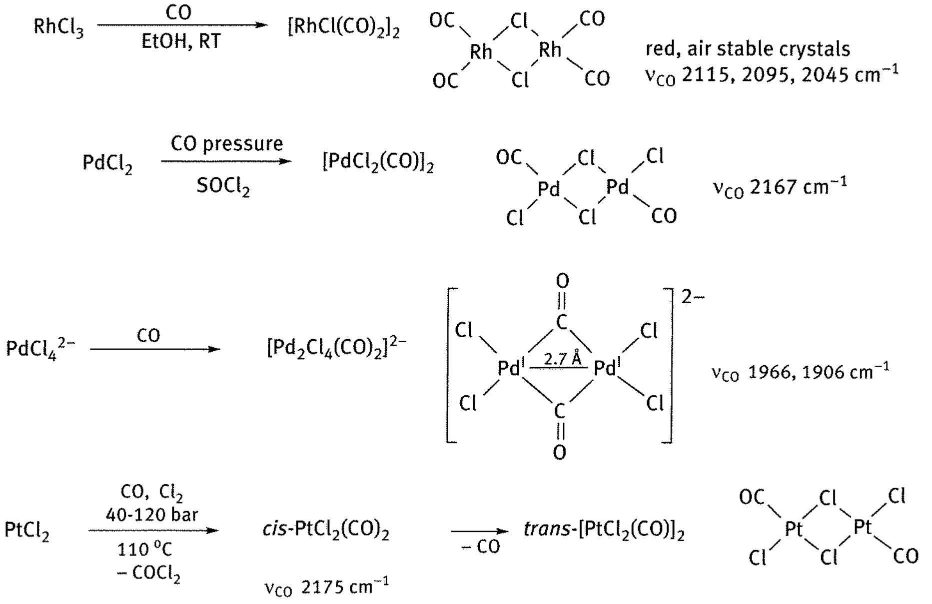
It has been argued that a similar decrease of back-bonding and increase in polarization occurs in vibrationally excited ordinary metal carbonyls, so that in these excited states the occupation of the CO π* orbitals is much diminished. As explained in Box 2.4.1, this would enable nucleophiles to attack coordinated CO ligands, whereas back-bonding would disfavour this interaction. This helps explain the CO activation in catalytic processes.

2.5.6 Metal Carbonyl Halides

The reaction of metal carbonyl complexes with halogens X_2 leads to oxidative addition and formation of M–X bonds. This is an easy way to functionalize carbonyl complexes.



From metal halides. This route is only important for the formation of CO complexes of noble metals. The halides of these elements are easily reduced to give lower valent complexes. $Pt(CO)_2Cl_2$ was the first metal carbonyl ever to be prepared (P. Schützenberger, 1868). A Pt(0) carbonyl $Pt(CO)_4$ analogous to $Ni(CO)_4$, is only stable in an argon matrix at low temperatures; it decomposes to give higher nuclearity Pt carbonyl clusters. Palladium is apparently reduced to Pd(I). $[Rh^{I}Cl(CO)_2]_2$ is made similarly from $RhCl_3$ using CO or ethanol solvent as reducing agent; it is an important catalyst precursor. Substitution with PPh_3 gives *trans*-$RhCl(CO)(PPh_3)_2$, an important precursor for hydroformylation catalysts.



$RhCl_3 \xrightarrow[\text{EtOH, RT}]{\text{CO}} [RhCl(CO)_2]_2$

red, air stable crystals
ν_{CO} 2115, 2095, 2045 cm^{-1}

$PdCl_2 \xrightarrow[SOCl_2]{\text{CO pressure}} [PdCl_2(CO)]_2$

ν_{CO} 2167 cm^{-1}

$PdCl_4^{2-} \xrightarrow{\text{CO}} [Pd_2Cl_4(CO)_2]^{2-}$

ν_{CO} 1966, 1906 cm^{-1}

$PtCl_2 \xrightarrow[\substack{110\ ^{\circ}C \\ -\ COCl_2}]{\substack{CO,\ Cl_2 \\ 40\text{-}120\ bar}} cis\text{-}PtCl_2(CO)_2 \xrightarrow[-\ CO]{} trans\text{-}[PtCl_2(CO)]_2$

ν_{CO} 2175 cm^{-1}

2.5.7 Metal Carbonyl Hydrides

2.5.7.1 Syntheses

The protonation of metal carbonyl anions leads to metal carbonyl hydrides, $H_xM(CO)_y$. Classical examples are:

$$Co(CO)_4^{-} + H^{+} \longrightarrow HCo(CO)_4$$

$$HFe(CO)_4^{-} + H^{+} \longrightarrow H_2Fe(CO)_4$$

Monomeric hydrides of first row transition metal carbonyls are volatile liquids which are stable under an atmosphere of CO at low temperature but in the absence of CO liberate H_2. The hydrides of the heavier metals within a triad are much more stable. $HCo(CO)_4$ was the first metal hydride to be discovered; it is a member of the cobalt-catalysed olefin hydroformylation cycle (cf. Section 3.4.1).

Strong acids are required for the protonation of neutral metal carbonyl complexes. The susceptibility to protonation increases as CO ligands are replaced by more electron donating ligands such as phosphines; for example, unlike $CpCo(CO)_2$, $CpCo(PMe_3)_2$ is a strong organometallic base that deprotonates ammonium salts.

$$Fe(CO)_3(PPh_3)_2 + H_2SO_4 \longrightarrow [HFe(CO)_3(PPh_3)_2]^+[HSO_4]^-$$

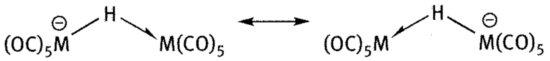
$$CpCo(PMe_3)_2 + NH_4PF_6 \longrightarrow [CpCo(PMe_3)_2H]^+PF_6^- + NH_3$$

Careful protonation of highly reduced metal carbonyl anions, such as $[Mn(CO)_4]^{3-}$, allows the isolation of dihydrido anions:

$$Na_3[Mn(CO)_4] \xrightarrow[\text{HMPA}]{\text{EtOH, AsPh}_4\text{Cl}} [AsPh_4]^+[H_2Mn(CO)_4]$$

Anionic clusters may be protonated to give products in which the H atom is encapsulated into the cluster metal framework, this '**interstitial hydrogen**' is evidence for the ease with which H atoms can migrate through metal lattices. In $[HCo_6(CO)_{15}]^-$, the hydride is located in the centre of the Co_6 octahedron.

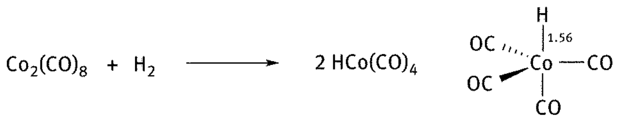
A general route to hydrides is by reduction of metal carbonyl halides and H^- addition to carbonyls. The anions $[M_2(\mu\text{-}H)(CO)_{10}]^-$ (M = Cr, Mo, W) are examples of bent M–H–M bridged systems without the support of M–M bonds or bridging CO, the hydride is part of a 2-electron-3-centre bond.

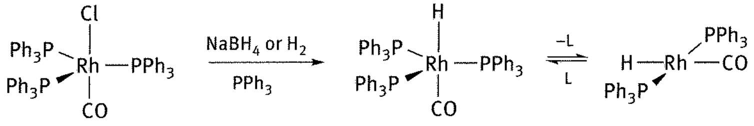


The half-arrow formalism shown here indicates that the M–H σ-bond acts as donor to the second M centre.

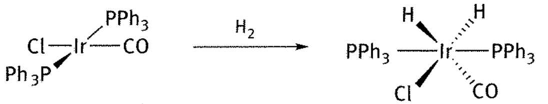
With a bond enthalpy of 450 kJ mol^{-1}, the H–H bond in H_2 is one of the strongest chemical bonds, far stronger than a C–C bond, and the H_2 molecule lacks polarity. Nevertheless, metals are able to react with H_2 under H–H bond scission and formation of M–H bonds. This hydrogen activation is the basis of many important catalytic reactions. Since H is more electronegative than most metals, the hydride ligand is formally regarded as anionic, so that H_2 addition to a metal is an oxidative addition process in which the metal centre increases the formal oxidation state by two units.

$HCo(CO)_4$, one of the first metal hydrides to be discovered (W. Hieber, 1930s), is thermally unstable and decomposes at its melt temperature (ca. –26 °C). It was one of the first hydroformylation catalysts. The analogous Rh complex is much more active, particularly when stabilized by phosphine ligands. Hydrogenation of *trans*-$RhCl(CO)(PPh_3)_3$ forms the analogous carbonyl hydride which is an isolable and highly active catalyst for the hydroformylation of alkenes. Note that under these conditions Rh does not form a Rh(III) hydride, unlike the Ir analogue. Heating $RuCl_3$ with PPh_3 in a high boiling alcohol also generates a hydrido carbonyl complex. In this case the solvent is partially dehydrogenated and acts as source of CO. $RuH(Cl)(CO)(PPh_3)_3$ is a potent hydrogenation catalyst.



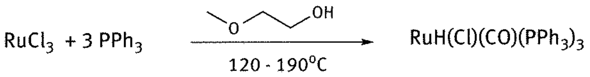


ν(Rh-H) 2041, ν(CO) 1923 cm^{-1}



Vaska's compound
Ir(I), d^8, 16 VE, square-planar
ν(CO) 1944 cm^{-1}

Ir(III), d^6, 18 VE, octahedral
ν(Ir-H) 2098, 2022 cm^{-1}



Ru(II), d^6, 18 VE, octahedral
ν(Ru-H) 2020 cm^{-1}

Acidity of metal carbonyl hydrides. Even though the term 'hydride' would seem to imply the accumulation of negative charge on the H ligand, the strongly electron withdrawing character of the CO ligands in metal carbonyl hydrides leads to a polarization of the M–H bond, with a partial positive charge on H. In polar solvents metal carbonyl hydrides are therefore **acidic**.

Hydride acidity: $HCo(CO)_4$ versus $HCo(PR_3)_4$

Acidities decrease with substitution of CO by phosphines or Cp ligands; e.g. although $HCo(CO)_4$ is comparable in acidity in aqueous solution to dilute HCl, $HCo(PMe_3)_4$ is a strongly reducing hydride (as well as highly sensitive). Acidities also decrease in the series first row < second row < third row metals, as the stability of the M–H bond increases.

Some indicative pK_a values are given in Table 2.5.7.1. Dihydrides have two pK_a values; for example, for $H_2Fe(CO)_4$ removal of the first proton decreases pK_{a2} by 10 orders of magnitude, while the acidity of a cationic dihydride $[L_nMH_2]^+$ may be 10^{20} times higher than that of its neutral counterpart L_nMH.

The M–H stretching frequencies are close to the ν_{CO} region; however, they tend to give a much weaker response in the infrared spectrum and are often difficult to detect.

2.5.7.2 Reactions

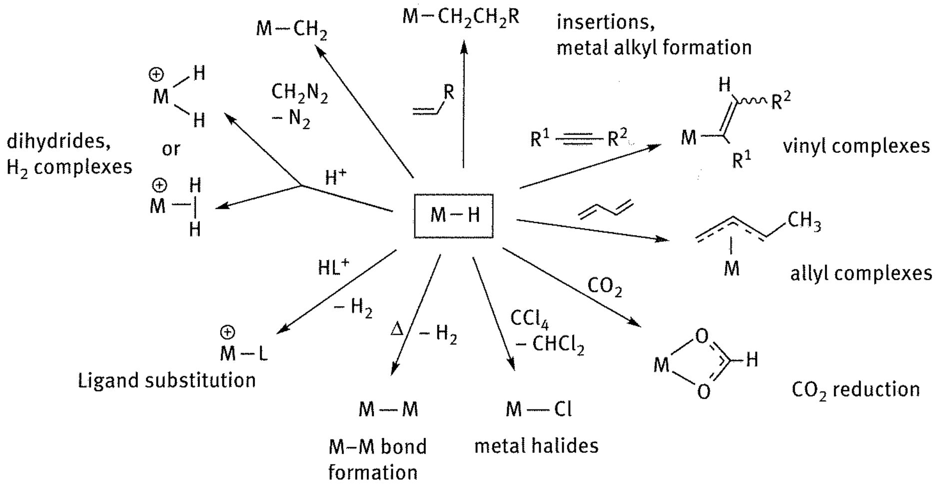
Metal hydrides are highly reactive and involved in numerous organic transformations and catalytic cycles. Terminal M–H bonds are the most reactive; the reactivity decreases in the series terminal H >> μ_2-H > μ_3-H > interstitial H. Their reaction with unsaturated substrates generates metal–alkyl, –vinyl, and –allyl bonds and is key to hydrogenations and reduction processes.

Table 2.5.7.1 Spectroscopic and acidity data for metal carbonyl hydrides.

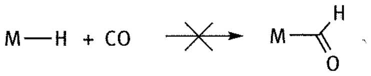
Complex	ν(M–H) [cm^{-1}]	δ ^{1}H NMR/ppm[a]	pK_a (H_2O)	Acidity comparable to
$HCo(CO)_4$	1934	−10.7	1	HCl
$HCo(CO)_3(PPh_3)$		−12.1	7	H_2S
$HMn(CO)_4$	1783	−7.5	7.1	H_2S
$H_2Fe(CO)_4$		−11.1	4.4	acetic acid
$[HFe(CO)_4]^-$		−8.7 (THF)	14	water
$[HTa(CO)_5]^{2-}$		−2.2		
$CpW(CO)_3H$	1854	−7.5	9.0	boric acid
$CpW(CO)_2(PMe_3)H$		−7.9 (*cis*), −8.0 (*trans*)	19.1[b]	*t*-butanol
$[CpW(CO)_2(PMe_3)H_2]^+$		−2.48 (CD_2Cl_2)	−1.9[b]	$MeSO_3H$

[a] The ^{1}H NMR chemical shifts of the hydride ligands are also included; metal hydride chemical shifts cover a very wide range from about −50 to +20 ppm and must ***not*** be regarded as an indication of hydridic character. The negative 'hydridic' shift is a consequence of the paramagnetic current localized in the adjacent metal fragment.

[b] Recalculated from values determined in acetonitrile on the basis pK_a(MeCN) = pK_a(H_2O) + 7.5: S. S.Kristjáhnsdóttir, J. R.Norton: *Transition Metal Hydrides*. Wiley-VCH, 1991.



The insertion of CO into M–C σ-bonds to give metal acyl products is very general. By contrast, the insertion of CO into a M–H bond is **endothermic**, ΔH ≈ +20 kJ mol^{-1}, and therefore does not occur. Formyl complexes are however accessible by other routes, such as intermolecular H^- attack on coordinated CO.

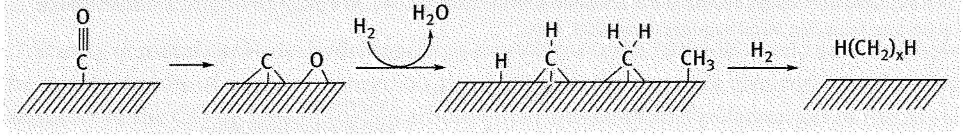


Box 2.5.7 CO Reduction: the Fischer–Tropsch process

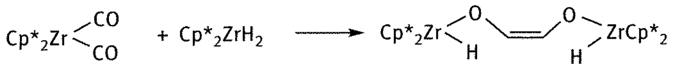
Heterogeneous M–CO chemistry: Surface carbide, methyne, methylene

Metal carbonyl clusters allow fundamental processes to be studied that occur on the surfaces of heterogeneous catalysts. For example, the reversible formation of CO bridges is responsible for the mobility of CO on catalyst surfaces. Studies of clusters allow such fluxional processes to be observed in detail, to identify preferred pathways and the reaction of CO with surface hydrides.

An example of an important reaction catalyzed by heterogeneous iron, cobalt, or ruthenium catalysts where metal carbonyl surface species play an essential role is the reaction of CO and H_2 to saturated hydrocarbons (**Fischer–Tropsch reaction, FT**). The catalyst is supported on a high-surface area oxide such as silica; the reaction is usually operated at 150–300 °C under pressure. The process involves cleavage of CO on the surface and reduction to surface-bound CH and CH_2 species which migrate and combine to give a statistical distribution of hydrocarbons. The products also tend to contain incompletely deoxygenated compounds such as alcohols, ethers, and esters ('oxygenates'). CO/H_2 mixtures, referred to as '**synthesis gas**', are available from any hydrocarbon source including coal. The FT reaction allows the production of liquid fuels and chemical feedstocks from coal, and is important in countries without natural oil resources. Metal carbonyl clusters have enabled key steps of the CO hydrogenation to be monitored.



The reduction of CO with metal hydrides is however possible if subsequent reaction steps give a favourable energy balance overall, as in the reductive coupling of CO to give enolate complexes:

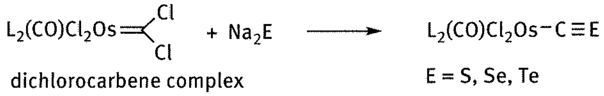


2.5.8 **Related π-Acceptor Ligands**

2.5.8.1 CS, CSe, and CTe

C≡E

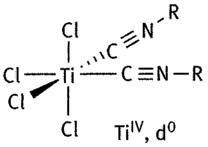
These heavier homologues of CO do not exist in the free state but can be synthesized within the metal coordination sphere. They are mainly of interest in terms of theory and bonding. They are stronger σ-donors as well as better π-acceptors than CO, and the lone pair on C seems to have a distinctly C–E antibonding character (E = S, Se, Te). CS complexes can be obtained by reducing CS_2 complexes with phosphines, for example, reduction of $CpMn(CO)_2(\eta^2\text{-}CS_2)$ gives $CpMn(CO)_2(CS)$; $CpMn(CS)_3$ is also known. Terminal C–S vibrations occur in the region of 1400–1150 cm^{-1}, i.e. they are in the fingerprint region of the IR spectrum where they overlap with other ligand vibrations and are therefore less diagnostic than ν_{CO}. CSe and CTe can be made by nucleophilic substitution, for example:



2.5.8.2 Isocyanide Complexes

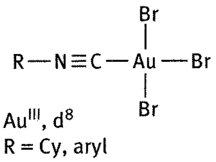
C≡N−R

Isocyanides (= isonitriles) C≡N–R are more basic and stronger σ-donors than CO but much weaker π-acceptors. They are therefore capable of making stable complexes with metals in high oxidation states which do not make stable complexes with CO, and where back-bonding is unimportant or impossible, as in the case of d^0 metals. Some examples:



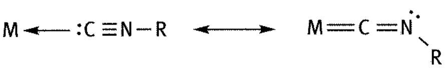
$[Mn(CNR)_6]^{2+}$

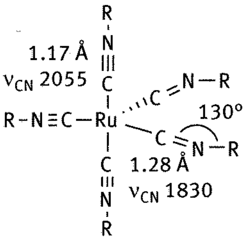
Mn^{II}, d^5



Unlike CO, isocyanides carry a substituent R which can readily be modified. Usually bulky substituents are used to give isolable complexes, such as Bu^t, Cy, or 2,6-$Me_2C_6H_3$.

Isocyanide ligands may be terminal or bridging, bent or linear, depending on the electronic requirements of the metal centre:

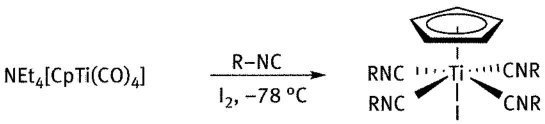




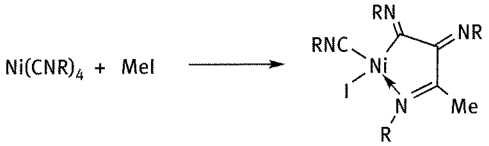
Isocyanide complexes are accessible by ligand substitution:

$$Ni(CO)_4 + 4\ PhNC \longrightarrow Ni(CNPh)_4 + 4\ CO$$

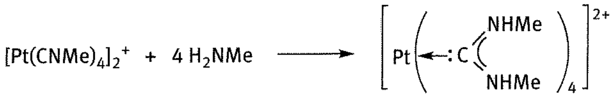
$$FeCl_2(CNR)_4 + RNC \xrightarrow{Na/Hg} Fe(CNR)_5$$



Unlike CO, isocyanides are capable of multiple insertions into metal–alkyl bonds.



The reaction of isocyanide complexes with nucleophiles is a widely used route to non-cyclic, N-stabilized carbene complexes.



Some isocyanide complexes are very stable and soluble in aqueous media. For example, isocyanide complexes of radioactive technetium, $[Tc(CNR)_6]^{2+}$, are used in nuclear medicine as *radio imaging agents* and can be made specific for accumulation in certain organs (e.g. imaging of heart or liver).

2.5.8.3 Nitrosyl Complexes

NO

Nitric oxide is a radical $NO^\bullet$ and therefore contains one electron more than CO. Consequently it can act as both 1- and 3-electron donors. Because of the lone pair on N, the 1-electron coordination geometry is indicated by a bent structure.

linear: θ ca. 160–180° bent: θ ca. 120–140°

As 3-electon donors, two NO ligands can replace three CO ligands. There is therefore a complete series of isoelectronic metal carbonyls and nitrosyls, like the tetrahedral complexes $ML_{4-n}L'_n$: $Cr(NO)_4$, $Mn(NO)_3(CO)$, $Fe(CO)_2(NO)_2$, $Co(NO)(CO)_3$, $Ni(CO)_4$.

The unpaired electron in NO resides in a π^* orbital. Oxidation gives the stable nitrosonium cation NO^+, which is isoelectronic with CO and forms a stable, commercially available salt, $NO^+BF_4^-$. NO^+ is a strong π-acceptor. The bonding characteristics are reflected in the N–O IR frequencies:

NO^+: 2e
NO: 1e or 3e
NO^-: 4e

Free NO	1876 cm^{-1}
$NO^+ BF_4^-$	2387 cm^{-1}
L_nM-NO	1950–1500 cm^{-1} (terminal NO)
	1650–1300 cm^{-1} (bridging NO)

The IR frequencies in metal complexes vary widely however and cannot be used as reliable indicators for the NO bonding geometry.

In the anion $[Fe(CO)_3(NO)]^-$, the NO ligand has a low stretching frequency of 1630 cm^{-1} and is best regarded as NO^- anion, a 4-electron donor. The metal centre is therefore Fe(0), 18 VE.

NO complexes are made either by treatment of complexes with NO gas, or by reaction with NO^+ salts. The chemistry of NO complexes generally follows that described for metal carbonyls, and similar structures are obtained. The so-called *nitroprusside* ion, $[Fe(CN)_5(NO)]^{2-}$, is used as an analytical reagent in qualitative spot tests for reducing substrates, with which it gives characteristically coloured products, for example in the detection of S^{2-}, HS^-, or SO_3^{2-}. NO^+ also forms a number of salts with complex metal anions in which it is not bonded to the metal, e.g. $[NO]_2FeCl_4$.

Key points

CO complexes demonstrate the mechanistic principles of ligand substitution.

CO substitution in octahedral metal carbonyls proceeds stereoselectively, *cis* to an anionic ligand.

Ligand exchange in square-planar d^8 complexes shows a pronounced *trans* effect.

Odd-electron metal carbonyls undergo ligand exchange orders of magnitude faster than even-electron compounds. CO can be substituted by alkenes, alkynes, Cp, and arenes.

Back-bonding increases in the order $[M(CO)_n]^- > M(CO)_n \gg [M(CO)_n]^+$.

Metal carbonyl hydrides are acidic; M–H bonds readily insert alkenes, alkynes, and dienes.

Whereas double CO insertion into M–C bonds is endergonic, i.e. does not take place, double isocyanide insertion is facile.

Isocyanides are stronger donors and weaker acceptors than CO. RNC complexes do not rely on back-bonding for stability.

Acceptor strength decreases for $NO^+ > CO > RNC$.

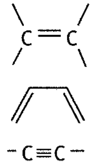
Exercises

1. Metal carbonyl alkyls $R{-}M(CO)_x$ insert CO to give the corresponding acyl complexes. By contrast, treating metal carbonyl hydrides $HM(CO)_x$ with CO fails to give the formyl complex, $(CO)_xM{-}CHO$. Rationalize this observation.
2. Irradiating $ClRe(CO)_5$ under an atmosphere of ^{13}CO gives a ^{13}C-containing product. Show the stereochemistry of this reaction.
3. Identify the products and write the chemical equations for the following reactions of $Mn_2(CO)_{10}$:
   (i) treatment with an excess of pyridine to give product **A**;
   (ii) reaction with 1 Br_2 to give **B**;
   (iii) reaction with sodium amalgam to give **C**.
   (iv) Treatment of product **C** with MeI gives **D** and an inorganic salt. Exposure of **D** to CO gives product **E**, which shows C–O stretching modes in the IR spectrum at 2115, 2011, 2003, and 1664 cm^{-1}.

Identify products **A**–**E** and draw the reaction pathways.

4. $PtCl_2(CO)_2$, a carbonyl of a third row M^{II} metal, shows $\nu_{CO} = 2175\ cm^{-1}$. $Cp_2W(CO)_2$, another third row M^{II} carbonyl, shows $\nu_{CO} = 1872$ and $1955\ cm^{-1}$. What do these differences indicate in terms of M–CO bonding?
5. Why is the rate of CO substitution of $Co_2(CO)_8$ much faster than that of $Ni(CO)_4$, even though the latter has fewer ligands?
6. What is the water-gas shift reaction and how is it catalysed?

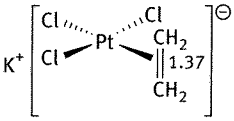
2.6 L-Type π-Acceptor Ligands: Alkenes, Dienes, and Alkynes

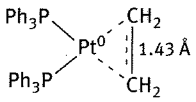


Unsaturated hydrocarbons can act as donors via their π-electron systems. As described in Section 2.3.2, they can also participate in metal-to-ligand back-bonding. Their π-acceptor strength increases with the degree of unsaturation: alkenes < conjugated dienes < alkynes.

Coordination to a metal centre induces polarity in otherwise non-polar molecules like alkenes and alkynes. This makes them susceptible to nucleophilic attack and hence functionalization. Apart from their role as ligands, C=C and C≡C compounds are therefore the basis of most catalytic transformations and industrial processes.

The first organometallic π-complex was $K[PtCl_3(\eta^2\text{-}C_2H_4)]$, **Zeise's salt**, first reported in 1827 although the structure was not confirmed until about a century later. The compound was originally formed by heating $K_2Pt^{IV}Cl_6$ in ethanol, which acts as reducing agent and, after dehydration, as the source of ethylene. Higher yields are obtained by treating $K_2Pt^{II}Cl_4$ with ethylene in the presence of catalytic amounts of $SnCl_2$. The structure is typical for a d^8 metal: **square-planar**, with little back-bonding to the ethylene ligand and only marginal elongation of the C–C bond compared to free ethylene. The degree of back-bonding depends strongly on the nature of the metal and the oxidation state. For Pt(II) (as in Zeise's salt) back-bonding is unimportant and the alkene ligand is oriented perpendicular to the coordination plane to minimize steric interactions. This may be compared with the in-plane orientation in the Pt(0) compound $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$, which shows significant C–C bond elongation since the in-plane orientation maximizes overlap with the occupied d-orbitals.





Due to back-bonding, the stability of a given alkene complex is related to the energy difference between the metal HOMO level and the alkene π*-orbital (ΔE_π), and increases with increasing ΔE_π. Generally the energy of the alkene π*-level is more sensitive to substituent effects than the π-level. The trend in ΔE_π is reflected in the equilibrium of the ligand displacement in NiL_4 complexes with various alkenes (Table 2.6.1):

$$\mathrm{NiL_4} + \text{alkene} \xrightleftharpoons{K_1} \mathrm{L_3Ni(alkene)} + \mathrm{L} \qquad \mathrm{L} = \mathrm{P(OPh)_3}$$

Table 2.6.1 π–π* Energy separation and association constants for Ni(0) alkene complexes

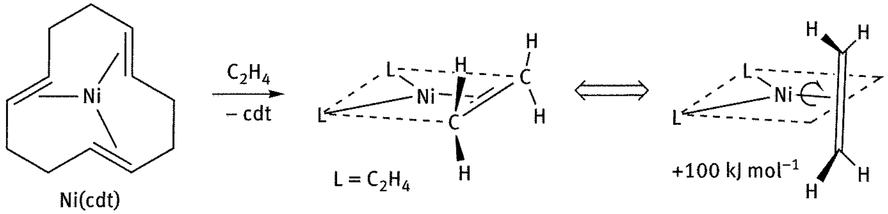
Alkene	$E(\pi^*)$	ΔE_π [eV][a]	K_1
$CH_2{=}CH{-}CN$	−4.48	−3.1	4.0×10^4
$CH_2{=}CH_2$	−3.24	−4.4	4.0×10^2
$CH_2{=}CHMe$	−2.63	−5.4	5.3×10^{-1}

[a] Based on $E_{HOMO}(NiL_3) = -7.6$ eV.

Donation and back-bonding result in a change in the hybridization of the C atoms from sp^2 towards sp^3. In cyclic olefins this relieves ring strain, and highly strained cycloolefins are therefore stronger donors than non-cyclic ones.

Just as the geometry of alkene complexes is dictated by maximizing the back-bonding interaction (apart from the inevitable steric factors), so is their reactivity. For example, in Ni(cdt) (cdt = *trans,trans,trans*-1,5,10-cyclododecatriene) the cyclic ligand is twisted, making it impossible for the three C=C bonds to achieve an optimal in-plane orientation. Although polydentate ligands are usually difficult to displace, this complex is therefore very labile, and the cdt ligand can even be displaced by ethylene. The ease of ligand displacement in Ni(cdt) has led to its description as ***'naked nickel'***.

MO calculations for $Ni(C_2H_4)_3$ have shown that the perpendicular orientation of an ethylene ligand is 100 kJ mol^{-1} less favourable than the in-plane orientation.

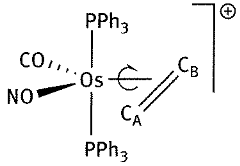


Ni(cdt)

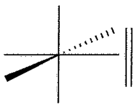
Alkene fluxionality. One aspect of donor–acceptor bonding in alkenes and alkynes is the existence of a **barrier to ligand rotation**. Alkene ligands rotate about the M–C bond; an interchange that amounts to a rotation about the C=C axis is only possible by a dissociation–reassociation process. These processes, and the energy barriers involved, can be measured by variable-temperature NMR spectroscopy.

The nature of alkene rotation could be shown by recording the ^{13}C NMR resonances of the ethylene C atoms in the asymmetric complex $[Os(C_2H_4)(NO)(CO)(PPh_3)_2]^+$. At low temperatures there are two C_2H_4 ^{13}C NMR signals, C_A and C_B, coupled to the two ^{31}P nuclei. On warming, the two resonances merge into one, with the C–P coupling being maintained. This is consistent only with rotation about the M–C bond.

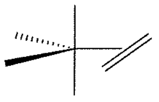
Alkene rotation exchanges positions 1 and 1′ but not 1 and 2:



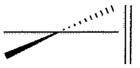
Depending on the d-electron configuration, alkene complexes exist in a number of geometries: d^6 metal centres will prefer octahedral geometries, while d^8 compounds may be square-planar or trigonal-bipyramidal, and d^{10} alkene complexes have a strong preference for a trigonal-planar structure. Alkyne ligands show similar geometries.



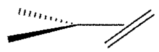
octahedral
d^6



trigonal-bipyramidal
d^8



square-planar
d^8



trigonal planar
d^{10}

Table 2.6.2 Rotational barriers of alkene complexes as a function of d-electron configuration.

Complex type	Geometry	d-Electron configuration	Rotational barrier [kJ mol^{-1}]
L_2M(alkene)	trigonal	d^{10}	76–105
L_4M(alkene)	tbp	d^8	42–63
L_5M(alkene)	octahedral	d^6	29–42

Rotational barriers provide information about the energies required to disturb these ground state geometries; they will be highest where the electronic stabilization through back-bonding is greatest. This is likely to be the case where few ligands compete for electron density with the alkene, and barriers will become lower as the coordination number increases. It is also obvious that the difference between the most and least favoured conformations will be greatest for a trigonal-planar and least for an octahedral geometry. This is borne out by the range of rotational barriers observed (Table 2.6.2).

2.6.1 Alkene Complexes

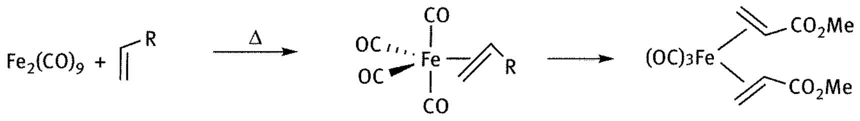
Alkene complexes are accessible by either thermal or photochemical ligand substitution from low-valent complexes such as metal carbonyls or phosphines complexes, or by reduction of metal salts. Alkene ligands are bonded much less strongly than CO or phosphines, and therefore alkene complexes provide convenient starting materials for further synthetic or catalytic applications.

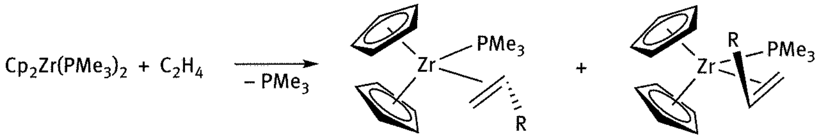
2.6.1.1 Synthesis of Alkene Complexes

Where starting materials with labile donor ligands are available, alkene complexes can be prepared by ligand displacement. Metal carbonyl complexes require either heating or photolysis. Substitution of PMe_3 in $Cp_2Zr(PMe_3)_2$, or the reaction of Cp_2ZrCl_2 with BuMgBr in the presence of a ligand L and an alkene, gives the adducts $Cp_2Zr(L)$(alkene).

With mono-substituted alkenes $CH_2{=}CHR$, two rotamers are obtained. The fact that they are slow to interconvert at room temperature is a measure of the strength of back-bonding: since alkene rotation by 90° would imply the loss of this back-bonding stabilization, there is a significant electronic barrier to ligand rotation. As the crystal structure of $Cp_2Zr(C_2H_4)(py)$ shows, back-bonding from Zr^{II} with high-lying occupied d-orbitals results in significant C–C bond elongation, and the bonding can be represented by a metallacyclopropane resonance form.

Synthesis by L displacement:



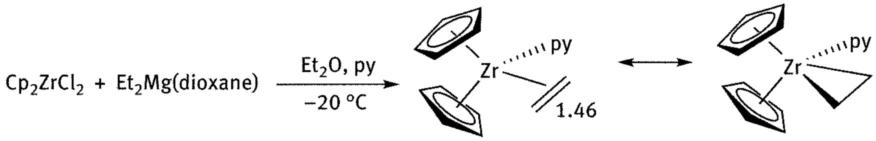


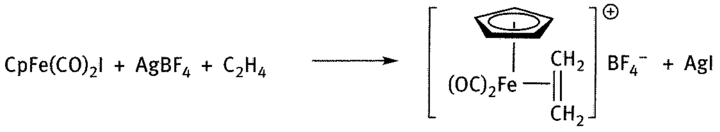
Synthesis by halide displacement with and without reduction:

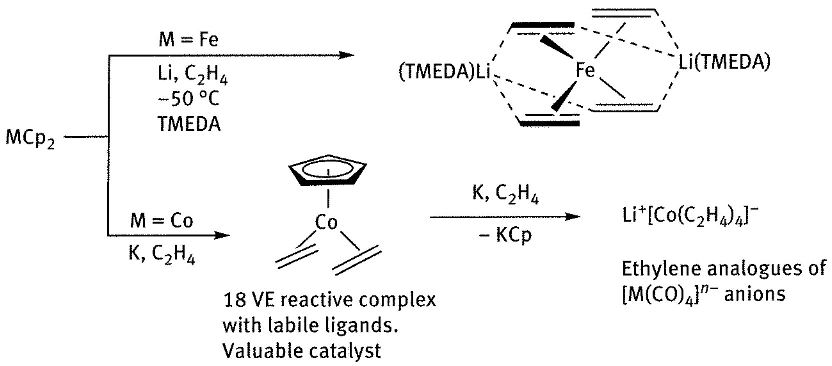
Generally the most convenient route to alkene complexes is the reduction of metal salts in the presence of the alkene, with or without other stabilizing ligands. Alkene complexes of noble metals in oxidation states I and II (Rh^I, Pt^{II}, d^8) are air and moisture stable and are therefore convenient starting materials. The synthesis of alkene complexes of Pt(II), for example Zeise's salt, can be conducted in water, e.g. by treating aqueous solutions of platinum salts with alkenes and collecting the precipitate. Since the d-levels of Group 10 metals are substantially lower in energy than those of Group 4 or 5 metals, the extent of back-bonding and hence the C–C bond elongation tends to be rather less. The alkene complexes shown in the following diagram are accessible by ligand substitution.

The reduction of metallocenes MCp_2 (M = Fe, Co) by alkali metals under an ethylene atmosphere at low temperatures leads to the highly sensitive compounds $Li_2[Fe(C_2H_4)_4]$ and $K[Co(C_2H_4)_4]$, which are analogous to the carbonyl anions $[M(CO)_4]^{n-}$. The metals are formally in oxidation states –II and –I, respectively. The iron complex catalyses the cross-coupling of aryl chlorides with alkyl Grignard reagents.

The 1,5-cyclooctadiene (COD) ligand provides stability through the ***chelate effect*** (it can be considered as two ethylene ligands tied together) but is labile enough to be readily displaced. COD complexes are therefore valuable starting materials for ligand substitution and oxidative addition reactions. $Ni(COD)_2$ in particular can be made easily in good yield and is a valuable starting material and catalyst precursor. The differences in lability and oxidation sensitivity between ethylene complexes of members of the same group, Co and Rh, illustrate the greater affinity and more covalent character of the alkene–metal bond of second and third row noble metals.

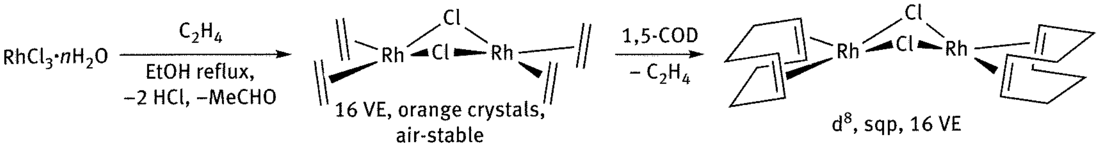






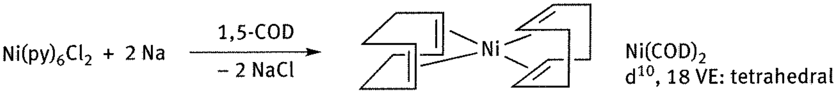
18 VE reactive complex
with labile ligands.
Valuable catalyst

Ethylene analogues of
$[M(CO)_4]^{n-}$ anions

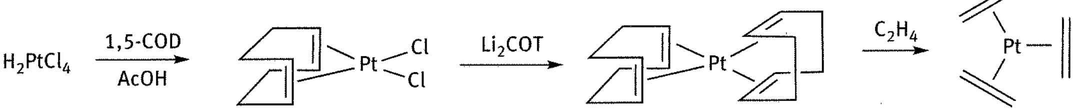


16 VE, orange crystals,
air-stable

d^8, sqp, 16 VE

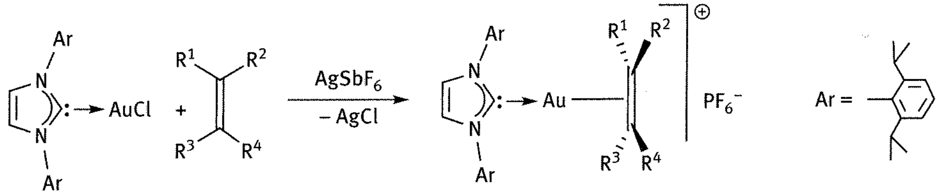


$Ni(COD)_2$
d^{10}, 18 VE: tetrahedral

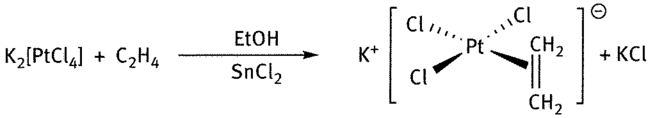


d^8, sqp, 16 VE

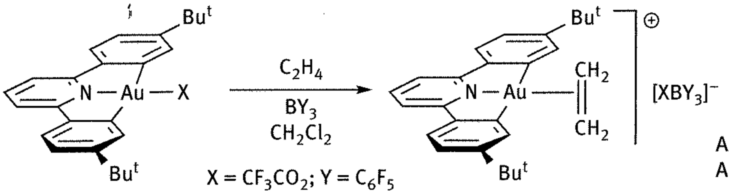
Pt(0), d^{10}, 16 VE
trigonal-planar,



Au(I), d^{10}, 14 VE: linear

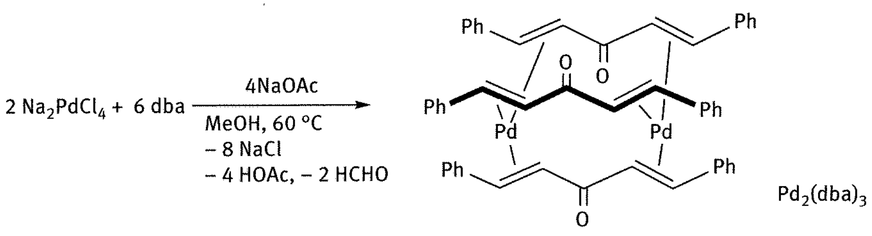


Zeise's salt
Pt(II), d^8, sqp

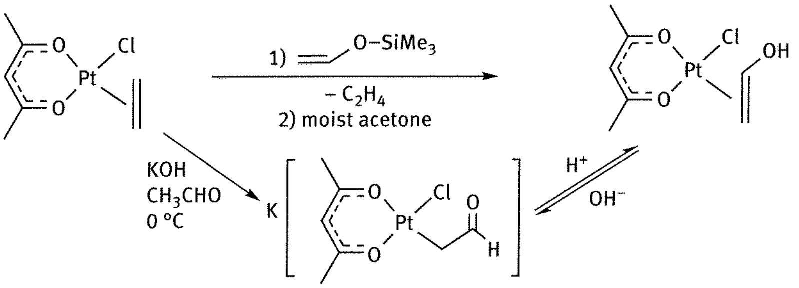


Au(III) pincer complex, d^8:
Au analogue of Zeise's salt

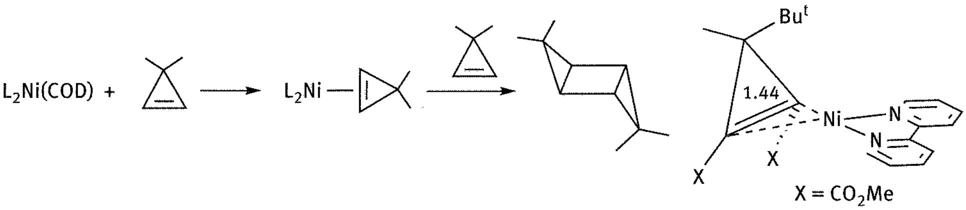
Another useful olefinic ligand is benzylideneacetone (dba = 1,5-diphenyl-1,4-pentadien-3-one), a good π-acceptor that allows the synthesis of stable complexes where COD does not. It is mostly used as a source of zero-valent palladium as an entry into Pd-catalyzed synthesis. The dba ligand is readily displaced by other donor ligands, e.g. to give catalytically active Pd(0) phosphine complexes.



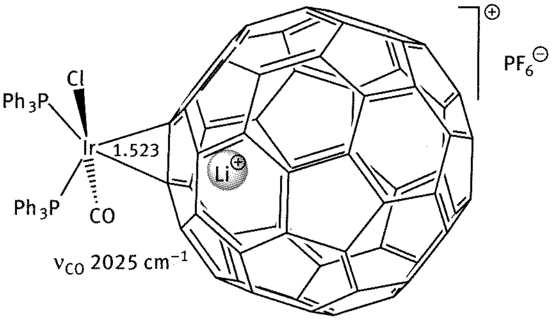
Olefin complexes with functional groups are also accessible, for example Pt complexes of vinyl alcohol, which are relevant in the context of the Pt-catalysed oxidation of ethylene to acetaldehyde (Wacker process, Chapter 3.5).



Strained olefins like cyclopropenes also form complexes and indeed are good donors and acceptors; however, the ring strain does lead to subsequent reactions. An example is the nickel-catalysed dimerization of 1,1-dimethylcyclopropene. A model for the intermediate cyclopropene complex has been structurally characterized and shows the expected lengthening of the C–C bond.



A special case of alkene ligands are the so-called buckminsterfullerenes (or simply fullerenes, named after the architect Buckminster Fuller). These are football-shaped hollow spheres of carbon based on 5- and 6-membered rings. The simplest such molecule is C_{60}. Unlike graphite, the 6-rings have little aromatic character. Fullerenes are good electron acceptors and bind to transition metals via C=C bonds like olefins. The metal coordinates to the most electron-rich C–C bond. Coordination is accompanied by significant C–C bond elongation. One C_{60} molecule can bind up to six PtL_2 moieties. Similar complexes have been obtained from the higher homologue C_{70}. Since fullerenes are empty spheres, it is possible to encapsulate metal ions during their high temperature synthesis, to give endohedral complexes, formulated as $M^{n+}@C_{60}$. Iridium and platinum adducts of $[Li^+@C_{60}]PF_6$ have been isolated; due to electrostatic effects in the complex the Li^+ ion is attracted to the transition metal centre, which leads to changes in the ^7Li NMR chemical shift. $Li^+@C_{60}$ is a stronger π-acceptor than C_{60} itself, as seen on coordination of $IrCl(CO)(PPh_3)_2$, which raises the ν_{CO} frequency from 1944 to 2025 cm^{-1}.



The strong coordination of fullerenes to palladium has been used to prepare materials with compositions $C_{60}Pd_n$ (n = 1, 2, 3, 4, 5) by mixing C_{60} with $Pd_2(dba)_3$ in various ratios; they were found to be strong absorbers of hydrocarbon vapours even at ppm levels.

2.6.1.2 Reactions of Alkene Complexes

Metal alkene complexes can undergo several key reactions:

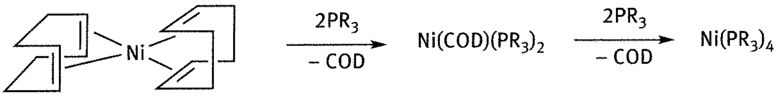
- ligand substitution
- reactions with nucleophiles
- reactions with electrophiles
- C–H activation reactions.

These reactions are commonly employed to introduce functional groups into molecules and are part of some of the most important catalytic cycles.

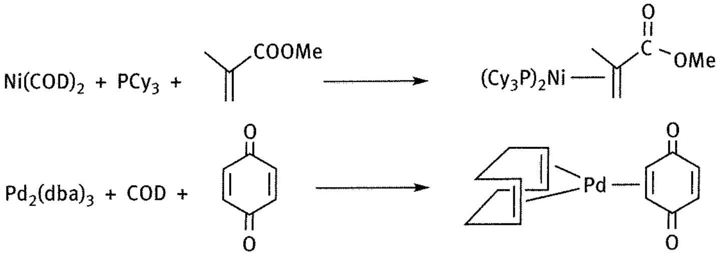
Ligand substitution. This reaction takes advantage of the fact that many alkenes are labile and act as placeholders, generating coordinatively unsaturated species. In these reactions, the alkene is not itself involved in further reactions. For example, this is used to generate metal phosphine complexes or allow oxidative addition reactions. Substitution with phosphines proceeds stepwise. Although in the solid state phosphine complexes of nickel and palladium (as examples of commonly used catalyst precursors) usually have the composition ML_4, in solution 16 VE species ML_3 often prevail (as shown in the following diagram for the example of $Ni(PEt_3)_4$); these coordinatively unsaturated species are capable of much faster reactions than 18 VE compounds, e.g. in oxidative additions of electrophiles.

Formation of 16 VE species may be seen by colour change: for L = PEt_3, NiL_4 is colourless, NiL_3 burgundy red.

The coordinated alkenes may carry functional groups. Complexes of metals typically used in organic synthesis (Ni, Pd) show bonding to C=C but not O functionalities.



$$\underset{\text{solid}}{Ni(PEt_3)_4} \rightleftharpoons \underset{\text{solution}}{Ni(PEt_3)_3 + PEt_3}$$

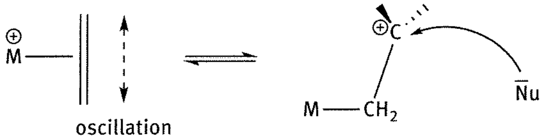


methacrylate complex: C=C not C=O bonded

quinone complex

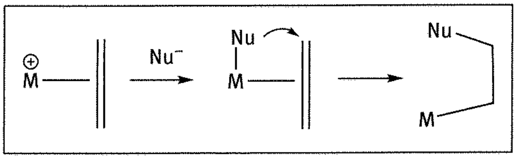
Reactions with nucleophiles. The most important consequence of metal–olefin bonding is that this coordination makes low polarity C=C substrates highly susceptible to nucleophilic attack.

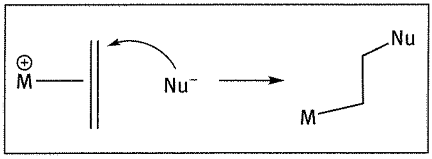
As discussed for carbon monoxide (Section 2.4.1), back-bonding populates the π^* orbitals needed for the reaction with nucleophiles and should therefore make nucleophilic attack less likely. The opposite is the case. The reason for the activating effect of metal–alkene bonding is that molecules are not static. Any ligand in a complex oscillates around its equilibrium position. For alkenes a vibration perpendicular to the M–alkene vector induces a redistribution of charge, and therefore bond polarity. In the extreme, this can be described as the accumulation of carbocationic character on one of the olefinic C atoms:



This polar resonance form readily explains the observed reactivity enhancement. Reactivity, in the case of alkenes in this example but for other ligands quite generally, is coupled to an **enhancement of bond polarity**.

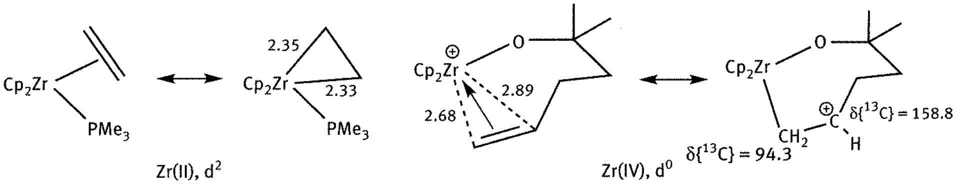
This is the case whether the nucleophilic attack occurs in ***inter*molecular** or ***intra*molecular** fashion, i.e. whether the nucleophiles was bonded to the metal centre before the reaction or not. Both pathways are possible, and it is often not easy to distinguish between them.





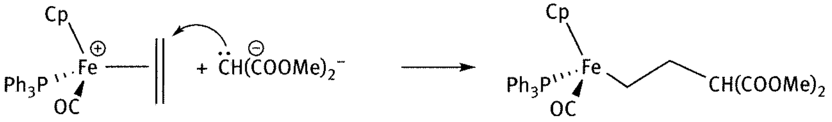
There are numerous cases where it can be seen that a coordinated alkene is asymmetrically bound to the metal, even in the ground state; one M–C bond is distinctly longer than the other. This leads to drastic changes in the ^{13}C NMR signals for the two C atoms, so that asymmetric alkene bonding can be detected spectroscopically.

The relationship between reactivity and C=C bond polarity can be illustrated by structurally characterized examples. Zr(II) complexes like $Cp_2Zr(C_2H_4)(PMe_3)$ show extensive back-bonding (cf. Section 2.6.1). Although one C-terminus is next to P and the other is not, both Zr–C bond lengths are similar, the polarization of the C–C bond is small, and the complex is comparatively stable and isolable. On the other hand, d^0 compounds like the cations $[Cp_2Zr(X)(L)]^+$ cannot stabilize themselves in this way. Any coordinated alkene is highly reactive, and it is no accident that these cationic metallocenes are the active species in certain olefin polymerization catalysts. Cationic zirconium alkoxides bearing a pendent alkenyl substituent could however be isolated; they show a strongly asymmetric coordination of the C=C bond, which is reflected in a large downfield shift of the metal-bonded C_1 and deshielding of C_2, indicative of partial carbocationic character (for comparison, the ^{13}C NMR resonance of C_2H_4 is δ 122.8 ppm); C_2 is therefore highly susceptible to nucleophilic attack.

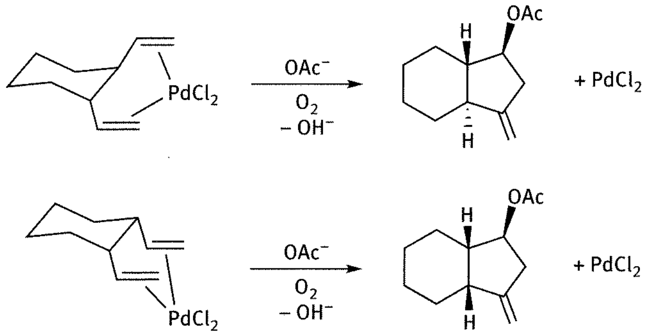


In the case of 1,1-disubstituted alkenes, the asymmetric bonding is particularly pronounced since the alkyl substituents R on the $-CR_2$ terminus stabilize the positive charge on C. For this reason isobutene $CH_2{=}CMe_2$ is readily polymerized via a carbocationic mechanism, with $-CH_2-C^{(+)}Me_2$ as propagating species.

In stoichiometric reactions, pre-formed alkene complexes can be used, for example those of the chiral-at-metal auxiliary $[CpFe(CO)(PPh_3)]^+$. The resulting iron alkyl is an 18 VE compound and is air stable.



Nucleophilic attack can proceed stereospecifically. An example is the palladium-mediated oxidative cyclization of *cis*- and *trans*-1,2-divinylcyclohexanes:

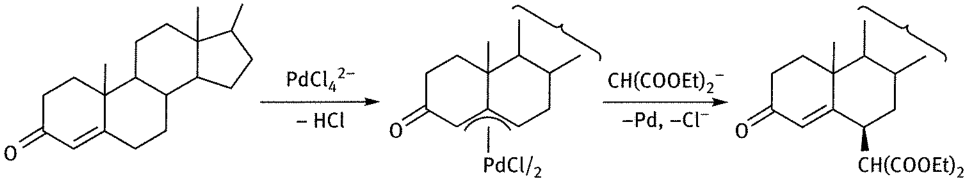


Detailed studies have shown that nucleophiles can be divided into two classes:

(1) external (**inter**molecular) attack *trans* to metal by relatively weak-field ligands: OH^-, H_2O, carboxylates RCO_2^-, alkoxides RO^-, amines;

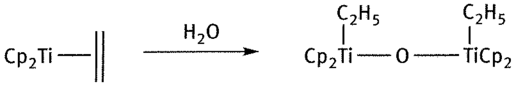
(2) metal pre-coordination and **intra**molecular *cis*-attack by strong σ-donors: hydride H^-, alkyl, and aryl ligands.

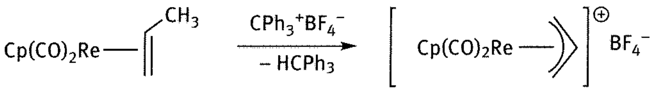
Palladium olefin complexes are readily converted into palladium η³-allyl products on treatment with a base. These allyl complexes are then susceptible to nucleophilic attack in the 1- or 3-position. This is a widely applied standard reaction for the conversion of non-substituted alkenes into derivatives bearing substituents in allylic position:



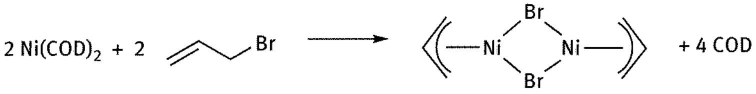
Reactions with electrophiles. Alkene complexes may be protonated or react with CPh_3^+ under hydride abstraction. They may also act as sources of low-valent metal complexes suitable for oxidative addition reactions. These oxidizing agents may include organic electrophiles such as alkenes and alkynes.

These principles are exemplified by the controlled H_2O addition to $Cp_2Ti(C_2H_4)$ to give an oxo-bridged Ti–Et product (an excess of H_2O would lead to Ti–C bond cleavage). The electrophilic abstraction of H^- by treating complexes of alkenes such as propene (or higher) with trityl (CPh_3^+) salts generates η³-allyl complexes.

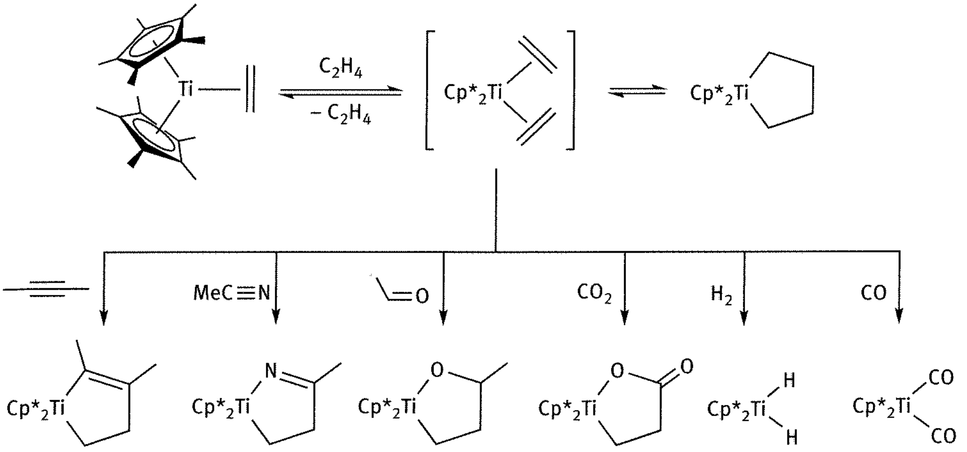




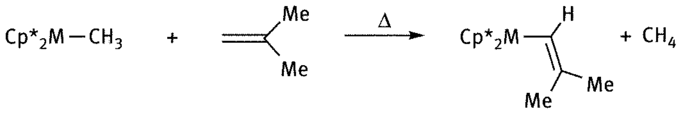
More commonly, alkene complexes act as soluble sources of M(0) species that react with electrophiles by oxidative addition, for example, $Ni(COD)_2$ or $Pd_2(dba)_3$ will add allyl bromide to give metal(II) allyl complexes.



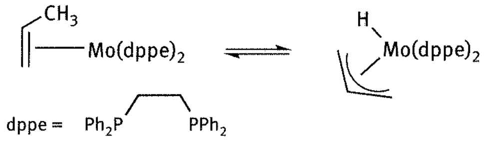
Electron-rich alkene complexes of early transition metals, e.g. Ti(II) and Zr(II) (d^2), react with organic electrophiles to form addition compounds. Since these metals have a strong tendency to achieve the highest possible oxidation state, even alkenes can act as oxidizing agents. The reactions involve C–C bond formation to give metallacyclopentane derivatives where the metal attains oxidation state IV. Synthetically very versatile is the reaction of $Cp^*_2Ti(C_2H_4)$ with organic electrophiles such as alkynes, nitriles, CO_2, and the like. The Cp* (= C_5Me_5) rings act primarily as bulky protecting ligands and facilitate isolation. The coupling of two ethylene ligands is reversible, and in the absence of an excess of ethylene, the mono-alkene complex is regenerated. Exposure to dihydrogen leads to the hydrogenolysis of both Ti–C bonds under very smooth conditions, with formation of $Cp^*_2TiH_2$; the by-product is ethane.

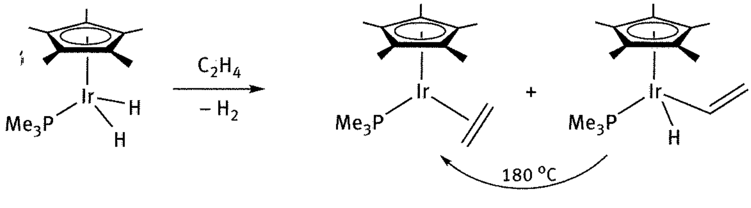


C–H activation reactions. Highly electrophilic metal centres may react with alkenes under C–H bond cleavage. In some cases the preceding alkene complex may not be detectable. Classic examples are the reactions of lanthanide complexes with alkenes.



If the energy difference between the olefin complex and the C–H activation product is small, both types of compounds may be in equilibrium:





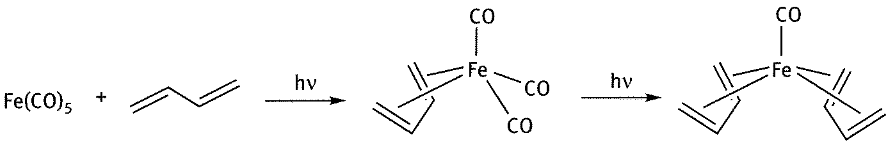
2.6.2 Diene Complexes

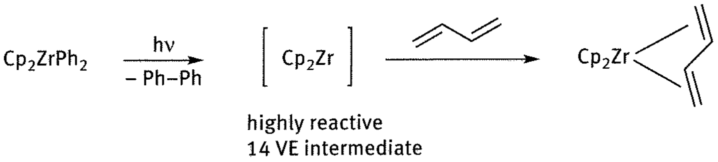
2.6.2.1 Synthesis of Conjugated Diene Complexes

Conjugated dienes are 4-electron donors and better π-acceptors than non-conjugated alkenes. They are highly reactive reagents or intermediates in stoichiometric and catalytic reactions.

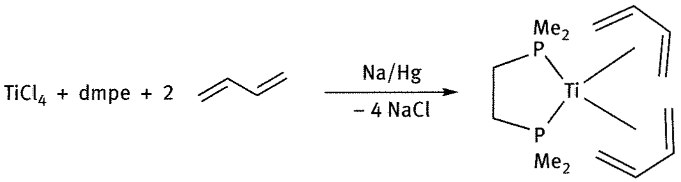
The synthetic methods resemble those used for the synthesis of alkenes. Photolysis and reduction methods are most common. Metal atom synthesis, a method where metal atoms are evaporated under vacuum and co-condensed with an excess of ligands onto a cold (−196 °C) surface, has also produced a range of diene complexes that were otherwise difficult to access.

By photolysis:



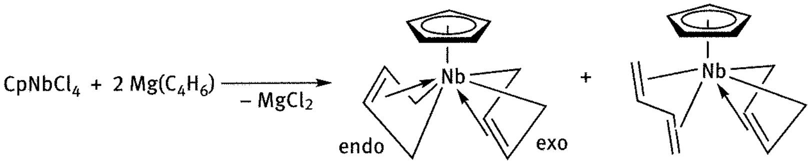


By reduction:



By alkylation:

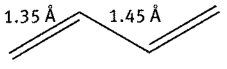
Magnesium butadiene (2-butene-1,4-diylmagnesium) acts as alkylating agent to give diene complexes:



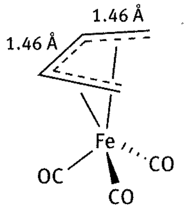
2.6.2.2 Bonding in Complexes of Conjugated Dienes

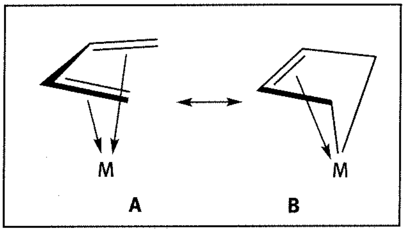
Dienes have lower lying π^* orbitals than mono-enes and are therefore stronger π-acceptors. It is this that enables bis(diene) complexes of titanium—formally Ti(0)—to be prepared, while the analogous tetra-ethylene complexes are unknown. With few exceptions, coordinated dienes prefer the s-*cis* conformation. The classical example is $(\eta^4\text{-}C_4H_6)Fe(CO)_3$, which has a half-sandwich or 'piano stool' structure.

The distribution of C–C bond lengths in free butadiene and in the complex provides information about the bonding situation. In butadiene there is a short-long-short pattern, while in the Fe complex all bond lengths are about the same.

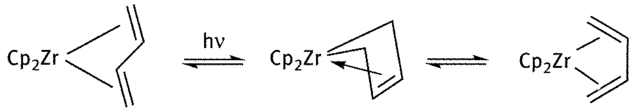


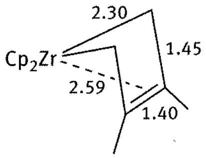
1,3-butadiene



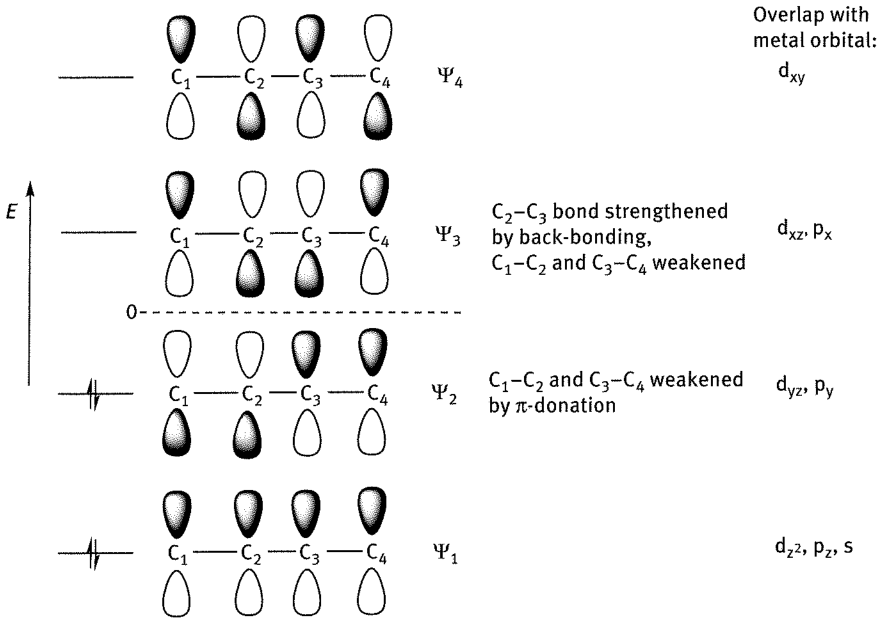


The s-*trans* coordination of butadiene to the zirconium and niobium complexes is unusual. On irradiation the $Cp_2Zr(s\text{-}trans\text{-}C_4H_6)$ interconverts with the s-*cis* form, via a Zr(IV) metallacyclopentene intermediate. The change in oxidation state of the metal during this equilibrium is evident from the crystal structure of the 2,3-dimethyl derivative: whereas in the butadiene complexes the C_1–C_2 and C_3–C_4 bonds are shorter than C_2–C_3, the inverse is the case in the metallacyclopentene. The '**folded envelope**' conformation due to C=C π-donation is typical of compounds of this type.



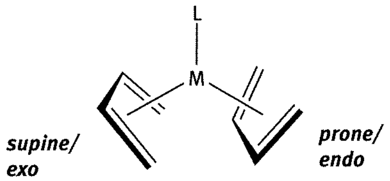


The bonding in the complex can be described by two resonance structures. The MO scheme of a conjugated diene shows qualitatively the π-orbital ordering shown in the following diagram; Ψ_1 and Ψ_2 are occupied and Ψ_3 represents the LUMO. Structure **B** above corresponds to the population of the LUMO of butadiene by metal d-electrons:

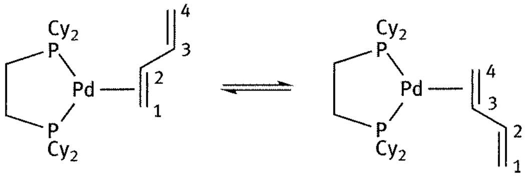


In the case of the $(C_4H_6)Fe(CO)_3$ complex, this synergistic action results in approximately equal C–C bond lengths in the diene. In complexes of early transitions metals (Groups 4 and 5) back-bonding is even more pronounced, and, as the example of the Cp_2Zr(diene) structure showed, as a consequence the bond orders of C_1–C_2 and C_3–C_4 are reduced to ~1, while C_2–C_3 gains double bond character and coordinates to the metal centre.

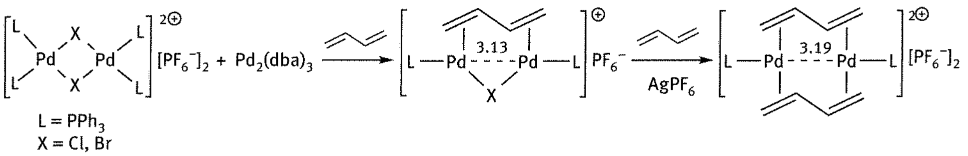
Dienes and their metallacyclopentene equivalents can adopt two orientations relative to a reference ligand, *supine* (*exo*) and *prone* (*endo*), in addition to the s-*trans* conformation.



If only one coordination site is available, butadiene may also be bound in η^2-fashion. In $L_2Pd(\eta^2$-butadiene) complexes the metal fluctuates between 1,2- and 3,4-bonding.



The comproportionation of Pd(II) and Pd(0) in the presence of butadiene gives binuclear Pd(I) compounds which contain s-*trans* butadiene ligands that bridge two metals. Although such binuclear Pd(I) compounds usually contain a Pd–Pd bond of 2.5–2.8 Å length, the dicationic compound shown in the following diagram contains a Pd–Pd distance that is difficult to interpret as a metal–metal bond (sum of van der Waals radii: 3.26 Å). This theme is further elaborated in Box 2.6.2.2.



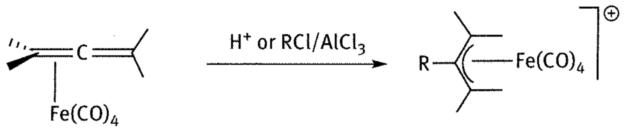
2.6.2.3 Reactions of Conjugated Diene Complexes

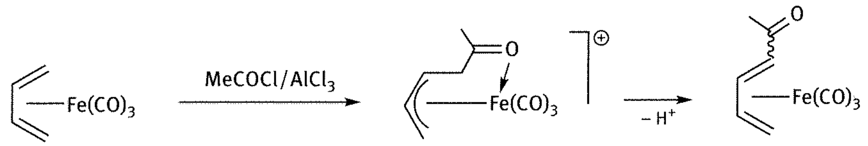
Typical reactions include:

- reactions with electrophiles;
- reactions with nucleophiles;
- cycloadditions.

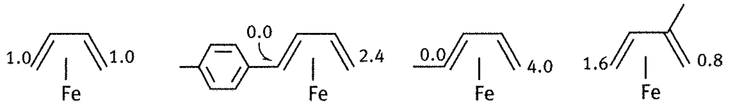
For the rules of nucleophilic attack, see Box 2.6.2.3.

Reactions with electrophiles. Protonation of olefinic complexes can lead to cationic metal enyl products. This reaction is usually seen for dienes including allenes, for example:

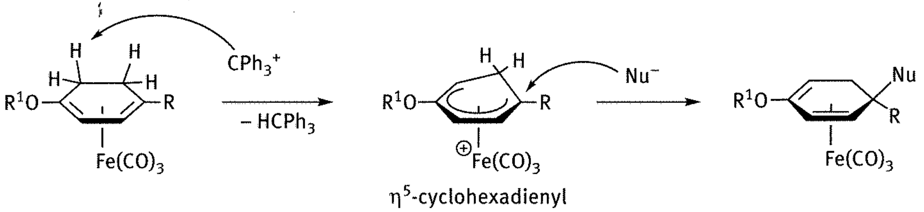




Relative rate of attack:

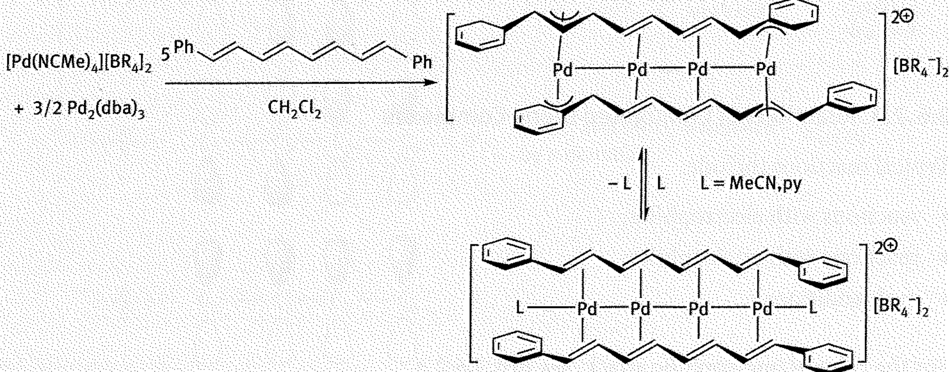


The reaction of cyclohexadiene complexes of iron carbonyls with electrophiles is useful as a means of generating cationic cyclohexadienyl derivatives. The reactions can proceed regio- and stereoselectively as part of an electrophilic/nucleophilic synthesis sequence.

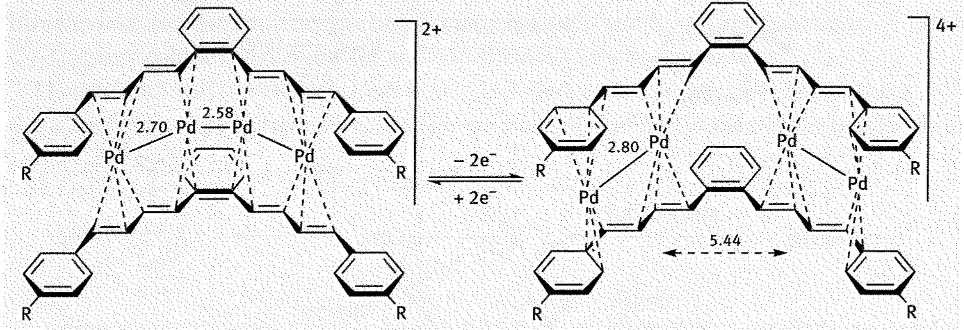


Box 2.6.2.2 Molecular wires and switches

The synthesis of conjugated diene complexes can be extended to polyenes. A tetraene example is shown in the following diagram. Extended polymetallic 1D structures can be obtained, supported by the polyene scaffolds ('molecular wires'). The crystal structure suggests an allylic η^3-coordination in the solvent-free complex and alkene bonding in the solvent-coordinated structure, which leads to a rather uncertain assignment of oxidation states for Pd.



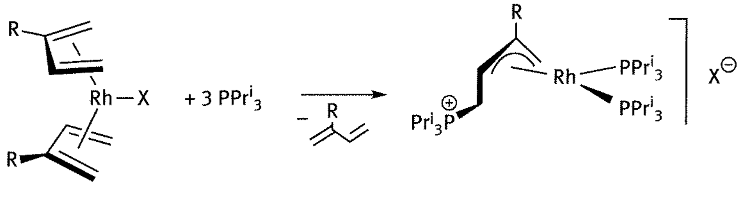
These systems can be turned into molecular redox switches: the metal arrangement moves reversibly along the C=C chain, breaking and re-forming M–M bonds on oxidation and reduction, while the metal oxidation states fluctuates between +0.5 and +I.



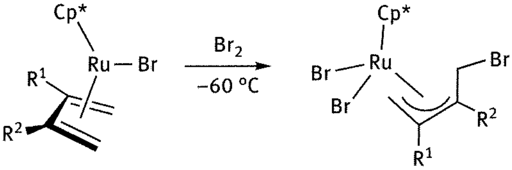
For diene dimerization combined with nucleophilic attack, see Box 2.7.1: Telomerization

Reactions with nucleophiles. Nucleophilic attack on coordinated diene ligands is a versatile method for generating C–X and C–C bonds. The pathway may involve external attack, or proceed following coordination to the metal centre. This is often apparent from the resulting stereochemistry.

Attack by phosphines:

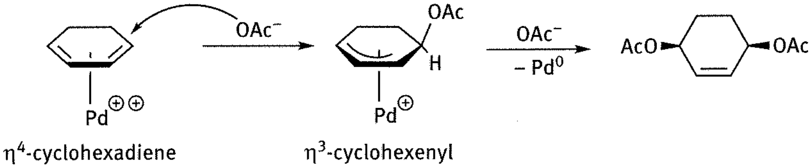


Attack by halide: This reaction leads to Br^- attack on the diene only if the substituents R are small, otherwise an ion pair results with Br^- as anion.

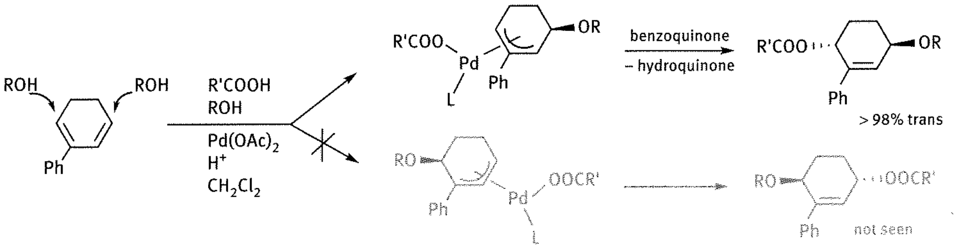


$R^1 = R^2 = H$
$R^1 = Me, R^2 = H$

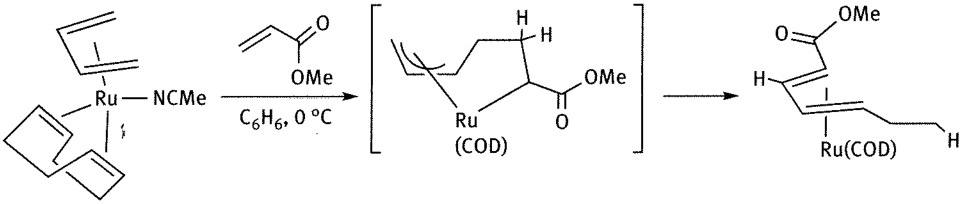
Nucleophilic attack on coordinated cyclohexadienes can lead to stereoselective double substitution. The palladium metal formed can be re-oxidized to Pd^{2+} to close the catalytic cycle.



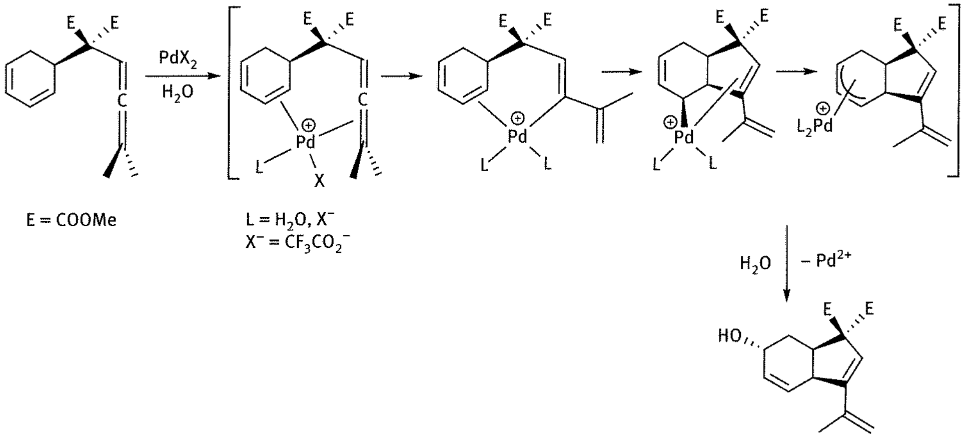
The stereoselectivity is a consequence of the direction of nucleophilic attack. In the Pd-mediated oxidative double-functionalization of cyclohexadienes with both alcohols and carboxylic acids, the alkoxide acts as external nucleophile, while the carboxylate is coordinated to Pd and attacks from the opposite side. As a consequence the *trans*-disubstituted isomer is produced in stereoselectivities of >98%.



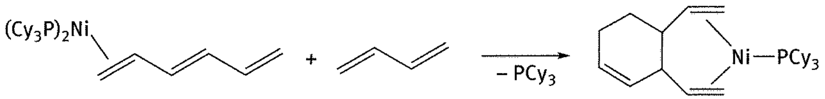
Attack with C–C coupling: Diene complexes of Ru(0) react with activated acrylate esters under C–C coupling. This method generates a multitude of carboxylate-functionalized dienes. Attack is followed by H-migration steps.



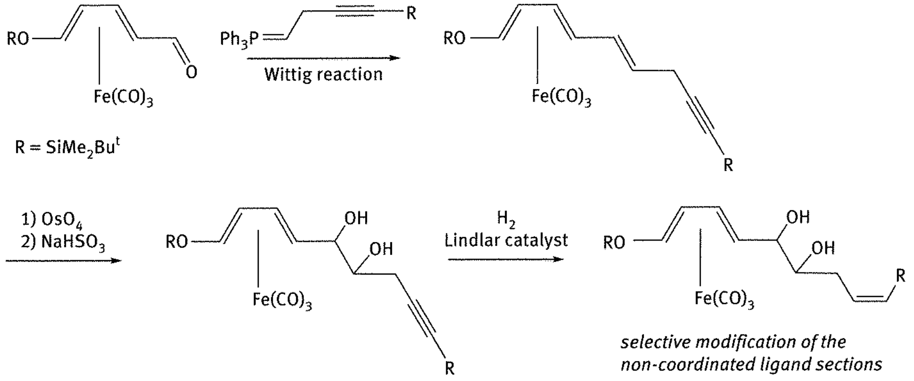
The examples shown so far have involved 1,3-dienes. Equally reactive are 1,2-dienes (allenes); they, too, can react with coordinated alkenes and 1,3-dienes under C–C bond formation. This reaction has been used for palladium-catalysed cyclizations, for example:



Cycloadditions. Dienes and diene complexes may undergo [4+2] cycloadditions, for example:



Diene coordination as protection. The coordination of a conjugated diene to a metal fragment such as $Fe(CO)_3$ can be used to protect the diene while carrying out modifications of alkenes or alkynes elsewhere in the molecule. An example is the Fe complex of the alkynyltriene shown in the following schematic:



selective modification of the non-coordinated ligand sections

Box 2.6.2.3 Nucleophilic attack on π-ligands: the Davies–Green–Mingos rules

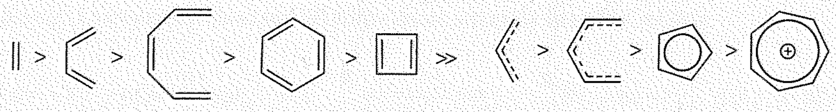
π-Ligands with different numbers of unsaturated coordinated carbon atoms, open or cyclic π-systems, and ligands with or without a charge react with nucleophiles at different rates. Often several such ligands are present in the same complex, so what guides the selectivity of nucleophilic attack?

The chemical behaviour can be summarized by three simple rules (S. G. Davies, M. L. H. Green, D. M. P. Mingos, 1978):

1. **Even before odd.** If a complex contains π-ligands, one with an even and one with an odd number of C atoms, the even-numbered ligand will be attacked.
2. **Open before closed.** Non-cyclic π-ligands will be attacked in preference to cyclic ones.
3. **Even at terminus, odd at terminus or internal.** Even-hapticity ligands will be attacked at a terminal carbon. Odd-hapticity ligands will be attacked at the terminus if the metal is electron rich, or at an internal carbon if that carbon carries a partial positive charge (electropositive metals).

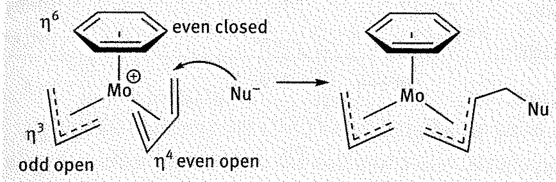
The reactivity trend is '**even >> odd**'.

Even hapticity		Odd hapticity	
open	closed	open	closed

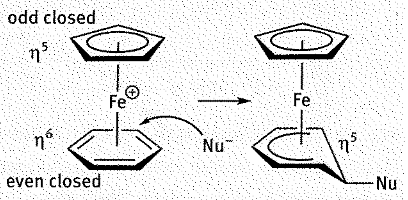


Therefore in a complex containing η^3-, η^4-, and η^5-ligands, it will be the η^4-diene that reacts with the nucleophile (even and open > odd and open > even closed > odd closed):

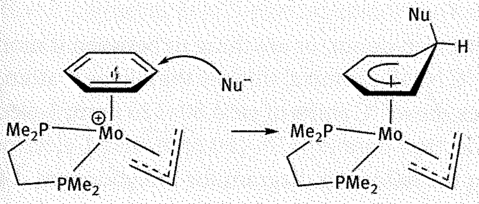
even open > odd open:



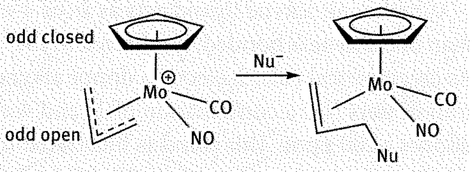
even closed > odd closed:



even closed > odd open:



odd open > odd closed:



2.6.3 Alkyne Complexes

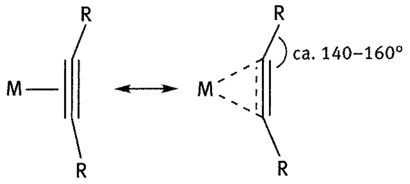
Most of today's chemical industry is based on petrol-derived products, mainly olefins and arenes obtained from cracking crude oil. Before crude oil became abundantly available, the chemical industry was based on coal and its gasification products, CO and acetylene, and there is therefore a very comprehensive chemistry of commodity chemicals based on transformations of acetylene. Heating solid carbon sources (coal, coke) with lime to high temperatures (2000–2100 °C) gives calcium carbide, which is hydrolysed to acetylene:

$$CaO + 3\,C \rightarrow CaC_2 + CO$$

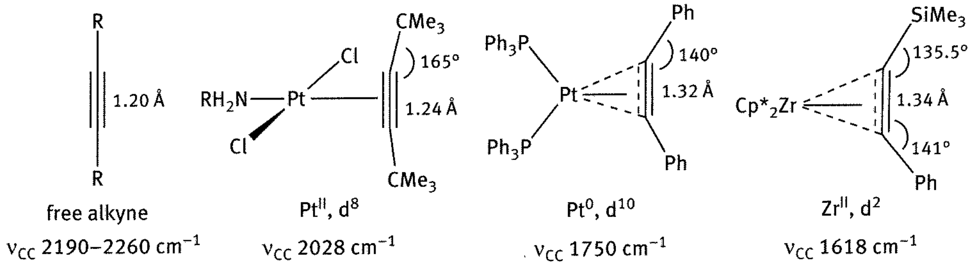
$$CaC_2 + H_2O \rightarrow C_2H_2 + CaO$$

Acetylene itself is weakly acidic (pK_a 25). The C≡C triple bond of alkynes is significantly more reactive than the C=C bond of alkenes.

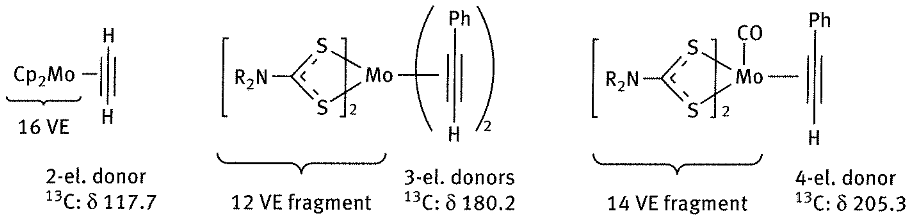
Acetylenes possess two orthogonal π-systems and can therefore act as both **2- and 4-electron donors**. This may be the case even when coordinated to only one metal centre. Like alkenes, the bonding of alkynes to metals consists of π-donation and π-acceptance. Back-donation leads to a change in the hybridization of the C atoms, from sp more towards sp^2, as indicated by the reduction of the C–C–R angles from 180° to about 140–160°.



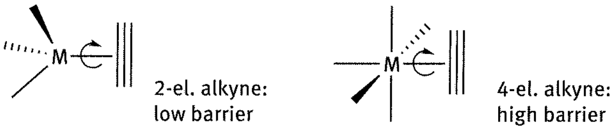
The deviation from linearity in coordinated alkynes depends on the metal electron count and its propensity for back-bonding, e.g. Zr(II) ≈ Pt(0) > Pt(II). As the examples in the following diagram show, there is a qualitative correlation between the degree of back-bonding and the IR C–C stretching frequency.



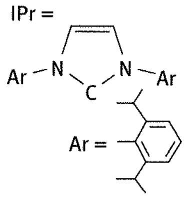
Whether an alkyne ligand acts as 2- or 4-electron donor, or anything in between if more than one alkyne is bonded, is reflected in the ^{13}C NMR chemical shifts of the alkyne C atoms. As an empirical rule, 2-electron donor alkynes show ^{13}C shifts of ca. δ 80–120 ppm, 3-electron donors (i.e. a combination of 2- and 4-electron donors) 170–180 ppm, and 4-electron donors >200 ppm. This trend is illustrated in the following diagram for molybdenum. ^{13}C NMR shifts in the region of δ 80–90 for 2-electron and δ 260–270 for 4-electron donor alkynes have been found for other metals.



Back-donation and behaviour as a 4-electron donor are expected to be reflected in the barrier of rotation about the M–alkyne bond. For 2-electron alkynes in mononuclear complexes, $\Delta G^{\ddagger}_{rot} \approx 40$ kJ mol^{-1}, while for 4-electron alkynes $\Delta G^{\ddagger}_{rot} \approx 50–70$ kJ mol^{-1}.

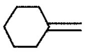
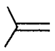
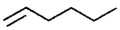
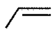
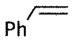


The binding strengths of alkyne and alkene ligands can be estimated in cases where an equilibrium is established that can be measured by NMR spectroscopy. For example, the displacement of the weakly coordinating nitrile $N{\equiv}CAr^F$ [$Ar^F = 3{,}5\text{-}(CF_3)_2C_6H_3$] in $[(IPr)Au(NCAr^F)]^+$ SbF_6^- with alkynes or alkenes in dichloromethane at –60 °C gave the association equilibrium constants, K_{eq}, shown in the following table, which show dramatic differences between similar ligands; e.g. 3-hexyne binds about 90 times more strongly than PhC≡CMe.

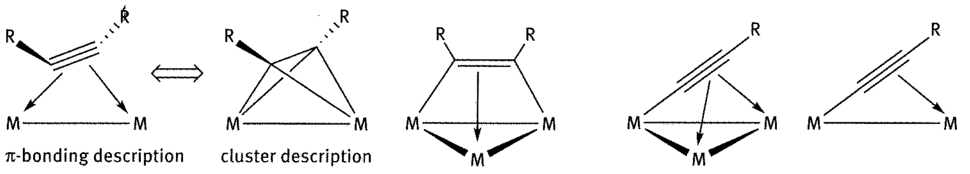


$$\left[\mathrm{IPr{-}Au{-}NCAr^F}\right]^{\oplus}\mathrm{SbF_6^-} + \mathrm{L} \underset{\mathrm{CH_2Cl_2},\,-60\,^\circ\mathrm{C}}{\overset{K_{eq}}{\rightleftharpoons}} \left[\mathrm{IPr{-}Au{-}L}\right]^{\oplus}\mathrm{SbF_6^-} + \mathrm{NCAr^F}$$

Relative C=C and C≡C binding strength

L	EtC≡CEt				MeC≡CMe			PhC≡CH
K_{eq}	780±62	90±7	67±4	25±1	24±1	6.8±0.3	1.7±0.4	0.21

In metal clusters, the C–C bond lengths of what may formally be regarded as a bridging alkyne is often reduced to the value of a C–C single bond, and it is more apt to describe such a compound as a cluster consisting of two metal and two C atoms. Alkynes may be found in metal carbonyl clusters in various positions bridging two or more metals. Cluster-bonded acetylides $RC{\equiv}C^-$ can act as 3- or 5-electron donors (= 4 or 6 electrons in the ionic counting convention).

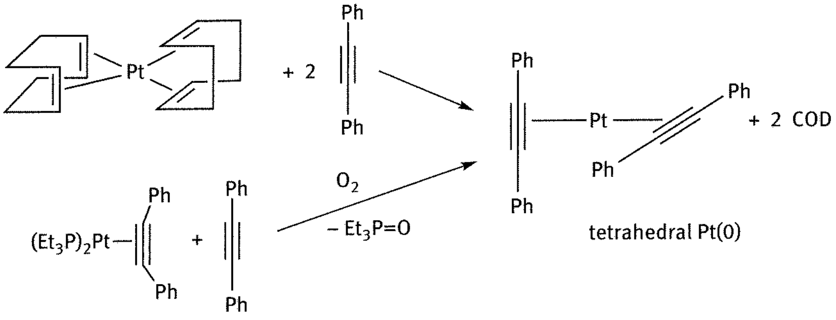


2.6.3.1 Synthesis of Alkyne Complexes

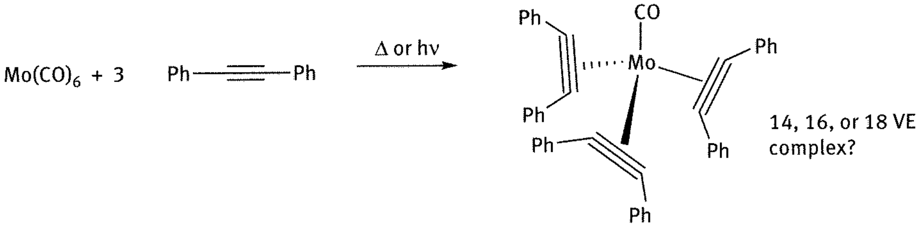
Since alkynes bind more strongly than alkenes, most alkyne complexes are made by ligand substitution, often using alkene compounds as starting materials.

An unusual, but synthetically convenient, route is the synthesis of platinum alkyne complexes from phosphine complexes by the oxidation of the phosphines to the phosphine oxide.

Unlike $Pt(C_2H_4)_3$, platinum(0) bis(alkyne) complexes are tetrahedral. The alkynes act here as 4-electron donors.

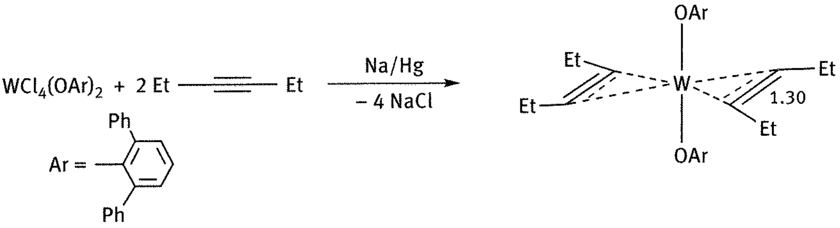


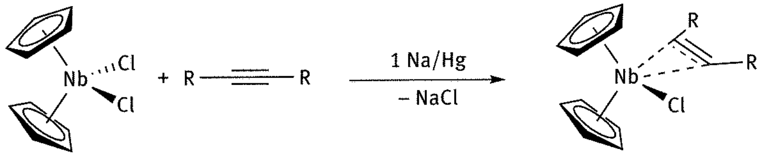
tetrahedral Pt(0)

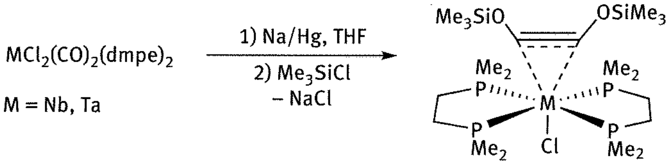


14, 16, or 18 VE complex?

By reduction: Note that alkyne complexes may also arise from the reductive coupling of CO ligands.

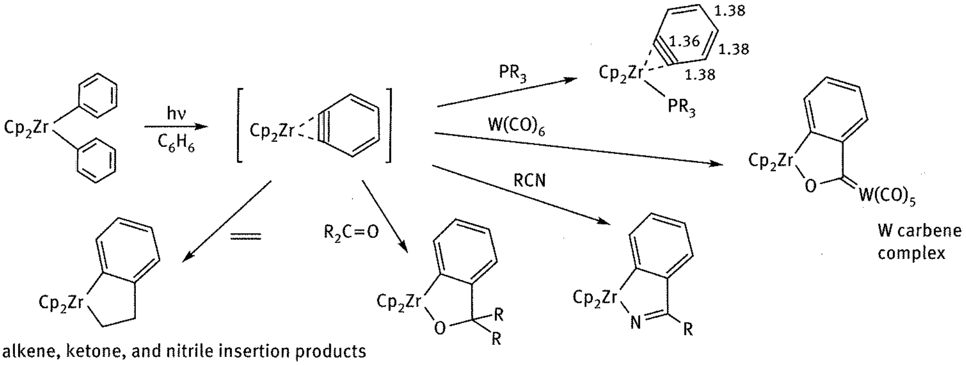




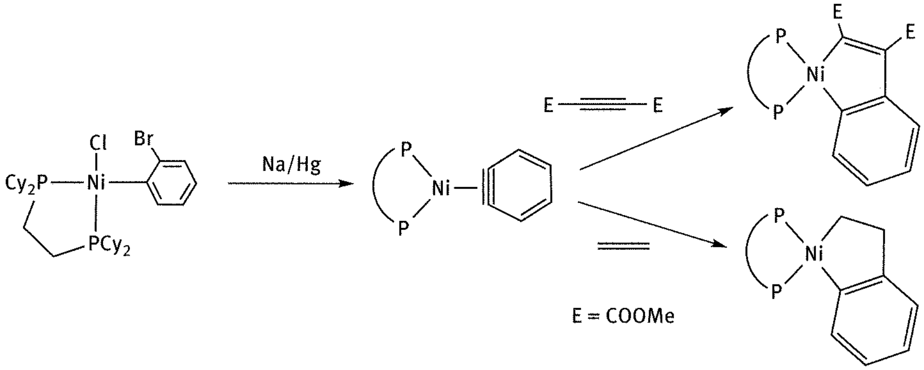


Benzyne complexes. The abstraction of two neighbouring H atoms from benzene gives benzyne, C_6H_4. In the free state this highly strained molecule is not stable; however, benzyne complexes can be generated in the coordination sphere of a metal. Although we follow the convention here to depict benzyne complexes with a C–C triple bond, the effect of back-bonding is such that the C_6H_4 ring shows very similar C–C bond distances for all ring carbons, which are almost identical to those of benzene itself. Coordination makes the C_6H_4 ring essentially strain-free.

Benzyne complexes can be generated, for example, by photochemical C–H activation or by reduction processes and trapped with phosphines or nitriles, alkenes, or alkynes to give [2+2] cycloaddition products.



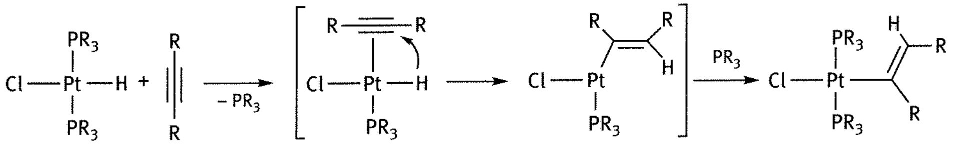
alkene, ketone, and nitrile insertion products



2.6.3.2 Reactivity of Alkyne Complexes

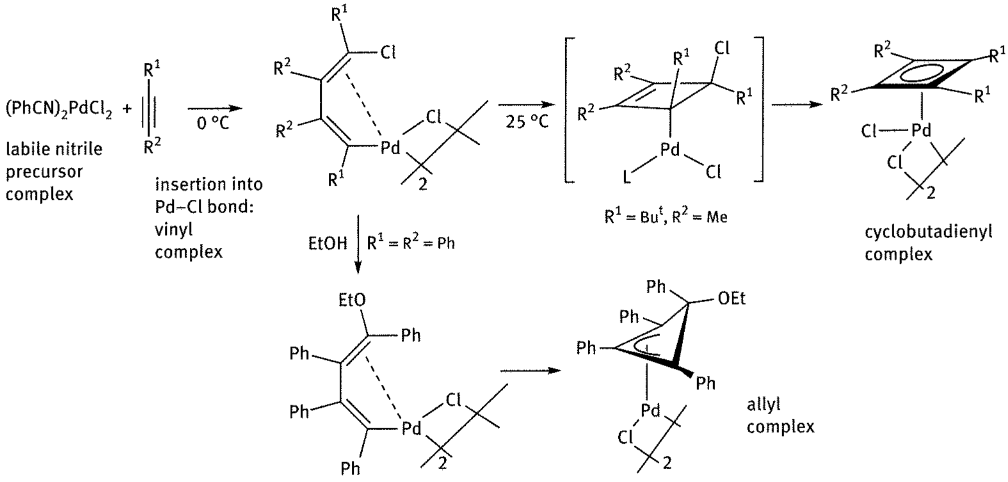
Alkynes undergo a multitude of insertion reactions. The reaction with M–H bonds gives vinyl complexes via ***cis*-insertion**, while successive insertions of alkynes into

M–C bonds gives linear or cyclic products that lead to the synthesis of arenes or heteroarenes.

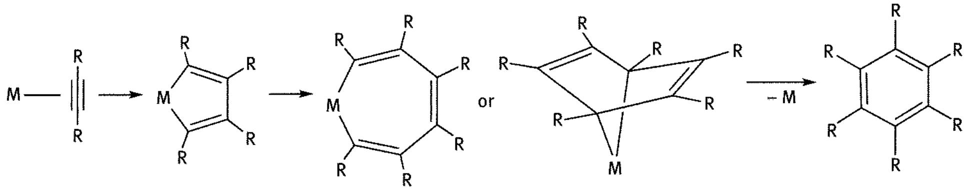


Alkyne Coupling Reactions: Insertions, Cycloadditions

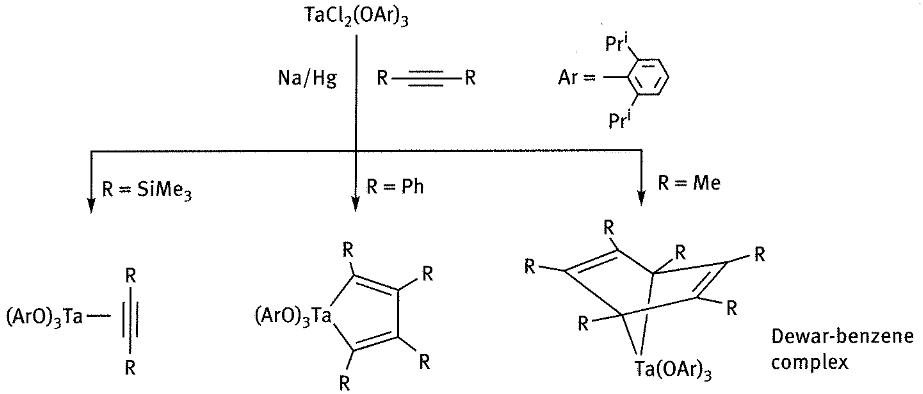
Alkynes can undergo single and multiple insertion reactions with metal–X bonds including M–Cl. Many transition metals will also polymerize C_2H_2, as well as mono-substituted acetylenes. $Ti(OR)_4/AlEt_3$ mixtures (Ziegler-type catalysts) have been used to make polyacetylene, a polyconjugated polymer that becomes electrically conducting on doping. Palladium salts can polymerize phenylacetylene. Disubstituted acetylenes are more stable but can react to give metal **vinyl, cyclobutadienyl, metallacyclopentadienyl, and arene complexes**. Key reaction pathways are outlined in the following diagram.



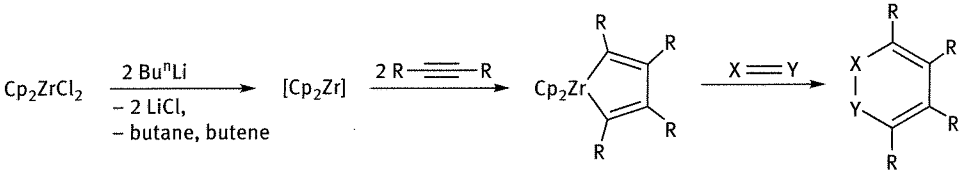
Many metal complexes, such as Ni, Pd, Nb, and Ta halides, as well as half-sandwich complexes $CpML_2$ (M = Co, Rh) catalyse the **cyclotrimerization** of alkynes to arene derivatives. The reaction goes stepwise, via metallacyclopentadienes and metallacycloheptatrienes. This is a very convenient route to highly substituted arenes C_6R_6.



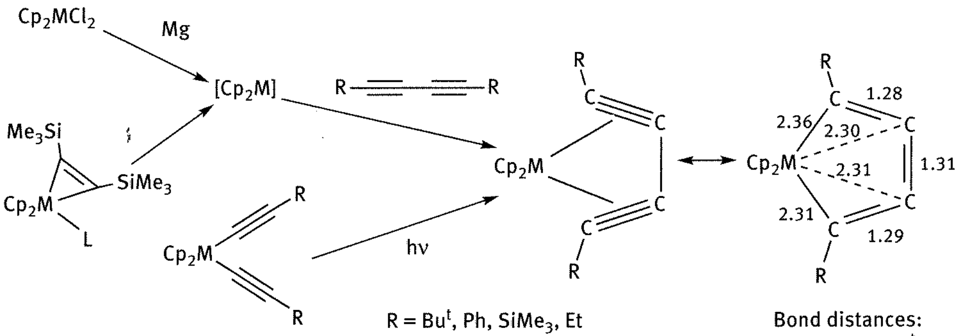
In some cases these intermediates could be isolated, depending on R:



Many low-valent metal complexes oxidatively add two acetylenes to give metallacyclopentadienes. A much-used example is the reduction of Cp_2ZrCl_2 with two equivalents of $LiBu^n$ in the presence of alkynes. The resulting metallacycles have been used for the synthesis of cyclopentenones and heterocycles.



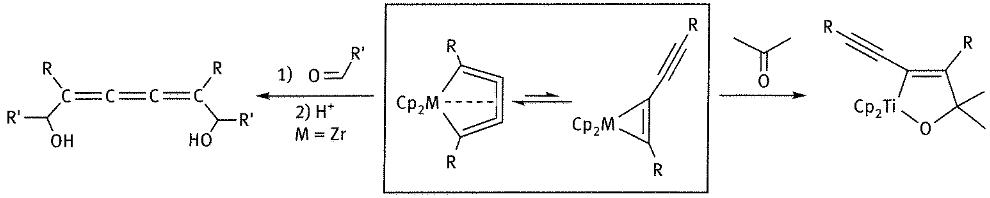
The same reduction of Cp_2MCl_2 in the presence of a di-acetylene R–C≡C–C≡C–R also leads to a 5-ring product, but since the carbon atoms in 2- and 3-positions do not carry any substituents, the resulting structure is a ***metallacumulene***. The MC_4 ring is planar, and although one can in principle formulate it as a bis-C≡C adduct, the bond length distribution indicates extensive delocalization to alleviate the ring strain. In particular, there are almost identical bonding interactions between the metal and all four carbon atoms. Each C atom in the cumulene has an electron in a p-orbital perpendicular to the ring. In addition, C_2 and C_3 share a π-orbital in the ring plane, which acts as donor towards the metal. According to calculations, this metallacumulene geometry is more stable than the more conventionally bonded $M(C{\equiv}CR)_2$ isomer.



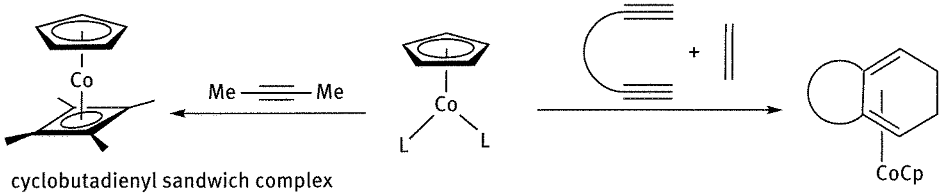
R = Bu^t, Ph, SiMe$_3$, Et

Bond distances:
M = Zr, R = Bu^t

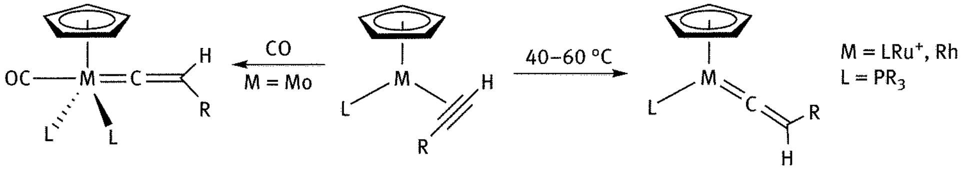
Metallacyclopentatrienes are in equilibrium with di-alkyne complexes, as indicated by some of their reactions:

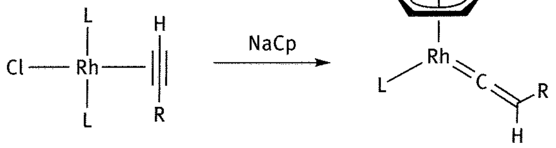


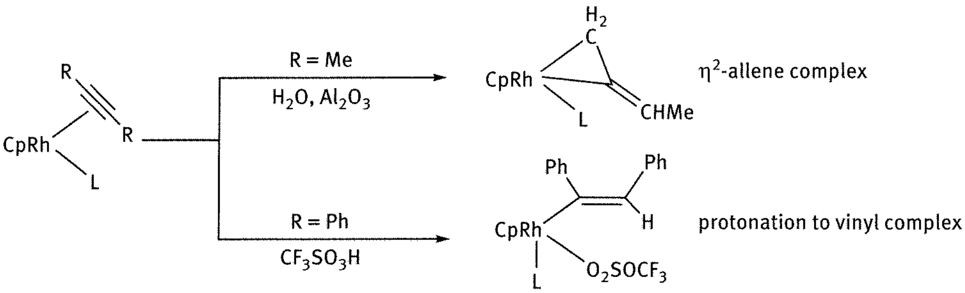
CpCo-catalysed cyclizations can involve enyne condensations and alkyne trimerizations. The reactions are facilitated by a source of the [CpCo] fragment with labile ligands L; e.g. the 1,5-COD ligand in CpCo(COD) is easily displaced and gives far smoother reactions than using $CpCo(CO)_2$, which requires photochemical dissociation of the CO ligands.



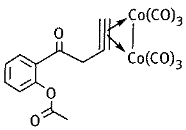
Alkynes can isomerize to allenes. Similarly, alkyne complexes can rearrange to vinylidene or allene complexes:







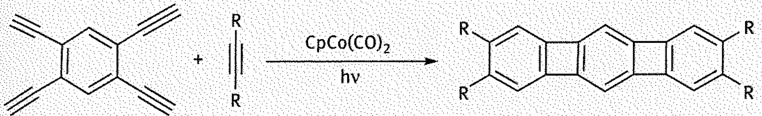
Co alkyne complex with anti-tumour activity

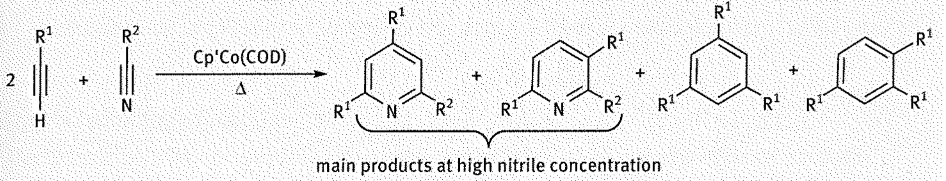


Synthetic applications of metal alkyne reactions are illustrated in Box 2.6.3.

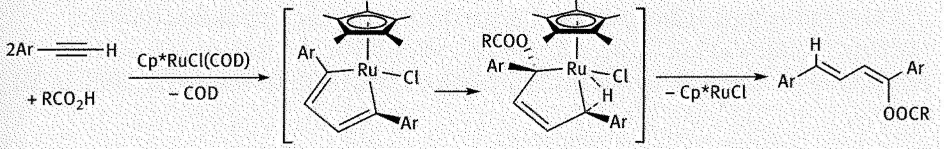
Box 2.6.3 Alkyne complexes in organic synthetic methodology

The 14-VE fragment CpCo is a highly efficient catalyst for the trimerization of alkynes and the co-trimerization of alkynes with nitriles to give pyridine derivatives. CpCo can be generated by photochemical CO dissociation from $CpCo(CO)_2$, or, more conveniently, using CpCo(1,5-COD) as precursor.

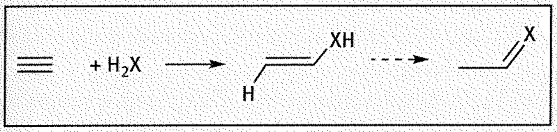


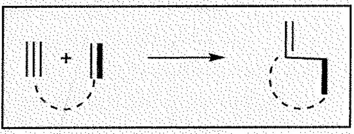


Metallacyclopentadiene intermediates are involved in the Ru-catalysed hydrocarboxylation of alkyne dimers:



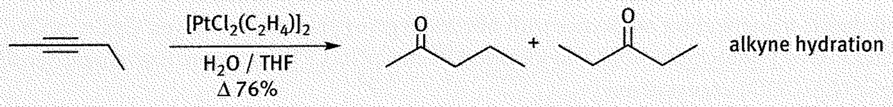
Electrophilic metal centres coordinate to alkynes and enable nucleophilic attack either by heteroatoms or by other carbon moieties. This has been exploited extensively for both inter- and intramolecular transformations. A few representative examples are given in the following diagrams.

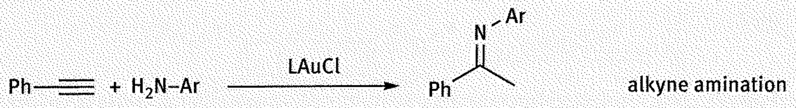




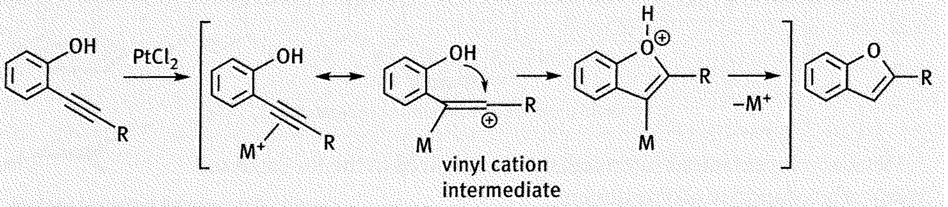
The reaction principle is invariably that coordination of M^+ to C≡C induces the formation of a reactive vinyl cation, which sets off a cascade of carbocationic rearrangements. Although in principle these reactions could also be initiated simply by H^+, the metal has a significant influence over the course and the outcome. The mechanisms are in most cases plausible rather than experimentally supported proposals.

Platinum and gold compounds are particularly widely used, either in the form of the simple halides ($PtCl_2$, AuCl, $AuCl_3$) or as complexes with donor ligands (phosphines, alkenes, NHCs) for enhanced solubility. Both act as sources of metal cations M^+ which coordinate to the triple bond of alkynes. Such a complex can be described by a resonance form which places the positive charge on the C atom in β-position to the metal, i.e. formation of a vinyl cation, which is susceptible to attack by nucleophiles. This enables the addition of HX across the C≡C triple bond, for example the hydration of alkynes to ketones, and the addition of primary amines to give imines.

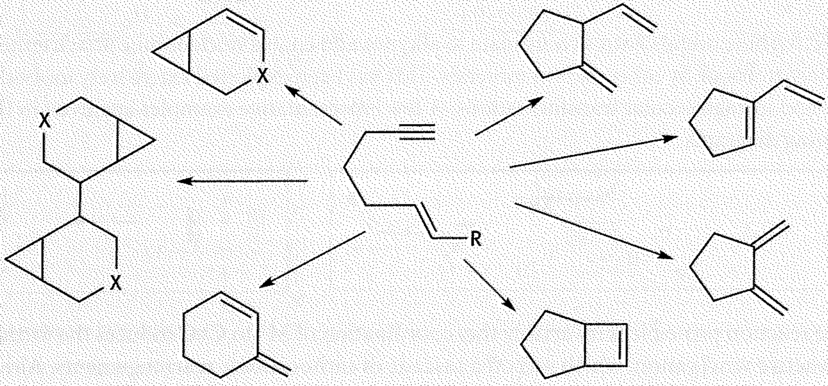


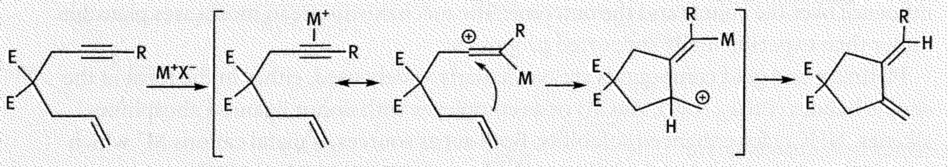


The same reaction principles can be applied to alkynes attached via a linker to amino or OH functions. Intramolecular cyclizations lead to a variety of heterocycles, for example:



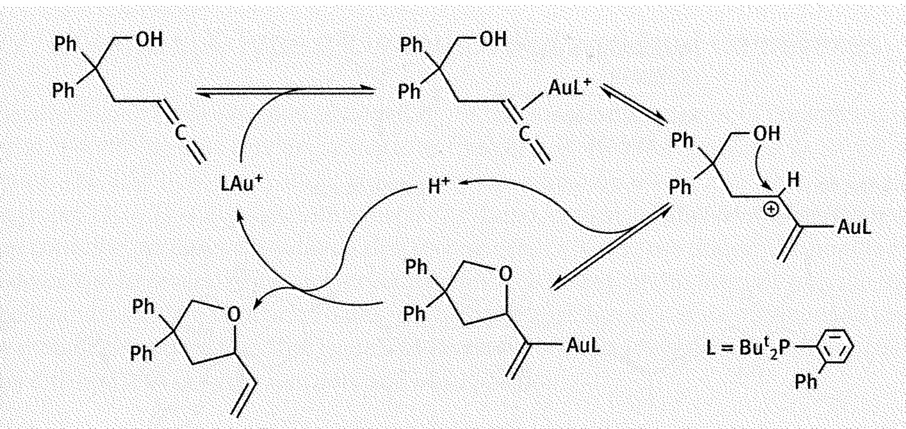
A very widely studied group of reactions are those of alkynes with alkenes ('enyne reactions'). These lead to C–C bond formation and cyclization. A number of skeletal reorganizations have been carried out by activating alkenyl-alkynes with electrophilic metal centres:





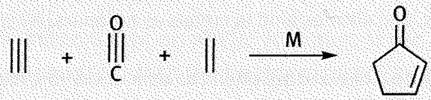
[MX = IrCl(COD), HOAc; E = CO_2Et]

Allenes are alkyne equivalents and show similar reactivity. The catalytic cycle in the following schematic has been studied in detail. C–O bond formation is fast but reversible.

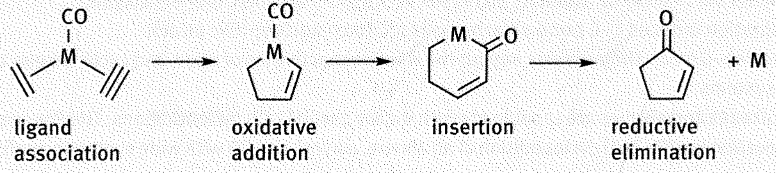


The Pauson–Khand reaction

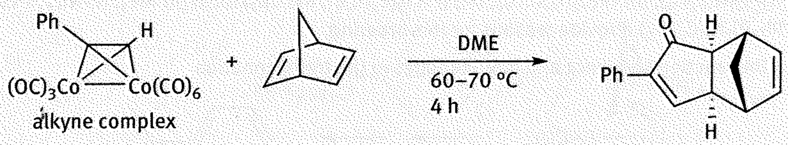
The formation of cyclic products by coupling alkynes with alkenes can be extended to incorporate CO, in a [2+2+1] cycloaddition reaction.



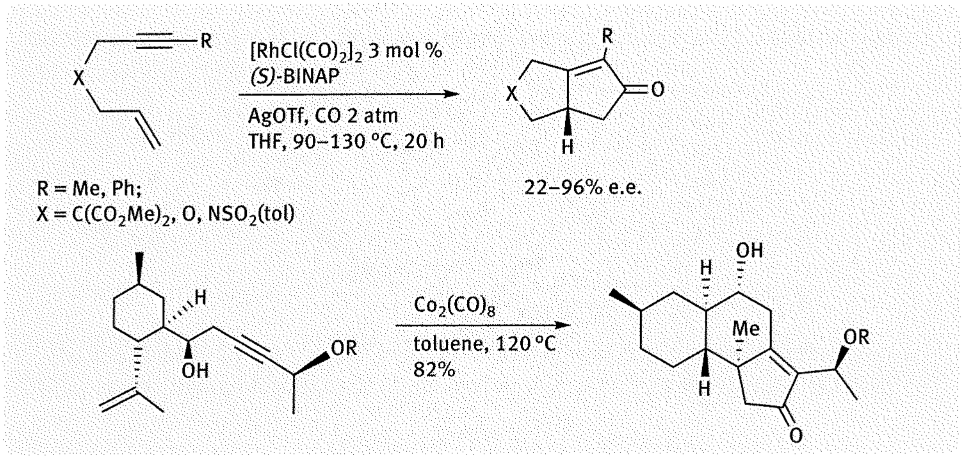
In principle, the mechanism includes the following key steps:



The reaction was originally discovered during attempts to react $Co_2(CO)_6(PhC_2H)$ with norbornadiene. Alkyne complexes of cobalt carbonyls form stable tetrahedral $Co_2(CR)_2(CO)_6$ clusters. The reaction requires forcing conditions. CO pressure is required to ensure a high yield of CO insertion product; on the other hand, high CO concentrations also retard the reaction since CO blocks the reactive coordination sites on the metal that are required for substrate binding. Nevertheless, numerous variants have been developed, using the metal carbonyl either in stoichiometric or catalytic quantities. A wide range of metals (Ti, Mo, W, Fe, Ru, Co, Rh, Ir, Pd) have been used.



The same reaction can be accomplished (93% yield) using (η^5-indenyl)$Co(CO)_2$ as catalyst. Intramolecular catalytic versions have been developed, and the reaction has been successfully applied to control the stereochemistry in asymmetric synthesis.



Key points

Alkenes, conjugated dienes, and alkynes bind to metals as π-donors. Alkynes can act as 2- and 4-electron donors.

Alkene complexes tend to be labile and are often convenient starting materials or reactive catalyst precursors. Alkene complexes are the starting point of numerous catalytic cycles.

Back-bonding is the most important component in C=C and C≡C ligand bonding. For a given set of substituents the π-acceptor capacity increases in the order alkene < diene ≤ alkyne.

Coordination induces C–C bond polarity and facilitates nucleophilic attack.

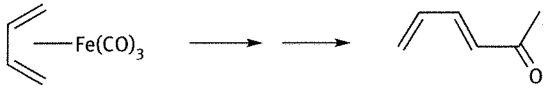
The *Davies–Green–Mingos rules* set out the relative reactivities of open and cyclic alkene and alkenyl systems.

Both alkenes and alkynes are capable of synthetically useful [2+2] cycloadditions. The *Pauson–Khand reaction* is a [2+2+1] cycloaddition of an alkene, alkyne, and CO with wide synthetic applications.

Exercises

1. Explain why the addition of catalytic amounts of $SnCl_2$ facilitates the synthesis of Zeise's salt $K[PtCl_3(C_2H_4)]$ from $K_2[PtCl_4]$ and ethylene.
2. Order the following compounds according to increasing rotational barriers of the alkene or alkyne ligands:

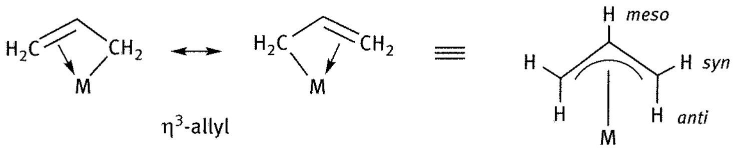
   (i) $(Ph_3P)_2Ni(C_2H_4)$, (ii) $Fe(C_2H_4)(CO)_4$, (iii) $[PtCl_3(C_2H_4)]^-$, (iv) $Cp_2Zr(C_2H_4)(PMe_3$, (v) $Ni(1,5\text{-}COD)_2$, (vi) $(Ph_3P)_2Ni(C_2Ph_2)$. Provide reasons for this ordering.
3. Show the reaction sequence and intermediates in the transformation



4. Discuss the bonding in $Pt(C_2Ph_2)_2$. Which electron count best describes the complex, and why is it not planar?
5. Draw the reaction steps and intermediates in the Co(I)-catalysed formation of pyridines from internal alkynes and nitriles.

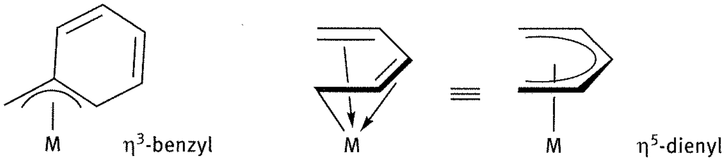
2.7 LX- and L$_2$X-Type π-Ligands: Allyl and Enyl Complexes

The allyl ligand (2-propenyl, $CH_2CH{=}CH_2$) is the simplest of a series of conjugated noncyclic π-donor ligands carrying a negative charge; it is therefore classified as an LX-type ligand. The allyl ligand can adopt either an η^1-coordination mode, as it does in Grignard reagents $CH_2{=}CH{-}CH_2MgX$ with a metal–C σ-bond, or form η^3-allyl compounds. For electron counting purposes a π-bonded allyl is considered a 3-electron donor. The bonding can be described by several resonance structures; since all three C atoms interact with the metal, a half-sandwich-type structure results in which the allyl ligand is close to perpendicular to the metal-centroid vector. Allyl ligands are available with a variety of substitution patterns. One differentiates between *syn*, *anti*, and *meso* positions:



Benzyl ligands (CH_2Ph) often adopt an allylic structure if the metal centre is coordinatively and electronically unsaturated, with the phenyl ring acting as a 2-electron π-donor.

Dienyls also form sandwich-type π-structures and act as L$_2$X ligands.

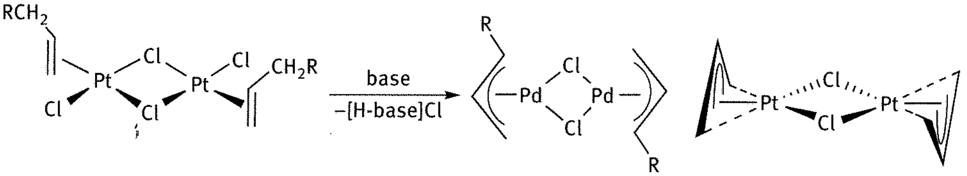


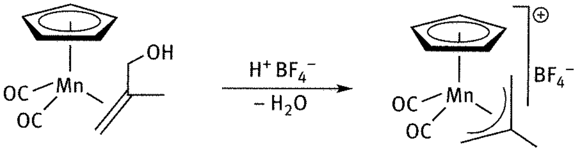
2.7.1 Metal Allyl Complexes

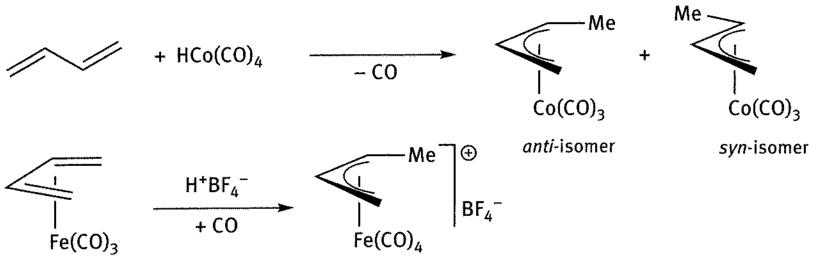
2.7.1.1 Synthesis

Metal-bound substituted alkenes can often be deprotonated to give allyl complexes. A classic example is $[(\eta^3\text{-allyl})PdCl]_2$. Similar complexes can be made by the protonation of dienes or diene complexes. All three carbon atoms are about equidistant to Pd, and the allyl ligand can be thought to occupy two coordination sites in a square-planar complex.

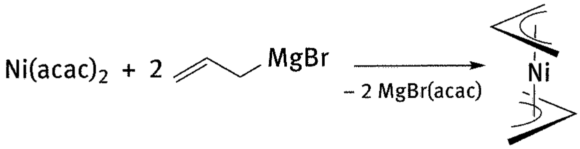
From alkene and diene complexes:



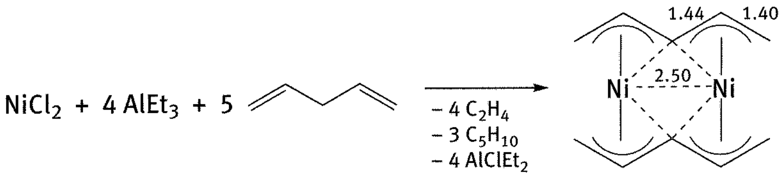


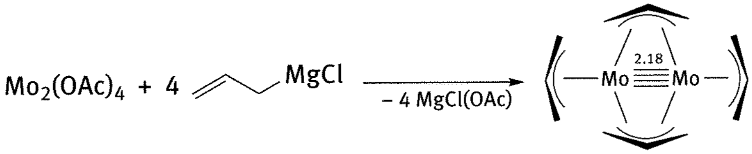


By allyl transfer:

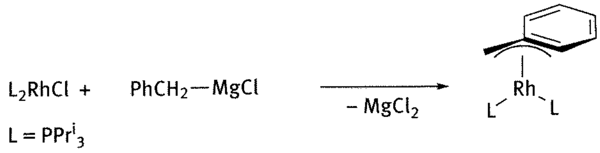


bis(allyl)nickel
volatile, orange crystals
temperature sensitive

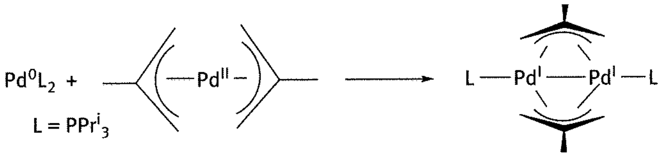




allyl ligands sandwiching
two metal centres

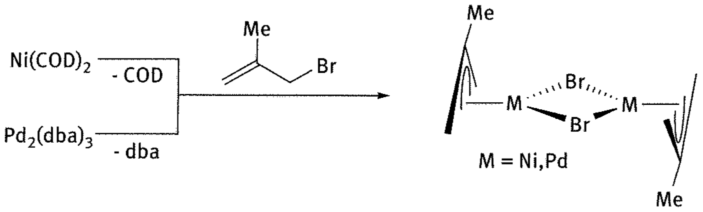


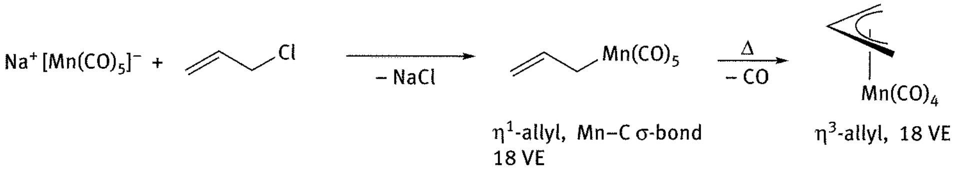
η^3-benzyl complex

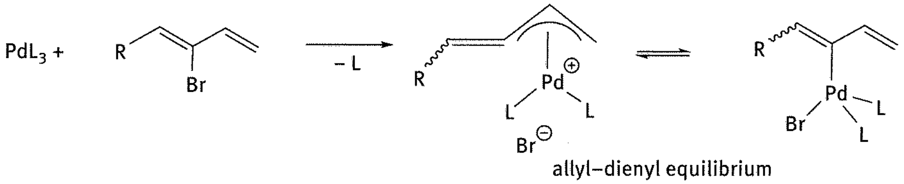


Ligand exchange
and comproportionation

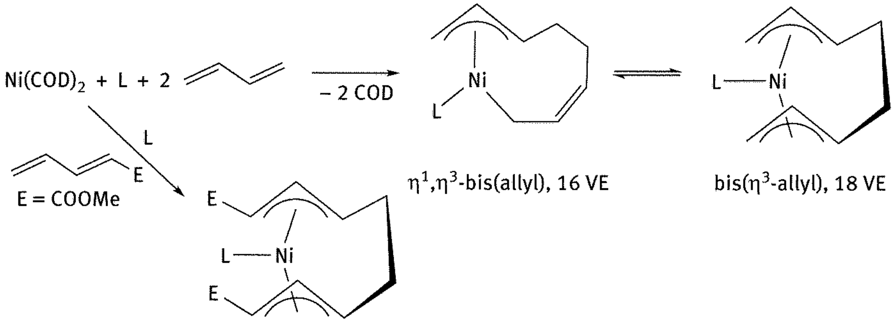
By oxidative addition of allyl halides:

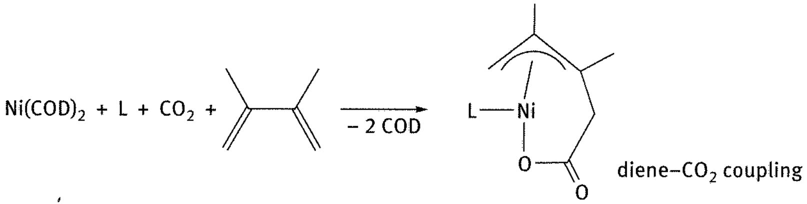






By oxidative C–C coupling: A particularly interesting and important aspect of nickel allyl chemistry is that dienes add oxidatively to Ni(0) to give C–C coupling products. This principle has been used for the construction of selectively functionalized organic molecules.





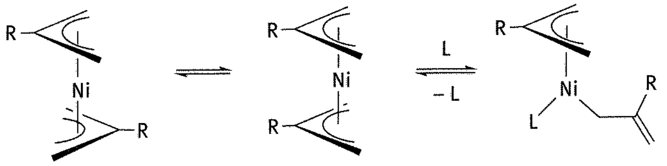
2.7.1.2 Properties

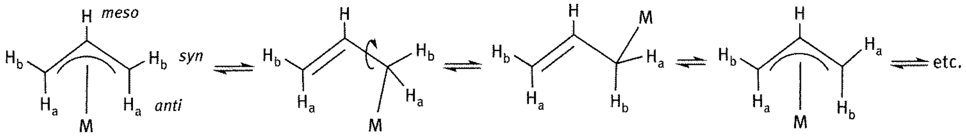
Allyl ligands are typically bonded π-fashion. In the chloro-bridged dimer [(methallyl) PdCl]$_2$ the allyl ligands sandwich the planar Pd_2Cl_2 moiety; the dihedral angle between best planes of the allyl and the Pd_2Cl_2 core is 111.6° (rather than 90°). The methyl substituent is slightly inclined towards the metal. Here and in other complexes the allyl ligand occupies effectively two coordination sites.

Ni(allyl)$_2$ was the first homoleptic metal allyl to be isolated; it has a sandwich structure. The 16 VE complex is highly air-sensitive and so volatile that it co-distils with diethyl ether at low pressure. It decomposes thermally below room temperature with reductive elimination of hexadiene to give metallic nickel and can be used as a source for Ni(0). Other first row metal allyls [Cr(allyl)$_3$, Co(allyl)$_3$] are even more temperature sensitive. By contrast, Rh(allyl)$_3$ is stable at room temperature and above and is not attacked by air or moisture. It is also volatile. This increase in stability mirrors the situation for alkene complexes, where compounds of second and third row metals are also much more stable to air and moisture than their first row analogues.

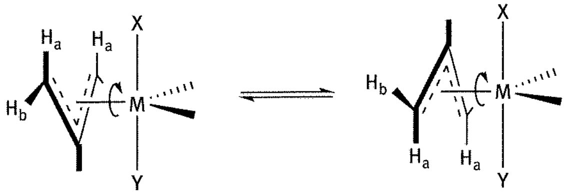
First row metal allyl complexes in low oxidation states and with an 18 VE electron count are more stable, for example CpNi(η^3-allyl).

Allyl ligands show several fluxional processes that affect their reactivity and stereoselectivity. Firstly, since π-allyls rotate about the allyl–metal vector, bis(allyl) complexes exist as a mixture of *syn*- and *anti*-isomers. Secondly, η^3- and η^1-structures may interconvert. This process interchanges *syn*- and *anti*-hydrogens. If donor ligands L are present, mixtures of η^3- and η^1-allyls may be present in various relative concentrations, which may affect the stereochemical outcome of subsequent reactions, such as diene insertions and oligomerizations.



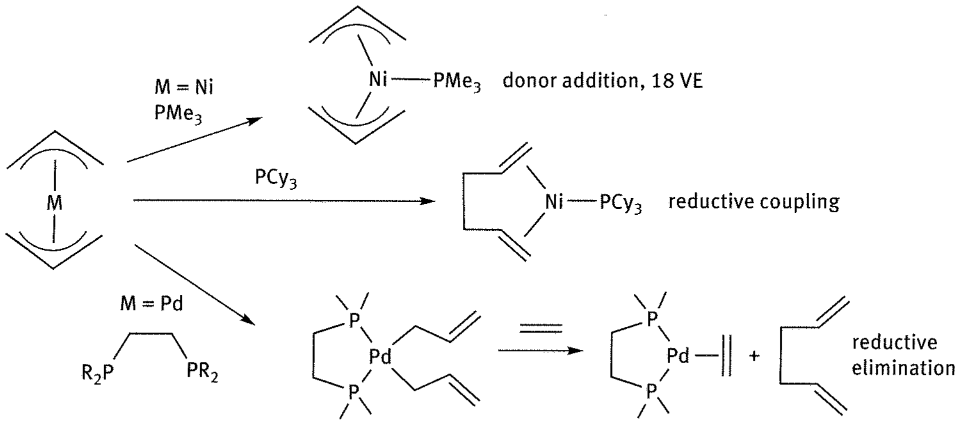


On the other hand, rotation of an allyl ligand without η^3 to η^1 interconversion cannot exchange the *syn*- and *anti*-hydrogen atoms. If the rotation is sufficiently slow on the NMR time scale, two isomers and two sets of resonances for the allylic H atoms may be observed, which on warming may coalesce, following the pattern of a two-site exchange.

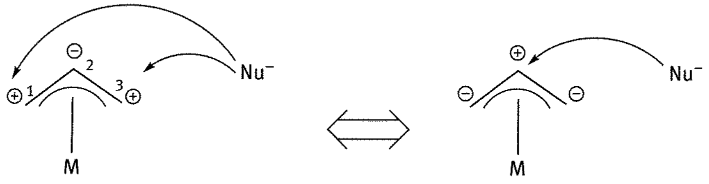


2.7.1.3 Reactivity of Allyl Complexes

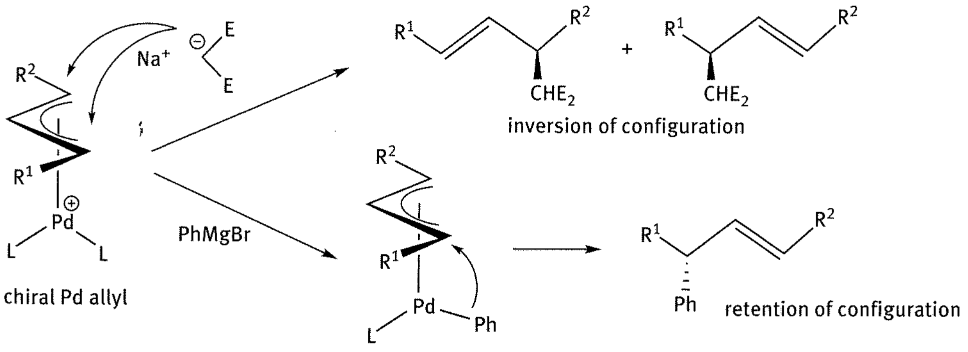
With phosphines. The addition of phosphine donor ligands to 16 VE complexes like Ni(allyl)$_2$ increases the stability of the complexes and gives 18 VE adducts, Ni(η^3-allyl)$_2$(PR$_3$). The allyl ligands are co-planar. Further addition of donor ligands may lead to reductive elimination, giving low-valent metal compounds and C–C coupling products; for example:



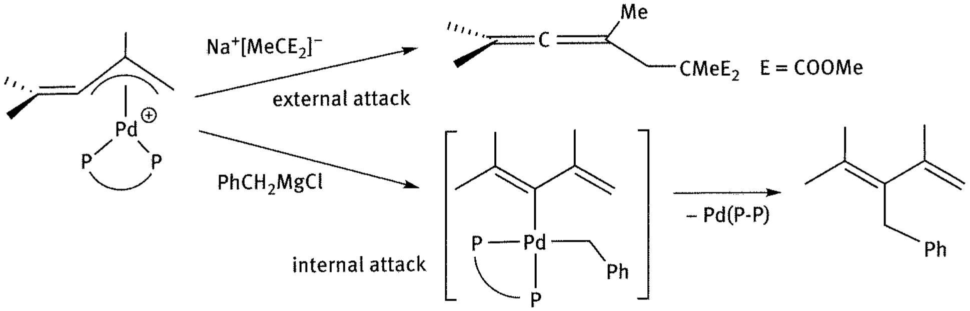
With nucleophiles. Allyl complexes can react with both electrophiles and nucleophiles. Nucleophilic attack is commonly used to introduce functional groups or to achieve C–C bond formations. In principle, there are two sites of attack: on the termini in 1 and 3 positions, or on the central C_2 atom. The site of attack depends on the charge distribution on the allyl ligand. In most cases where allyl complexes are employed in synthesis, the metal is electron rich, as in palladium allyls, and nucleophilic attack occurs on one or both of the termini. The regiochemistry will depend on the substitution pattern. However, where the allyl carries electron-withdrawing substituents, or where the metal is electropositive and the termini carry significant partial negative charge, the nucleophile will attack the middle C atom.



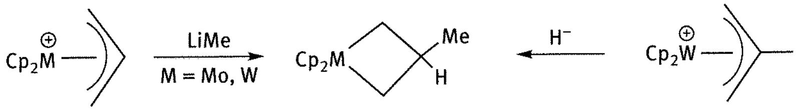
The stereochemistry of nucleophilic attack depends on whether the reaction occurs by intermolecular attack on the ligand, or by way of coordination to the metal, followed by intramolecular reductive elimination. If the Pd atom is the centre of chirality, in the first case there will be *inversion* of configuration, in the second *retention*.



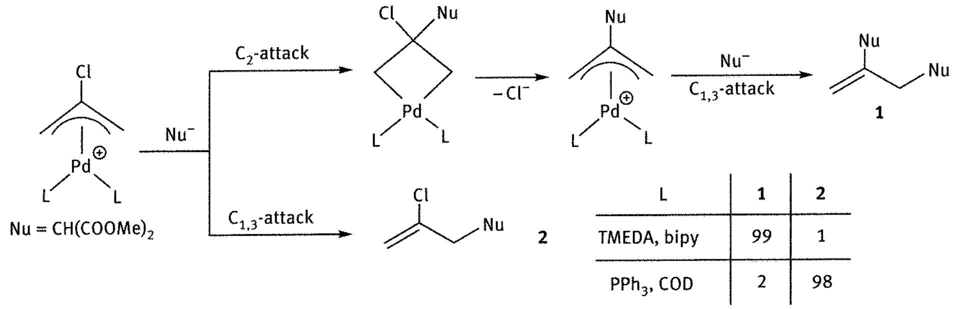
This principle has, for example, been used for the selective synthesis of allenes and dienes. Other examples are shown in Section 2.6.2.3 (diene reactions).



Attack on the central C is found for cationic allyl complexes of Mo and W.

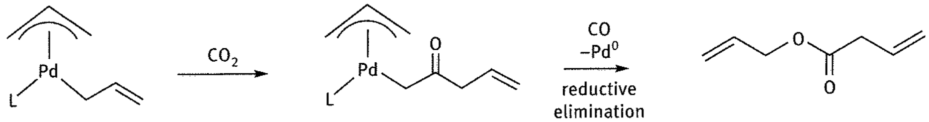


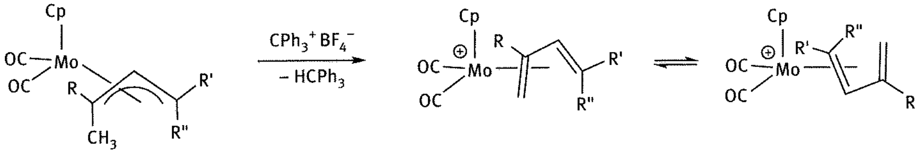
Although most reactions of nickel and palladium allyls with nucleophiles result in terminal attack, palladium allyls with 2-chloro substituents may also display C_2 regioselectivity, depending on the σ-donor strength of neutral ligands L. The regioselectivity correlates with the ^{13}C NMR chemical shift difference between the terminal and central C atoms: a large difference, implying more positive charge on the central C, favours C_2-attack.



L	1	2
TMEDA, bipy	99	1
PPh_3, COD	2	98

With electrophiles. Allyl complexes can insert electrophiles like CO_2 or aldehydes. The reaction with CPh_3^+ proceeds with hydride abstraction to give cationic diene complexes. Subsequent reaction of these with nucleophiles is a method of introducing further substituents, with regeneration of a π-allyl complex.

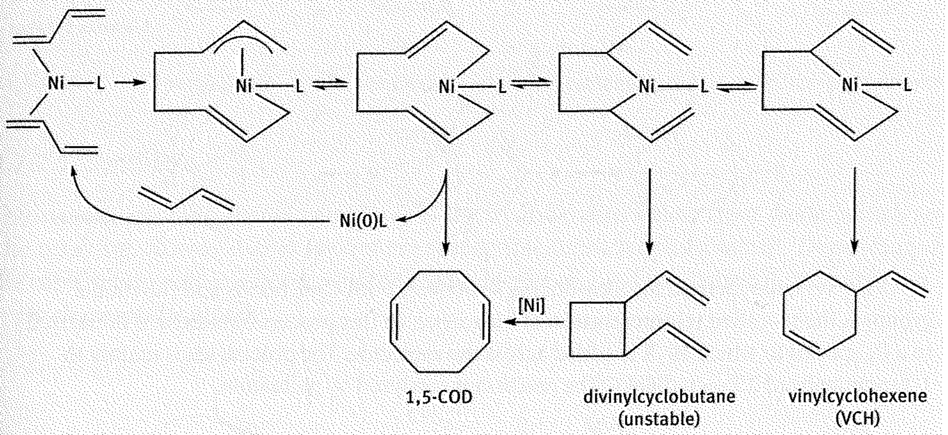




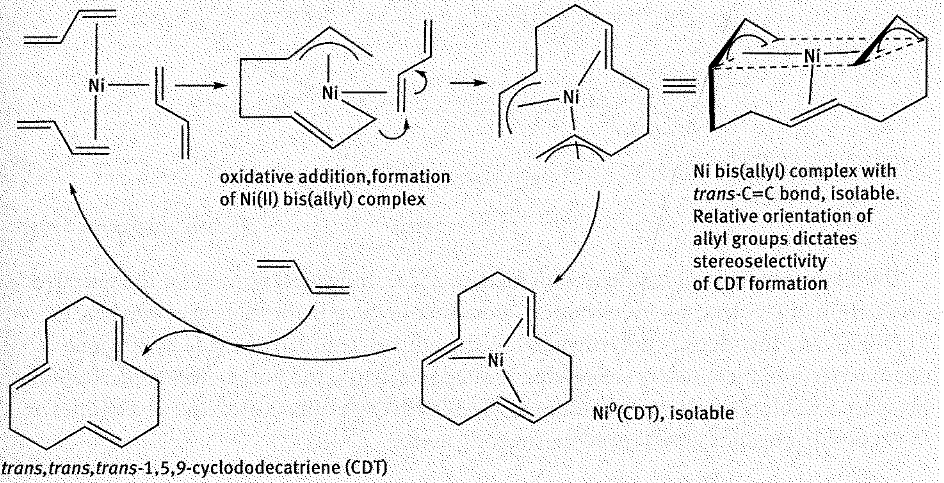
Box 2.7.1 Metal allyl catalysts

Metal allyl complexes are the active species in the oligomerization, polymerization, and functionalization of conjugated dienes. The most important of the diene substrates are 1,3-butadiene and isoprene (2-methyl-1,3-butadiene), the building block of terpenes and natural rubber. The best studied catalysts for diene oligomerizations are nickel and palladium complexes.

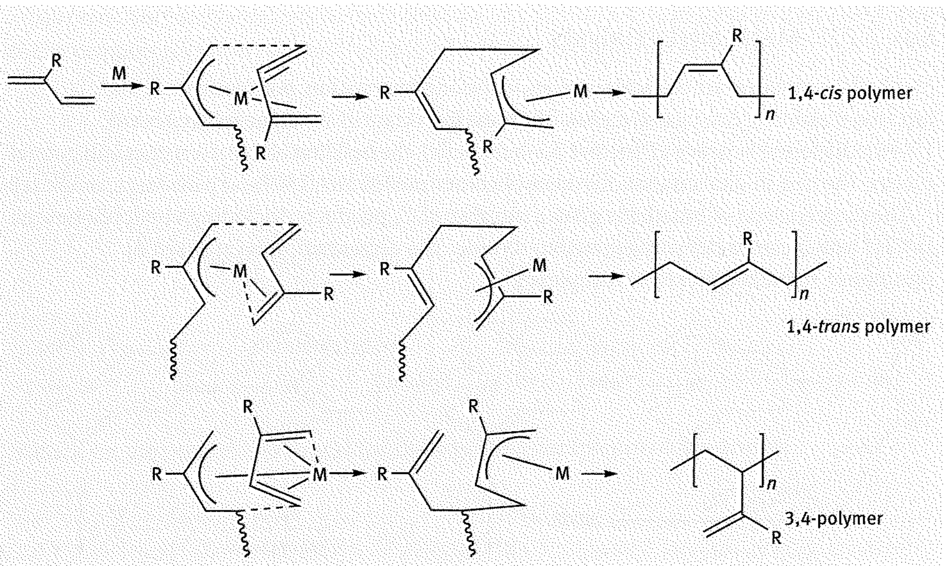
The dimerization of butadiene gives a number of C_8 products, including vinylcyclohexene (VCH) which can be dehydrogenated to styrene. The dimerization is catalysed by phosphine-stabilized nickel(0) complexes.



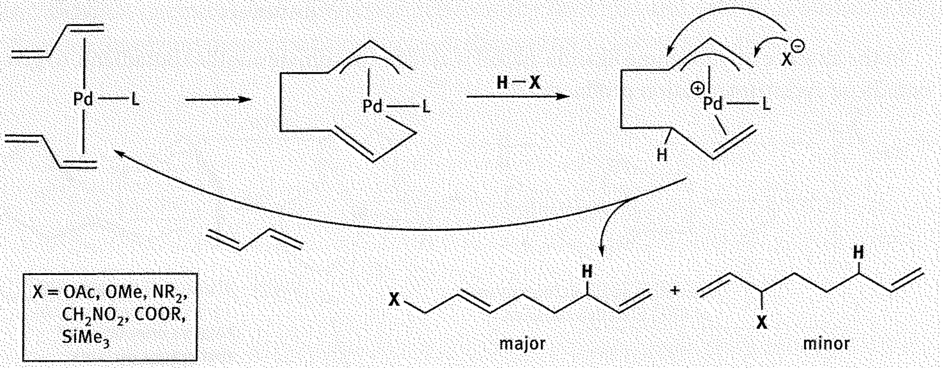
In the absence of phosphine ligands, nickel is able to coordinate another butadiene, to give butadiene cyclotrimerization products.



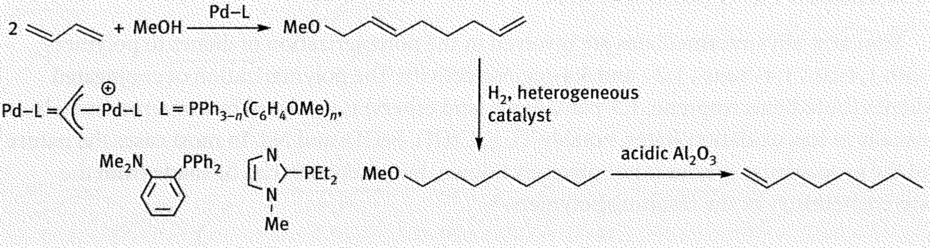
Similar π-allyl intermediates are involved in the polymerization of dienes to polymers with 1,4-*cis*-, 1,4-*trans*-, 1,2-, and 3,4-regioselectivity. The polymerization of conjugated dienes (butadiene, isoprene, 1,3-pentadiene, and others) is catalysed by numerous metals usually in low oxidation states, notably Ti, V, Cr(II), Fe(II), and Nd. In most cases the nature of the propagating species is not precisely known, but inferences can be made from the stereochemistry of the resulting polymers.



A very versatile method for introducing selectively both C=C bonds and functional groups is the so-called **telomerization** of butadiene. In this process butadiene is dimerized to a C_8 species to which H–X is added across the molecule. The process leads mainly to 1-functionalized 2,7-octadienes. The reaction is catalysed by palladium.

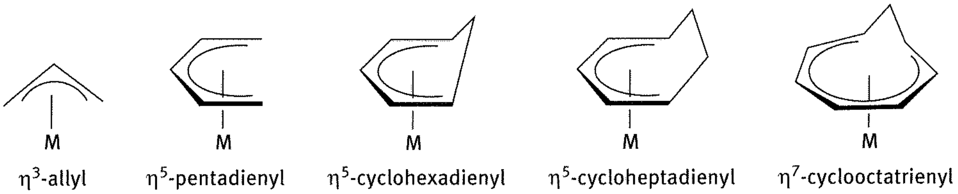


The telomerization of butadiene with methanol is an industrial process for the selective production of 1-octene, an important co-monomer in the polymerization of ethylene to LLDPE (linear low-density polyethylene). Although 1-octene can be made by ethylene oligomerization, these routes suffer from limited selectivity, and butadiene telomerization provides a viable alternative. Palladium catalysts with OMe-substituted aryl phosphines or P–N chelating ligands have proved particularly useful:



2.7.2 **Metal Dienyl and Trienyl Complexes**

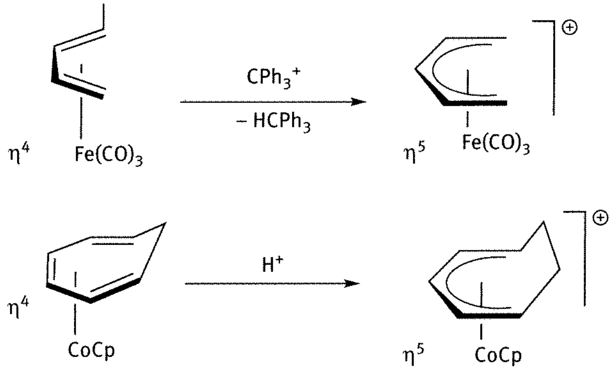
Dienyls and trienyls extend the series from η^3-allyl to η^5- and η^7-bonded, formally anionic π-ligands. They may form open delocalized structures, or the termini of these π-systems may be bridged by a saturated linker. Closed $(4n+2)\pi$ Hückel aromatic systems (cyclopentadienyls, arenes) are considered in Chapters 2.8 and 2.9.



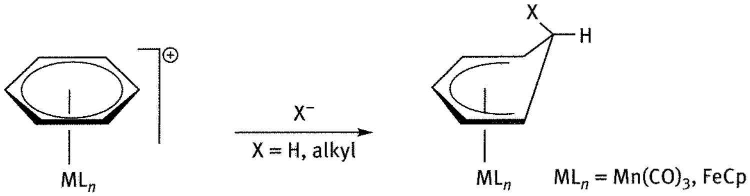
2.7.2.1 Synthesis

The classical route to dienyl complexes is the hydride abstraction from diene complexes. The resulting cationic dienyl species are susceptible to nucleophilic attack. Depending on the substitution pattern, this is a highly regioselective method for diene functionalization.

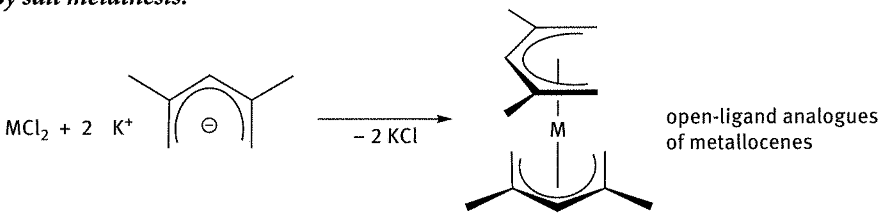
By electrophilic attack:



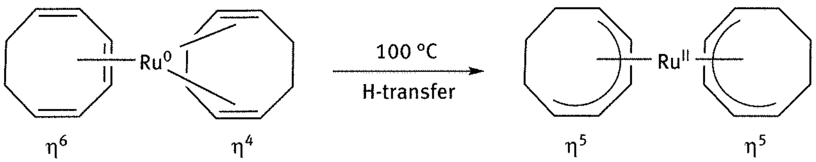
By nucleophilic attack:



By salt metathesis:

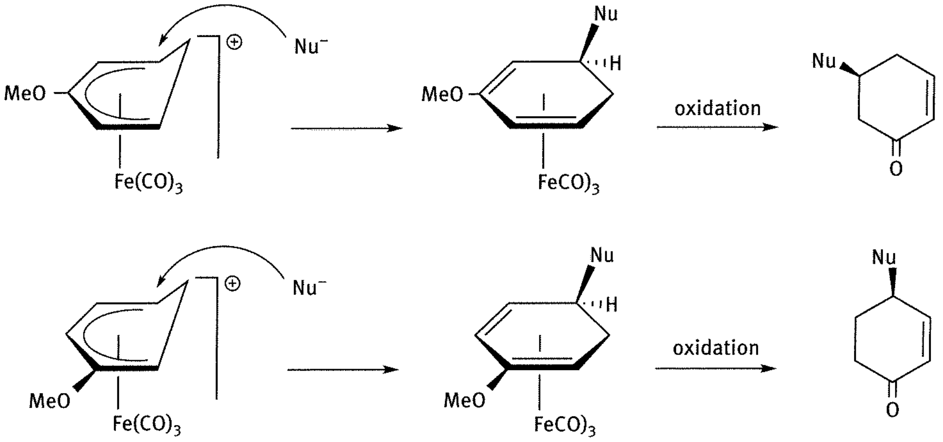


By isomerization:



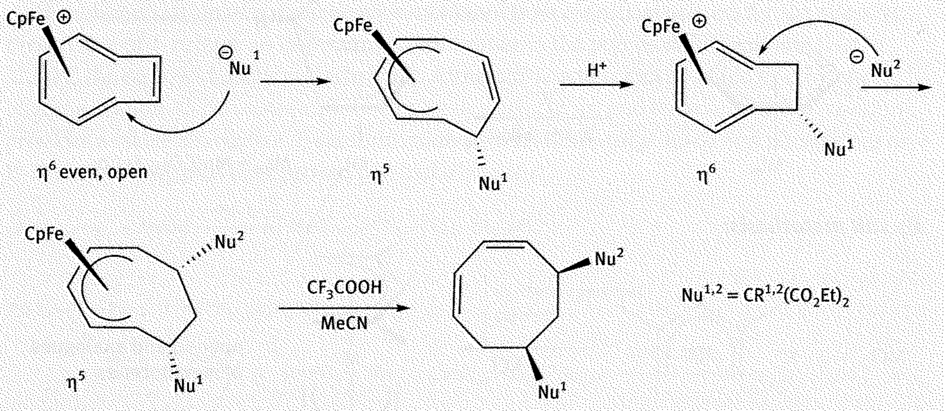
2.7.2.2 Reactivity

Dienyl complexes, particularly those of Fe and Mn carbonyls, have important applications in stereoselective synthesis. The strategy is to use a succession of $[\eta^4] \rightarrow [\eta^5]^+ \rightarrow [\eta^4]$ or $[\eta^6]^+ \rightarrow [\eta^5]$ conversions (for $Fe(CO)_3$ and FeCp compounds, respectively) to introduce selective functionalizations.

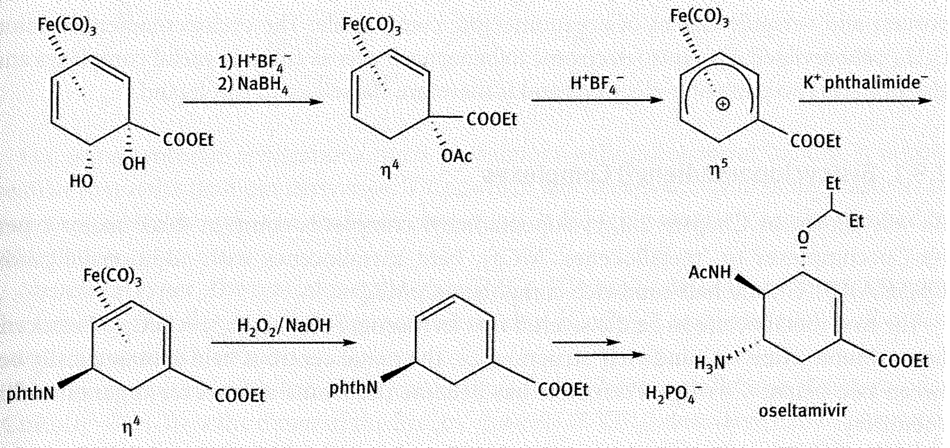


Box 2.7.2 Metal dienyl complexes in organic synthesis

Successive nucleophile addition and protonation steps allow the conversion of a cyclooctatetraene complex into a stereoselectively difunctionalized diene:



A similar reaction sequence has been used to synthesize a core constituent of the anti-influenza agent oseltamivir. The starting diene in this case is a product of the microbial oxidation of benzene.



Key points

Allyls and dienyls coordinate to metals in most cases as π-ligands donating 3 and 5 electrons, respectively. These ligands are regarded as monoanionic, LX and L_2X ligand classes.

Allyls are often generated from alkenes and conjugated dienes as part of catalytic cycles (double bond isomerization, diene oligomerization and polymerization, synthesis intermediates).

They are susceptible to nucleophilic attack, most commonly in 1- and 3-positions (see also Davies–Green–Mingos rules).

The formation of allyls and dienyls allow the regio- and stereoselective functionalization of unsaturated substrates.

Important catalytic applications involving π-allyl complexes include:

(i) catalytic butadiene dimerization and trimerization;

(ii) butadiene dimerization with HX addition: telomerization;

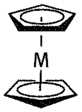
(iii) butadiene and isoprene polymerization to elastomeric polymers.

Exercises

1. What is the product of the reaction of $[(n^2\text{-}C_3H_6)PdCl_2]_2$ with a base?
2. Nickel(0) complexes catalyse the dimerization of 1,3-butadiene to 4-vinylcyclohexene (VCH), which can be oxidized to produce styrene. Draw all intermediates and describe each reaction step of VCH formation.
3. Draw the reaction steps and intermediates in the following transformation, mediated by $PdCl_2$ in the presence of a nucleophile HNu:

2.8 L_2X-Type π-Acceptor Ligands: Metallocene Complexes

Complexes containing one or more cyclopentadienyl ligands constitute one of the most important and versatile classes of organometallic compounds. The cyclopentadienide anion $C_5H_5^-$, abbreviated Cp^-, is isoelectronic to benzene; it acts as anion in metal complexes and also donates two pairs of π-electrons and is therefore classed as an L_2X ligand.

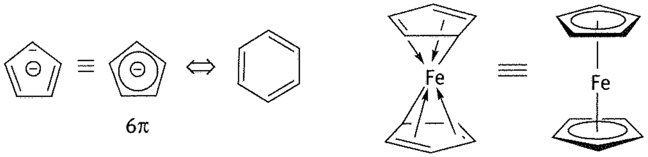


Nobel Prize 1973 to E. O. Fischer and G. Wilkinson: Discovery of sandwich complexes

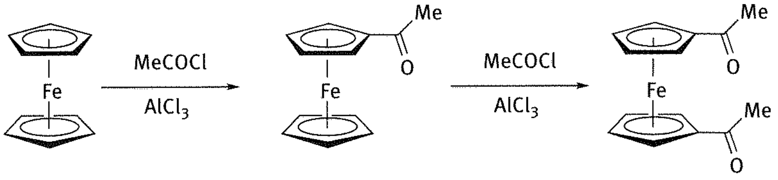
2.8.1 Bis(cyclopentadienyl) Complexes

As was shown in Chapter 2.2, cyclopentadienyl complexes come in three major types: bis-Cp complexes or 'metallocenes', MCp_2, bent metallocenes with additional ligands, $Cp_2M(A)(B)(C)$, and half-sandwich complexes, $CpML_z$.

The first metallocene to be discovered was ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2 = FeCp_2$. Ferrocene has a 'double-cone' or 'sandwich' structure, i.e. the metal centre is held symmetrically between two planar C_5 rings. Ferrocene has become the iconic symbol for organometallic chemistry.



The name ferrocene was coined in recognition that it behaved chemically rather like benzene or a three-dimensional arene molecule. For example, the Friedel–Crafts acylation of ferrocene is even more facile than that of benzene:

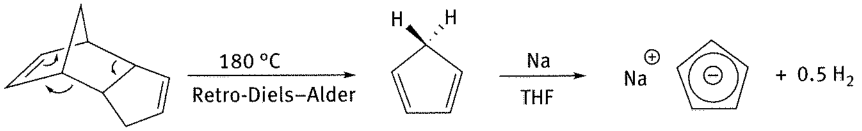


The fact that Cp rings can bear a multiplicity of substituents has contributed much to the success of metallocenes.

For examples, see Chapter 2.2

It was soon realized that the sandwich-type bonding was a general structural principle. Not only could bis-Cp complexes be made for many different metals, the isoelectronic relationship between Cp and benzene could also be used to postulate and synthesize other systems, e.g. complexes of benzene as neutral Cp^- analogues. $Cr(benzene)_2$ is the prime example. Sandwich complexes now exist with ring sizes from 3–9.

The cyclopentadienide anion is made by deprotonation of cyclopentadiene, C_5H_6. This exists under normal conditions as its Diels–Alder dimer, from which it can be generated by thermal cracking. It is a C–H acidic compound ($pK_a = 16$); it reacts therefore with alkali metals or alkali metal hydrides with evolution of H_2 and formation of the corresponding metal–Cp compounds. The alkali compounds are colourless salts (usually coloured pink due to trace impurities of oxidation products). Substituted cyclopentadienes are more stable as monomers.

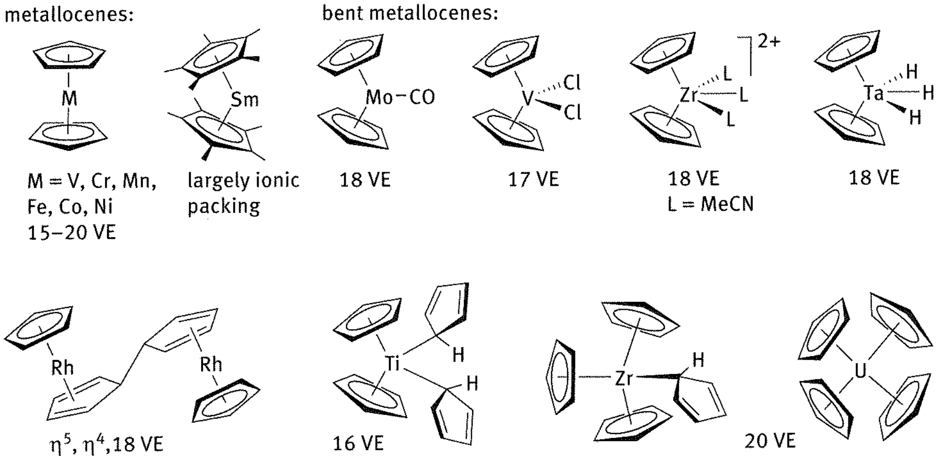


For some synthetic applications, such as reactions with noble metal halides, it is convenient to use the thallium derivative, TlCp, which has the advantage of being stable to air and moisture (although, as a thallium compound, it is highly toxic). It can be purified by sublimation.

For TlCp see Section 1.5.3.2.

Structural types. The typical metallocenes $[MCp_2]^{n+}$ may be neutral or cationic. Among the first row metallocenes, only ferrocene itself and $[CoCp_2]^+$ are diamagnetic; all others have 1–5 unpaired electrons.

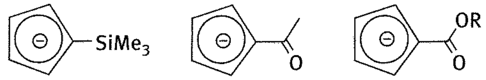
Not all complexes with the empirical formula MCp_2 have metallocene structures, e.g. $[CpRh(\eta^4\text{-}C_5H_5)]_2$ is the dimer of the $RhCp_2^{\bullet}$ radical (18 VE). Some large metals like zirconium $[r(Zr^{4+}) = 0.91$ Å, the largest of the transition metals] and uranium $[r(U^{4+}) = 1.17$ Å] are capable of π-coordination to more than two Cp ligands. By contrast, $TiCp_4$, with its much smaller metal centre $[r(Ti^{4+}) = 0.74$ Å], contains two η^5- and two η^1-bonded Cp ligands.



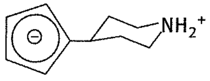
Ligand types. The introduction of substituted Cp rings provides a facile and convenient way to modify the electronic and steric properties of metal complexes. The pentamethyl-Cp ligand, C_5Me_5 (usually abbreviated Cp*) greatly increases steric hindrance since the five CH_3 substituents roughly double diameter and thickness, compared to C_5H_5. As a result, in cases where the $M^+\cdots Cp^-$ interactions have a strong ionic component and the unsubstituted compounds form dimeric or polymeric $[MCp_2]_x$ structures (Mn^{II}, lanthanides), the Cp* analogues are monomeric and molecular. Due to the positive inductive effect of methyl substituents, Cp* is also a much stronger electron donor than Cp. Pentahalo-Cp ligands C_5X_5

(X = Cl, Br, I) have the opposite effect, as does C_5Ph_5. The $C_5(CN)_5^-$ ligand is so weakly basic that it acts as anion in salts, e.g. $[Ni(DMF)_6]^{2+}[C_5(CN)_5^-]_2$. Complexes of halo-substituted Cp derivatives are however useful for the preparation of functionalized Cp derivatives.

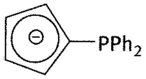
Benzo-annulation of the Cp skeleton (i.e. adding an aromatic C_6 ring) tends to increase the stability of the complexes; e.g. $(\eta^5\text{-indenyl})_2TiMe_2$ is thermally much more stable than Cp_2TiMe_2. On the other hand, as pointed out in Section 2.5.3.1, in cases where the indenyl ligand is bound to electron-rich metals that allow $\eta^5 \rightarrow \eta^3$ slippage, indenyl complexes may prove far more reactive than their Cp counterparts. Chiral substituents are frequently used to induce stereoselectivity in Cp complexes.



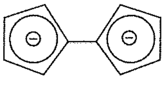
increased lipophilicity

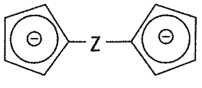


water soluble

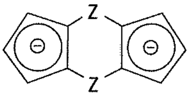


Cp with P-donor function

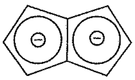

fulvalene dianion

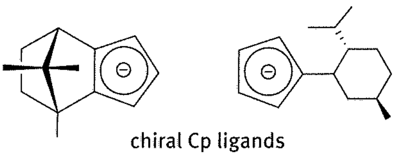


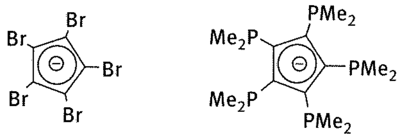
chelate ligand; Z = CH_2, CR_2, $SiMe_2$



double bridge; Z = $SiMe_2$


pentalenediyl dianion

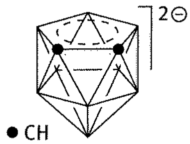

chiral Cp ligands



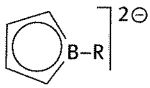
susceptible to nucleophilic substitution

There are numerous Cp analogues based on heterocycles, notably carboranes and boron-containing rings. Those with B–N bonds correspond closely to the C_5 parent compounds, while rings containing one or more BR units in place of CH are electron-deficient. The $[C_2B_9H_{11}]^{2-}$ system has frontier orbitals very similar to those of Cp^-, and series of complexes analogous to metallocenes exist.

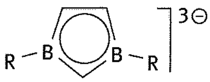
Cp analogues:



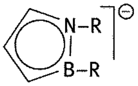
$[C_2B_9H_{11}]^{2-}$
Cp analogue



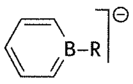
borolyl anion



1,3-diborolenyl

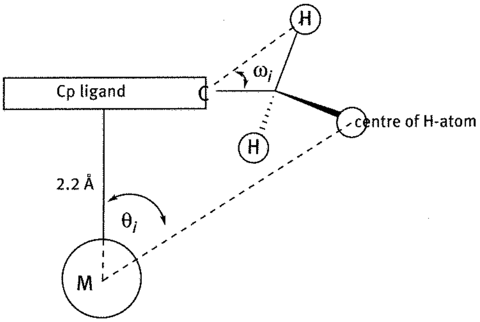


1,2-azaborolyl



boratabenzene

Steric effects. As was discussed for phosphines and carbenes, steric parameters can be assigned to cyclopentadienyl ligands to describe their **steric influence** on a metal complex. Since Cp ligands can carry different numbers of substituents, and since each substituent may be able to adopt more than one conformation to minimize steric repulsion, it is difficult to summarize the total effect in a single number. Usually two angles are measured (or calculated) based on crystal structures, the angle about the metal $\boldsymbol{\Theta = 2/5\ \Sigma\theta_i}$ (i = 1–5), and the angle $\boldsymbol{\Omega = \Sigma\omega_i}$ (i = 1–3) describing the bulk of a substituent.



This leads to the following ordering of Cp ligands according to increasing steric demand. A good measure for this is the rotational barrier of the corresponding ferrocene. Where two values are close to one another, the sequence may vary (Table 2.8.1).

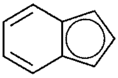
Electronic effects. The electronic effect of Cp substituents is more difficult to assess since the influence of conformational changes, such as the dihedral angle of best planes through the Cp ligands, are substituent-dependent and do not necessarily give a linear relationship. A good general method is to measure the average of the symmetric and antisymmetric ν_{CO} stretching frequencies of $(Cp^R)_2Zr(CO)_2$ complexes. The values decrease as the number of substituents with a +I effect increases. Each CH_3 substituent reduces ν_{CO} by 3.2 cm^{-1} on average. By this measure, the electron donating power of substituents decreases in the sequence

$$\mathbf{Bu^t > Pr^i \approx Et \approx Me > SiMe_3 > H}$$

There is a good correlation with the σ_{meta} Hammett parameter, in agreement with the operation of an inductive effect.

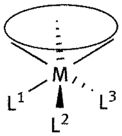
Fluxionality and ring slippage of Cp complexes. Cp complexes show four types of fluxional behaviour:

Table 2.8.1 Steric (°) and electronic (ν_{CO} av) parameters of Cp ligands.[a]

Ligand:	C_5H_5	C_5H_4Me		C_5H_4–$SiMe_3$				C_5Me_5
θ [°]	88.2	95.1	102.6	104.3	116.2	132.0	146.4	167.4
Ω [°]	0	49.0	0	95.6	100.7	99.8	85.9	88.6
ν_{CO} av	1932	1926.5	1942	1929.0	1913.0			1899.5

[a] Steric parameters are derived from $(Cp^R)Zr(\eta^7\text{-}C_7H_7)$, ν_{CO} values [cm^{-1}] from $(Cp^R)_2Zr(CO)_2$.

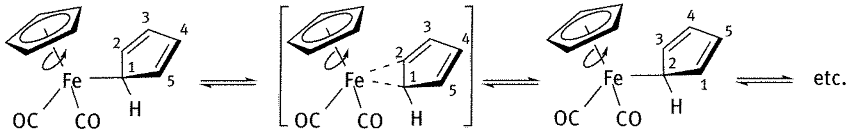
(i) Cp ring rotation;
(ii) σ-bond shift in η^1-Cp ligands;
(iii) η^1/η^5 hapticity interchange;
(iv) η^5/η^3 ring slippage.



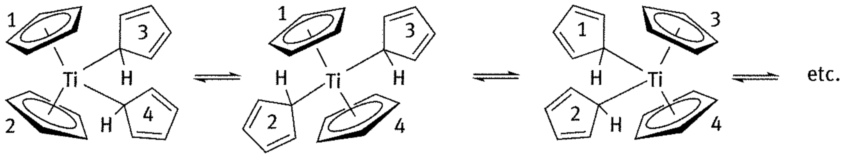
Coordination site occupation by Cp in octahedral complexes

A pentahapto (η^5) coordinated Cp ligand can be regarded as occupying three coordination sites in an octahedral complex. Although in the crystal such a ligand may adopt a preferential conformation relative to the other ligands, in solution Cp ligands are not static and rotate very rapidly about the M–Cp(centroid) vector. With very few exceptions the rotational barrier of a C_5H_5 ring is very small, of the order of ~2 kJ/mol, so that even on cooling to very low temperatures all Cp-hydrogen atoms are equivalent in the NMR spectrum. In ferrocene the rotational barrier is only about one-third of that of ethane.

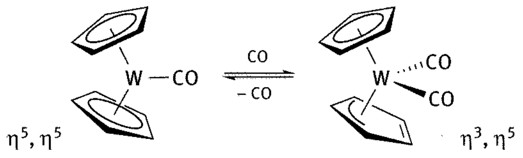
η^1-Cp bonding and σ-bond shift have been discussed in the case of $Hg(\eta^1\text{-}Cp)_2$, which shows rapid interchange of the M–C σ-bonds between all five Cp carbons (Section 1.4.3.2). For transition metals this situation is exemplified by $(\eta^5\text{-}Cp)Fe(CO)_2(\eta^1\text{-}Cp)$. Here the η^1-Cp ligand undergoes a succession of sigmatropic shifts (both 1,2- and 1,3-shifts are possible), so that at room temperature and above all five C-H moieties are identical on the NMR time scale. At 30 °C the ^1H NMR spectrum of this complex consists of two sharp singlets, one of which broadens on cooling to show the expected 1:2:2 signal pattern. The signal for the η^5-Cp ligand remains unaffected and sharp.



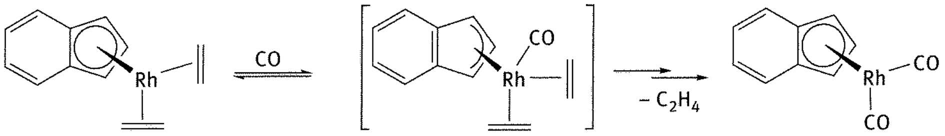
A second type of fluxionality is seen in $TiCp_4$. The 18-electron rule and the small size of Ti(IV) imply that four η^5-Cp ligands could not be accommodated. At 60 °C the compound displays a single ^1H NMR signal; this broadens on cooling and splits into two singlets. In this case two Cp ligands are η^1- and the other two η^5-bonded, and all four participate in the exchange process. There are therefore three fluxional processes operative here: η^5-Cp rotation, η^1/η^5 hapticity interchange, and sigmatropic shifts over the η^1-Cp rings.



η^5/η^3-Ring slippage can be the result of a competition for coordination sites between Cp and other ligands. A classical case is the CO uptake by $Cp_2W(CO)$ to give $Cp_2W(CO)_2$. This is apparently a 20 VE species; however, CO coordination is associated with $\eta^5 \rightarrow \eta^3$ slippage of one of the Cp rings, so that the 18 electron count is maintained.



While such a slippage is unusual for Cp, in indenyl ligands this process is facilitated by the gain in aromaticity of the six-membered ring. The importance of η^5/η^3-indenyl ring slippage for the kinetics of ligand substitution has been discussed in Section 2.5.3.1. It is particularly important for indenyl complexes of Co and Rh. For example, whereas $CpRh(C_2H_4)_2$ is very reluctant to exchange the ethylene ligands for CO, $(Ind)Rh(C_2H_4)_2$ reacts instantaneously:



2.8.1.1 Synthesis of Metallocene Complexes

The most general method of preparing metallocenes is the reaction of metal salts with alkali metal cyclopentadienides.

$$MCl_2 + 2\,Na^+Cp^- \xrightarrow[Et_2O\text{ or }THF]{} MCp_2 + 2\,NaCl$$

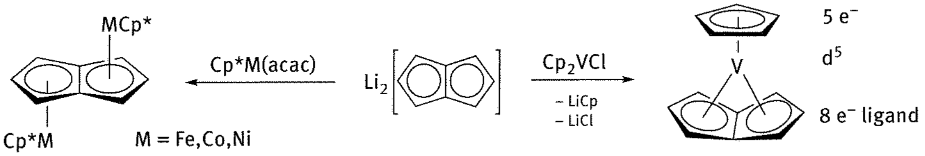
M = V, Cr, Mn, Fe, Co, Ni

$$Ni(acac)_2 + 2\,CpMgBr \xrightarrow[Et_2O]{} NiCp_2 + 2\,MgBr(acac)$$

For stable metallocenes like ferrocene it is possible, and certainly more convenient, to generate the required (small) concentrations of Cp^- anions in situ, from cyclopentadiene and a base like Et_2NH or KOH in DMSO.

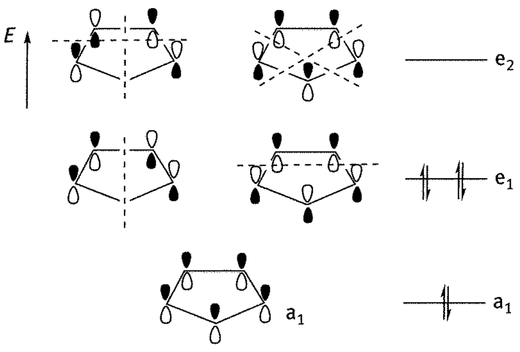
$$FeCl_2\cdot 6H_2O + C_5H_6 + 2\,Et_2NH \longrightarrow FeCp_2 + 2\,Et_2NH_2^+Cl^-$$

The pentalene-diyl anion consists of two edge-sharing Cp rings. It can act as sandwich as well as bridging ligand:



2.8.1.2 Structure and Bonding in MCp_2 Complexes

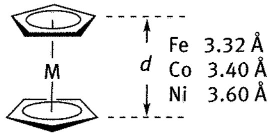
The Cp ligand acts as π-donor and acceptor by virtue of relatively low-lying e_2 levels:



Magnetism

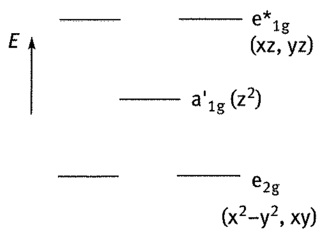
For the MO diagram of sandwich-type metallocenes MCp_2 the combination of Cp and d-orbitals gives the following splitting pattern which determines the **magnetism** of the complexes. The magnetic moment of manganocenes is strongly dependent on the Cp substitution pattern. The 18-VE compounds $FeCp_2$ and $CoCp_2^+$ are diamagnetic (Table 2.8.1.2).

The electron count of metallocenes increases from 15 (VCp_2) to 20 ($NiCp_2$), i.e. the nickel compound exceeds the 18-electron rule. Nevertheless, it has true metallocene structure (as opposed to the η^5- / η^3-Cp alternative). However, the additional electrons weaken the Ni–Cp bond. There is an increase in the distance between the two Cp planes from in the sequence Fe < Co > Ni, contrary to the trend in atomic radii.

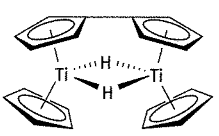


Missing in the series of simple metallocenes MCp_2 is $TiCp_2$, **titanocene**. This would be a highly unstable 14 VE species. Instead, cleavage of the C–H bonds of a Cp ligand occurs, to give a Ti(III) fulvalene hydride complex. The sterically stabilized $Ti(\eta^5\text{-}C_5Me_5)_2$ exists, but even this is in equilibrium with a C–H activated 'tuck-in' isomer. The introduction of bulky substituents is necessary to produce isolable, stable titanocenes. Linear titanocenes (d^2) are

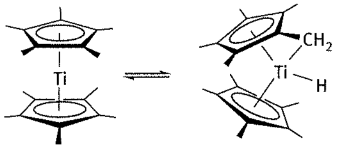
Table 2.8.1.2 Electron configuration and magnetic properties of metallocenes.

Partial qualitative MO diagram for MCp_2		d-level occupancy	VE count	Unpaired electrons	μ_{eff}, spin-only value	Found [Bohr magnetons]
	Cp_2V	$(e_{2g})^2(a'_{1g})^1$	15	3	3.87	3.84
	Cp_2Cr	$(e_{2g})^3(a'_{1g})^1$	16	2	2.83	3.20
	Cp_2Fe^+	$(e_{2g})^3(a'_{1g})^2$	17	1	1.73	2.34
	Cp_2Mn	$(e_{2g})^2(a'_{1g})^2(e^*_{1g})^2$	17	5	5.92	5.81
	Cp_2Co	$(e_{2g})^4(a'_{1g})^2(e^*_{1g})^1$	19	1	1.73	1.76
	Cp_2Ni	$(e_{2g})^4(a'_{1g})^2(e^*_{1g})^2$	20	2	2.83	2.86

paramagnetic; Ti(η^5-C_5Me_4Ph)$_2$ shows a magnetic moment of μ_{eff} = 2.7 B.M., close to the spin-only value for 2 electrons of 2.83 B.M.

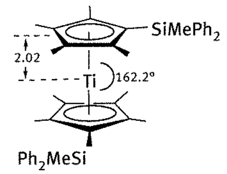


'titanocene', Ti(III), 15 VE, diamagnetic



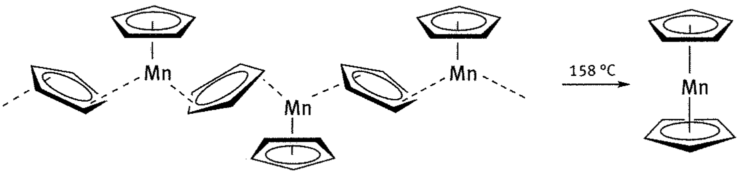
14 VE, Ti(II), yellow, paramagnetic

16 VE, Ti(IV), green, diamagnetic



14 VE, greenish-brown, mp. 105 °C, paramagnetic

Manganese(II) has a half-filled d-shell which in the high-spin state implies ionic character and zero ligand field stabilization. Consequently, in the solid state **manganocene MnCp$_2$** has a polymeric structure with bridging Cp$^-$ anions, reminiscent of more ionic Cp compounds like those of Zn^{2+}. As a further expression of its ionic character, MnCp$_2$ forms 19–21 VE mono- and bis-adducts with donor ligands, such as Cp$_2$Mn(THF)$_2$ and Cp$_2$Mn(PMe$_3$). MnCp$_2$ exists in two phases: at 158 °C the amber polymeric low temperature modification is converted into the pink monomeric metallocene structure.

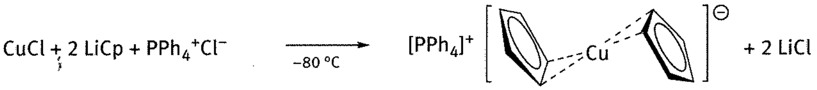


In Mn(C_5H_4Me)$_2$ high-spin (HS) and low-spin (LS) states are energetically very close, so that small changes in temperature or solvent can affect changes in magnetism. The HS/LS cross-over brings with it profound changes in the degree of covalent character of the Mn–Cp bond; the high-spin d^5 form is ionic with a large Cp(centroid)–Mn–Cp(centroid) distance (4.1 Å), whereas the low-spin form is covalent, with Mn–Cp distances comparable to ferrocene.

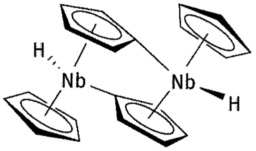
Na[MnCp*$_2$] is a powerful one-electron reductant (E1/2 = -2.17 V vs SCE)

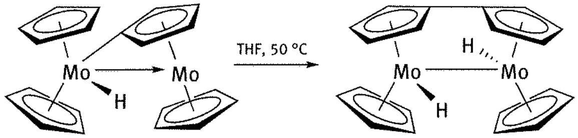
MnCp*$_2$ is a monomeric 17 VE complex with the expected sandwich structure. Because of the higher field strength of Cp*, the compound is low-spin (S = ½, μ_{eff} = 2.18 B.M.). It can be oxidized to [MnCp*$_2$]$^+$ and reduced to the 18 VE anion [MnCp*$_2$]$^-$.

There is no metallocene of Cu(II) but Cu(I) (d^{10}) forms a bis-Cp complex in which the Cp ligands are η^2-bonded and form a 'slipped-sandwich' structure. Unlike the other bis-Cp complexes discussed here, [CuCp$_2$]$^-$ salts are thermally unstable and decompose in solution above 0 °C.



Second- and third-row early transition metal metallocenes, like Nb, Mo, and W, show C–H activation similar to titanocene and give a variety of isomeric metallocene hydride structures with bridging η^1,η^5-C_5H_4 ligands. Some representative examples are shown in the following diagram. $ReCp_2$ (17 VE) is unstable but $ReCp^*_2$ is isolable. Only Ru and Os form simple metallocenes analogous to ferrocene.





2.8.1.3 Reactions of MCp_2 Complexes

Metallocenes MCp_2 (i.e. excluding complexes with further L or X-type ligands) show mainly four types of reactivity:

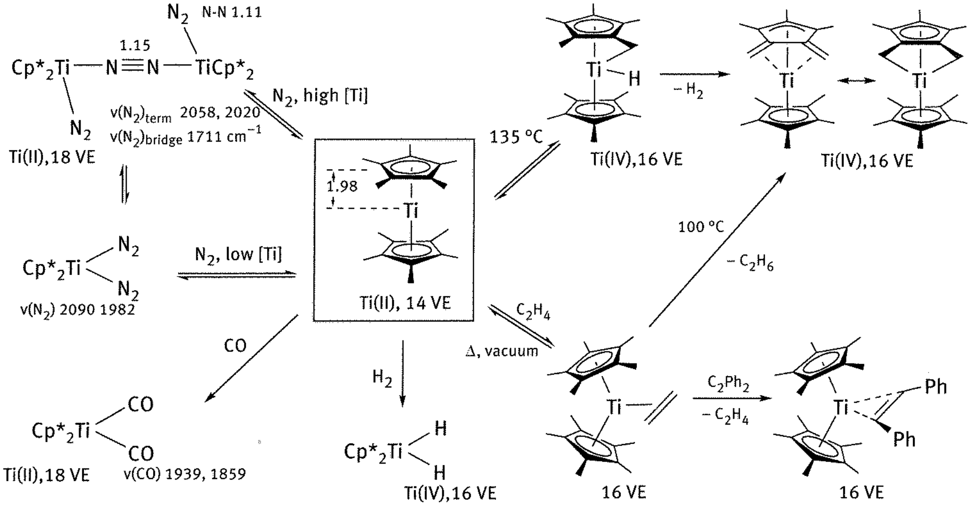
(i) Electron-deficient metallocenes will add ligands to gain a higher electron count. This reactivity pattern is illustrated in the following diagram for Group 4 metallocenes.

(ii) Electron-rich metallocenes are redox-active and show reversible 1-electron oxidations and reductions.

(iii) The reactivity of 18 VE metallocenes like ferrocene is dominated by modification of the Cp ligand, without affecting the metallocene structure itself.

(iv) Electron-rich metallocenes show ligand exchange behaviour to achieve an 18 VE configuration.

(i) Early transition metal metallocenes. The reactivity is exemplified by the 14 VE species $M(C_5Me_5)_2$ (M= Ti, Zr) which coordinate alkenes, alkynes, H_2, CO, and even N_2 to achieve a 16–18 VE electron count and oxidation state IV.



Groups 5 and 6: Vanadocene VCp_2 (15 VE) adds CO to give $Cp_2V(CO)$. Chromocene $CrCp_2$ (16 VE) has a strong tendency to retain the metallocene structure and forms a CO adduct at low temperature. Under CO pressure both react with ligand substitution to give

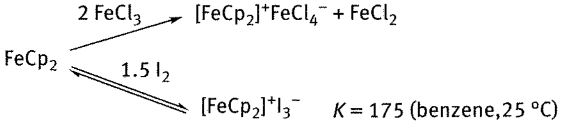
$CpV(CO)_4$ and $[CrCp_2]^+[CpCr(CO)_3]^-$, respectively. $CrCp_2$ is oxidized by iodine or allyl iodide to give $[CrCp_2]^+I^-$,while heating with CCl_4 leads to oxidation coupled with partial substitution of a Cp ligand, to give $[CrCp_2]^+[CrCpCl_3]^-$.

(ii) Redox reactions. The most widely utilized metallocene is **ferrocene** (Fc), and its most characteristic reaction is the oxidation of the orange ferrocene (Fe^{II}, d^6, 18 VE) to the dark blue ferrocenium cation (Fe^{III}, d^5, 17 VE), $E_{1/2} = +0.34$ V (ethanol, 25 °C) and +0.31 V (MeCN) vs. SCE (SCE = standard calomel electrode).

$$FeCp_2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [FeCp_2]^+$$

The Fc/Fc^+ couple is often used as electrochemical reference standard. Each methyl substituent on the Cp ring shifts the potential by 0.048 V to more negative values.

Ferrocene oxidation occurs with numerous reagents, including $FeCl_3$. The reaction with iodine is an equilibrium.



$$FeCp_2 \xrightarrow{2\,FeCl_3} [FeCp_2]^+FeCl_4^- + FeCl_2$$

$$FeCp_2 \overset{1.5\,I_2}{\rightleftharpoons} [FeCp_2]^+I_3^- \quad K = 175 \text{ (benzene,25 °C)}$$

Ferrocene forms a charge-transfer adduct with electron-poor alkenes like tetracyanoethylene (TCNE). The more easily oxidized $FeCp^*_2$ reacts with electron acceptors like TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) under electron transfer to give conducting salts $[Fe^{III}Cp^*_2]^+[TCNQ]^-$.

Cobaltocene. $CoCp_2$ is a 19 VE species; it is stable in an inert gas atmosphere but air-sensitive. It is an excellent 1-electron reducing agent ($E_{1/2} = -0.87$ V vs. SCE), and the black-purple $CoCp_2$ is oxidized to yellow $[CoCp_2]^+$, which is isoelectronic to ferrocene. Cobaltocene oxidation with O_2 in the presence of water gives the hydroxide, $[CoCp_2]^+OH^-$. The cobalticinium cation is remarkably stable, even to strong aqueous alkali and strong acids, and the cation behaves like a large alkali ion. It is resistant to further oxidation; for example, treatment of $[Co(C_5H_4Me)_2]^+$ with concentrated nitric acid oxidizes the methyl substituents to give $[Co(C_5H_4COOH)_2]^+$ but leaves the metallocene core intact.

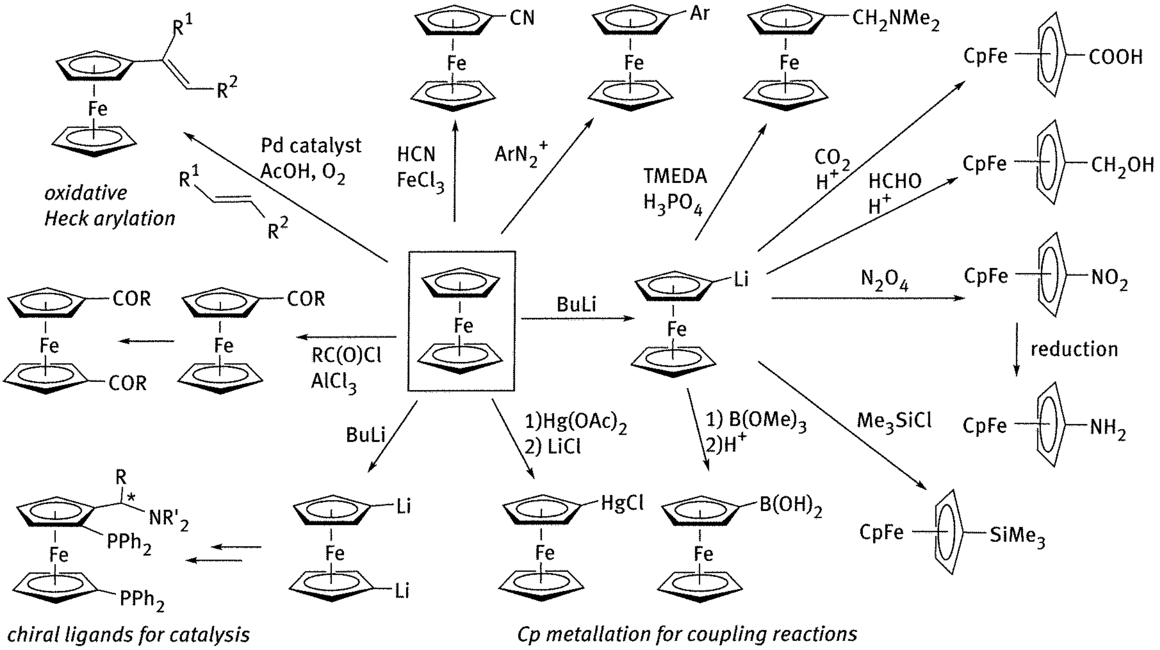
$$CoCp_2 \xrightarrow[H_2O]{O_2} [CoCp_2]^+OH^-$$

Nickelocene (20 VE) shows two oxidation steps. Although the $[NiCp_2]^{2+}$ dication is an 18 VE species, it is difficult to generate and not stable (Ni^{IV}!).

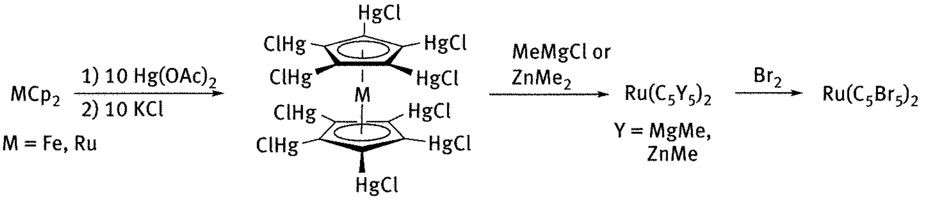
$$NiCp_2 \overset{+0.1\text{ V}}{\rightleftharpoons} [NiCp_2]^+ \overset{+0.74\text{ V}}{\rightleftharpoons} [NiCp_2]^{2+}$$

(iii) Substitution reactions on the Cp ring. As pointed out earlier, ferrocene behaves like an aromatic compound, and standard organic synthetic methods have been applied to generate a huge arsenal of derivatives for many applications in synthesis, materials science, and medicine. Ferrocene is more electron rich than benzene, and Friedel–Crafts acylations for example proceed about 10^6 times faster. The Cp ring can be lithiated, and the resulting

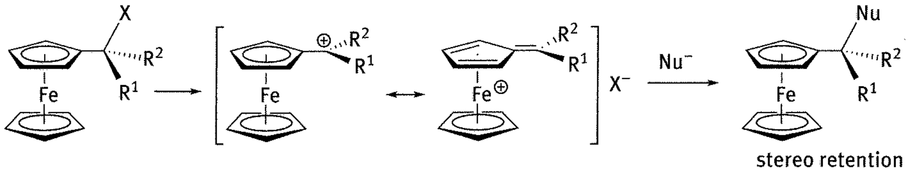
$CpFe(C_5H_4Li)$ behaves like a conventional lithium aryl in its reactions with electrophiles. The following scheme provides an overview of the diverse reactivity patterns.



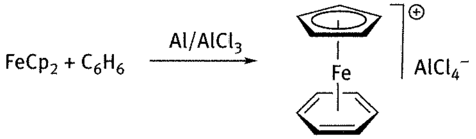
Metallation of the Cp ligands in $FeCp_2$ and $RuCp_2$ has been shown to proceed with complete substitution of all 10 H atoms. This can be achieved by electrophilic mercuration with $Hg(OAc)_2$ or $Hg(O_2CCF_3)_2$. The mercury can in turn be substituted by Li, Mg, Zn, or halides:



The ferrocenyl unit stabilizes carbocations bound to a Cp ring, e.g. the $[Fc\text{–}CPh_2]^+$ cation is isolable. This facilitates substitution in α-position to the ring:

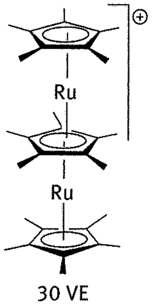


A general method for exchanging one Cp ring in ferrocene by an arene is the treatment of $FeCp_2$ with a mixture of the arene, $AlCl_3$ and aluminium powder to give the corresponding cationic mixed-ligand sandwich complex:



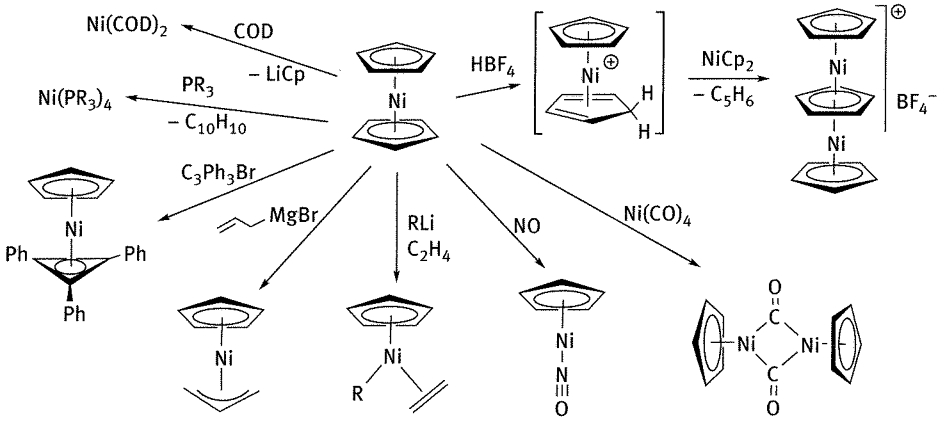
(iv) Reactions of nickelocene. The reactivity of this 20 VE species is driven by the energetic advantage of obtaining an 18-electron count. This can be achieved by ligand substitution, where one of the Cp rings is replaced by a 3-electron donor, and also by comproportionation with Ni(0) complexes. Treatment of $NiCp_2$ with an excess of phosphines or 1,5-COD leads to reduction and formation of Ni(0) compounds.

An interesting reaction is observed on protonation of $NiCp_2$ with HBF_4, i.e. an acid containing a non-coordinating anion. Addition of H^+ to Cp gives C_5H_6, which dissociates, leaving the highly reactive $[CpNi]^+$ fragment. This can react with further nickelocene to give a stacked complex, $[Ni_2Cp_3]^+$, the first triple-decker complex to be isolated. Similar triple-deckers are known for other metals; for example, the stacking reaction of $[Cp^*Ru(NCMe)_3]^+$ with $RuCp^*_2$ gives $[Ru_2Cp^*_3]^+$. This is a 30 VE multi-stack, the binuclear equivalent of 18 VE and a stable bonding situation. By contrast, $[Ni_2Cp_3]^+$ has 34 VE; the additional electrons weaken cluster bonding and elongate the Ni–Ni distance.



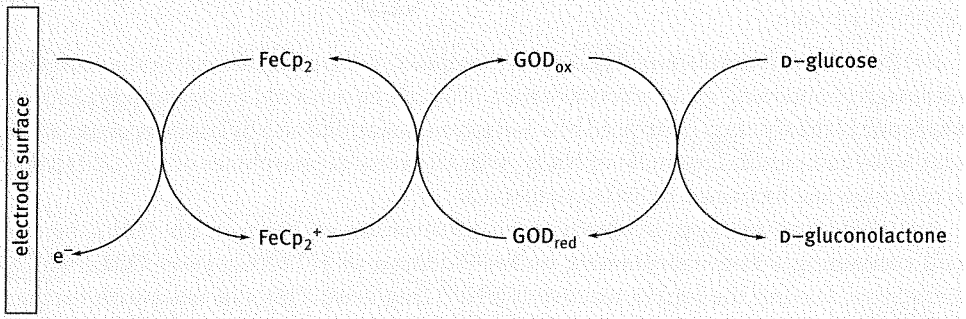
30 VE

See Section 2.5.2

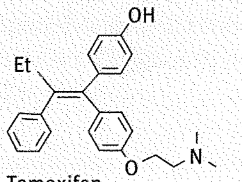


Box 2.8.1 Ferrocenes in medicine and catalysis

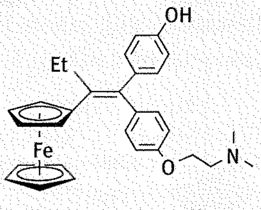
Blood glucose sensors. There are about 350 million diabetes sufferers worldwide. The fast and easy determination of blood sugar levels is a daily need. The enzyme glucose oxidase (GOD) is highly sensitive and specific; however, the direct determination of the oxidation process by electrochemical methods is impeded since the enzyme does not react with the electrode surface directly. This difficulty can be overcome by employing ferrocene as a redox catalyst which mediates the quantitative oxidation of glucose to D-gluconolactone, the resulting current is proportional to the glucose concentration. The redox potential and kinetics can be optimized by suitable Cp ring substitution. It has been estimated that in the 30 years since the invention of this sensor system in 1982 some 25 billion test strips have been sold. The system involves several interlinked redox cycles:



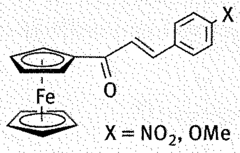
Anti-cancer drugs. Given the increasing problem of resistance of many diseases to established medicines, drugs containing organometallic components are increasingly being tested. Ferrocene derivatives in particular are frequently employed to modify or enhance anti-tumour drugs, with many structural motifs being explored. The approach may be illustrated for example, by the tamoxifen-inspired hydroxyferrocifen (**A**). Tamoxifen is a standard treatment against breast cancer but tumours can develop resistance. In such cases the ferrocene derivative **A** is effective and inhibits the growth of hormone-independent breast cancer cells. Compounds of type **B** are active against liver cancer. Ferrocenyl ethers **C** are being tested against prostate cancer, among many others, while type **D** operates by targeting aberrant kinase activity (protein phosphorylation) in cancer cells.



Tamoxifen

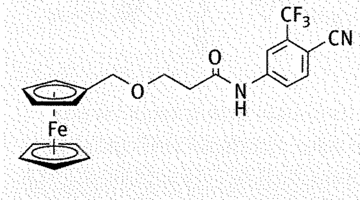


A hydroxyferrocifen

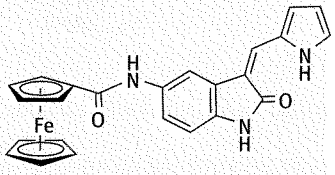


$X = NO_2$, OMe

B

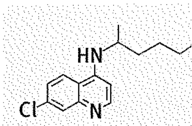


C ferrocene bicalutamide

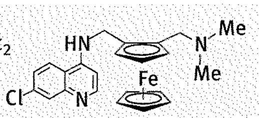


D

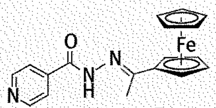
Malaria and tuberculosis. Apart from cancer, malaria and tuberculosis are increasingly threatening and a major cause of mortality worldwide. Multi-drug resistant bacterial strains make conventional treatment difficult. The ferrocene derivative **E** is active against chloroquine-resistant malaria pathogens. Compounds of types **F** and **G** have been reported to show promise against multiply-resistant strains of tuberculosis.



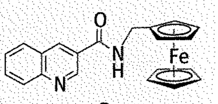
Chloroquine



E Ferroquine anti-malaria drug

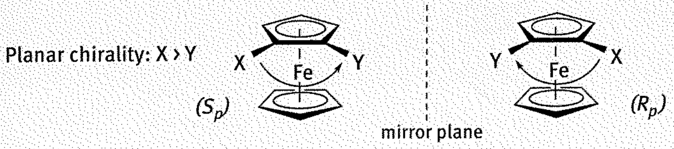


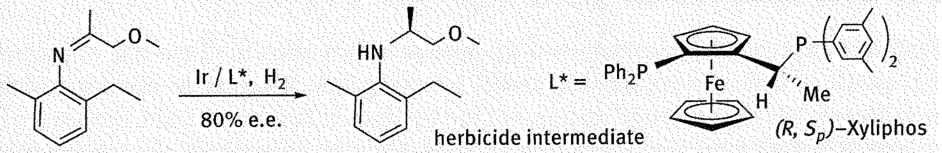
F



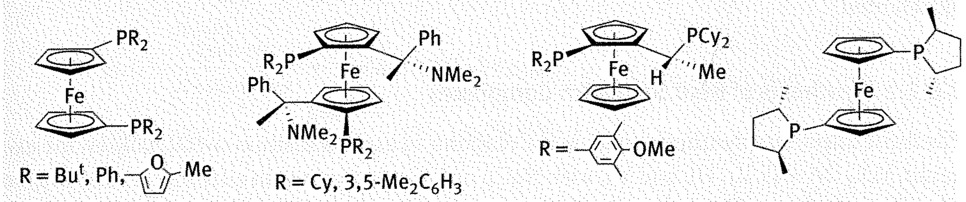
G

Ferrocene-derived ligands for asymmetric catalysis. Since both rings in ferrocene can be substituted independently, one or more chiral substituents per Cp ring afford chiral auxiliaries. Introducing two substituents on one ring allows the construction of ligands with planar chirality. Ligands of this type are for example being used in the asymmetric iridium-catalysed imine hydrogenation, a large-scale industrial process for the production of a herbicide intermediate.

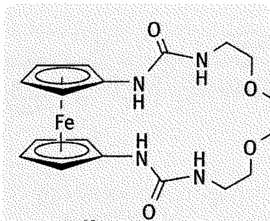




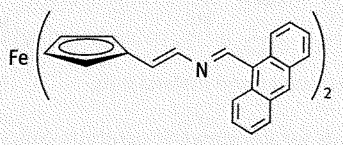
There are numerous variations of bidentate chiral phosphines with a ferrocenyl backbone. The examples in the following diagram stand for a large number of ferrocene-type ligands and are commercially available, as are many others.



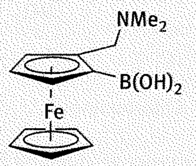
Ferrocene complexes as chemosensors. Metal complexes are widely exploited as selective sensors for metal ions, anions, or various other substrates including biomolecules, none more so than ferrocene derivatives. Sensing responses can be gathered from multiple channels: by UV/vis spectroscopy, fluorescence, or electrochemical responses, i.e. shifts in the Fc/Fc^+ redox potential. For example, the crown ether-like ferrocene **H** is selective for Li^+ ions in the presence of other alkali metals, **I** gives selective electrochemical and UV/vis responses for Zn^{2+} in the presence of Cd^{2+}, while the boronic acid derivative **J** is a sensor for HF as well as for carbohydrates. Complex **K** is a colorimetric sensor for the enantioselective detection of chiral secondary alcohols, and **L** detects trinucleotides, both by hydrogen bonding to their respective substrates.



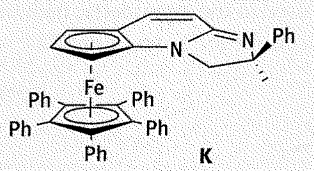
H



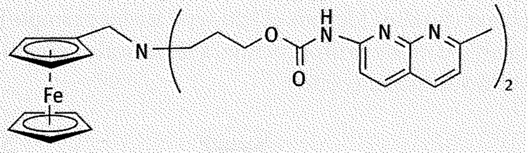
I



J

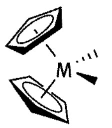


K



L

2.8.2 Bent Metallocene Complexes



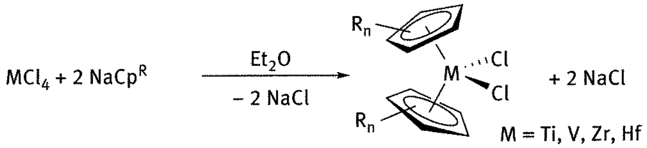
Bent sandwich complexes contain two Cp ligands, which often fulfil the role of protecting ligands, as well as one or more X- and/or L-type ligands. Whereas the chemistry of the metallocenes MCp_2 concerned reactions of the Cp ligands, here the X and L ligands are of interest. X-ligands form typically M–halide, M–H, M–O, M–N, and M–C single or multiple bonds, while L-type ligands may be CO, phosphines, alkenes, or alkynes. Bent metallocenes include the important area of metallocene-type Group 4 olefin polymerization catalysts (Section 3.7.2). This is also a complex type where lanthanides and actinides are prominently represented.

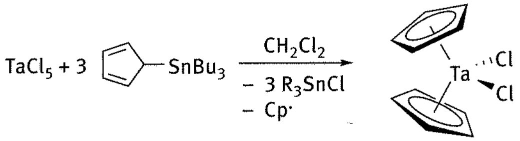
2.8.2.1 Synthesis of Bent Sandwich Complexes

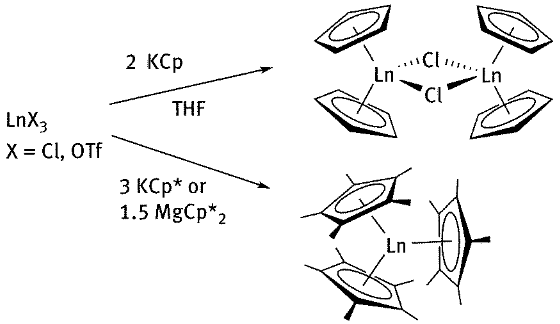
Group 4 Cp_2MX_2

The most important synthetic route is the reaction of early transition metal halides, for example MX_4 (M = Ti, Zr, Hf, and V), with NaCp or LiCp derivatives in a 1:2 molar ratio to give Cp_2MX_2 complexes. The analogous reaction of the heavier Group 5 metal halides would be expected to give M(V) complexes Cp_2MX_3 (M = Nb, Ta); these exist but are easily reduced to the Cp_2MX_2 which are sterically less congested; these d^1 compounds are paramagnetic. $CpSiMe_3$ and $CpSnR_3$ (R =Me, Bu^n) are mild Cp transfer agents that react with Lewis acidic metal halides smoothly to give mono- or bis-Cp complexes. $(Cp^R)_2NbCl_2$ complexes are also accessible from $NbCl_4(THF)_2$ and $LiCp^R$.

Lanthanide halides give compounds of the types Cp_2LnX and $LnCp_3$, depending on the stoichiometry. Cp_2LnX complexes are halide-bridged dimers. The $LnCp_3$ compounds with unsubstituted Cp ligands are polymeric with Cp-bridged structures. However, the compounds depolymerize on heating and can be purified by sublimation. The Cp* analogues are mononuclear.

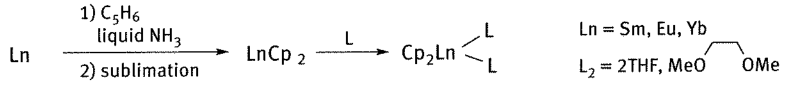






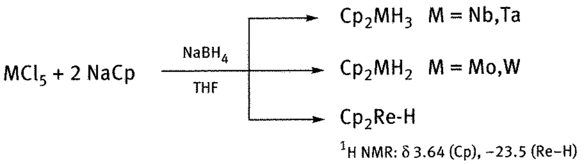
Lanthanides Cp_2Ln, Cp_2LnX Cp_3Ln

The lanthanide elements samarium, ytterbium, and europium are known for the relative stability of oxidation state +II. They give metallocenes Cp_2Ln from the metals; coordinating solvents form adducts Cp_2LnL_2. These compounds are thermally very stable but highly sensitive to oxidation.



$$Yb + 2\,TlCp \xrightarrow{DME} Cp_2Yb(DME) + 2\,Tl$$

The reaction of $ReCl_5$ with NaCp in the presence of $NaBH_4$ gave access to the first organometallic metal hydride complex. The method is general, e.g. for the synthesis of Cp_2MH_2 (M = Mo, W) and Cp_2MH_3 (M = Nb, Ta).

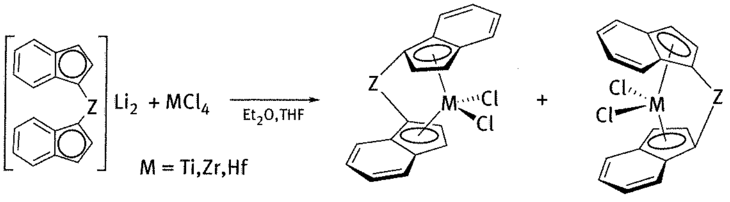


Groups 5, 6

A particularly important class of bent sandwich complexes are Ti, Zr, and Hf compounds where the Cp ligands are connected by a linker group, the so-called *ansa*-metallocenes (from Latin *ansa* = handle). Complexes with substituted Cp ligands may form *rac* and *meso* stereoisomers; the former are important pre-catalysts for the **stereoselective polymerization**

of 1-alkenes, while the latter show low activity without stereocontrol. For example, the C_2-symmetric *rac*-Z(Ind)$_2$ZrCl$_2$, when mixed with suitable catalyst activators, gives isotactic polypropene polymers (Z = linker: e.g. Me$_2$Si, C_2H_4, Me$_2$C). Ligand variation includes complexes with C_s symmetry (e.g. for the syndio-specific polymerization of propene) and more open Cp-amido complexes. For catalytic applications see Section 3.7.2.

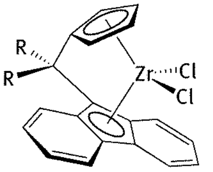
ansa-metallocenes



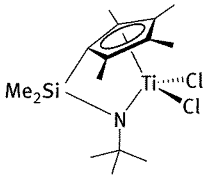
rac-isomer

meso-isomer

Z = SiMe$_2$, CMe$_2$, CH$_2$CH$_2$, etc.



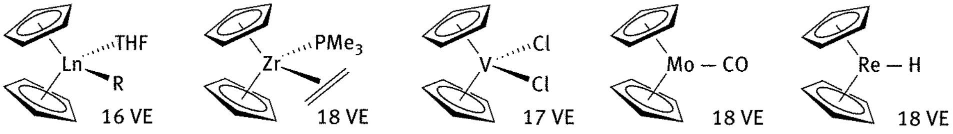
C_s-symmetric precatalyst



Cp-amido "constrained geometry" complex

2.8.2.2 Structures of Bent Metallocene Complexes

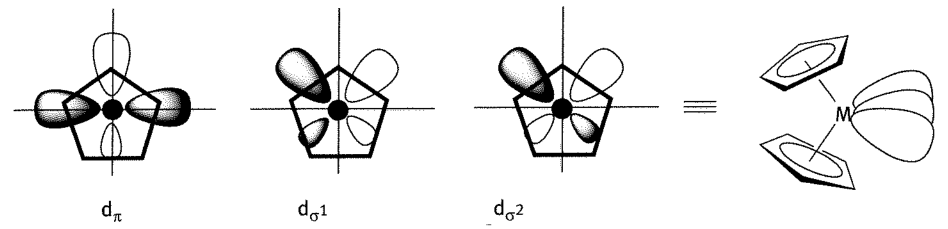
Because of the 18-electron rule, bent bis-Cp complexes are restricted to metals with low numbers of d-electrons. The range of complexes is illustrated by the following characteristic types:

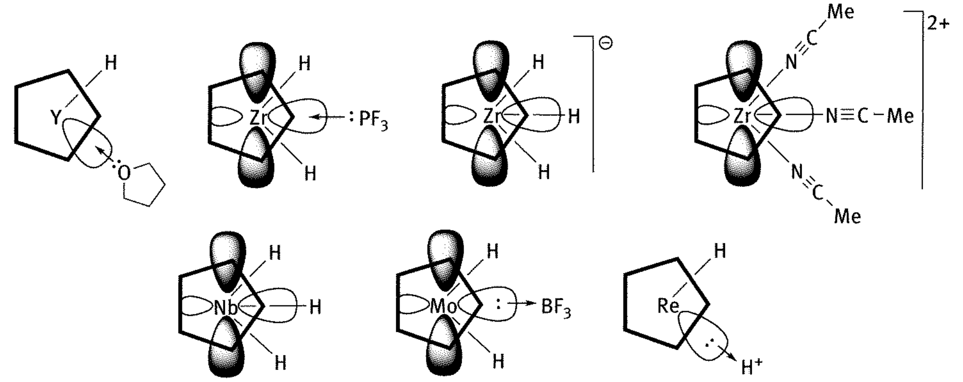


Ln = Group 3, lanthanides
R = alkyl

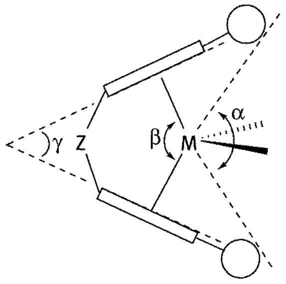
dπ, dσ frontier orbitals

The orbitals responsible for the chemical reactivity of bent metallocenes are oriented in the 'equatorial plane', i.e. the plane bisecting the Cp–M–Cp angle. Compounds like Cp$_2$MX$_2$ (M = Ti, Zr, Hf) also have a LUMO in this plane, capable in principle of accepting π-donors (and therefore labelled d_π). In addition there are two orbitals involved in making two M–X σ-bonds, denoted d_σ. A bent metallocene fragment Cp$_2$M therefore has these three orbitals available, which may be occupied with varying numbers of electrons. Depending on the electron count of the metal, they may be employed in binding up to three ligands. If all three orbitals are vacant, three donor ligands can bind. If one of these equatorial orbitals contains two electrons, it may act as a base. There is therefore a systematic change in chemical properties on going from Group 3 to Group 7 metallocenes. The number of ligands that may be bound is restricted by steric interactions and the size of the metal centre; e.g. while Zr forms [Cp$_2$Zr(NCMe)$_3$]$^{2+}$, the smaller titanium can only bind two nitrile ligands, [Cp$_2$Ti(NCMe)$_2$]$^{2+}$.





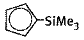
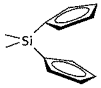
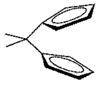
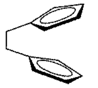
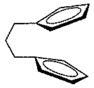
The energy of these frontier orbitals can be varied by adjusting the angle between the two Cp ligand planes. This effect is important in *ansa*-metallocenes where the Cp ligands are connected by a linker Z. Here the coordination geometry of the metal can be described by the dihedral angle formed by the best planes through the C_5 rings, γ, the centroid–M–centroid angle β, and the angle α formed between the van der Waals surfaces of the Cp ligands and the metal, referred to as the **coordination gap aperture** (CGA) of the metal.



coordination gap aperture,α, and characteristic angles in *ansa*-metallocenes

In the case of a short single-atom linker, e.g. Z = CH_2, the energy of the frontier orbitals is raised and the metal becomes more Lewis acidic. Conversely, longer linkers reduce α, and apart from steric interactions the metal becomes in effect more electron rich. Of course, substituents exerting a more or less strong inductive (+I) effect will have the opposite effect. This influence of electron donating substituents and ring tilt angles can for example be seen considering the average ν_{CO} frequencies [cm^{-1}] of $L_2Zr(CO)_2$ complexes (Table 2.8.2). The increase in Lewis acidity by introducing a restraining linker Z explains for example the sometimes dramatically increased 1-alkene polymerization activity of *ansa*-metallocene catalysts compared to similar non-linked metallocene complexes.

Table 2.8.2 Steric and electronic properties of Cp ligands.

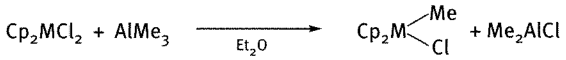
L =	Cp	Cp*					
γ =	53.5	43.7		60.1	71.4	56.4	50.2
ν =	1932.0	1899.5	1929.0	1939.5	1935.0	1931.0	1928.5

2.8.2.3 Reactivity of Bent Metallocene Complexes

Halide metathesis. The most important reaction in terms of synthetic utility and catalytic applications is the exchange of halide ligands by alkyls.

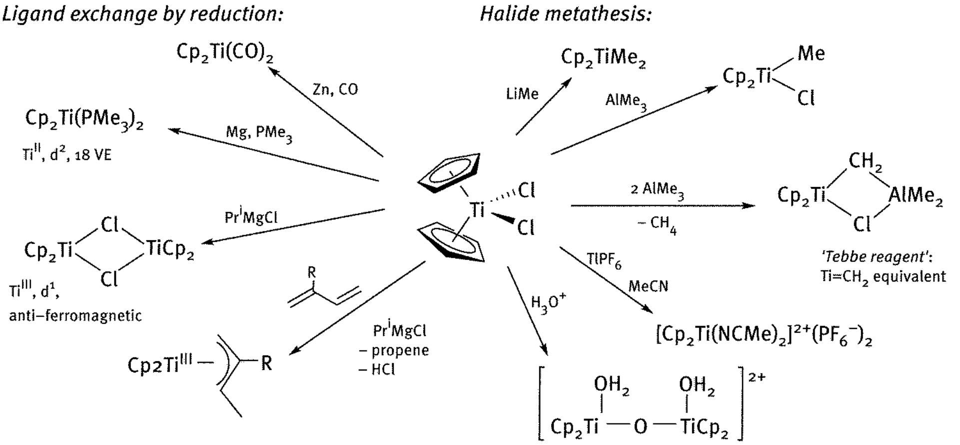
$$Cp_2MCl_2 + 2\ RLi \xrightarrow[Et_2O]{} Cp_2MR_2 + 2\ LiCl$$

R = Me, CH_2SiMe_3, aryl, alkynyl, etc.



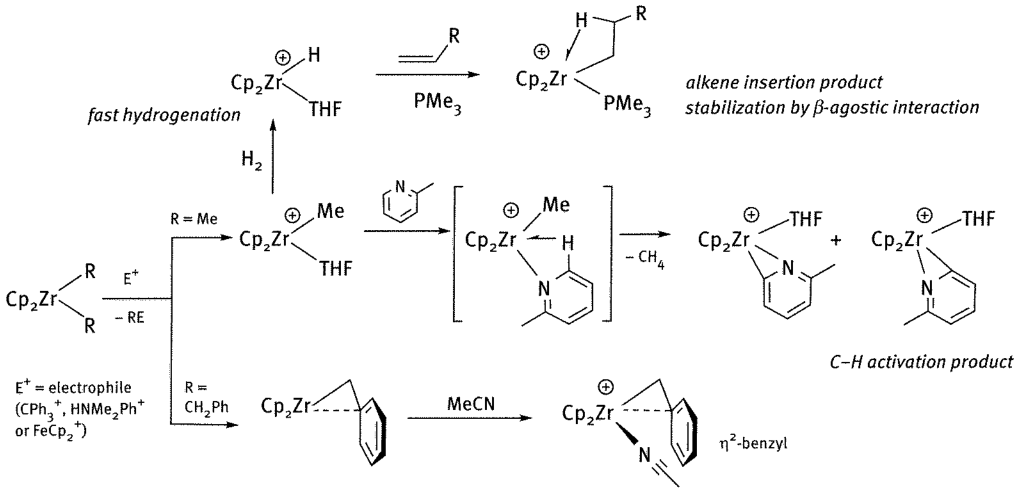
$$Cp_2MCl_2 + AlMe_3 \xrightarrow[Et_2O]{} Cp_2M(Me)(Cl) + Me_2AlCl$$

Similarly, replacing halide by hydride opens the way to new reactivity. M–Cl, M–H, and M–C bonds of early transition metals are prone to hydrolysis to give bridging or terminal oxides. The reduction of metallocene halides allows the coordination of alkenes or phosphines. The reactivity pattern is illustrated in the following diagram for titanocene dichloride.

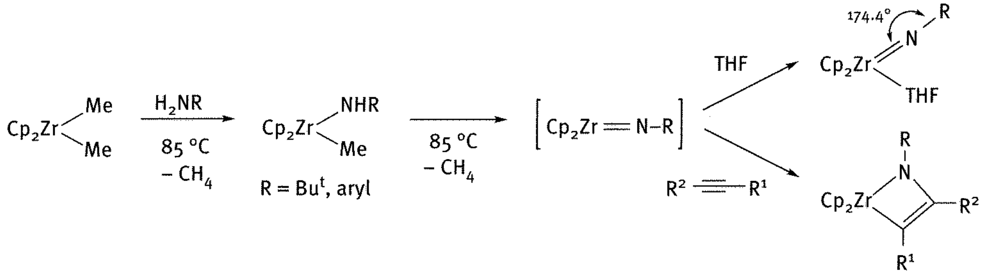


Abstraction of one alkyl ligand in Cp_2MR_2, by either H^+, CPh_3^+, or $FeCp_2^+$ salts of non-coordinating anions, gives access to highly reactive, electron-deficient (14 VE) cationic Group 4 metal alkyls. The effects of electron deficiency can be seen in the reaction pattern and the structures that these compounds adopt. In the case of R = benzyl, the electron deficiency is alleviated by π-interaction with the phenyl ring. Stabilization by **agostic interactions** between the metal and a C–H bond in β-position is another way of reducing electron deficiency.

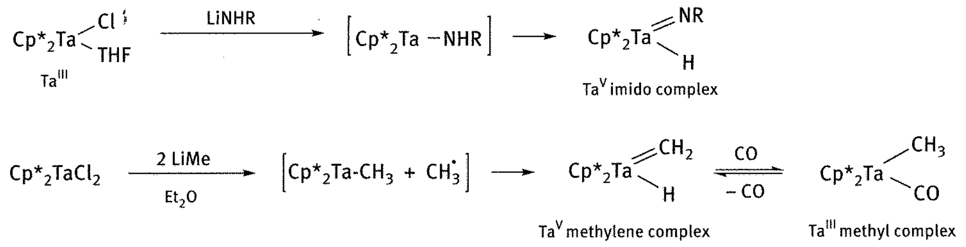
Cationic metallocene alkyls are far more reactive than neutral analogues and are capable of **activating C–H bonds**. They also readily insert alkenes and alkynes.



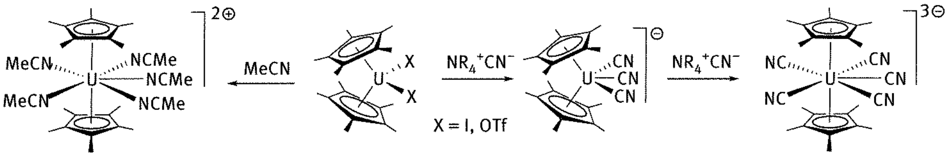
Group 4 metal complexes with double bonds to heteroatoms (O, N) are uncommon but can be generated by thermal methane elimination from the methyl amido complex $Cp_2ZrMe(NHR)$. The intermediate $Cp_2Zr{=}NR$ can be stabilized by THF coordination or trapped with alkynes to give metallacycles:



In contrast to Group 4, Group 5 metals frequently favour M=E double bonds. Compounds of this nature often form spontaneously by α-H elimination processes, as illustrated by the facile formation of tantalum imides and methylene complexes. α-H elimination is reversible, and the precursor complexes may be trapped by donor ligand addition:

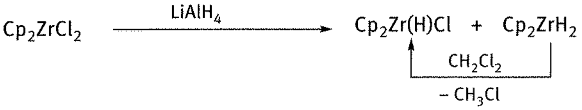


Very large metal centres like U(IV) are able to increase their coordination numbers beyond those found for transition metals and give pentagonal-bipyramidal complexes:

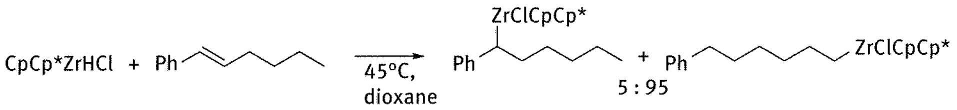


Hydrozirconation

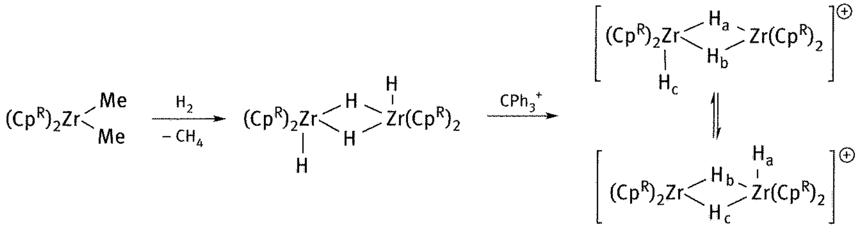
Metallocene hydrides. Zirconocene chlorohydride, $Cp_2Zr(H)Cl$, is known as the Schwartz reagent and has widespread use in synthesis. It hydrozirconates alkenes and alkynes. With internal alkenes, C=C insertion is followed by isomerization steps, so that a primary alkyl zirconocene results. This can be useful for the introduction of functional groups with **anti-Markovnikov** regiochemistry.



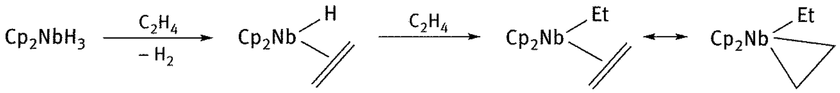
$$Cp_2ZrCl_2 \xrightarrow{LiAlH_4} Cp_2Zr(H)Cl + Cp_2ZrH_2$$
$$Cp_2ZrH_2 \xrightarrow[-\,CH_3Cl]{CH_2Cl_2} Cp_2Zr(H)Cl$$



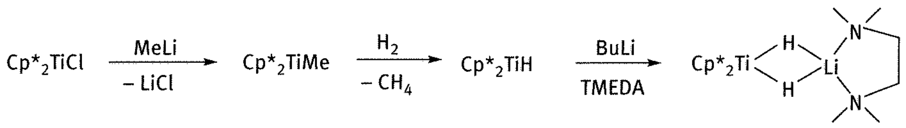
Zirconocene dihydrides are accessible by the hydrogenolysis of the corresponding dimethyl complexes. They are dimeric, $[Cp^R{}_2Zr(H)(\mu\text{-}H)]_2$, unless the Cp ligands are very bulky. Hydrido cations $[(Cp^R{}_2Zr)_2(H)(\mu\text{-}H)_2]^+$ are formed if H^- is abstracted with $CPh_3{}^+$ salts of non-coordinating anions; they are fluxional and are potent initiators for the polymerization of isobutene to butyl rubber.



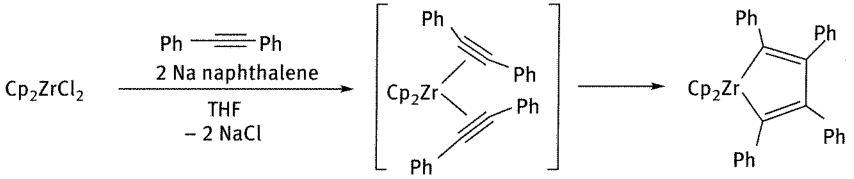
Metallocene hydrides often react under elimination of H_2; this can be a convenient and clean route to CO and alkene complexes. For Groups 5 and 6 metals adducts of π-acceptor ligands are characterized by strong back-donation, which makes ethylene complexes of Nb(III), for example, very stable and unsuitable for further ethylene insertion reactions. Such compounds are therefore inactive as polymerization catalysts.



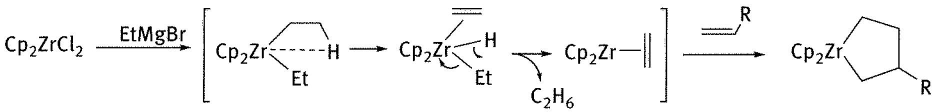
Ligand exchange by reduction. Reduction of Cp_2TiCl_2 by Al, Zn, or Pr^iMgCl gives the deep green Ti(III) chloride, $[Cp_2Ti(\mu\text{-}Cl)]_2$. The metal centres have d^1 electron configuration and are antiferromagnetically coupled. The Cp* analogue is monomeric and readily exchanges the halide ligand for alkyls or hydride. Ti(III) complexes are highly sensitive to oxidation.



The reduction of metallocene dichlorides in the presence of alkenes or alkynes is typically followed by oxidative addition to give metallacycles. This is a useful method for C–C bond formation:



The reduction of Cp_2ZrCl_2 with alkylmagnesium reagents bearing β-H atoms gives thermally unstable zirconocene alkyls. β-H elimination and reductive elimination steps lead to Zr(II) alkene complexes. This is a route to organic synthetic Zr mediated transformations. The Zr(II) species are invariably generated in situ, without isolation. This reaction sequence leads eventually to the carbomagnesation of alkenes.

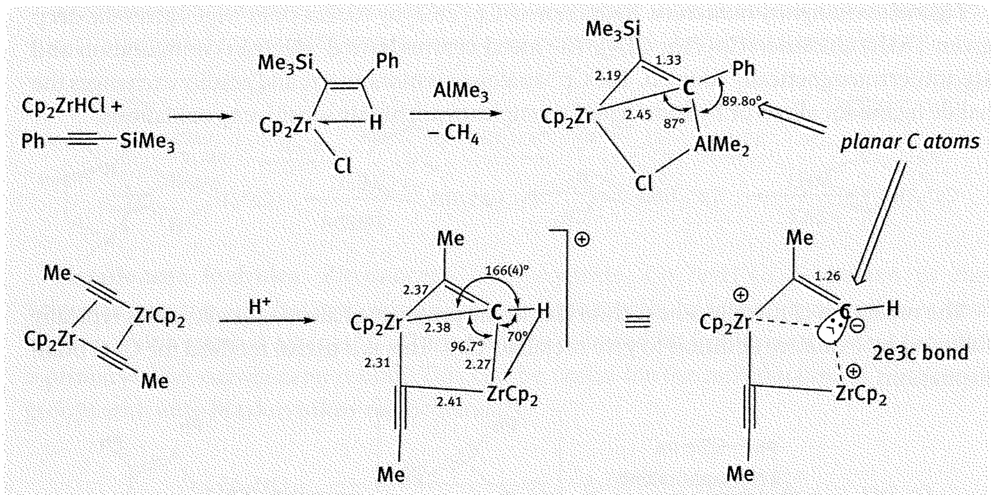


The reduction of metallocene halides of more electron-rich metals is a convenient means of generating adducts with donor ligands, including N_2 complexes:

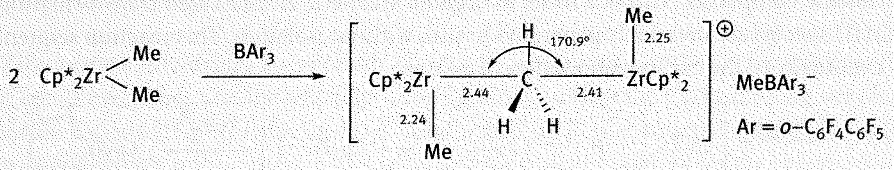
$$Cp_2MoCl_2 \xrightarrow[L]{Na/Hg} Cp_2Mo{-}L \qquad L = CO,\ C_2H_4,\ PR_3,\ R{-}{\equiv}{-}R,\ N{\equiv}N$$

Box 2.8.2.1 Structural aspect of electrophilic metallocenes: square-planar and trigonal-bipyramidal C

Electrophilic metal centres are able to stabilize unusual coordination geometries such as **planar carbon** atoms. These can arise when an sp^2-hybridized C atom forms bonds with four substituents in the same plane—so-called '***anti*-van't Hoff–LeBel compounds**'. This requires 2e3c bonds, since six electrons are making four bonds. While under normal circumstances this bonding situation would be highly unfavourable, electron-deficient metal centres as substituents on C provide the necessary delocalization so that such an arrangement becomes the ground state. This has been realized using Cp_2Zr fragments:

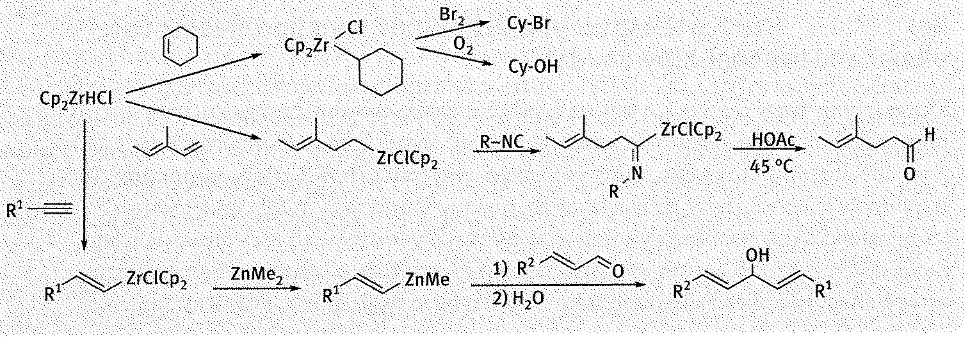


Electrophilic metallocene cations also stabilize **trigonal-bipyramidal carbon**. Many complexes L_2MMe_2 (M= Ti, Zr, Hf; L = Cp or anionic non-Cp ligand) react with strong electrophiles in the absence of coordinating anions to give cations $[L_2MMe]^+$, which add to a methyl ligand of L_2MMe_2 to form a methyl bridge. While this is in principle reminiscent of the electron-deficient μ-methyl bonding in Al_2Me_6 (see Section 1.5.2.2), these complexes contain a linear M–C–M arrangement.



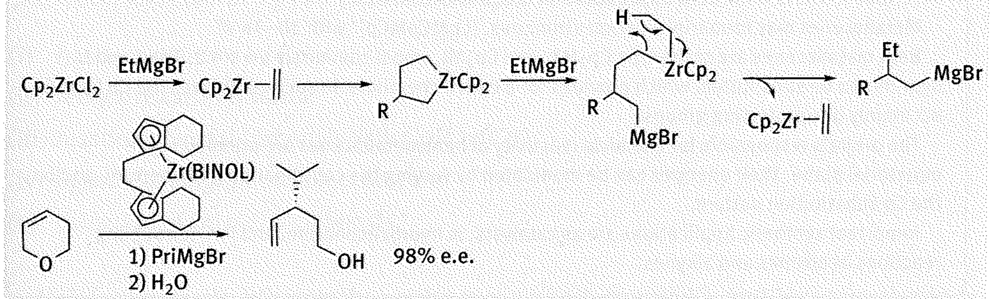
Applications of zirconocenes in organic synthesis

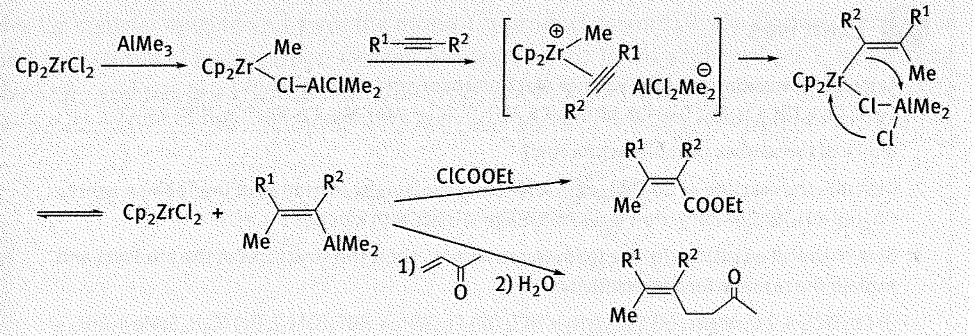
The hydrozirconation of alkenes and alkynes with Schwartz's reagent has found wide application. The Zr–C bond can be used for introducing a variety of functional groups. Hydrozirconation may be followed by the insertion of CO or an isocyanide. The reaction can also be coupled with transmetallation, for example to a zinc reagent, for more facile coupling with organic carbonyl compounds.



As explained in the main section, the zirconocene-mediated **carbometallation** of alkenes involves the reduction of Cp_2ZrCl_2 to a $Cp_2Zr(alkene)$ fragment. These react with further alkenes to give a metallacyclopentane intermediate which is cleaved by Al or Mg reagents under transmetallation. With chiral zirconocenes the reaction can be used for asymmetric syntheses. Alkynes can be similarly carbometallated with AlR_3 to give reactive vinyl aluminium reagents.

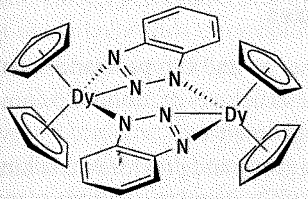
E. Negishi: Nobel Prize 2010 for contributions to C–C coupling methodology

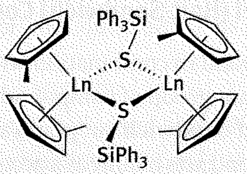




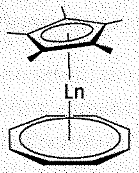
Box 2.8.2.2 Metallocene materials: single-molecule magnets (SMMs)

The high spin and the slow relaxation of magnetization of 4f ions makes compounds of lanthanides attractive molecular targets for potential high-density magnetic data storage. The ligand environment controls the electronic structure and the degree of magnetic interactions between ions. Single-ion magnets (SIMs) are also known. Some examples:





Ln = Gd, Dy



Ln = Dy, Ho, Er

single-ion magnet

Key points

Complexes where the metal is sandwiched between two Cp ligands are known as metallocenes.

Group 5–8 transition metals form metallocenes of composition MCp_2, with 15–20 VE.

The most important metallocene is ferrocene, $FeCp_2$ (Fc). It is electrochemically active; the Fc/Fc^+ redox couple is used as an electrochemical reference standard and as an electron-transfer catalyst.

Ferrocenes have important applications in drugs and as sensors.

Metallocenes may form triple-decker structures, $[CpMCpMCp]^+$ with 30–34 VE.

Bent metallocenes are of the type Cp_2MX_n and Cp_2ML_y; most commonly $n = y = 2$. The X and L ligands can be substituted, which provides for a varied chemistry. In such complexes the Cp ligands act mainly like protecting groups.

The orbitals responsible for chemical reactivity of bent metallocenes are oriented in the equatorial plane. Their energies can be modulated by varying the coordination gap aperture, and by the Cp substitution pattern.

Important synthetic applications are as catalysts, in hydrozirconation, and in C–C coupling reactions of alkenes and alkynes.

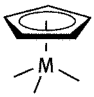
Exercises

1. Calculate the oxidation state, valence electron count, and magnetism of Cp_2V, $Cp^*{}_2TiH$, $Cp_2Zr(CO)_2$, Cp_2NbCl_2, $[Cp_2WH_3]^+$, $(C_5H_4Me)_2Mn$, Cp_2Ru, $[Cp_2Ni]^+$, Cp_2Co.

   Which of these obey the 18-electron rule?
2. Describe the reaction of Cp_2TiCl_2 with $AlMe_3$ and explain the formation of the Tebbe reagent, $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$. How does this reagent react with ketones $R_2C{=}O$?
3. Give chemical equations for the following reactions, show the structures of the products and explain the reasons for this reactivity:

   (i) Cp_2TiCl_2 + 2 CpMgBr; (ii) $Cp^*{}_2ZrH_2$ + HCl; (iii) Cp_2WH_2 + $HBF_4(OEt_2)$; (iv) $(C_5H_4SiMe_3)_2ZrH_2$ + $CPh_3{}^+$; (v) Cp_2HfCl_2 + 2 LiEt; (vi) Cp_2ZrCl_2 + 2 EtMgBr + 1-hexene; (vii) $[Cp_2ZrMe(THF)]^+$ + 1) H_2 and 2) 1-hexene.
4. Explain the fluxional processes observed in the product of reaction 3(i).
5. What is an *ansa*-metallocene and what are the characteristics and applications of this type of compound?

2.8.3 Mono-Cyclopentadienyl (Half-Sandwich) Complexes



Complexes containing one Cp ligand in combination with other X- and L-type ligands constitute a very diverse and important group of compounds. The structures of mono-Cp complexes are often described as **'half-sandwich'** or **'piano stool'** geometries.

With few exceptions, the Cp ligand acts mainly as a protecting group and provides steric hindrance and, with suitable substitution, chiral information. Mono-Cp complexes include many examples where the metal centre is in a high oxidation state and the back-donation contribution to metal–Cp bonding is minimal. In such cases the interaction is mainly due to Coulomb attraction between the Cp^- anion and the metal cation; Cp complexes differ in this respect from arene and alkene complexes. For structurally related mono-arene complexes, see Section 2.9.2.

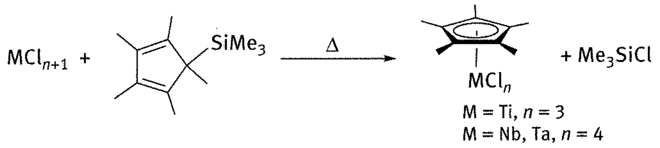
Apart from mononuclear mono-Cp complexes there are many bi- and polynuclear complexes. The bonding characteristics of some of these (such as $[CpFe(CO)_2]_2$) have been discussed in Section 2.5.2.

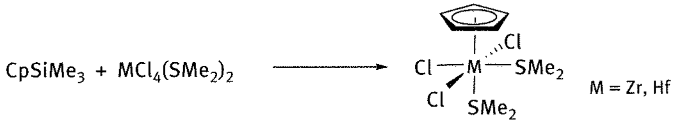
2.8.3.1 Synthesis of Mono-Cp Complexes

The synthesis of mono-Cp complexes can involve various routes:

(i) halide metathesis by Cp^-;
(ii) reductive carbonylation;
(iii) reaction of metal carbonyls with CpH or Cp^-;
(iv) ligand exchange of metallocenes; and
(v) oxidation of Cp metal carbonyls.

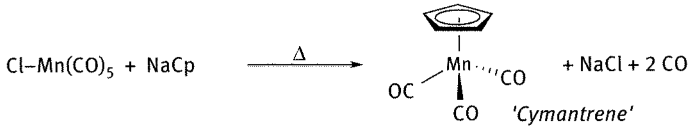
Halide metathesis. Whereas the synthesis of $CpTiCl_3$ from $TiCl_4$ and NaCp in ether at a 1:1 molar ratio gives mainly Cp_2TiCl_2 and unreacted $TiCl_4$, the less basic $CpSiMe_3$ is a selective Cp transfer reagent and gives the mono-Cp product quantitatively. The reaction works best in a saturated hydrocarbon solvent. Moderating the Lewis acidity of MCl_4 by forming the SMe_2 adducts is advantageous. This method also avoids the formation of alkali halide by-products which can reduce the yield, whereas Me_3SiCl is easily removed under vacuum.

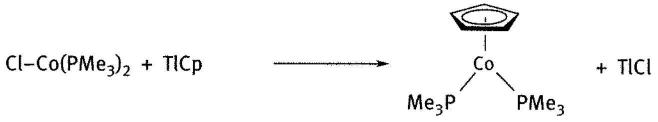


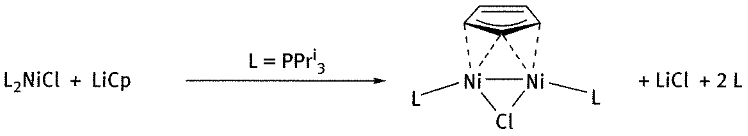


While these mono-Cp halides are electron deficient (12–16 VE), complexes containing CO or phosphines obey the 18-electron rule. The very stable $CpMn(CO)_3$ is also known under the trivial name of *cymantrene*; the C_5H_4Me analogue was at one time used as an anti-knock petrol additive. $CpCo(PMe_3)_2$ is electron rich and behaves as an inorganic base; it oxidatively adds electrophiles like MeI, quite unlike its CO analogue $CpCo(CO)_2$ which has no basic properties.

The reaction of the Ni(I) complex $NiCl(PPr^i_3)_2$ with LiCp provides an example of a Cp ligand bridging two metal centres; the bulky and basic PPr^i_3 ligand is required to stabilize nickel in the oxidation state +I. Cp complexes of Cu(I) of the type CpCuL can be conveniently obtained from $[CuOBu^t]_4$ which acts as base; unlike in the $[CuCp_2]^-$ anion, the Cp ligand in $CpCu(PR_3)$ is η^5-bonded to give an 18 VE structure.

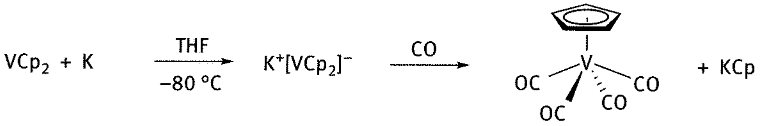






L = PMe3, PEt3, PPh3

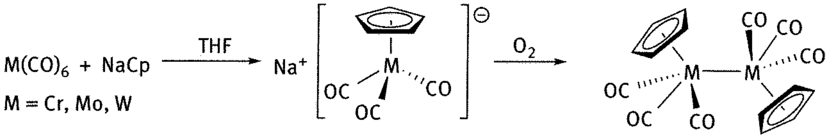
By reductive carbonylation. There are a number of routes to $CpV(CO)_4$ from VCl_3 but they require high CO pressures. The reduction of vanadocene under CO proceeds smoothly under mild conditions:

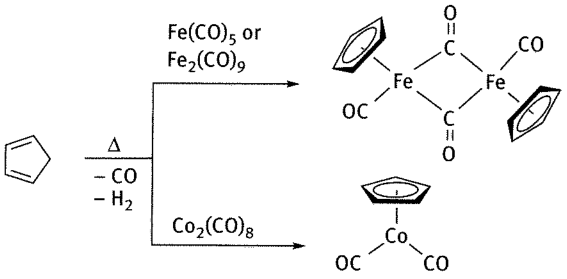


From metal carbonyls. Cp anions are capable of displacing CO ligands to give complex anions $[CpM(CO)_n]^-$; these may be protonated or reacted with electrophiles to a variety of successor products. Heating CpH (or its Diels–Alder dimer) at 150 °C with $Fe(CO)_5$ gives $[CpFe(CO)_2]_2$, often abbreviated Fp_2.

$$V(CO)_6 + Cp'H \longrightarrow Cp'V(CO)_4 + 2\,CO + 0.5\,H_2$$

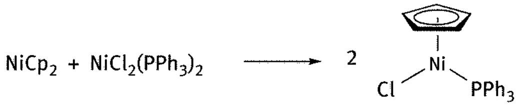
Cp' = alkyl-substituted Cp derivative



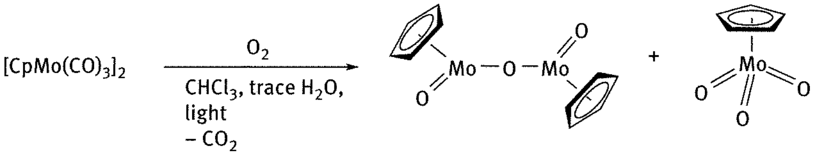


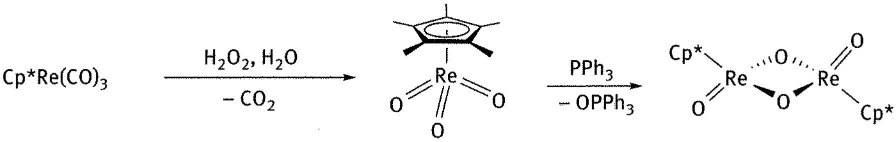
By ligand exchange of metallocenes. As a 20 VE species, nickelocene undergoes a variety of ligand exchange reactions to give 18 VE products. The structure and bonding of $[CpNi(\mu\text{-}CO)]_2$ (Ni^I, d^9) has been discussed in Section 2.5.2. Compounds of the type $Cp^RNi(X)(L)$ are also accessible, e.g. by reaction of $LiCp^R$ with $NiBr_2(PPh_3)_2$. Both the Ni products shown are useful starting materials.

$$NiCp_2 + Ni(CO)_4 \longrightarrow [CpNi(\mu\text{-}CO)]_2 + 2\,CO$$



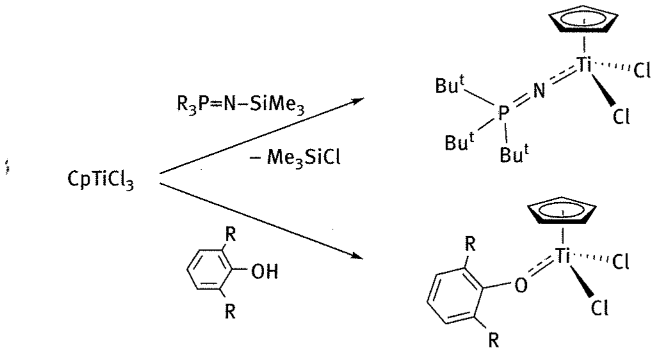
By oxidation of metal carbonyls.



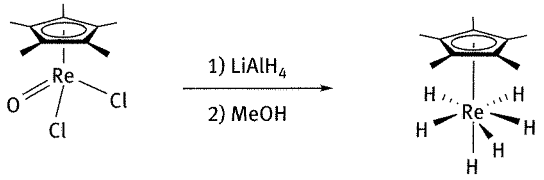


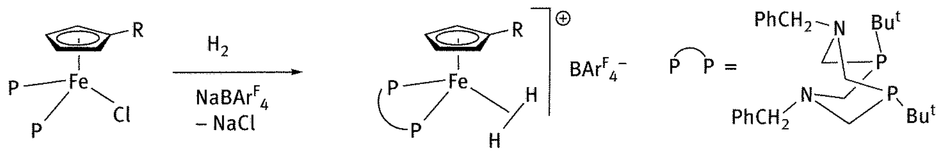
2.8.3.2 Reactivity of Mono-Cp Complexes

Halide substitution. The reactivity of mono-Cp complexes follows the principles outlined for bent metallocenes. Complexes with halide ligands are useful starting materials for a multitude of new compound classes. In the case of Lewis acidic, early transition metals, at least one chloride ligand can be conveniently removed by reaction with Me_3Si reagents. The volatile by-product Me_3SiCl is removed *in vacuo*. The CpTi phosphinimido and aryloxo examples shown in the following diagram are precursors to highly active ethylene polymerization catalysts and are used in industrial processes. The lone pairs on E = N or O provide some π-donation to the metal centre, which results in bond angles around E close to 180°.



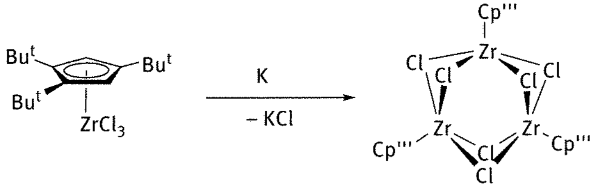
Mono-Cp halides and oxides react with hydride transfer agents to give hydride complexes. Alternatively, chloride abstraction leaves a vacant coordination site which, in the presence of a suitable donor ligand environment, can bind H_2. The iron dihydrogen complex shown in the following diagram is a highly efficient catalyst for the electrochemical oxidation of hydrogen to H^+, a reaction that is important in the context of utilizing H_2 as an energy source.

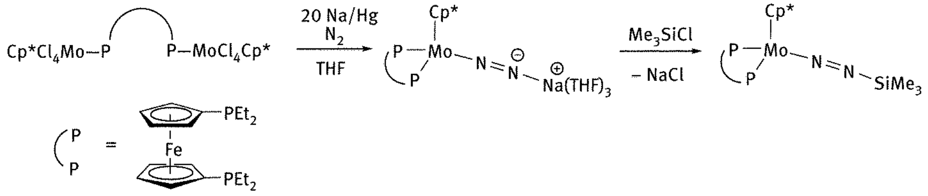




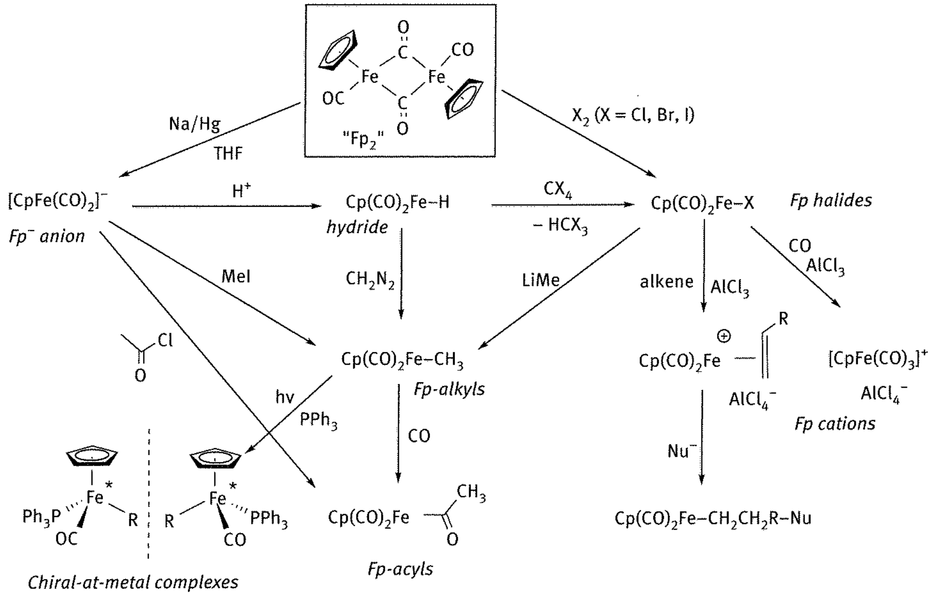
R = C_6F_5; Ar^F = 3,5-$C_6H_3(CF_3)_2$

Reductions. The reduction of the bulky Cp derivative $Cp'''ZrCl_3$ with potassium metal provides an example of a Zr(III) half-sandwich complex ($Cp''' = 1,2,4\text{-}Bu^t_3C_5H_2$). Reduction of complexes of the type $Cp^*MoCl_4(L)$ with sodium amalgam under N_2 enables the metal centre to bind N_2, followed by the reduction of coordinated dinitrogen to the diazenido anion $N{=}N^{2-}$.





Reduction with sodium amalgam is also a facile entry into the chemistry of binuclear Cp metal carbonyls, such as $[CpCr(CO)_3]_2$ and $[CpFe(CO)_2]_2$. Reduction generates 18 VE mononuclear Cp metal carbonyl anions, which can be protonated or alkylated with alkyl halides to give hydrides or metal alkyl derivatives. The binuclear complexes are also cleaved electrophilically by dihalogens. The complex $CpFe(CO)(PPh_3)R$ can be regarded as a tetrahedrally coordinated metal centre with four different substituents and is therefore chiral. Since inversion is slow, the enantiomers can be resolved and used in asymmetric synthesis. The typical reaction pattern is outlined in the following diagram for the iron compounds:



Redox reactions. Apart from alkali metal and thallium Cp complexes, which are frequently used to substitute halide ligands for Cp, cyclopentadienyl complexes can also be generated by redox transfer. For example, $CpCuPPh_3$ reacts with metallic lanthanide elements to give copper metal and lanthanide Cp complexes. This is also a clean, high-yielding path to mixed-ligand lanthanide mono-Cp compounds.

$$2\,\mathrm{CpCuL} + \mathrm{Yb} \xrightarrow[20\,^{\circ}\mathrm{C}]{\mathrm{THF},\ \mathrm{YbI_2}} \mathrm{Cp_2Yb} + 2\,\mathrm{Cu} + 2\,\mathrm{L} \qquad \mathrm{L} = \mathrm{PPh_3}$$

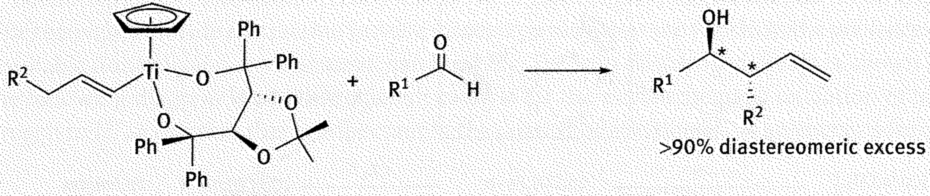
$$3\,\mathrm{CpCuL} + \mathrm{Ln} \xrightarrow[20\,^{\circ}\mathrm{C}]{\mathrm{THF},\ \mathrm{LnI_3}} \mathrm{Cp_3Ln} + 3\,\mathrm{Cu} + 3\,\mathrm{L}$$

$\mathrm{Ln} = \mathrm{Pr},\ \mathrm{Er}$

$$\mathrm{CpCuL} + \mathrm{SmI_2(THF)_2} \xrightarrow[20\,^{\circ}\mathrm{C}]{\mathrm{THF}} \mathrm{CpSmI_2(THF)_2} + \mathrm{Cu} + \mathrm{L}$$

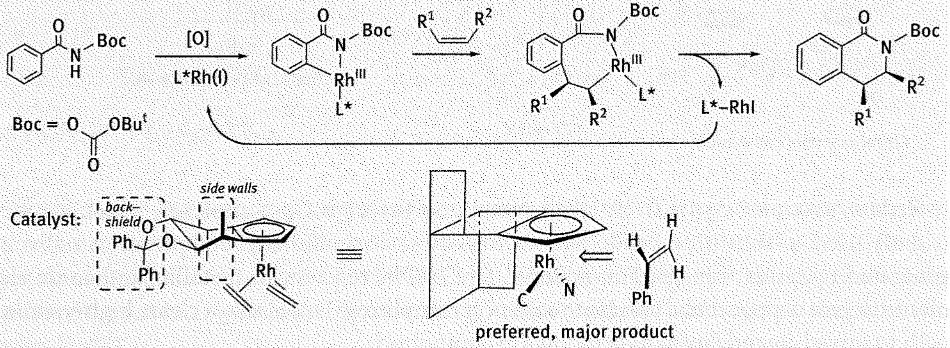
Box 2.8.3 Half-sandwich complexes in stereoselective synthesis

Mono-Cp complexes are widely used as catalysts and stereoselective reagents. There are two approaches: using the Cp ligand as a protecting group in combination with a second chiral ligand, or modifying the Cp ligand with chiral and stereo-directing substituents. The first approach is illustrated in the following equation for a chiral CpTi allyl complex, which produces a C–C bond to the more highly substituted C atom, generating two chiral centres with very high diastereoselectivity:



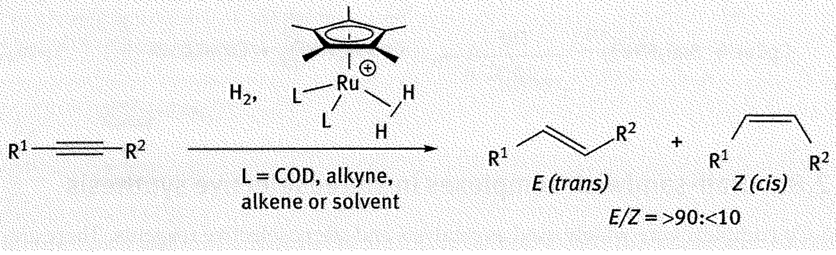
>90% diastereomeric excess

The second approach is employed in a Rh catalyst with modified Cp ligand. Here the position of substituents on the Cp ligand is used to control the orientation of the C–N substrate and the direction of the incoming alkene. Enantiomeric excesses of >90% are achieved. The reaction proceeds through oxidative cyclometallation to give a C–N bonded Rh(III) intermediate, followed by alkene insertion and reductive elimination, to produce the cyclic product and regenerate Rh(I).



preferred, major product

The hydrogenation of alkynes to alkenes usually proceeds by delivery of H_2 in *cis* fashion, to afford alkenes with *Z*-configuration. By contrast, some Cp* ruthenium(II) complexes have been shown to catalyze the production of *E*-(*trans*)-alkenes. A number of pre-catalysts can be used, although they all seem to generate $[Cp^*Ru(H_2)]^+$ cations stabilized by weakly-bonded ligands or solvent molecules (MeOH, CH_2Cl_2). A wide variety of functional groups is tolerated.



E/Z = >90:<10

Key points

Half-sandwich complexes contain one aromatic π-ligand plus a combination of X- and L-type ligands.

Mononuclear half-sandwich complexes containing CO ligands follow the 18-electron rule.

Binuclear mono-Cp complexes with bridging CO ligands are dimers with 30/34 valence electrons.

Most common and synthetically useful are the halides $CpMX_n$, which allow substitution of X by other anionic ligands to give complexes with M–C, M–O, or M–N bonds.

Complexes of electron-rich metals $CpML_n$ (L = phosphine, alkene) are widely used as catalysts and precursors for reactive CpM fragments.

CpM complexes find applications for example in polymerization, C–C coupling, and hydrogenation catalysis.

Exercises

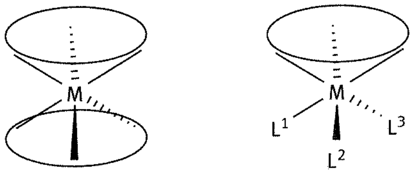
1. Give synthetic routes and equations for the synthesis of mono-Cp complexes starting from (i) $TiCl_4$; (ii) $Mo(CO)_6$; (iii) $Fe(CO)_5$; (iv) $[RhCl(C_2H_4)_2]_2$.
2. Devise synthetic routes to and discuss the structure and bonding of (i) $[CpNi(CO)]_2$; (ii) CpNi(NO); (iii) $[CpNi(PPh_2)]_2$; (iv) $[CpNi(PPh_3)_2]BF_4$; (v) $[CpNi(PEt_3)]_2$.
3. Explain why the substitution of ethylene ligands by CO in (η^5-indenyl)$Rh(C_2H_4)_2$ is orders of magnitudes faster than in $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$.

2.9 Arene Complexes

2.9.1 Bis(Arene) Sandwich Complexes

Arenes can form π-complexes that are structurally closely related to the cyclopentadienyl complexes described in Chapter 2.8, since both $C_5H_5^-$ and C_6H_6 are isoelectronic 6π Hückel aromatic systems. Like Cp^-, the arene ring can be considered to occupy three coordination sites, so that a bis(arene)metal complex can be regarded as octahedral.

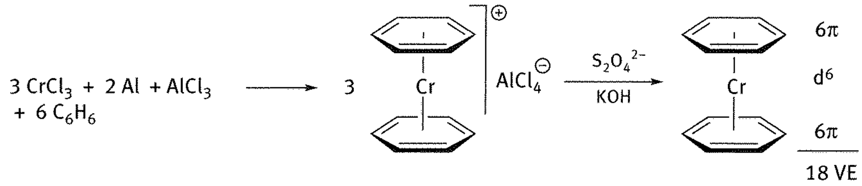
The C–C bonds in arene complexes are slightly elongated compared to the free arene, indicative of a back-bonding contribution. Since arenes are not charged, the electrostatic contribution to bonding that is an important feature in Cp complexes is absent, and arene complexes are therefore in general more labile. This is reflected in the metal–arene bond energy; whereas $D(Fe–C_5H_5)$ is 260 kJ mol^{-1}, $D(Cr–C_6H_6)$ is only 170 kJ mol^{-1}.



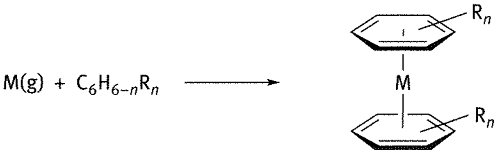
basic structure of bis(arene) and arene half-sandwich complexes

2.9.1.1 Synthesis and Structures

The classical example of an arene complex is bis(benzene) chromium, an 18 VE arene compound that is isoelectronic and isostructural to ferrocene. It was first made by E. O. Fischer in the 1950s by reduction of $CrCl_3$ with Al/$AlCl_3$ in benzene (Fischer–Hafner synthesis) to give a Cr(0) sandwich complex:

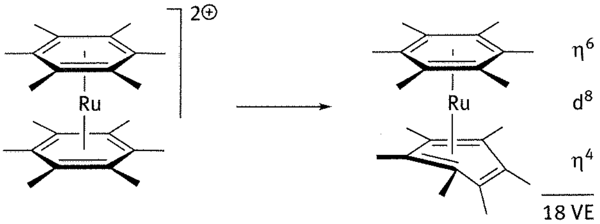


An alternative method to generate arene complexes is to co-condense atomic metal vapour with arenes under high vacuum on a cold (−196 °C) wall of the condensation reactor. This method has allowed a series of substituted bis(arene) complexes to be isolated, particularly with arene = 1,3,5-$R_3C_6H_3$ ($R = Pr^i, Bu^t$):



M = Ti, Zr, Hf, Nb, Cr,
lanthanides
R = H, Me, Bu^t, etc.

The stability of arene complexes increases with the degree of substitution; hexamethylbenzene in particular forms a range of bis(arene) complexes with 16–21 valence electrons. Compounds that appear to exceed the 18 VE count tend to be based on bonding modes which involve less than six electrons per arene ring; for example, Ru(C_6Me_6)$_2$ contains one η^6- and one η^4-bonded arene ring, so that the effective electron count of 18 is preserved. As is typical for such degenerate bonding situations, the compound is fluxional.

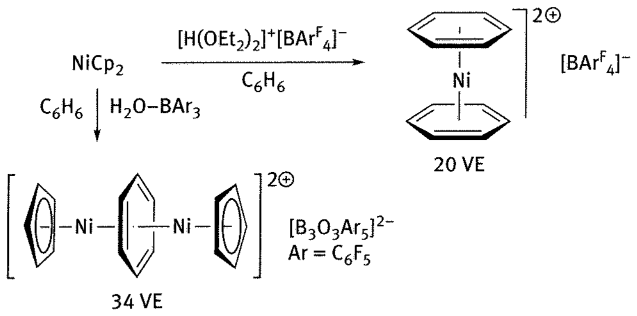


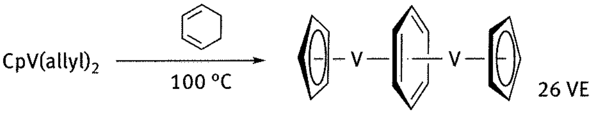
Many bis(arene) complexes deviate from the 18-electron rule and are paramagnetic. Some examples are collected in Table 2.9.1.

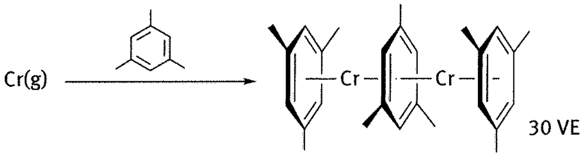
Arene complexes can be made from Cp complexes by ligand exchange. The arene ring can bridge two metals to give ***triple-decker structures***: The bonding is electron-deficient; e.g. the electron count per Cr atom in Cr_2(mesitylene)$_3$ is only 15. However, the bridging arene ring forms part of a M_2C_6 core held together by delocalized bonding.

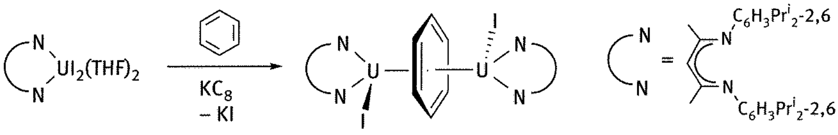
Table 2.9.1 Overview of first row bis(arene) complexes.

Complex	Electron count	Unpaired electrons	Comments
$Ti(C_6H_6)_2$	16	0	
$[V(C_6H_3Me_3)_2]^+$	16	0	
$[Ti(C_6H_5Ph)_2]^-$	17	1	
$V(C_6H_6)_2$	17	1	
$[V(C_6H_6)_2]^-$	18	0	
$Cr(C_6H_6)_2$	18	0	
$[Fe(C_6Me_6)_2]^{2+}$	18	0	orange, very stable
$[Fe(C_6Me_6)_2]^+$	19	1	deep purple
$[Co(C_6Me_6)_2]^{2+}$	19	1	
$Fe(C_6Me_6)_2$	20	0	probably η^6,η^4
$[Co(C_6Me_6)_2]^+$	20	2	yellow, η^6,η^6
$[Ni(C_6Me_6)_2]^{2+}$	20	2	red-brown









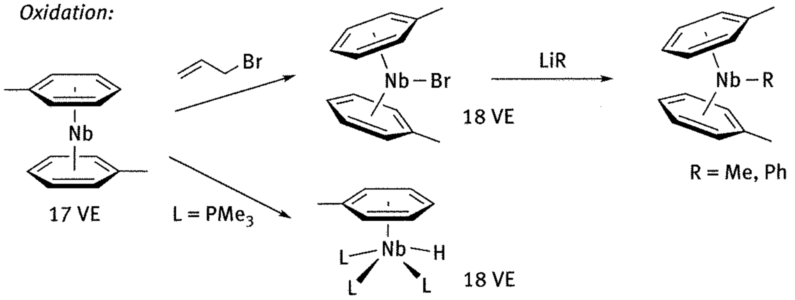
2.9.1.2 Reactivity of Bis(Arene) Complexes

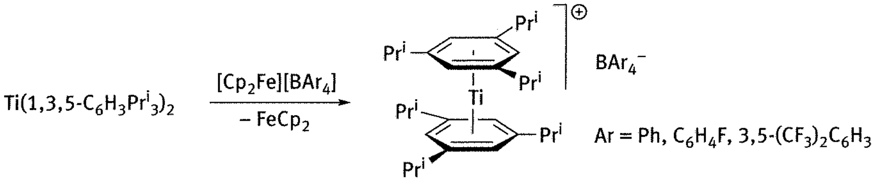
Arene complexes undergo reactions

(i) on the metal, by oxidation and reduction;
(ii) by ligand substitution;
(iii) on the arene ligand, by metallation and nucleophilic attack.

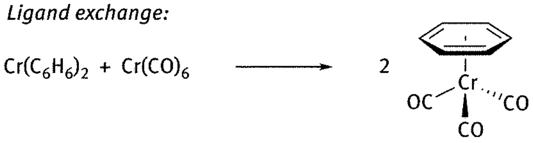
Reactions of the metal and ligand substitutions are exemplified by the redox reactions of Nb(η^6-toluene)$_2$. Low-valent arene complexes are easily oxidized, e.g. Ti($C_6H_3Pr^i_3$)$_2$ reacts with the 1-electron oxidant FeCp$_2^+$ to give a rare example of a Ti(I) complex, [Ti($C_6H_3Pr^i_3$)$_2$]$^+$, a 15 VE paramagnetic species with one unpaired electron. The reaction between Cr(benzene)$_2$ and Cr(CO)$_6$ leads to ligand exchange to give arene half-sandwich compounds:

Oxidation:



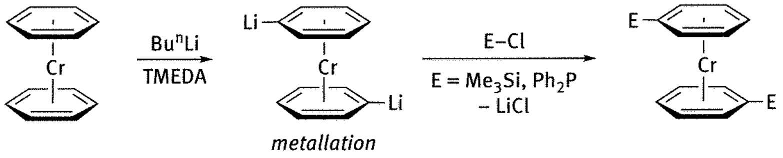


Ligand exchange:

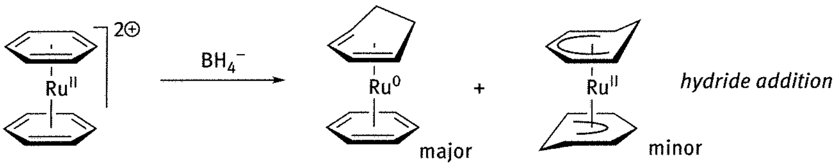


Attack on arene ligands:

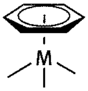
Ligand exchange:



Nucleophilic attack:



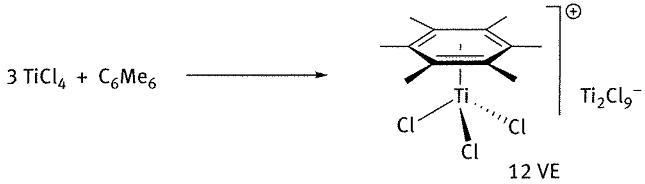
2.9.2 Arene Half-Sandwich Complexes

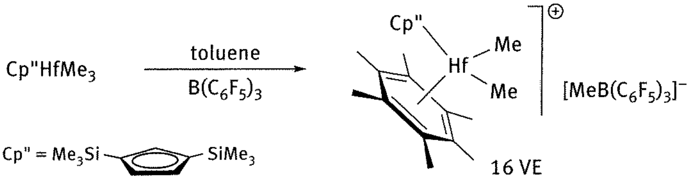


By far the largest and most important group of arene complexes are half-sandwich compounds with 'piano stool' geometry, analogous to Cp complexes. These exist in combination with X-type ligands, as (arene)metal halides, and with L-type ligands, particularly (arene) metal carbonyl complexes.

2.9.2.1 Synthesis and Structures of Mono-Arene Complexes

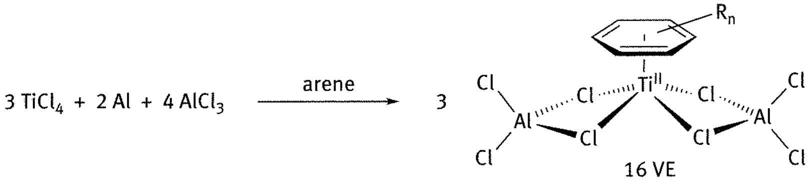
Halide complexes. Early transition metal halides possess sufficient Lewis acidity to form π-complexes with arenes. Electron-rich arenes such as C_6Me_6 form particularly stable adducts.

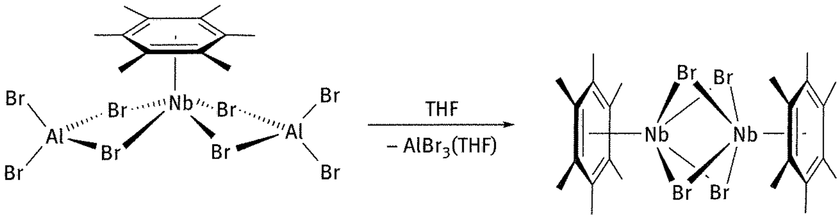




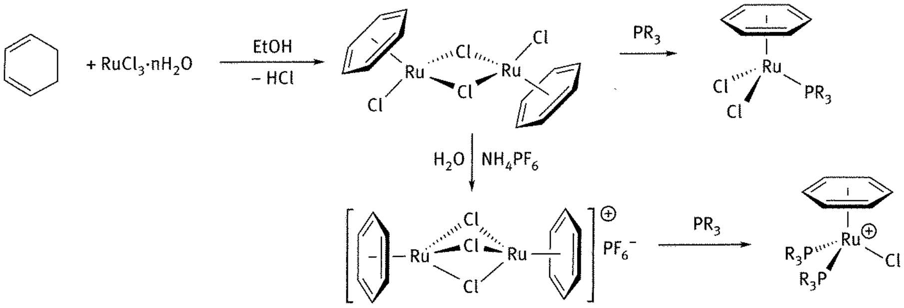
arene analogue of Cp_2MX_2 bent sandwich complex

Arene complexes of low-valent early transition metal halides are also known, often stabilized by AlX_3 (X = Cl, Br) and are generated by reducing metal(IV, V) halides with Al/AlX_3 mixtures in the presence of arene solvents.





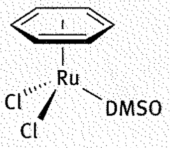
By contrast, arene complexes of noble metals may be prepared by dehydrogenation of dienes which act as reducing agents, e.g. to reduce Ru(III) to Ru(II). This leads to the important and varied class of (arene)$RuCl_2$(L) complexes.

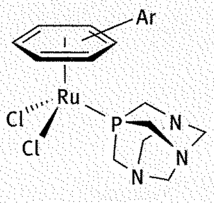


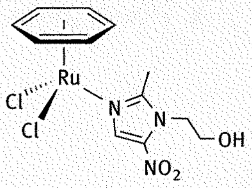
Mixed-ligand arene complexes. Diene complexes may be converted into arene compounds by hydride abstraction. Arenes are also capable of substituting labile ligands such as acetonitrile. Cationic arene analogues of CpNi(allyl) can be made from $[(\text{allyl})\text{NiCl}]_2$ by chloride displacement; unlike many other electron-rich nickel arene complexes (vide infra) the arene here is η^6-bonded to give an 18 VE product.

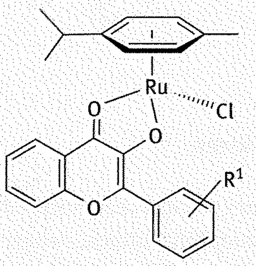
Box 2.9.2 Mono-arene complexes for cancer treatment

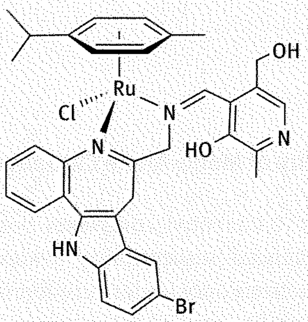
Many half-sandwich complexes, and particularly arene complexes of ruthenium, show promising anti-tumour activities. The ligands are selected partly to ensure solubility under physiological conditions, and partly because they are related to known anti-tumour drugs. Some examples:

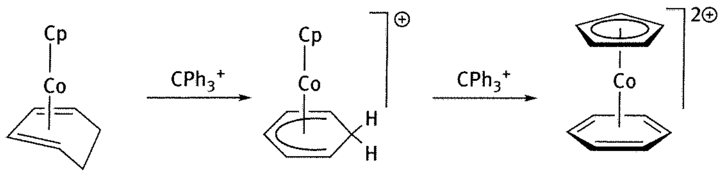


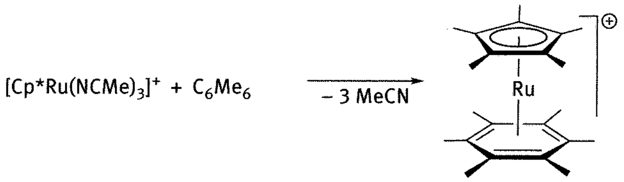


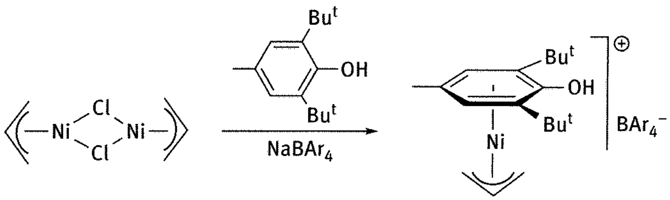




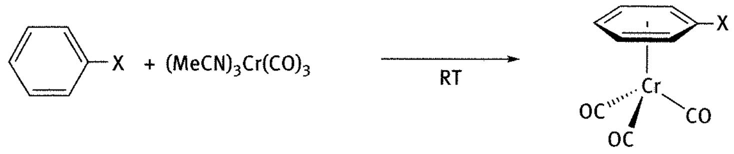


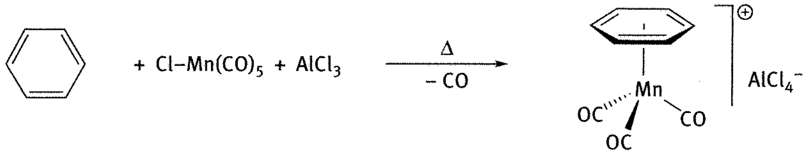






Arene metal carbonyls. This gives compound families that are particularly useful for synthetic purposes. The coordination to an electron-withdrawing M(CO)$_n$ fragment activates the arene ligands. Common synthetic approaches are ligand substitution and abstraction of halides from metal carbonyl halides with AlCl$_3$.



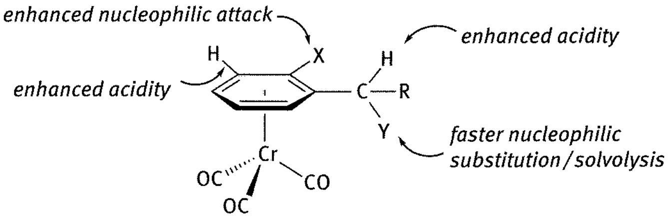


2.9.2.2 Reactivity of Mono-Arene Carbonyl Complexes

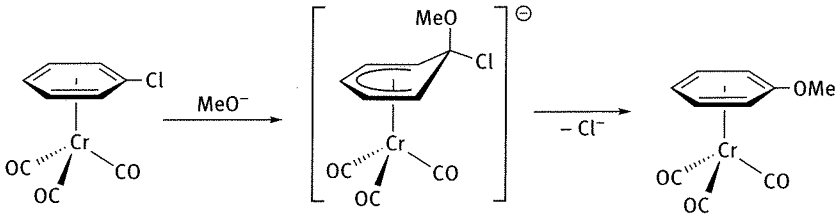
pK_a: PhCOOH 5.68
(PhCOOH)-Cr(CO)3
4.77
p-O$_2$N-C$_6$H$_4$-COOH
4.48

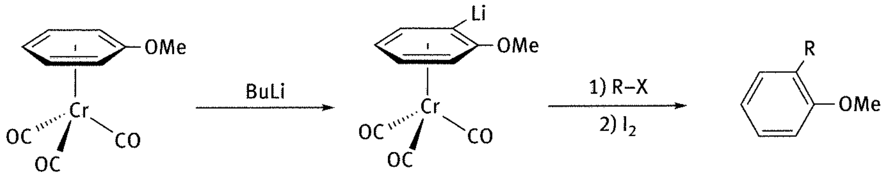
Arene chromium tricarbonyl complexes possess very varied reactivity. The coordinated arene shows enhanced susceptibility towards nucleophilic attack, whereas free arenes undergo such reactions only under very forcing conditions. The Cr(CO)$_3$ fragment also increases the C–H acidity of alkyl substituents as well as of the arene C–H bonds, thus giving more facile metallations, and coordination stabilizes carbocations in α-position to the ring, so that benzylic nucleophilic substitutions and solvolysis reactions are accelerated (Y = leaving group). As judged from a comparison of the pK_a values of benzoic acids, coordinating the phenyl ring of PhCOOH to $Cr(CO)_3$ exerts about the same electronic influence as the introduction of a nitro group.

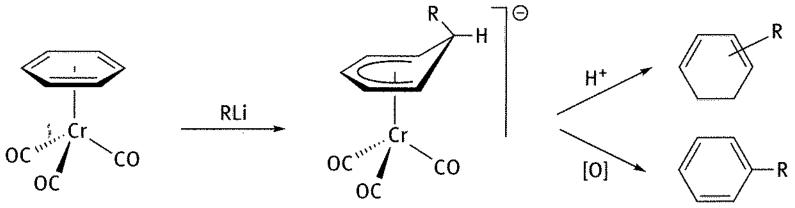
Effects of $Cr(CO)_3$ coordination:

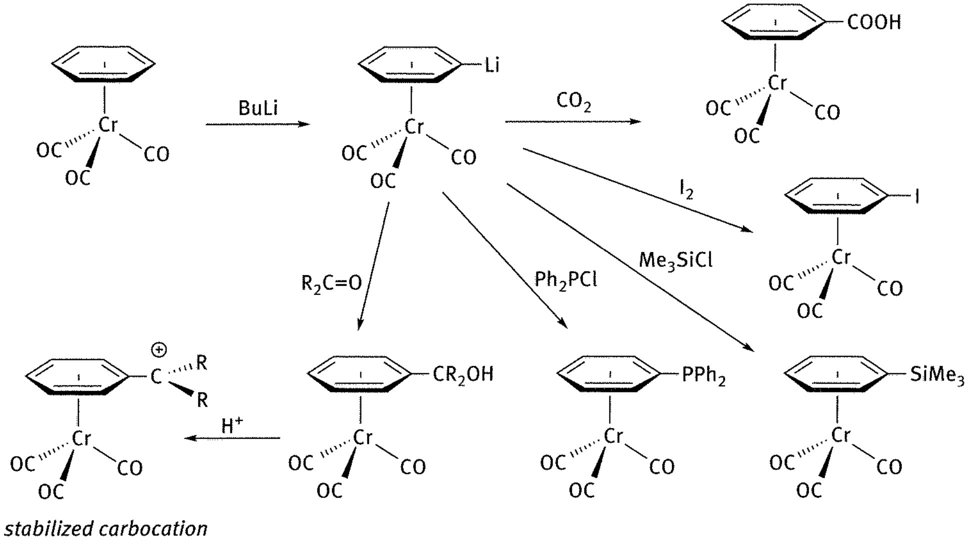


These properties can be exploited in numerous ways. For example, even chloroarenes, which are otherwise chemically extremely inert, undergo nucleophilic substitutions if coordinated to $Cr(CO)_3$ and the introduction of an alkyl substituent can be 100% regioselective:

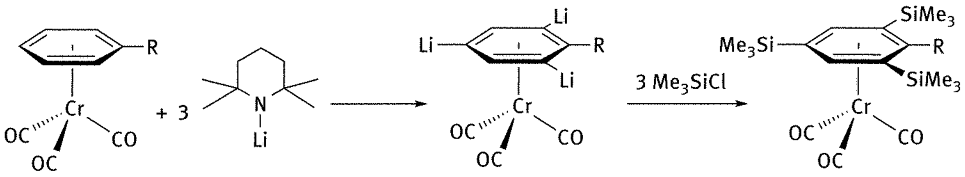


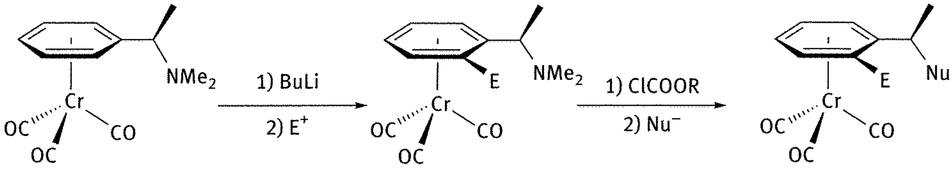




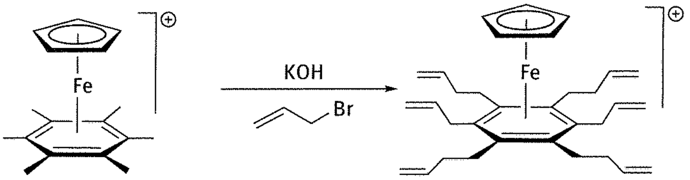


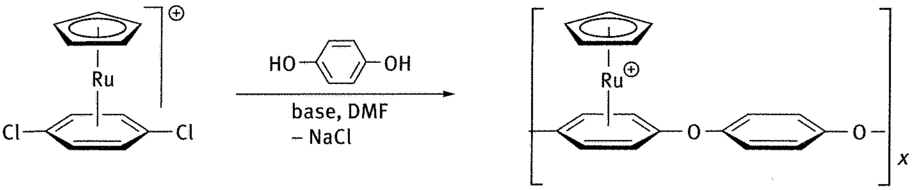
Multiple metallations are also possible, as are chiral substitutions on the ring (planar chiral system) and in benzylic position. Some examples:





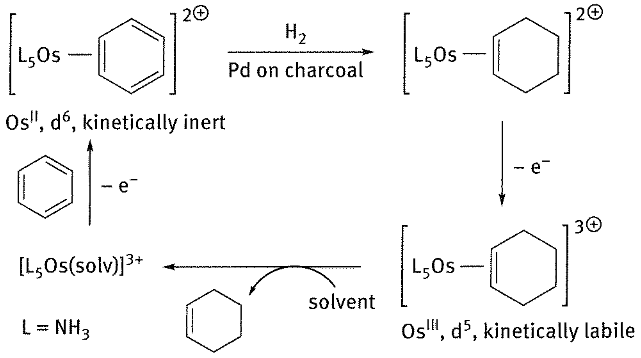
Arene coordination to cationic CpM^+ fragments has an activating effect similar to $Cr(CO)_3$ and facilitates nucleophilic attack, even with chloroarenes. In the case of C_6Me_6, the combination of base (here: KOH) with an activated allylic halide leads to multiple C–C bond formations.



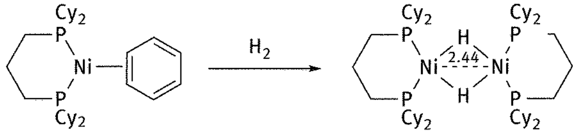


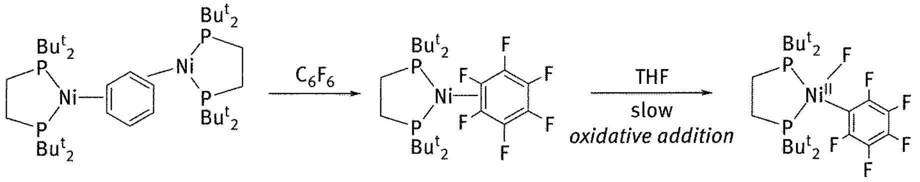
2.9.3 Arene Complexes with Less Common Coordination Modes

While the η^6-coordination mode is most common for arene complexes, other coordination types may be adopted. The fluxional η^4-bonding mode of $Ru(C_6Me_6)_2$ has been mentioned (Section 2.9.1.1). An example of an η^2-benzene ligand is the kinetically inert complex $[Os(C_6H_6)(NH_3)_5]^{2+}$. Here the coordinated C=C bond is protected while the non-coordinated bonds of benzene can be selectively hydrogenated, resulting in a cyclohexene complex. The alkene ligand may be released after oxidation of Os(II) (d^6) to the kinetically labile Os(III), so that a stepwise cyclic process can be devised:

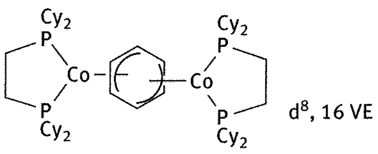


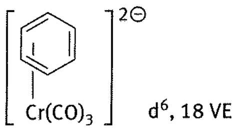
Other η^2-benzene complexes are known, for example for nickel(0) supported by bulky, strongly donating phosphines, where hydrogenation leads to Ni(I) hydrides. Bridging η^2:η^2 arenes have also been observed. The benzene ligand in these electron-rich complexes can be replaced by the electron-acceptor C_6F_6, which undergoes slow oxidative addition of the C–F bond. The reaction suggests η^2-arene complexes as intermediates in oxidative additions of arene C–X bonds.



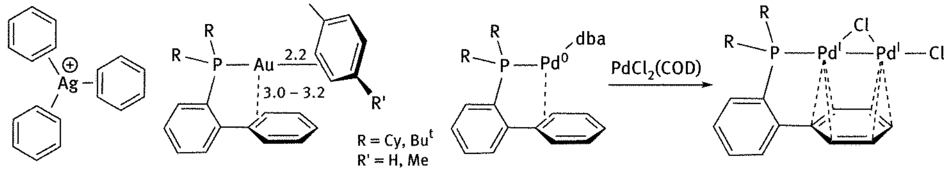


In related arene-bridged, bis-phosphine cobalt compounds the arene is η^3:η^3-coordinated, while in the thermally unstable anion $[(C_6H_6)Cr(CO)_3]^{2-}$, the benzene is η^4-bonded, all a reflection of the electronic requirements of the metal centre.



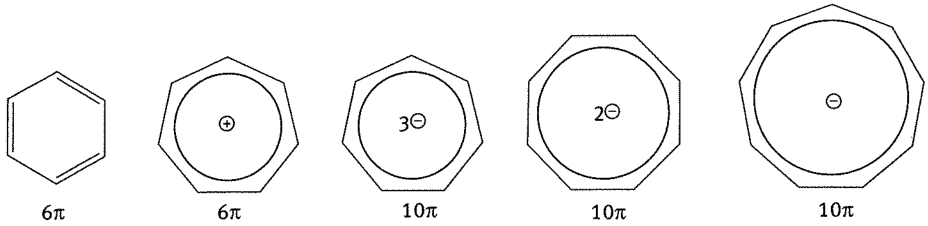


The ability of Ag^+ salts in aqueous solution to bind to arenes has long been known. More recently, several examples of such complexes have been isolated and structurally characterized, confirming that three benzene molecules are bonded very much like ethylene. Gold(I) arene complexes require the support of strongly donating phosphines with a biphenyl substituent; there is a short bond to the η^2-arene as well as a much longer and weaker interaction with a C=C bond of the biphenyl. Such gold complexes act as electrophilic catalysts for organic transformations. The same ligand supports arene η^2 and $\mu_2,\eta^3:\eta^3$-coordination to Pd(0) and Pd(I). These complexes are useful catalyst precursors for Suzuki–Miyaura C–C cross-coupling reactions.

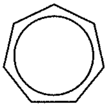


2.9.4 Larger Arene Ligands: 7-, 8-, and 9-Membered Rings

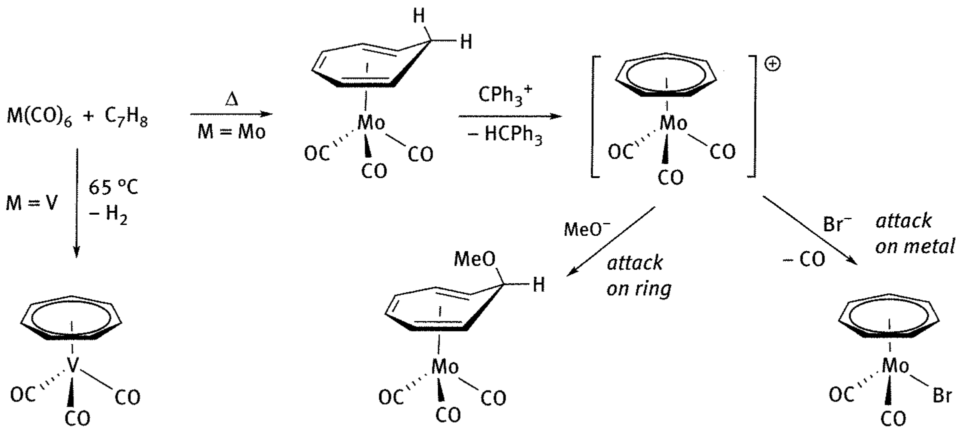
Extending the size of arene rings leads to planar Hückel-aromatic π-systems with 6 and 10 π-electrons:



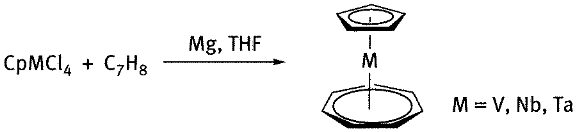
2.9.4.1 π-C_7H_7 Complexes



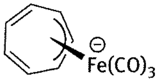
The cycloheptatrienyl ring can be regarded either as the 6π tropylium cation $C_7H_7^+$ or as the 10π trianion $C_7H_7^{3-}$, depending on the nature of the metal centre to which it is coordinated. The precursors are cycloheptatriene complexes, such as $(\eta^6\text{–}C_7H_8)M(CO)_3$ (M = Cr, Mo, W), which readily undergoes hydride abstraction to give $[(\eta^7\text{–}C_7H_7)M(CO)_3]^+$. Such cationic complexes are susceptible to nucleophilic attack, which may take place either externally on the ring or on the metal centre. These pathways are outlined in the following reaction scheme for $Nu^- = MeO^-$ and Br^-.

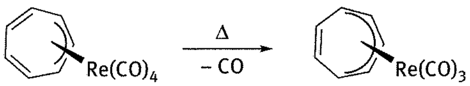


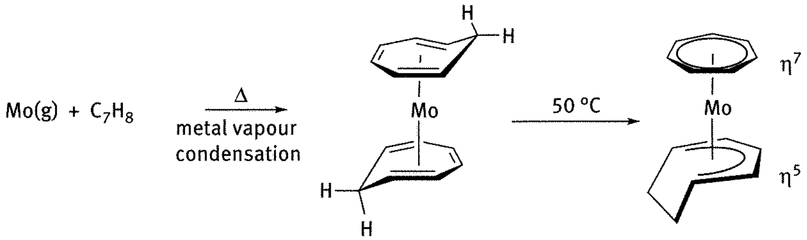
The reduction of $CpMCl_4$ (M = V, Nb, Ta) in the presence of cycloheptatriene gives the sandwich complexes $CpM(C_7H_7)$, which are more appropriately regarded as M(IV) compounds with $C_7H_7^{3-}$ anions.



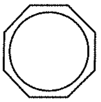
In some instances, the electron demand of the metal centre is partially satisfied by other ligands, so that it may only be able to interact with a few C atoms of the C_7 ring, as in $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]^-$ or $(\eta^5\text{-}C_7H_7)Re(CO)_3$. The η^6,η^6 sandwich complex $Mo(C_7H_8)_2$ rearranges thermally by H-transfer to give $Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$.





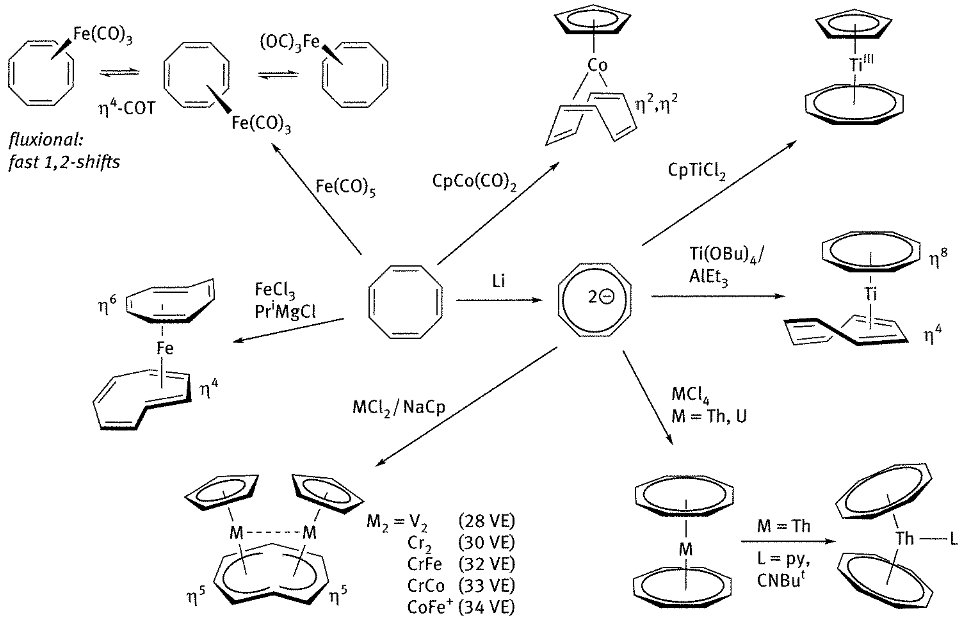


2.9.4.2 π-C_8H_8 Complexes



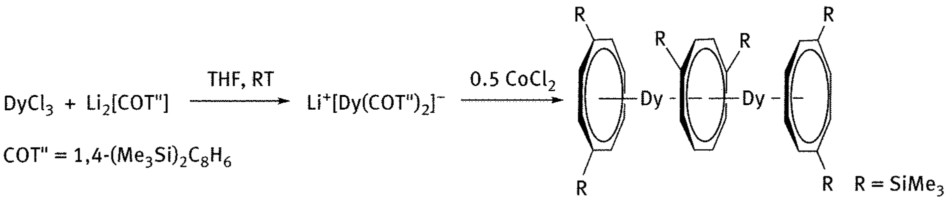
Cyclooctatetraene (COT) is a versatile ligand that can bind to metals as the non-planar, antiaromatic neutral tetraene or as the planar 10π COT^{2-} dianion. There are numerous compounds where only one or two C=C bonds of COT are coordinated to a metal centre. The large size of the C_8 ring means that the ligand is able to bridge across two metal centres and give binuclear compounds.

Large ions, such as lanthanides and actinides, form COT sandwich complexes. The best-known COT complex is '**uranocene**', $U(\eta^8\text{-}C_8H_8)_2$, which has attracted theoretical attention because of its structural similarity to metallocenes and the possibility of f-orbital contribution to ligand bonding. Whereas COT complexes of lanthanide metals have a highly ionic character and are very sensitive to hydrolysis, $U(\eta^8\text{-}C_8H_8)_2$ is stable to water and the bonding is more covalent; the participation of 6d as well as 5f orbitals in the actinide-ligand bonding has been proposed. **Actinidocenes** $M(\eta^8\text{-}C_8H_8)_2$ exceed the 18-electron rule, with electron counts ranging from 20 (M = Th) to 25 (M = Am). The thorium and plutonium complexes are diamagnetic, while uranocene and the others are paramagnetic. The following scheme gives an overview of synthetic routes, COT bonding modes, and types of COT complexes.



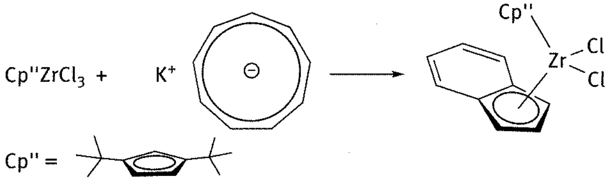
The binuclear compounds $(CpM)_2(\mu\text{-}C_8H_8)$ have been described as 'twinnocenes', and on the basis of the 18-electron rule M–M multiple bonds have been postulated. However, studies of the magnetic behaviour have shown that only for the electron-poor 28 and 30 VE species is there a single metal–metal σ-bond. Unpaired spins are essentially localized on the metal centres. Singlet and triplet states are energetically very close, giving rise to unusual magnetic behaviour.

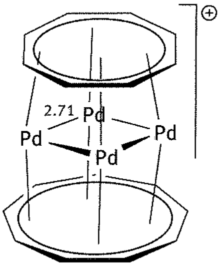
COT complexes of lanthanides have been extensively studied as ***single-molecule magnets (SMMs)***. The SMM behaviour of Cp*Er(COT) has been mentioned in Section 2.8.2.3. Other examples are the mono- and binuclear dysprosium COT complexes shown in the following diagram (with $SiMe_3$ substituents for increased solubility). DFT calculations suggest strongly covalent metal–COT bonding; the ions show magnetic interactions across the COT bridge.



2.9.4.3 π-C_9H_9 Complexes

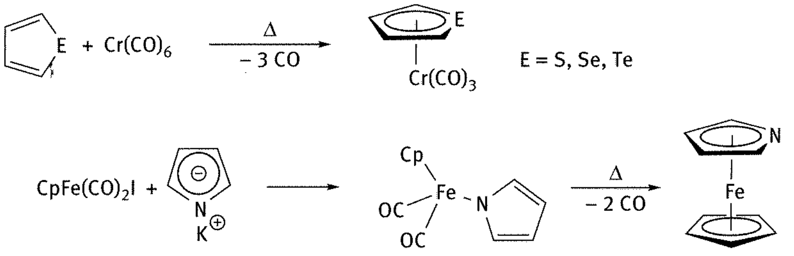
Extending the line of aromatic planar cycles further leads to the cyclononatetraenyl anion, $C_9H_9^-$. This is too large to form sandwich-type complexes with most ions and shows a tendency to condense to indenyl, as in the reaction of K[C_9H_9] with Cp''ZrCl_3. The size of the C_9 ring is best illustrated by its ability to sandwich a raft of four palladium atoms, as in the Pd(I) compound $[Pd_4(\eta^8\text{-}C_8H_8)(\eta^9\text{-}C_9H_9)]^+[BAr^F{}_4]^-$.

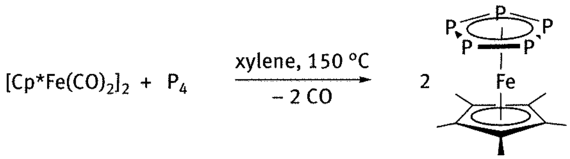




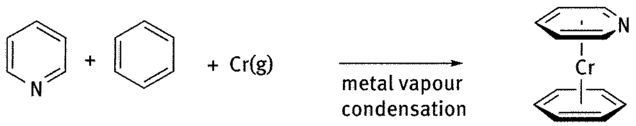
2.9.4.4 π-Complexes of Heterocycles

Aromatic systems incorporating heteroatoms with a lone pair usually act as 2-electron n-donors but are also capable of forming π-complexes. Since they are more electron rich than arenes, they can be useful for modifying the redox behaviour of metal centres. Complexes of thiophenes have been studied in the context of the catalytic hydrodesulfurization of coal derivatives. The reaction of $[CpFe(CO)_2]_2$ with P_4 under reducing conditions gives a ferrocene analogue containing the P_5^- anion, which is isostructural and isoelectronic with Cp^-. Heterocycles incorporating a B–N moiety are isoelectronic with arenes and show a similar coordination chemistry; the B–N bond carries double bond character but is more polar than a C=C bond. A few representative examples are shown in the following diagram.

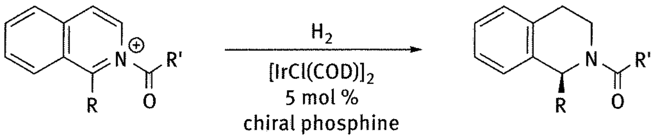


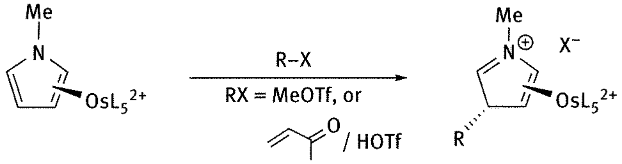


Pyridine has a strong preference for κ^1-coordination via the N atom. Nevertheless, Cr(η^6-pyridine)$_2$ has been prepared but is unstable towards solvolysis. The mixed sandwich Cr(pyridine)(benzene) is much more stable.

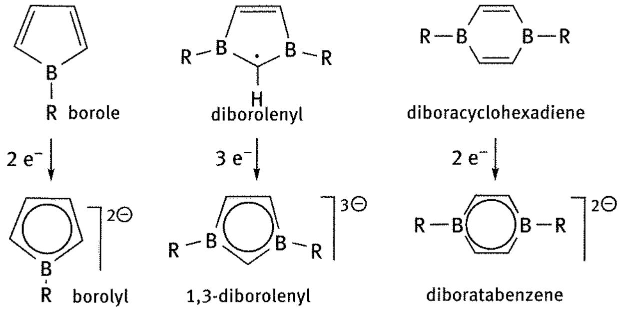


While π-complexes of heteroarenes like pyridine have not achieved the synthetic prominence of their arene congeners, they are important in asymmetric hydrogenation for the synthesis of drugs based on saturated N-heterocycles. Five-ring heteroarenes are more easily derivatized; for example, the uncoordinated C=C bond of the kinetically inert complex $[(\eta^2\text{-}C_5H_4NMe)Os(NH_3)_5]^{2+}$ is readily attacked by electrophiles:



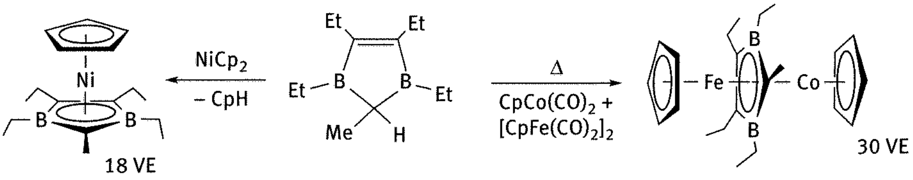


Heterocycles containing B in place of C have been mentioned in Section 2.8.1. They are electron-deficient and accept electrons from metal–ligand fragments ML$_n$ to achieve a 6π Hückel aromatic configuration. These electrons are frequently supplied by two different metals, giving rise to ***multi-decker structures*** with electron counts beyond the 18-electron rule: the 'magic numbers' are **30 VE** for triple-deckers and **42 VE** for tetradeckers.



In the reaction of 1,3-diborolenes, three electrons are provided either by one CpNi fragment, or by a combination of CpFe + CpCo, following the rules outlined in Section 2.5.2. This synthetic principle is extendable, and penta- and hexadecker complexes based on bridging 1,3-B_2C_3 rings have been synthesized.

Electron donation by ML_n:
$Mn(CO)_3$ = CpFe 1 e^-
$Fe(CO)_3$ = CpCo 2 e^-
$Co(CO)_3$ = CpNi 3 e^-



Key points

Arenes form sandwich complexes $M(arene)_2$ and half-sandwich compounds $(arene)ML_n$.

The metal–arene bond is covalent but lacks the Coulomb contribution of metal–Cp complexes.

Most mononuclear arene sandwich complexes follow the 18-electron rule.

Stacking $M(arene)_2$ complexes with further M(arene) fragments leads to triple-decker and tetra-decker structures which extend the 18 VE rule to **30** and **42 VE**, respectively.

Half-sandwich complexes $(arene)Cr(CO)_3$ and isoelectronic cations $[(arene)FeCp]^+$ are important as reagents in regio- and stereoselective synthesis. Coordination of the arene to $Cr(CO)_3$ increases C–H acidity, susceptibility to nucleophilic substitution, and ring metallation.

Mono-arene complexes of Ru are promising anti-cancer agents.

$C_7H_7^+$, $C_7H_7^{3-}$, and $C_8H_8^{2-}$ (COT) are larger, planar aromatic systems and form analogous complexes. $M(COT)_2$ sandwich compounds are formed with large M = Th, U, lanthanides.

Heterocycles form complexes of analogous structural types.

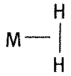
Exercises

1. Draw the structures and determine the oxidation states and electron count for
   (i) $[Cr(C_6H_6)_2]^+$;
   (ii) $Cr(C_6H_3Me_3)_2$;
   (iii) $Cr_2(C_6H_3Me_3)_3$;
   (iv) $(C_7H_7)Mo(CO)_2Br$;
   (v) $U(C_8H_8)_2$.
2. Using $(arene)Cr(CO)_3$ synthesis strategies, devise a route for the synthesis of 2-benzylanisole, $MeOC_6H_4$-2-CH_2Ph, from chlorobenzene.
3. Why is the COT ligand planar in CpTi(COT) but non-planar in CpCo(COT)?

2.10 Sigma Complexes

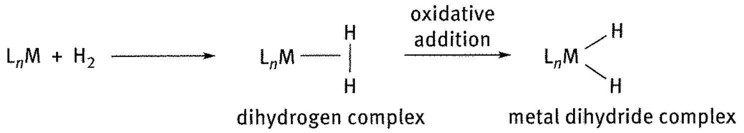
Apart from lone pairs and π-electrons, given the right combination of electrophilicity and back-bonding capacity, metal centres can coordinate to the σ-bonds of H–H and H–X molecules. The most important σ-ligand is H_2. Although metal hydrides and hydrogen complexes are not strictly organometallic, they play a key role in organometallic reactions and in catalysis and are therefore included here.

2.10.1 H_2 Complexes



The electron density of the σ-bonds is shared with the metal in a situation closely similar to 2e3c bonding. Since *n*d levels (*n* = 3–5) are comparable to or higher in energy than σ* orbitals of H–H and H–X bonds, there is a degree of back-bonding that leads to an elongation of the H–H or H–X bonds.

The coordination of H–X may be regarded as an arrested reaction: in most cases this is part of the oxidative addition sequence of H–X to a metal centre, with an M(HX) adduct as the transition state. However, in some cases the oxidative addition step is slow, as in the case where the metal centre is not electron rich. This is often the case in cationic complexes. In such cases the H–X adduct becomes the ground state and may be isolable.



The formation of an H_2 complex was first discovered when the apparently coordinatively and electronically unsaturated complex $W(CO)_3(PCy_3)_2$ was exposed to H_2. In this compound, the bulkiness of the two PCy_3 ligands results in a formally 16 VE species with a vacant coordination site. Closer inspection showed however that the electron deficiency was alleviated by the interaction of the metal with a C–H bond of one of the cyclohexyl substituents. This interaction is sufficiently weak to be displaced by H_2. On the other hand, the electron-withdrawing characteristics of the three CO ligands ensure that the metal is not electron rich enough for fast oxidative addition of H_2 and cleavage of the H–H bond, so that the intermediate could be isolated. Oxidative addition does occur but slowly.

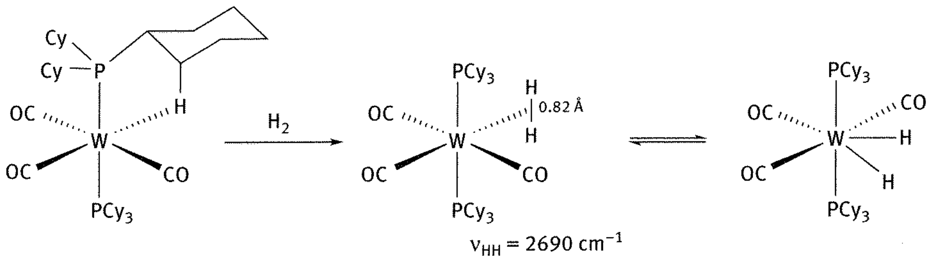


Table 2.10.1 Acidities of H_2 complexes

Compound	pK_a
H_2 (in THF)	>49
$Ru(H_2)(H)_2(PPh_3)_3$	36
$[Cp^*Ru(CO)_2(H_2)]^+$	−2
$[Os(H_2)(CO)(dppp)_2]^{2+}$	−5.7

Coordination elongates the H–H distance, from 0.74 Å in free H_2 to values of 0.8–1.0 Å in H_2 complexes. There are also complexes with 'elongated hydrogen', with H–H distances of up to 1.36 Å. The H_2 binding enthalpy in the classical complex $W(H_2)(CO)_3(PCy_3)_2$ is only 39.4 kJ mol^{-1} (by calorimetry), although in other complexes it was found to be 2–3 times larger. Nevertheless, H_2 is a weakly-bonded ligand that may be readily displaced.

There are many polyhydride complexes which contain one or more H_2 ligand. Whether or not an H_2 complex is formed depends on the electron donating or accepting nature of other ligands and on the metal. As the stability of high oxidation states increases down a transition metal triad, so does the tendency to form polyhydride rather than H_2 complexes. For example, whereas $RuH_4(PPh_3)_3$ is actually $Ru^{II}(H_2)(H)_2(PPh_3)_3$, the Os analogue is a tetrahydride, Os^{IV}.

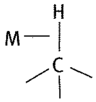
Since X-ray diffraction often struggles to locate hydrogen ligands and crystals suitable for neutron diffraction may not be attainable, the best method of differentiating between the $M(H_2)$ and $M(H)_2$ states is NMR spectroscopy, by measurement of the J_{HD} coupling constant of the partially labelled HD complexes. Coordination weakens the H–D bond and consequently lowers the value of the coupling constant, from 43 Hz for free HD to 35 Hz or lower. In principle the H–H vibration can also be detected by vibrational spectroscopy but is often weak.

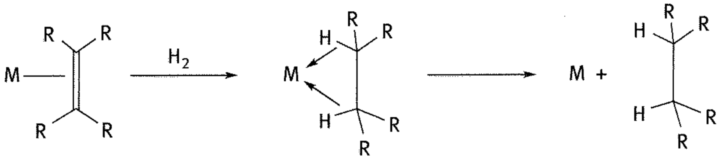
Coordination of H_2 to a metal centre drastically **increases its acidity**, particularly in cationic complexes, and can reach the strength of triflic acid (CF_3SO_3H) (Table 2.10.1). This increase in acidity plays a major role in H_2 activation, heterolytic H–H bond cleavage, and σ-bond metathesis reactions such as M–C bond hydrogenolysis.

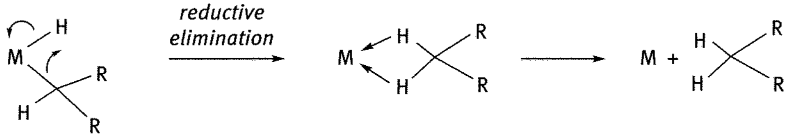
For acidity of metal carbonyl hydrides, see Section 2.5.7.

2.10.2 Alkane and Silane Complexes

Alkane complexes. As the structure of $W(CO)_3(PCy_3)_2$ shows, metal centres are in principle capable of binding to C–H bonds of saturated hydrocarbons in a donor–acceptor fashion. The same bonding interactions should be expected to be present in metal complexes of alkanes. Such species must, for example, be generated in the hydrogenation of alkene complexes and in the reductive elimination of alkanes from hydridometal alkyls. In most cases such complexes are too unstable to be detectable.

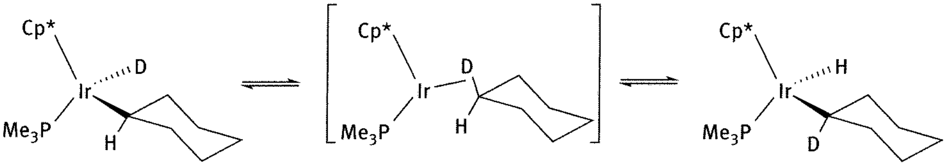


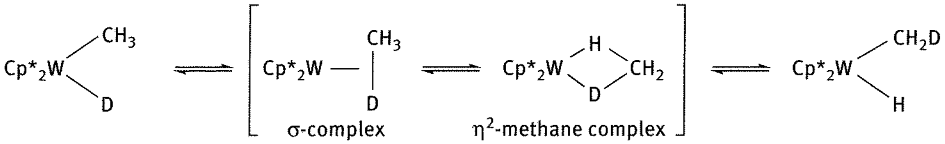




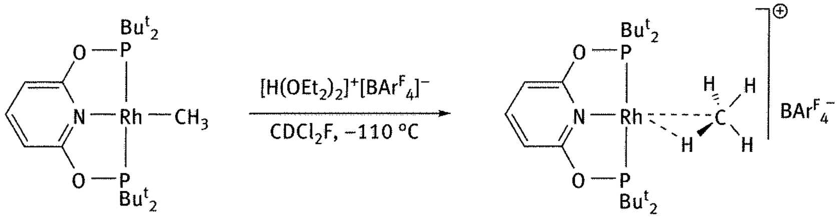
The ability of metal complexes to bind to alkanes has long been investigated, e.g. by flash photolysis of metal carbonyls in low temperature matrices; for example, the 16 VE species $W(CO)_5$ binds hexane with a dissociation energy of 11 kcal mol^{-1}. Such complexes are too labile to be isolated.

Alkane complexes have been postulated as intermediates in the H/D exchange of some metal alkyls:

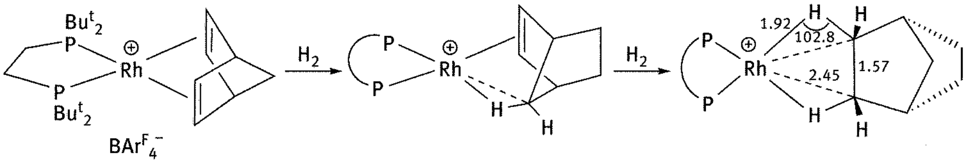




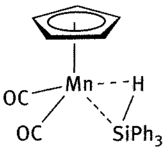
The protolysis of the pincer complex (PNP)Rh–CH_3 gave a cationic Rh(I) methane complex that was sufficiently stable and long-lived to be characterized by NMR spectroscopy. According to computational modelling, one Rh–H bond is much shorter than the other, with a possible Rh · · · C interaction. The compound is highly fluxional.

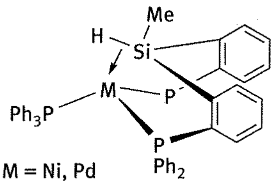


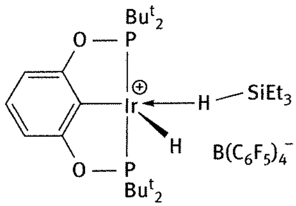
The characterization of an alkane complex by single-crystal X-ray diffraction became possible by the hydrogenation of a crystalline rhodium norbornadiene complex in the solid state, by a gas–solid reaction:



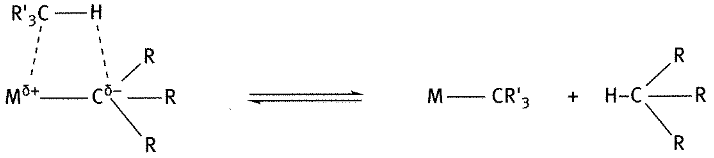
Si–H complexes. Silanes have similar characteristics to H_2, and the hydrosilylation of alkenes and alkynes follows very similar pathways to the hydrogenation process. It is therefore to be expected that silanes $R_3Si–H$ should form Si–H σ-complexes that resemble H_2 and alkane complexes. Such compounds were indeed detected; they are less labile than alkane complexes, and a number of noble metal compounds could be structurally characterized. Complexes with η^2-Si–H bonds as well as η^1-type bonding are known. σ-Complexes with borane B–H bonds also exist.





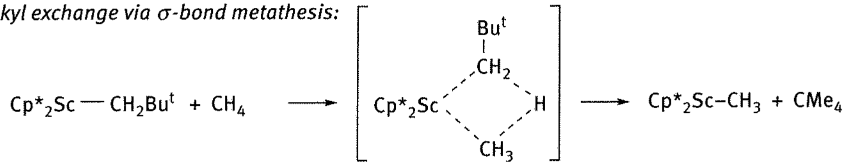


σ-Bond metathesis. C–H bonds can react with metal–alkyl bonds without oxidative addition via a process called σ-bond metathesis. This process takes place provided the metal centre is sufficiently electrophilic and in a high oxidation state.

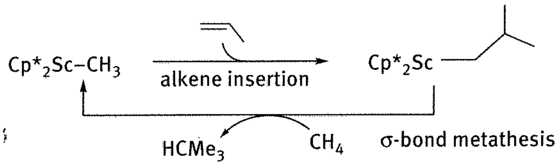


This process is often observed for Group 3 and lanthanide complexes and can lead to new alkyls or alkylation products. Even the usually very unreactive methane can be used as an alkylation agent.

Alkyl exchange via σ-bond metathesis:



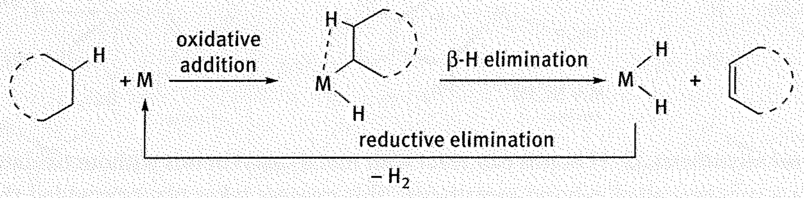
Methane activation:

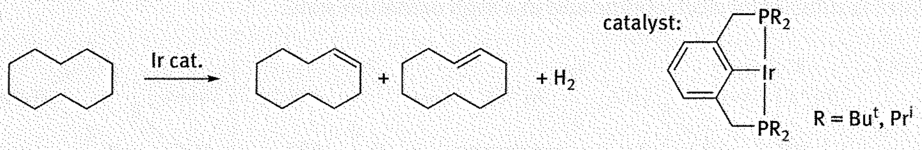


σ-Bond metathesis is industrially important for controlling the molecular weight of olefin polymers by adding judicious amounts of hydrogen to the reactor, to bring about M–C bond hydrogenolysis in Ziegler-type olefin polymerizations.

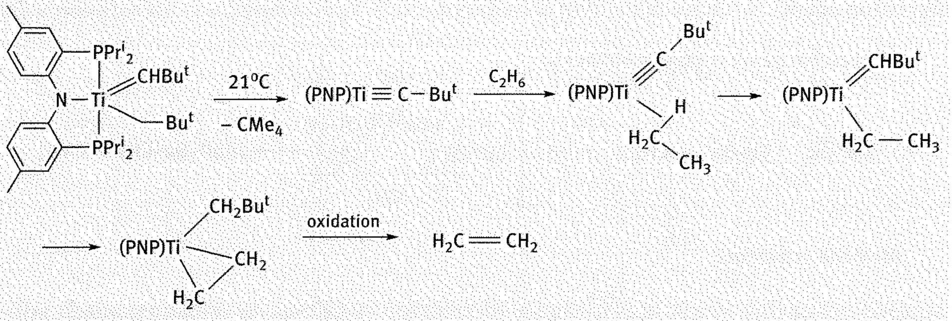
Box 2.10.2 Alkane dehydrogenation and functionalization

Alkane complexes must be involved prior to the activation of C–H bonds of saturated hydrocarbons by transition metals. This reaction generates metal alkyl hydrides, which undergo β-H elimination to give alkenes and metal dihydrides. Provided these MH_2 species reductively eliminate H_2 easily, the reaction results in the catalytic conversion of alkanes into alkenes + H_2. A variant of this reaction includes a sacrificial H_2 acceptor, although this is obviously much less atom-efficient. Low-valent noble metal complexes of pincer ligands carrying strongly donating dialkylphosphino substituents have proved particularly effective as catalysts for the 'acceptor-less' alkane dehydrogenation.

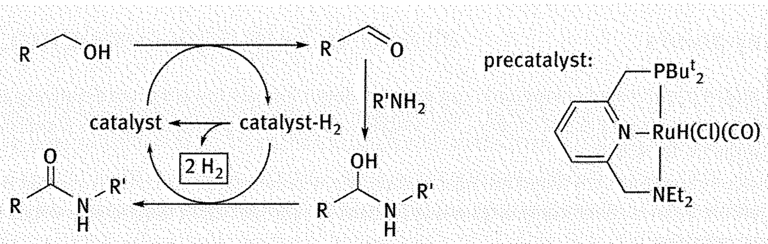




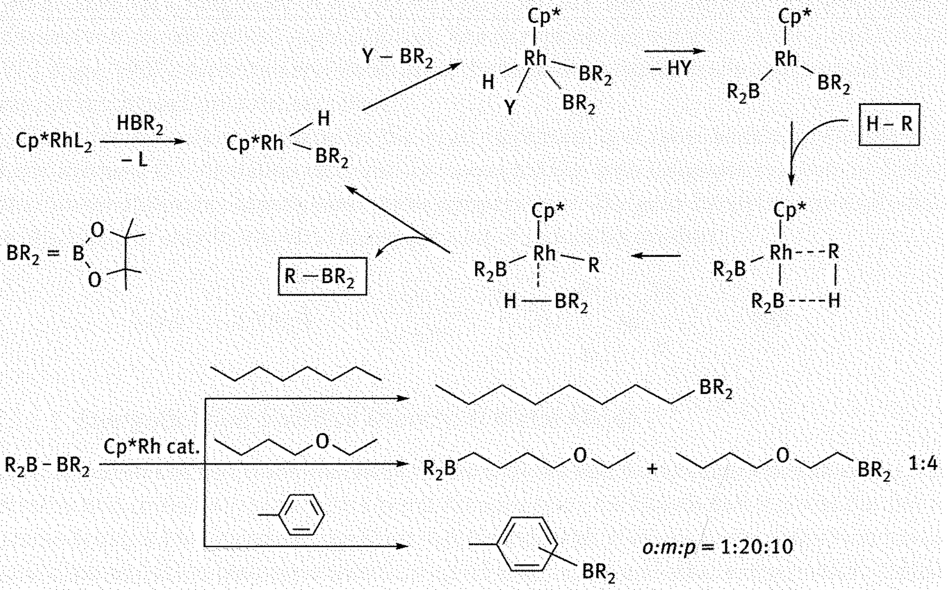
It has been possible to follow the reaction steps in the stoichiometric transformation of ethane into ethylene. In this particular case a titanium(IV) carbyne complex acts as intramolecular H-acceptor during the C–H cleavage. Here, too, tridentate pincer ligands proved useful to allow isolation of the species involved:



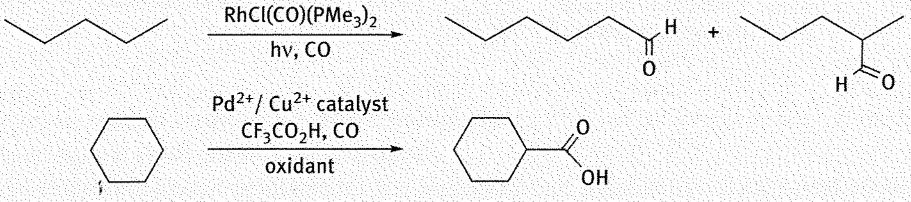
The alkane activation reaction by metal insertion into the C–H bond can be extended to the dehydrogenation of primary alcohols to give aldehydes. In contrast to conventional oxidation, the by-product here is H_2, not H_2O. The reaction can be used to build up complex molecules with H_2 as only by-product.



Alkane activation to give metal alkyl products can be coupled with reductive elimination, to give **functionalized alkanes**. For example, this reaction sequence enables boron substituents to be introduced, as in the Rh-catalysed borylation cycle shown here.



Combining alkane C–H activation with CO insertion, either under reductive hydroformylation conditions or the more general oxidative carbonylation, also gives functionalized alkanes. The reactions, although catalytic in metal, give however only limited turnover numbers.



Key points

The H–X bonds of saturated compounds can act as σ-donor ligands towards coordinatively and electronically unsaturated metal centres. The stability of such complexes decreases significantly in the sequence X = H › Si › C.

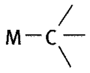
Dihydrogen complexes are found for most metals. Many polyhydride complexes contain H_2 as well as hydride ligands. Such complexes are important in hydrogenation reactions and hydrogen generation catalysis.

A number of silane complexes have been synthesized.

Alkane complexes can be isolated only in exceptional circumstances. They are intermediates in reductive elimination and the C–H activation of hydrocarbons.

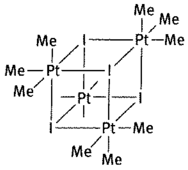
Evidence for alkane complex intermediates is provided by H/D exchange.

2.11 Complexes with M–C σ-Bonds



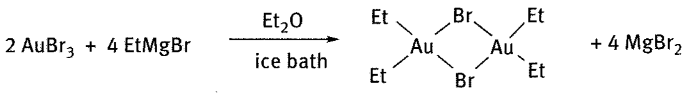
Metal-catalysed processes involve the making and breaking of metal–carbon bonds. This is also the main principle in stoichiometric transformations involving organometallic reagents for many organic synthetic applications. Whenever alkanes, alkenes, alkynes, or arenes are generated, hydrogenated, polymerized, or functionalized, metal alkyl intermediates are involved. The vast majority of all products generated by the chemical industry involves a catalytic step at some stage of the process.

The first deliberately synthesized metal alkyls were the zinc alkyls $ZnEt_2$ and EtZnI prepared by Edward Frankland from 1848 onwards. These were soon followed by other Main Group alkyls including those of silicon, tin, lead, mercury, and aluminium. Alkyl complexes of transition metals proved more difficult. The first examples were $[Et_2AuBr]_2$ and $PtMe_3I$ (W. J. Pope, 1907); the tetrameric structure of the latter with octahedrally coordinated Pt(IV) was not discovered until decades later.



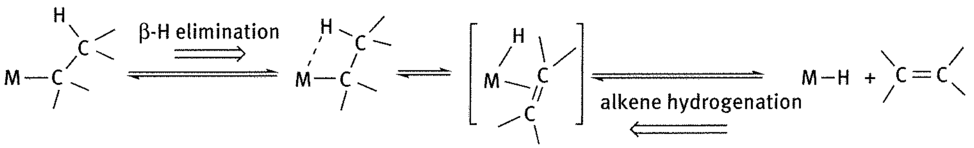
The first transition metal alkyls (Pope, 1907). The tetrameric structure was not discovered until about 50 years later.

These compounds were made by the most important and most widely applicable synthetic method, the alkylation of transition metal halides with Grignard reagents in diethyl ether under a nitrogen atmosphere at low temperatures. The gold diethyl compound could be obtained but only in low yield alongside a lot of reduction product.



2.11.1 Energetics and Stability Aspects of Metal Alkyls

Alkyl complexes of transition metals other than the Pt and Au examples mentioned in the introduction could not be made for several decades. It is now known that this was due not to thermodynamics but kinetics: transition metal alkyls with H atoms in the β-position have a facile decomposition pathway available, by β-H abstraction and alkene elimination. Unlike Main Group elements, for transition metals with unoccupied d-orbitals this **β-H elimination** process is very facile.



Principle of microscopic reversibility

The reaction steps involved in β-H elimination are equilibria; the reverse process is the hydrogenation of an alkene by a metal hydride.

An important design principle for the preparation of isolable transition metal alkyls is therefore the use of alkyl ligands without β-H atoms. Alternatively, stable metal alkyls can be prepared if all available coordination sites are occupied by firmly bound ligands such as Cp and CO, and an electron count of 18 is obtained.

Table 2.11.1 M–C bond dissociation energies[a]

Metal alkyl	D [kJ mol^{-1}]	Metal alkyl	D [kJ mol^{-1}]
$Ti(CH_2CMe_3)_4$	198	$Cp^*_2TiMe_2$	281±8
$Zr(CH_2CMe_3)_4$	249	$Cp^*_2ZrMe_2$	284±2
$Hf(CH_2CMe_3)_4$	266	$Cp^*_2HfMe_2$	306±7
$TaMe_5$	261±5	Cp_2MoMe_2	166±8
WMe_6	160±6	Cp_2WMe_2	221±3
$(OC)_5Mn–CH_3$	187±4	$(OC)_5Mn–Cl$	294±10
$(OC)_5Mn–Ph$	207±11	$(OC)_5Mn–Br$	242±6
$(OC)_5Mn–C(O)CH_3$	160±10	$(OC)_5Mn–I$	195±6
$(OC)_5Re–CH_3$	220±11		
cis-$(Et_3P)_2Pt(Cl)–CH_3$	251±30	$CH_3–I$	238±1
trans-$(Et_3P)_2Pt(Cl)–C_2H_5$	206	$CH_3C(O)–I$	209±3

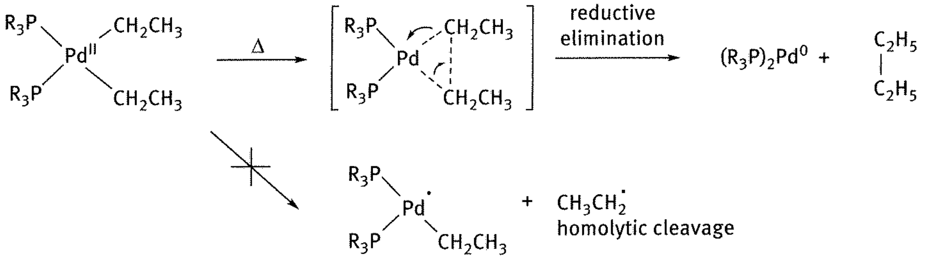
[a] From: J. A. M. Simões, J. L. Beauchamp, *Chem. Rev.* **1990**. *90*, 629.

For bond dissociation energies of Main Group metal alkyls, see Chapter 1.1

The bond dissociation energies D of transition metal–carbon bonds (Table 2.11.1) are comparable to those of Main Group metals. However, in contrast to Main Group elements, the ***bond strength increases down a group***.

As the data show, the M–C bond strengths are comparable to the carbon–iodine bond in alkyl or acyl iodides. Metal–methyl bonds are stronger than those of higher alkyls, confirming that the instability of some methyl complexes is kinetic, not thermodynamic. Bond strengths decrease in the order $M–C(sp^2) > M–C(sp^3) > M–C(O)R$.

In the presence of donor ligands, other decomposition pathways of metal alkyls may come into play. For example, ethyl complexes of palladium phosphine complexes are isolable. The coordination of phosphine ligands disfavours decomposition by β-H elimination, and unlike $PbEt_4$, decomposition by homolytic M–Et bond cleavage and formation of ethyl radicals is also not energetically feasible. Dialkyls of Pd (and other electron-rich metals) can decompose by an alternative process, the reductive C–C coupling of the two alkyl ligands to generate a hydrocarbon of twice the number of C atoms and a zero-valent Pd phosphine complex. This process is termed ***reductive elimination***; it is the termination step in Pd-catalysed C–C coupling reactions. For this reaction to proceed, the two alkyl ligands must occupy neighbouring coordination sites, i.e. they must be in ***cis* position** relative to one another. The process is associated with a significant activation barrier and usually requires heating; unlike β-H elimination, it is irreversible.



While the bond dissociation energies predict stable metal alkyls even if an 18 electron count is not achieved, the stability of metal alkyls like TiR_4 indicates the importance of other factors. $PbEt_4$ is an endergonic compound but can nevertheless be isolated and is stable at room temperature. $TiEt_4$ is exergonic but cannot be made due to facile β-H elimination, as explained in the previous section. However, although this process cannot operate for $TiMe_4$, this methyl compound is also thermally unstable and decomposes > −50 °C. The reason is that given the low electron count—$TiMe_4$ is an 8 VE compound—the metal centre is able to react with C–H bonds in α-position and initiates an α-H decomposition pathway. This implies that for electron-deficient compounds like TiR_4, alternative strategies have to be employed for stabilization.

2.11.2 Types and Bonding Modes of M–C σ-Bonded Ligands

2.11.2.1 M–R Ligand Types

The synthesis of stable transition metal alkyls can be achieved by two strategies:

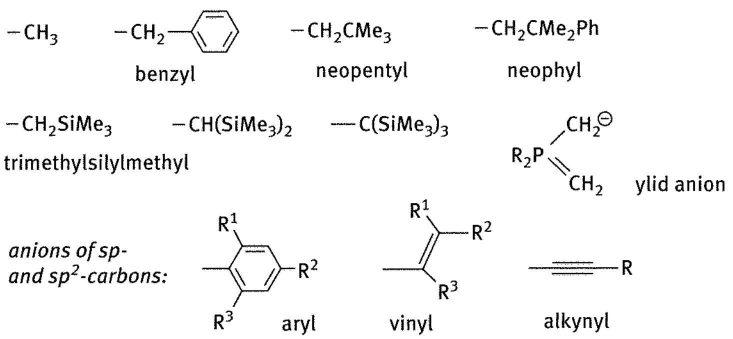
1. Blocking of Coordination Sites With Donor Ligands

A good example of this strategy are 18 VE alkyls like $CpFe(CO)_2$–R (R = Me, Et, etc.), which are air- and moisture-stable and can be isolated by column chromatography. For this reason the $CpFe(CO)_2$ fragment, usually abbreviated Fp, is widely used in organic synthetic applications. Chelating ligands such as 2,2′-bipyridyl (bipy) and mono- or polydentate phosphines fulfil the same purpose. For example, while tetrahedral $TiMe_4$ is thermally highly unstable, the octahedral adduct $TiMe_4$(dmpe) (12 VE) is stable at room temperature, even though it falls far short of the 18-electron rule (dmpe = 1,2-bis(dimethylphosphino)ethane, $Me_2PC_2H_4PMe_2$). There are numerous metal alkyl complexes with a 16 to 18 electron count. The alkyl anion itself may act as stabilizing donor ligand; for example, while $RhMe_3$ is unknown, salts of $[RhMe_6]^{3-}$ are isolable.

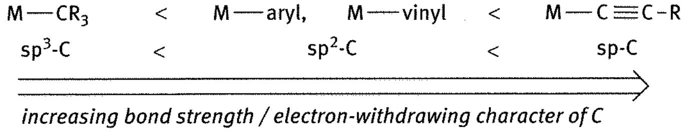
2. Using Alkyl Ligands Stable Towards β-H Elimination

Stability against β-H elimination can be achieved by an absence of β-H atoms, by high steric bulk and by making the β-H elimination step energetically unfavourable. Commonly used ligands include:

β-H free alkyls:

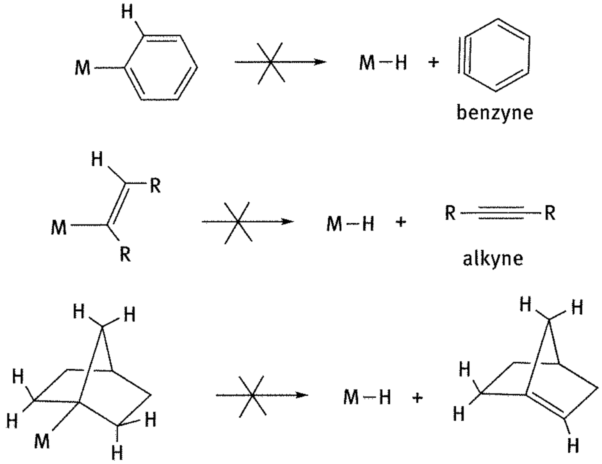


Generally, the metal–carbon bond strength increases with increasing s-character of C:



Aryls and vinyls may contain β-H atoms, but in these cases β-H abstraction is energetically highly unfavourable. The same is true for bridgehead alkyls like 1-norbornyl: although this alkyl has six β-H atoms, β-H abstraction does not occur since this would lead to a highly strained bridgehead alkene:

Bredt's rule: double bonds to bridgehead carbons are unfavourable



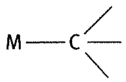
2.11.2.2 M–R Bonding Modes

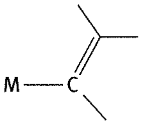
The following metal–alkyl bonding modes are commonly encountered. Terminal and bridging alkyl and aryl complexes are formed depending on the electron demand of the metal centre or centres. Electron-deficient metals may, in addition to the M–C σ-bond, form bonding interactions with C–H bonds in α-, β-, or γ-position to the metal; such bonding type has been termed **'agostic' bonding**. This bonding mode is indicated in structure drawings by a half-arrow.

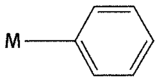
The term 'agostic' derives from a word used by Homer, αγοστω, to clasp, or hold to oneself.

Benzyl ligands contain phenyl substituents that can donate some of the π-electron density to an electron-deficient metal centre, to give η^2- or η^3-benzyl compounds. In η^2-benzyls the M–C–C angle is much more acute than the tetrahedral angle of 109.5°, usually around 90°. Since in such compounds the benzyl ligand is held rigidly, depending on the symmetry of the complex the two CH_2 protons may be inequivalent (diastereotopic) and appear in the ^1H NMR spectrum as an AB spin pattern.

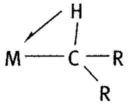
Terminal:



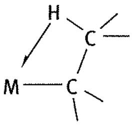




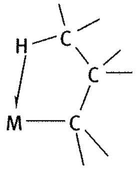
Alkyl bonding to electron-deficient metals:



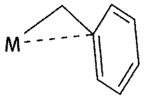
α-agostic



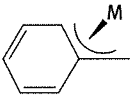
β-agostic



γ-agostic



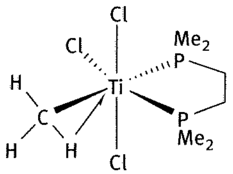
η^2-benzyl, indicated by narrow M–C–C angle

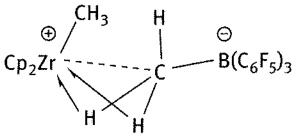


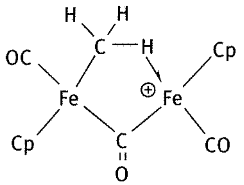
η^3-benzyl

Some examples of complexes with agostic bonding:

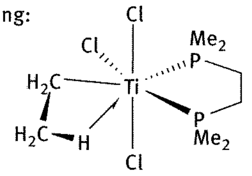
α-agostic bonding:

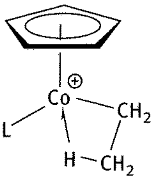






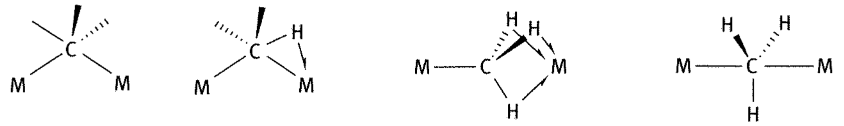
β-agostic bonding:





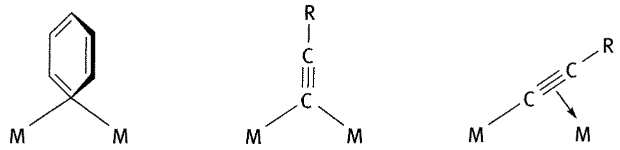
Bridging: Where there is a choice between an sp^3- and an sp^2-hydridized C atom to be placed in the bridging position between two metals, there is a strong preference for the sp^2-C. The same trend has been described for Main Group metals. Since bridging alkyls tend to form with electron-deficient metals, the bridge is often supported by a variety of agostic interactions.

Bridging in highly electrophilic systems:



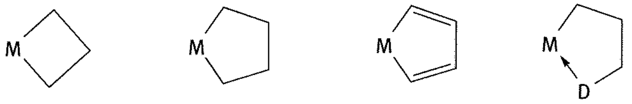
methyl bridges with single and multiple agostic M–H–C interactions

trigonal-bipyramidal 5-coordinate C in μ-CH_3 compounds

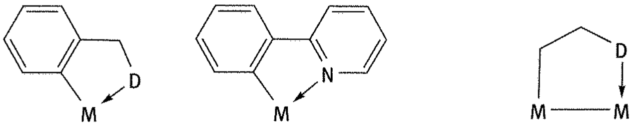


symmetrical and unsymmetrical bridging alkynyl

Metallacycles: Metal alkyls can also form a variety of metallacycles. Five-membered rings tend to be particularly stable. Metallacycles supported by a donor heteroatom are frequent. The heteroatom also directs the location of C–H activation that leads to cyclometallated phenyl pyridine or amino-substituted benzyl compounds.



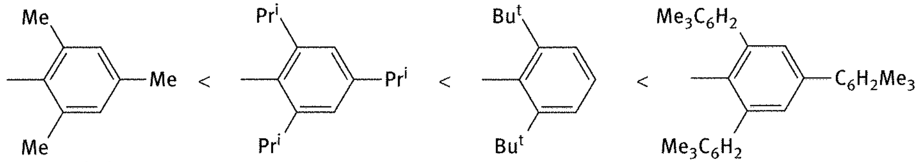
donor-stabilized alkyl



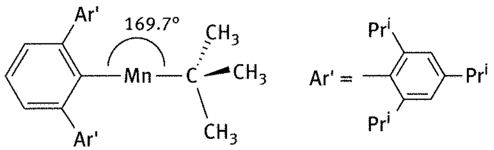
cyclometallated complexes

2.11.2.3 The Importance of Steric Hindrance

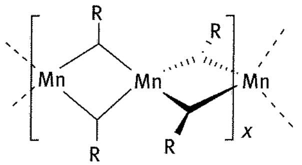
The stability of metal alkyls, particularly of complexes without additional donor ligands, increases with the steric bulk of the alkyl ligand. Thus $Ti(CH_2SiMe_3)_4$ is thermally very much more stable than $TiMe_4$. Bulky alkyls, as well as aryls with *ortho*-substituents, have been widely used to generate thermally stable complexes with low coordination numbers. Aryl ligands with electron-withdrawing groups like C_6F_5 resemble halide anions in their electronic characteristics. The degree of steric shielding provided by bulky, disubstituted aryls 2,6-$R_2C_6H_3$ is largely controlled by the *ortho*-substituents and increases in the sequence R = Me < Pr^i < $Bu^t \approx$ Ph < $C_6H_2R'_3$-2,4,6. The effect of bulky aryls can be seen for example in the mixed-ligand manganese(II) alkyl in the following diagram; although the metal carries a Bu^t ligand with nine β-H atoms, steric hindrance by the very bulky aryl prevents β-H abstraction and the compound is stable to 160 °C. Manganese(II) alkyls with smaller ligands are extremely air-sensitive and form coordination polymers $[Mn(\mu\text{-}CH_2R)_2]_x$, with an alkyl-bridged chain structure which resembles that of magnesium dialkyls.



mesityl 'isityl' 'super-mesityl', Mes*

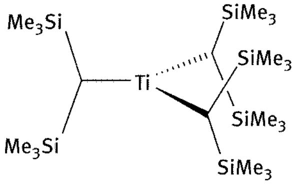


Monomeric, sterically encumbered Mn(II) dialkyl, 9 VE

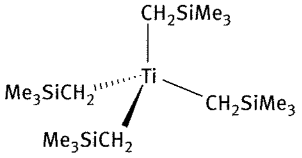


Polymeric Mn(II) dialkyl, e.g. R = Bu^t; 2e3c bonding

Steric hindrance influences the oxidation state a metal centre can attain; e.g. $Ti(CH_2SiMe_3)_4$ (Ti(IV), diamagnetic) can be made, but with even bulkier ligands paramagnetic Ti(III) alkyls result, such as trigonal-planar $Ti\{CH(SiMe_3)_2\}_3$.

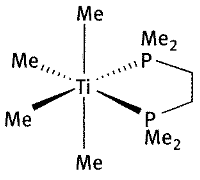


Ti^{III}, d^1, 7 VE, alkyl ligand too bulky to form TiR$_4$

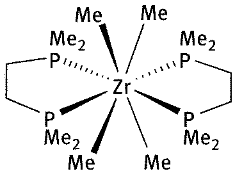


Ti^{IV}, d^0, 8 VE, tetrahedral; preferred geometry and oxidation state for smaller ligands

The interplay of the size of a metal ion, the alkyl ligand, and any donor ligands is also nicely illustrated by phosphine adducts of MMe_4 (M = Ti, Zr) on the one hand, and of Cr(II) dialkyls on the other. Zirconium, as the largest of the transition metals, can form alkyl complexes with coordination numbers as high as 8. For Cr(II), sterically undemanding phosphine ligands allow the formation of metal–metal bonded compounds, while chelate ligands with increasing steric hindrance favour six and four-coordinate mononuclear compounds, with correspondingly diverse magnetic states and reactivities.

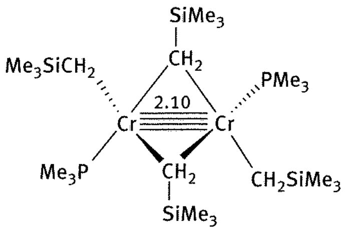


Ti(IV), $r = 0.61$ Å, 12 VE

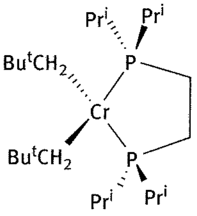


Zr(IV), $r = 0.72$ Å, 16 VE

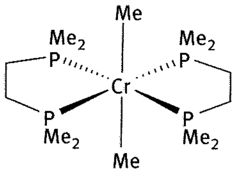
For phosphine-free Cr(II, III) alkyls, see Section 2.11.3



Cr(II), d^4, 14 VE,
distorted square-planar,
Cr–Cr quadruple bond,
diamagnetic



Cr(II), distorted square-planar,
12 VE, d^4, **high-spin**, $\mu_{eff} = 4.9$ B.M.



Cr(II), octahedral, 16 VE,
d^4, **low-spin**, $\mu_{eff} = 2.7$ B.M.

2.11.3 Synthesis of Metal Alkyls

2.11.3.1 Synthesis of Homoleptic Metal Alkyl Complexes

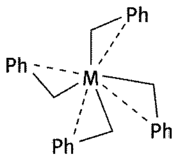
'homoleptic' = complexes containing only one ligand type.
'binary' = compounds consisting of just two different elements.

The most widely applicable synthetic method is the alkylation of transition metal halides with Main Group metal alkyls, both for **homoleptic** metal alkyls and for complexes stabilized by additional donor ligands.

$$TiCl_4 + 2\,Mg(CH_2SiMe_3)_2 \xrightarrow[-78\,°C\text{ to RT}]{Et_2O} \underset{\text{8 VE, yellow, diamagnetic}}{Ti(CH_2SiMe_3)_4} + 2\,MgCl_2$$

The alkylation of MCl_4 (M = Zr, Hf) with benzylMgCl gives the tetra-alkyls $M(CH_2Ph)_4$. Whereas a Main Group alkyl like $Sn(CH_2Ph)_4$ has a regular tetrahedral structure, the Zr and Hf complexes show a variety of M–C–C angles which are much more acute than the tetrahedral angle of 109.5°, in the range of 85–101°. This is indicative of π-interactions with the *ipso*-C atom of the phenyl ring of the benzyl ligands and helps to alleviate the electron deficiency of the complex (formally 8 VE).

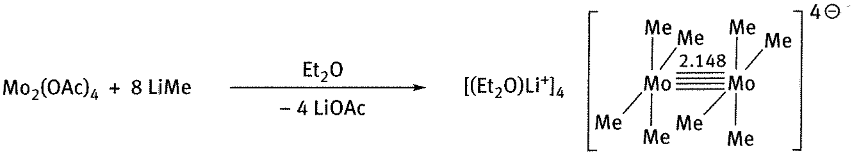
$$\underset{M = Zr, Hf}{MCl_4 + 4\,PhCH_2MgCl} \xrightarrow[-78\,°C\text{ to RT}]{Et_2O}$$



$$WCl_6 + 3\,Al_2Me_6 \xrightarrow[-\,Me_2AlCl]{} WMe_6 \xrightarrow{LiMe} Li[WMe_7]$$

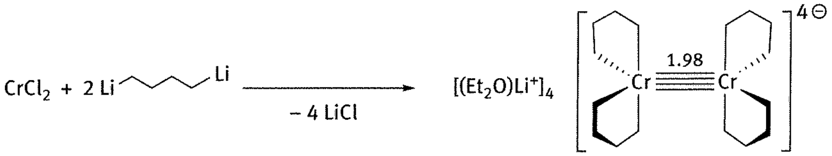
WMe_6: 12 VE,
colourless, diamagnetic
trigonal-prismatic, C_{3v}

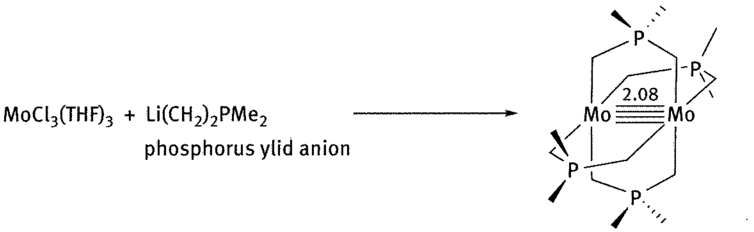
$Li[WMe_7]$: 14 VE anion,
capped octahedron



16 VE, M–M quadruple bond

This method is also suitable for the synthesis of metallacycles:





The **alkylation strength** of Main Group metal alkylating agents decreases with increasing electronegativity of the metal: **LiR** > **RMgX** > **AlR_3** > **R_2AlCl** ≈ **ZnR_2**. Weaker alkylating agents lead to metal alkyl halides:

$$\begin{tikzcd}
& MeTiCl_3 \arrow[r, "ZnMe_2"] & Me_2TiCl_2 \\
TiCl_4 \arrow[ur, "Me_2AlCl"] \arrow[dr, "LiMe"'] & & \\
& TiMe_4 &
\end{tikzcd}$$

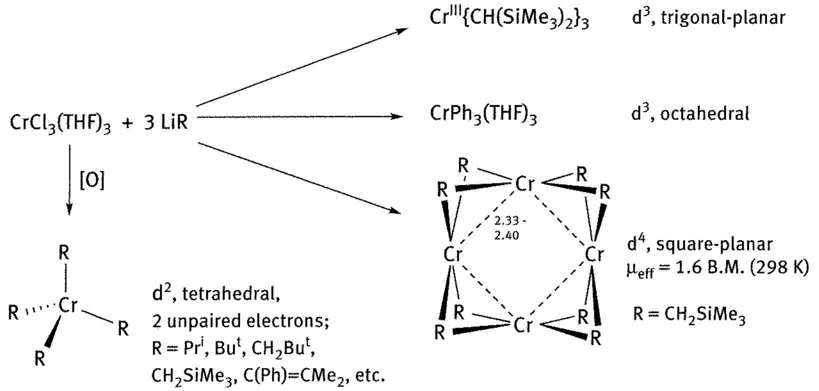
On the other hand, mixed-ligand alkyl halides are often best prepared by comproportionation:

$$TiCl_4 + 4\,PhCH_2MgCl \longrightarrow Ti(CH_2Ph)_4$$

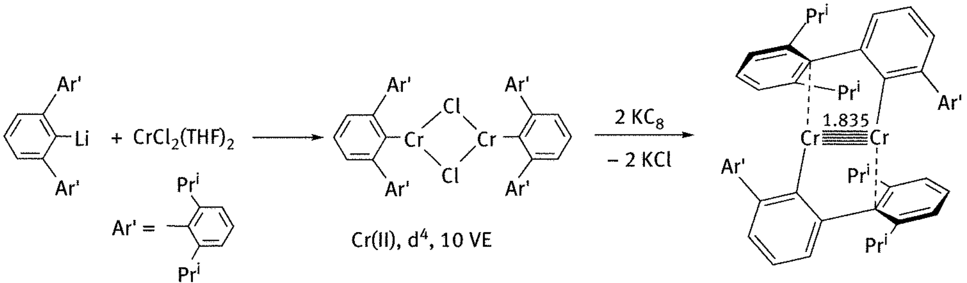
$$3\,Ti(CH_2Ph)_4 + TiBr_4 \longrightarrow 4\,TiBr(CH_2Ph)_3$$

Alkylation reactions may involve a change in oxidation state. For example, the alkylation of $CrCl_3$ is dependent on the size of R and results in Cr trialkyls which are easily oxidized to Cr(IV) products. Since Cr(IV) is a small ion (r = 0.55 Å), even the isopropyl and *tert*-butyl derivatives are surprisingly stable against β-H elimination. CrR_4 complexes are also stable towards hydrolysis. By contrast, smaller ligands like phenyl and coordinating solvents like THF give solvent-coordinated octahedral $CrPh_3(THF)_3$. The reaction of $CrCl_3(THF)_3$ with $LiCH_2SiMe_3$ leads to reduction and formation of tetrameric $[CrR_2]_4$, with square-planar Cr(II) centres held together by alkyl bridges. The compound (d^4) shows temperature-dependent paramagnetism through antiferromagnetic coupling of the metal centres.

Ionic radii:
Cr(II) 0.73 (low spin), 0.80 (high spin)
Cr(III) 0.62 Å
Cr(IV) 0.55 Å

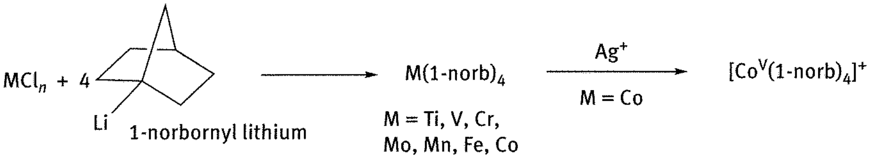


Ligands with high steric hindrance can be used to obtain complexes with very low coordination numbers, which usually implies high reactivity. Such compounds may display interesting bonding modes; for example, with very bulky aryls is has been possible to generate metal–metal bonded dimers where five electrons per metal centre are involved in M–M multiple bonding:



Cr(I) dimer, d^5,
Cr–Cr quintuple bond

With elimination-resistant bridgehead alkyls, the oxidation state of the metal is dictated by the steric requirement of the ligands. Since alkyls are strong σ-donors, they stabilize high formal oxidation states; for Co, oxidation states as high as Co(V) become possible:



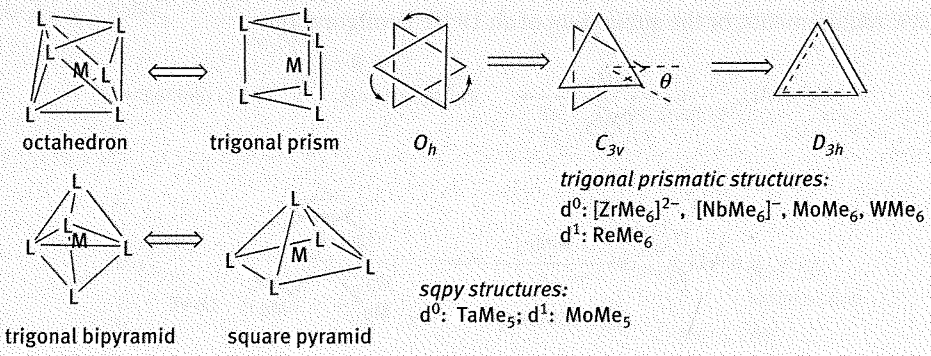
Box 2.11.3.1 The structures of homoleptic metal methyl complexes

Homoleptic complexes with six methyl ligands, like WMe_6 and $ReMe_6$, were originally thought to be octahedral. However, MO calculations have shown that complexes containing only σ-donor ligands should be **trigonal-prismatic**, and this was indeed found. These structures contradict the simple point-charges-on-a-sphere model of metal complexes and cannot be explained by considering steric interactions, ligand field theory or by conventional VSEPR (valence shell electron pair repulsion) theory.

Octahedral and trigonal-prismatic geometries can be interconverted by rotation of one triangular face relative to the other by an angle θ (**Bailar twist**), such that the octahedron represents one extreme ($\theta = 60°$) and the trigonal prism the other ($\theta = 0°$).

In most cases the complexes deviate from these ideals. While negatively charged anions like $[ZrMe_6]^{2-}$ are close to D_{3h} symmetry, presumably because of the repulsive influence of the charge, in neutral compounds some further stabilization can be achieved by reducing the symmetry to C_{3v}, as in WMe_6.

Similarly, the pentamethyls MMe_5 (M = Ta, Mo) are square-pyramidal rather than trigonal-bipyramidal. The general principle in these σ-donor complexes seems to be the avoidance of interligand angles of 180°.



trigonal prismatic structures:
d^0: $[ZrMe_6]^{2-}$, $[NbMe_6]^-$, $MoMe_6$, WMe_6
d^1: $ReMe_6$

sqpy structures:
d^0: $TaMe_5$; d^1: $MoMe_5$

By contrast, **ligands with π-bonding capability stabilize octahedral or tbp structures**. For this reason $W(CO)_6$ as well as halides like MoF_6 and WCl_6 are octahedral, as are alkoxides and amides. Complexes with σ-donors but high electron count are also close to octahedral, for example $[RhMe_6]^{3-}$ (d^6, 18 VE, $\theta = 45°$).

2.11.3.2 Synthesis of Heteroleptic Metal Alkyl Complexes

Metal alkyl complexes stabilized by additional L or LX-type ligands are also commonly made from the corresponding metal halides. However, there is less danger of β-H elimination if an electron count of 18 is achieved. Whereas homoleptic metal alkyl complexes are in most cases sensitive to oxidation and/or M–C bond hydrolysis, alkyl compounds like $CpFe(CO)_2(R)$ and related metal carbonyl alkyls are air and moisture stable. 16 VE species and Cp-stabilized metal alkyls of early transition metals are more sensitive to air and protic reagents; nevertheless, they are thermally more stable than homoleptic alkyls.

'heteroleptic': complexes containing more than one type of ligands.

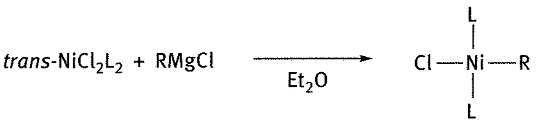
There are a number of alternative ways of generating M–C σ-bonds that do not involve salt metathesis reactions.

By alkylation of metal halides:

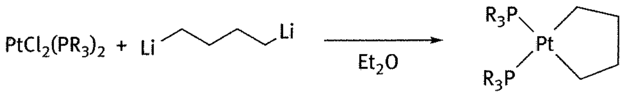
$$\mathrm{Cp_2MCl_2 + 2\,LiR \xrightarrow[-78\,^{\circ}C\ \text{to}\ RT]{Et_2O} Cp_2MR_2 + 2\,LiCl}$$

M = Ti, Zr, Hf

16 VE, yellow, diamagnetic



16 VE,
L = $\mathrm{PMe_3}$

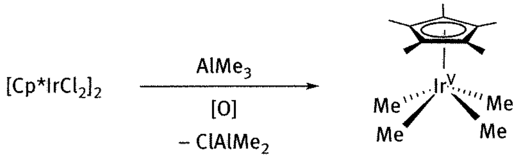


16 VE
colourless

Alkylation reactions may involve a change in oxidation state. The driving force may be steric requirements, or the attainment of an 18 VE configuration:

$$\mathrm{Rh^{II}{}_2(OAc)_4 \xrightarrow[PMe_3]{MgMe_2} Rh^{III}Me_3(PMe_3)_3}$$

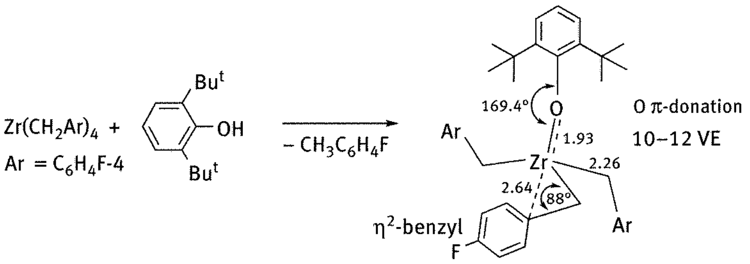
18 VE, diamagnetic



18 VE

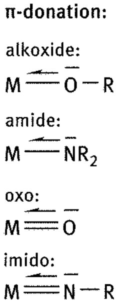
While metal alkyls stabilized by phosphine or cyclopentadienyl ligands are most common, there are also many examples of complexes stabilized by **π-donor ligands**, i.e. heteroatom ligands carrying a lone pair which interacts with a vacant metal orbital in π-donor fashion (see Section 2.4.3). These complexes contain metals in high oxidation states. The π-donation increases the electron count of the metal centre, although the exact extent of this contribution is not always unequivocally clear. The result is a shortening of the M–E bond length, while in metal alkoxides and aryloxides the M–O–C angles widen and approach 180°.

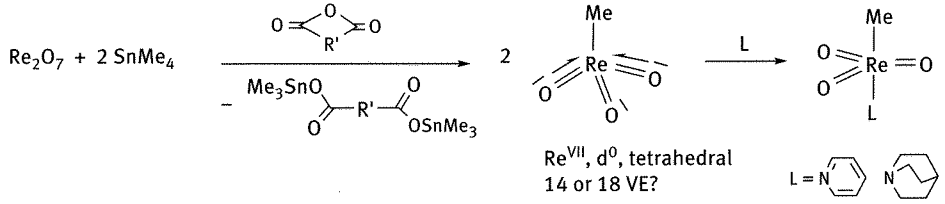
The zirconium benzyl complex shown in the following schematic also demonstrates the η^2-coordination of a benzyl ligand, which is typical for electron-deficient benzyl complexes.

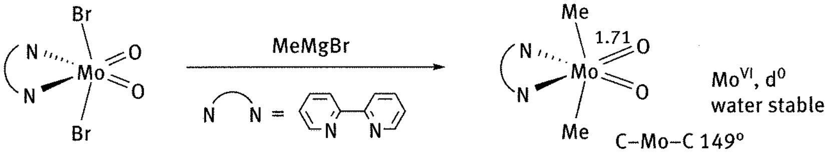


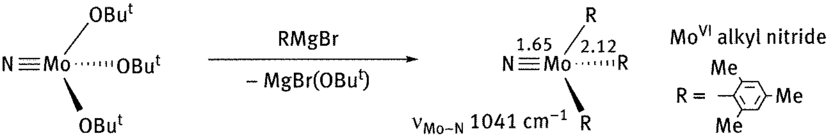
Metal alkyls with oxo and imido ligands are widely used in a number of catalytic reactions. These dianionic ligands form M=E double bonds and formally contribute two electrons, but through π-donation can act as 4-electron ligands. Complexes with M=O and M=N bonds are common for the Group 5–7 triads, particularly for second and third row elements.

A classic example is $MeReO_3$, a catalyst for oxidation and O-transfer reactions. The oxo ligands provide π-electron donation; however, this can be replaced by stronger donors such as pyridine, so that these complexes behave like Lewis acids.







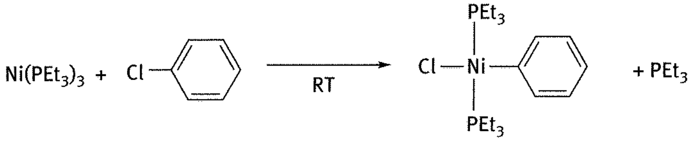


Oxidative addition. The addition of electrophiles H–X and R–X to low-valent transition metal complexes is a key reaction in many catalytic cycles. Since both R and X can formally be regarded as anionic, i.e. they consist of atoms with a higher electronegativity than the metal centre, the process amounts to an oxidation of the metal by two units. The reaction is facilitated by electron donating ligands, which help to generate metal centres with energetically high-lying occupied d-orbitals. Phosphine or carbene complexes of M^I (M = Co, Rh, Ir) and M^0 (M = Ni, Pd, Pt) metal centres are typical reaction partners. The classical example of a complex that undergoes oxidative addition with a multitude of substrates is **Vaska's complex,** $IrCl(CO)(PPh_3)_2$.

Oxidative additions often involve changes in coordination geometry: tetrahedral M^0 compounds (M = Group 10 metal) become square-planar M^{II} (d^8), and square-planar M^I (M = Group 9 metal) become octahedral M^{III} (d^6).

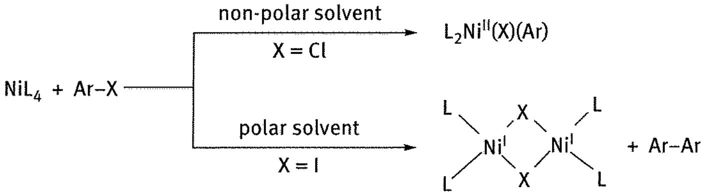
$$\underset{\text{Vaska's complex}}{Ir^{I}Cl(CO)L_2 + R\text{–}X} \longrightarrow \underset{\text{several stereoisomers possible}}{Ir^{III}R(Cl)(X)L_2 \quad L = \text{phosphine}}$$

Very electron-rich metal centres, like trialkylphosphine complexes of Ni(0), are able to oxidatively add even chemically inert bonds, such as C–Cl in chloroarenes, to give M-aryls under very mild conditions:



C–C coupling: Chapter 3.6

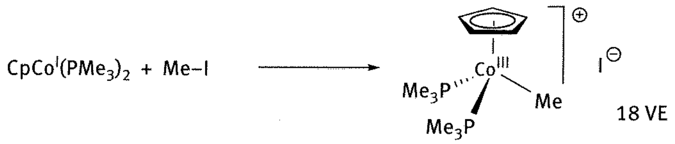
Oxidative addition reactions with Ni, Pd, and Pt complexes normally lead to the formation of M(II)–C bonds—indeed the widely used Pd-catalysed C–C cross-coupling reactions depend entirely on the success of this reaction. However, depending on the nature of the halide and the solvent, on occasions 1-electron pathways may compete with 2-electron oxidative addition reactions. Radicals may form, leading to metal products of intermediate oxidation states, e.g. Ni(I):

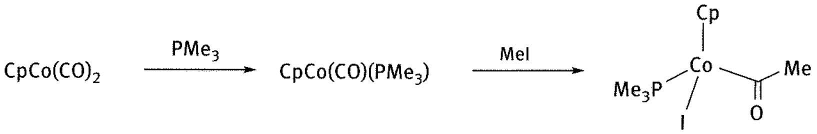


Oxidative addition of alkyl halides to Cr(II) salts leads to solvated Cr(III) mono-alkyls. These octahedral complexes are kinetically inert (d^3 electron configuration!) and are not attacked by acids or water.

$$Cr(ClO_4)_2 + PhCH_2Cl \xrightarrow{HClO_4,\ H_2O} [PhCH_2\text{–}Cr(OH_2)_5]^{2+}[ClO_4^-]_2$$

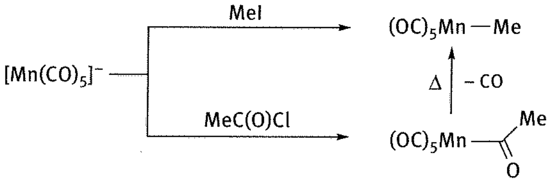
Tri-alkyl phosphines can make the metal centre highly basic, which aids oxidative addition. However, if the halide ligand cannot be accommodated in the coordination sphere, ionic products may result, as in the reaction of $CpCo(PMe_3)_2$ with MeI, which proceeds along the same lines as the quaternization of an amine. The unreactive electron-poor CO analogue $CpCo(CO)_2$ oxidatively adds MeI after activation with PMe_3, to give an acyl complex:



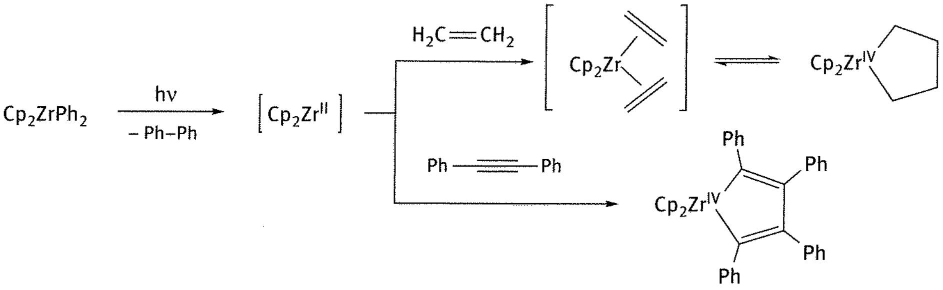


The reaction of metal carbonyl anions with organic halides to give metal alkyls or acyls also amounts to an oxidative addition to the metal. These are classical standard methods of M–C bond formation in 18 VE complexes. Since the products are coordinatively saturated with strongly bonded CO and Cp ligands, kinetic instability due to β-H elimination is not a problem, and ethyl or butyl derivatives are easily prepared.

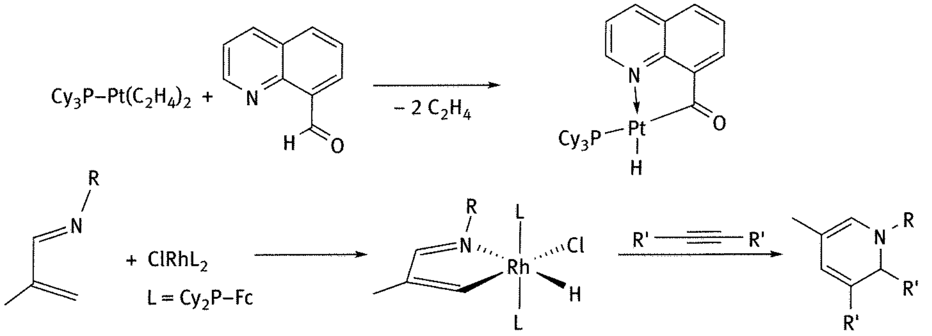
$$[CpFe(CO)_2]^- + Et{-}I \longrightarrow CpFe(CO)_2{-}Et + I^-$$



Early transition metals, with their high-energy d-levels, show a strong tendency to form complexes with the metal in the highest possible oxidation state. For example, the reaction of Zr(II) complexes with alkenes and alkynes in the absence of further donor ligands leads to oxidative C–C coupling and the formation of metallacycles of Zr(IV):

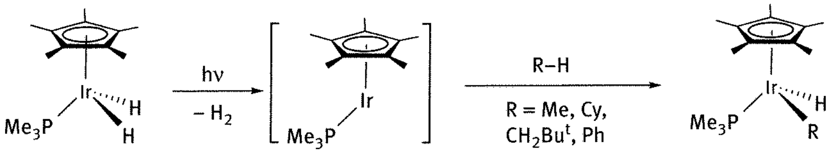


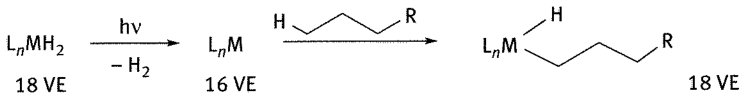
A special case of oxidative addition is the **addition of C–H bonds** to a low-valent metal. These allow functionalization of hydrocarbons and new C–C bonds to be formed without the need for organic halides. C–H bond activation of this kind is greatly facilitated by donor atoms in close proximity which allow the formation of 5-membered chelate rings. This reaction proceeds predominantly with sp^2-CH bonds. Some examples are shown in the following diagram; the Rh(III) metallacycle reacts further with alkynes in a catalytic route leading to variously substituted dihydropyridines which can be oxidized to pyridines.



See also alkane complexes, Section 2.10.2

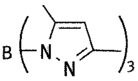
While most such oxidative additions involve sp^2-C–H bonds, electron-rich low-valent metal centres have been shown to be capable of oxidatively adding saturated hydrocarbons. These reactions were first demonstrated for Ir(I) which also reacts with CH_4, but many other 16 VE metal species with strong donor ligands display similar reactivity:



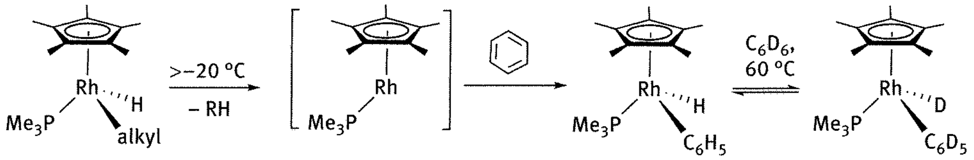


ML_n = $Fe(Me_2PC_2H_4PMe_2)_2$, $Cp^*Re(PMe_3)_2$, $Cp^*Rh(PMe_3)$, $Pt(Cy_2PC_2H_4PCy_2)$,

$Tp^*Rh(CNR)$; Tp^* = HB



Aromatic C–H bonds undergo oxidative additions to metals more readily than aliphatic C–H bonds. This is in spite of the fact that sp^3-C–H bonds (ca. 385–425 kJ/mol) are weaker than sp^2-C–H bonds (460 kJ/mol). Rhodium alkyl hydrides reductively eliminate much more readily than the Cp* iridium example shown here, and they can therefore be used as a facile source of the Cp*Rh(L) fragment, which reacts with arenes. Arene C–H activation, too, is reversible but requires more activation energy. Heating the resulting Rh hydrido phenyl complex in C_6D_6 leads to H/D exchange:

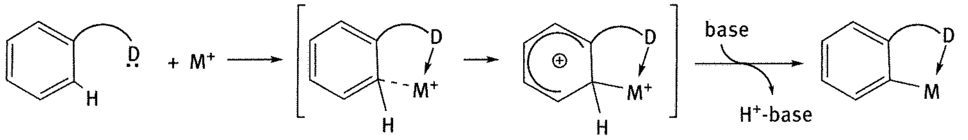


H/D exchange via reversible C–H addition/elimination

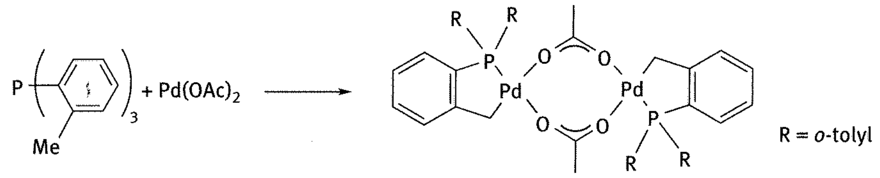
In competition experiments between benzene and *n*-propane, a mixture of Rh(H)(Pr^n) and Rh(H)(Ph) species are formed in a ratio of 1:4, even though both hydrocarbons have about the same statistical likelihood of C–H activation.

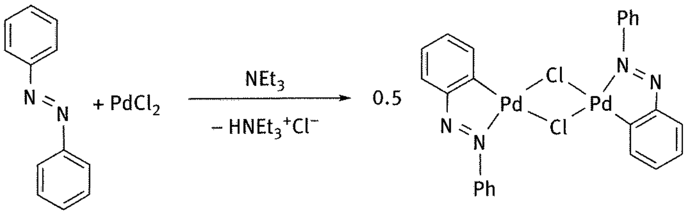
By electrophilic attack: cyclometallation. The reactions shown in the previous diagrams involve the oxidative addition of C–H bonds to give metal hydride complexes. It is more common, however, to generate similar complexes by the attack of an electrophilic metal centre on an sp^2-C–H bond, followed by deprotonation. In that sequence, the metal is in a sufficiently high oxidation state to act as an electrophile, and the oxidation state does not change during this process.

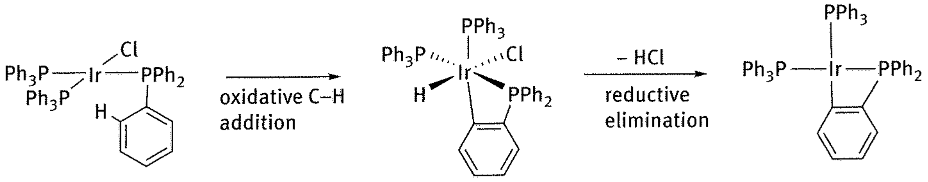
A similar process has been described in Section 1.4.3.1 between Hg^{2+} and arenes, which gives aryl mercury compounds. The attack of transition metal electrophiles is facilitated by a donor atom **directing group**, usually N or P, which coordinates to the metal so that the subsequent slower C–H activation reaction proceeds regioselectively in one of several possible positions. The outcome is the formation of a metallacycle with the M–C bond in *ortho* position to the substituent, the so-called ***ortho*-metallation** or **cyclometallation**. This is the driving force for very numerous subsequent functionalizations and C–C coupling reactions, which all rely on metallacycle formation by the *ortho*-metallation sequence.



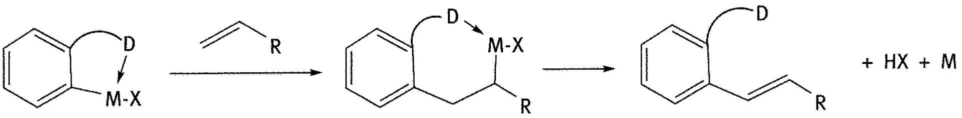
Ortho-metallation is common for palladium(II) compounds and has been widely exploited in synthesis. One of the earliest examples is the *ortho*-palladation of azobenzene. Phosphine ligands are also prone to *o*-metallation, both on the phenyl ring and on *o*-Me substituents.





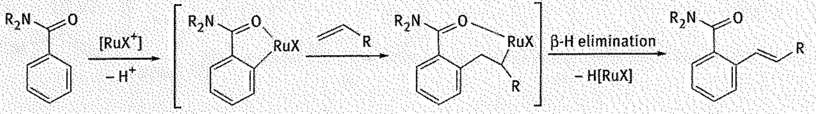


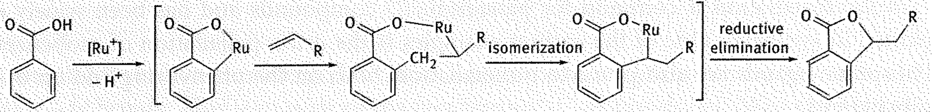
The *ortho*-metallation step may be followed by an insertion into the C–M bond, so that a new C–C bond in *ortho*-position is formed.



Cyclometallated complexes also have widespread applications as sensors and in organic light-emitting diodes (OLEDS).

Box 2.11.3.2 Synthetic examples of the *ortho*-metallation/alkene insertion sequence are the following Ru-catalysed transformations:





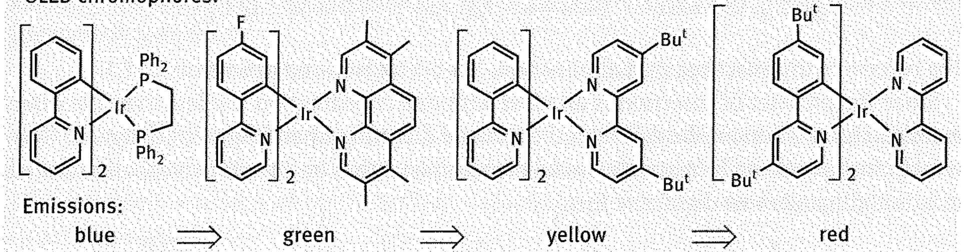
pre-catalyst: $[RuCl_2(p\text{-cymene})]_2/Cu(OAc)_2$

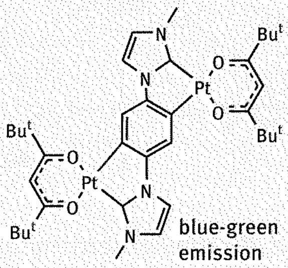
Cyclometallated aryl complexes for light emission devices and sensors

Complexes of electron-rich third row transition metals with cyclometallated ligands often show unusually strong photoluminescence. Strong σ-donors are required to push up the energy of the d-orbitals, and on photo- or electro-excitation these complexes emit light in a range of colours, depending on the ligand environment. The complexes can be incorporated as dopants into films of electroactive polymers to give organic light-emitting diodes (OLEDs) for flat screen displays and provide a way to tune the uniform emission of the polymer into a colourful display across the visible spectrum. Other applications are as white light sources, as luminescent probes for bio-imaging of cell structures, or as chemosensors. A few examples of luminescent chemosensors are shown in the following diagram; they either change their emission wavelengths when binding to the desired substrate, or the fluorescence is quenched. The key to all these applications is the design of the ligands.

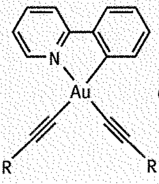
High ligand fields, i.e. strong bonding interactions, are produced by using **cyclometallated** aromatic ligands with low-lying π-systems, mostly based on a chelating phenylpyridine motif. The emission colour depends on the electron donating or withdrawing substituents. The structure of the complexes also influences the quantum yield and the lifetime of the excited state, which ranges from nanoseconds to microseconds (fluorescence to phosphorescence). Iridium^{III} (d^6) and Pt^{II} (d^8) have been particularly widely studied. Since OLED flat screen displays do not require back-lighting to be visible, they can be made flatter than liquid crystal displays and require less energy.

OLED chromophores:

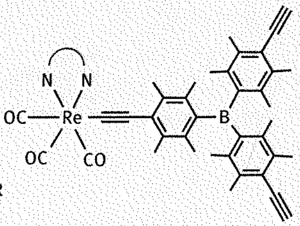




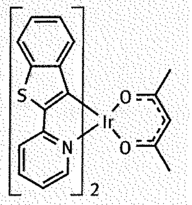
blue-green emission



blue-green to yellow emission

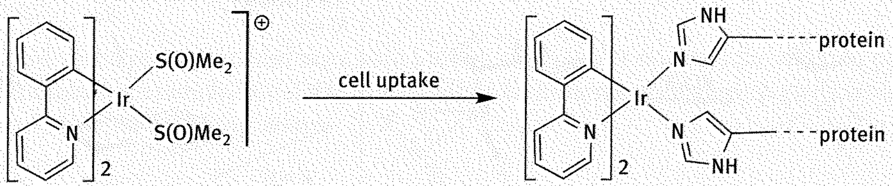


Fluoride sensor: yellow, F^- binding: deep orange



Mercury sensor: deep-red emission, quenched by Hg^{2+}

Cyclometallated iridium(III) complexes have also been used for fluorescence imaging of live cells. The DMSO complex $[(C^\wedge N)_2Ir(DMSO)_2]^+$ is non-emissive, but in cells it binds to histidine-containing proteins in nuclear membranes to give an intensely luminescent adduct. The compound accumulates rapidly in the nuclei.

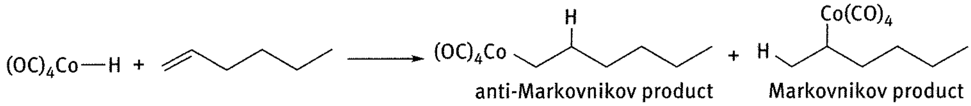


non-emissive

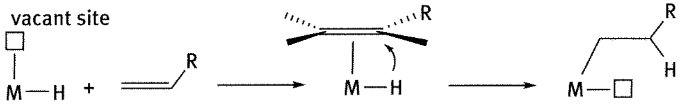
fluorescent

For alkene reactions with Schwartz's reagent, Cp_2ZrHCl, see Section 2.8.2.3.

M–C bonds by M–H insertion reactions. Alkenes and alkynes readily insert into M–H bonds to give metal alkyls or metal vinyls, respectively. The insertion of alkenes into M–H bonds is a key step in several catalytic reactions, such as hydrogenation, hydroformylation, carbonylations, and polymerizations.

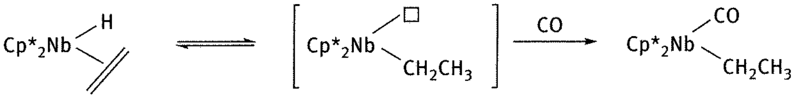


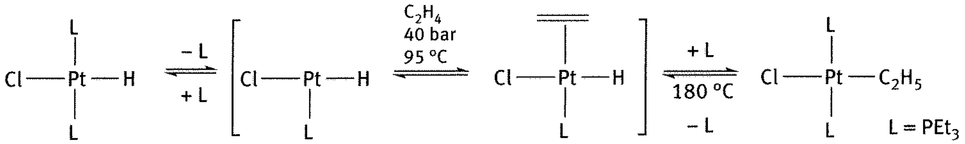
Mechanistically, alkene insertions constitute an intramolecular nucleophilic attack on a coordinated ligand, i.e. the reaction is a migration of H^- onto the unsaturated substrate. For this step to proceed, the hydride and the alkene must be mutually in *cis* position, so that the olefinic C atoms, H, and M are arranged in one plane.



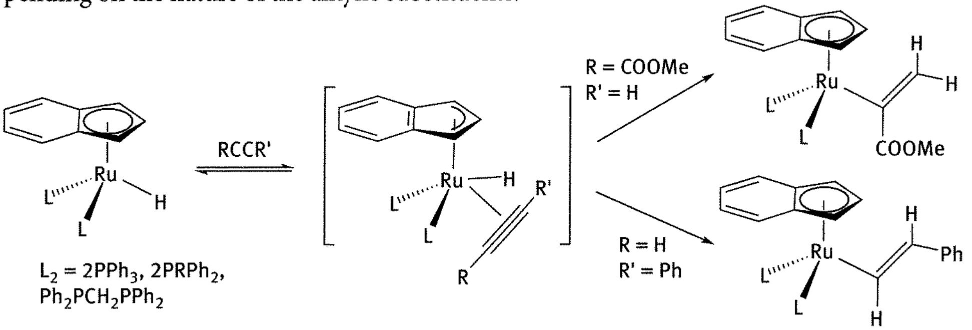
The reverse of this reaction, β-H elimination, has been discussed in Section 2.11.1.

Since the product of insertion is an alkyl with one coordination site less than the intermediate, the reaction can be driven in the forward direction by adding a donor ligand. Conversely, for the alkene to react, the metal centre must either be coordinatively unsaturated, or a donor ligand must dissociate first.

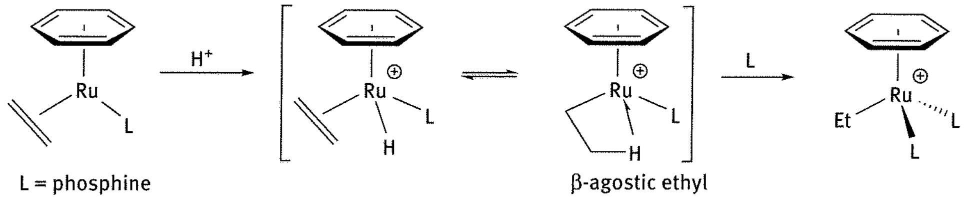


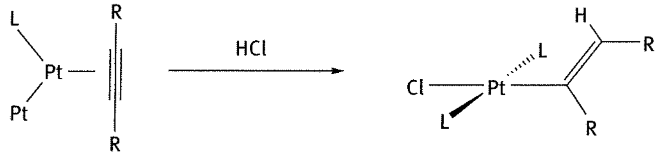


Alkynes insert into M–H bonds, particularly activated alkynes like dimethylacetylene dicarboxylate (DMAD). In case of 18 VE starting materials like $(Ind)RuHL_2$, either dissociation of L or indenyl ring slippage occurs to create the coordination site required for acetylene binding; the Cp analogue is much less reactive. The insertions proceed regioselectively, depending on the nature of the alkyne substituents.



The same process is followed in the protonation of metal alkene and alkyne complexes:

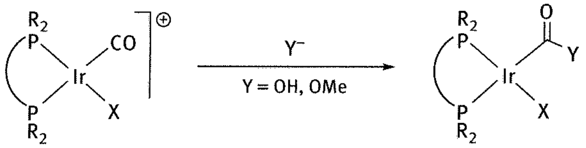


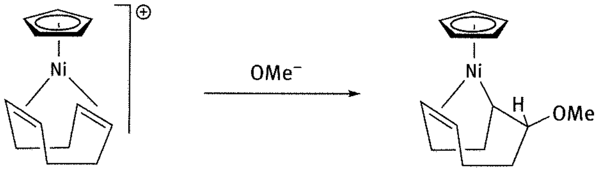


Another method of generating M–C bonds from hydrides is the insertion of carbenes. For example, diazomethane reacts with acidic metal carbonyl hydrides to give the corresponding methyl complexes:

$$\mathrm{CpMo(CO)_3H + CH_2N_2 \longrightarrow CpMo(CO)_3CH_3 + N_2}$$

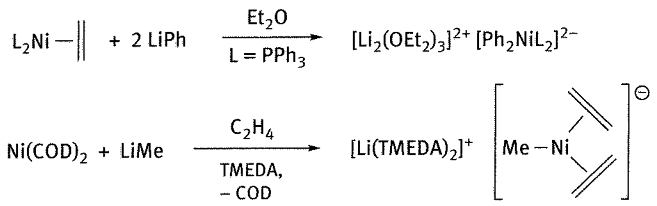
M–C bonds by nucleophilic attack. Unsaturated polar ligands like CO, isocyanides, alkenes, and alkynes are susceptible to nucleophilic attack to give M–C σ-bonded complexes. Like insertion reactions of metal hydrides, reactions of this type are frequently found in catalytic processes.





Zero-valent metals can also react with lithium alkyls under nucleophilic addition of the alkyl anion. For example, $Ni(COD)_2$ adds LiMe in the presence of ethylene to give the highly reactive $[Me\text{–}Ni^0(C_2H_4)_2]^-$ anion.

As Ni(0), d^{10} complexes, anions $[R_2NiL_2]^{2-}$ are tetrahedral, while $[MeNi(C_2H_4)_2]^-$ is planar.

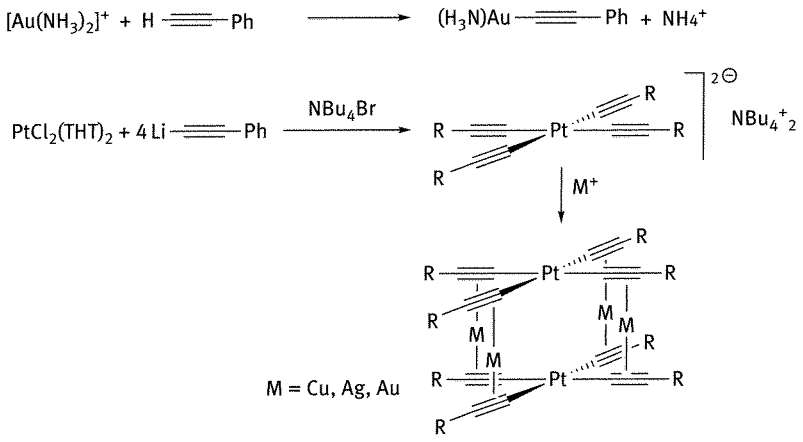


2.11.3.3 Alkynyl Complexes

pK_a (DMSO):
PhC≡C–H 28.8
C_2H_4 44
C_6H_6 43
$PhCH_3$ 41
CH_4 ~60

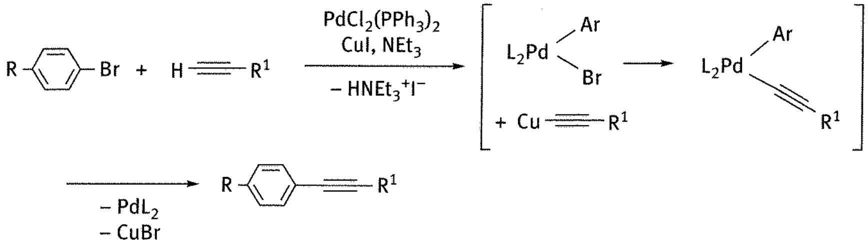
Terminal alkynes are very much more acidic that alkanes, alkenes, and arenes. As a result, the alkynyl anion is much more stable and coordinates to many metal complexes in a manner not dissimilar to cyanide. It is a good π-acceptor and forms stable complexes with most metals, including homoleptic metal alkynyl complexes where the corresponding alkyls are either not known or are very difficult to prepare. The increased acidity means that alkynyl complexes can be prepared from alkynes and metal salts by the addition of relatively weak base.

Since the alkynyl ligand contains two perpendicular π-systems, it can act as π- as well as σ-donor and often forms alkynyl-bridged higher aggregates. Metal alkynyl complexes can also act as π-ligands towards a number of other metal ions, often coinage metals, to give heterometallic alkynyl clusters with interesting light emission properties. For example, the Pt_2Cu_4 cluster shown here exhibits luminescence in the near-infrared region. The light emission of other polynuclear Au_xAg_y alkynyl clusters can be tuned from blue to red.

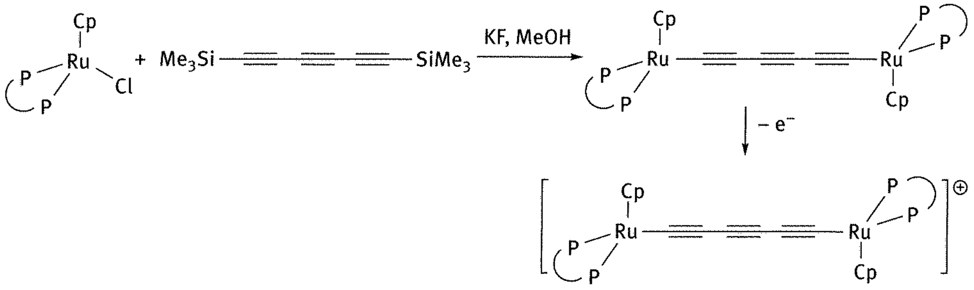


Sonogashira coupling

Metal alkynyl complexes are involved in the palladium-catalysed coupling of aromatic halides with terminal alkynes (*Sonogashira coupling*):



Dimetallic poly(alkynyl) complexes $L_nM–(C{\equiv}C)_x–ML_n$ form 'molecular wires'. They undergo redox reactions to give mixed-valence compounds. Structures of this type are of interest as switches in nanoelectronics and molecular logic devices. For example:



2.11.4 **Reactivity of Metal Alkyls**

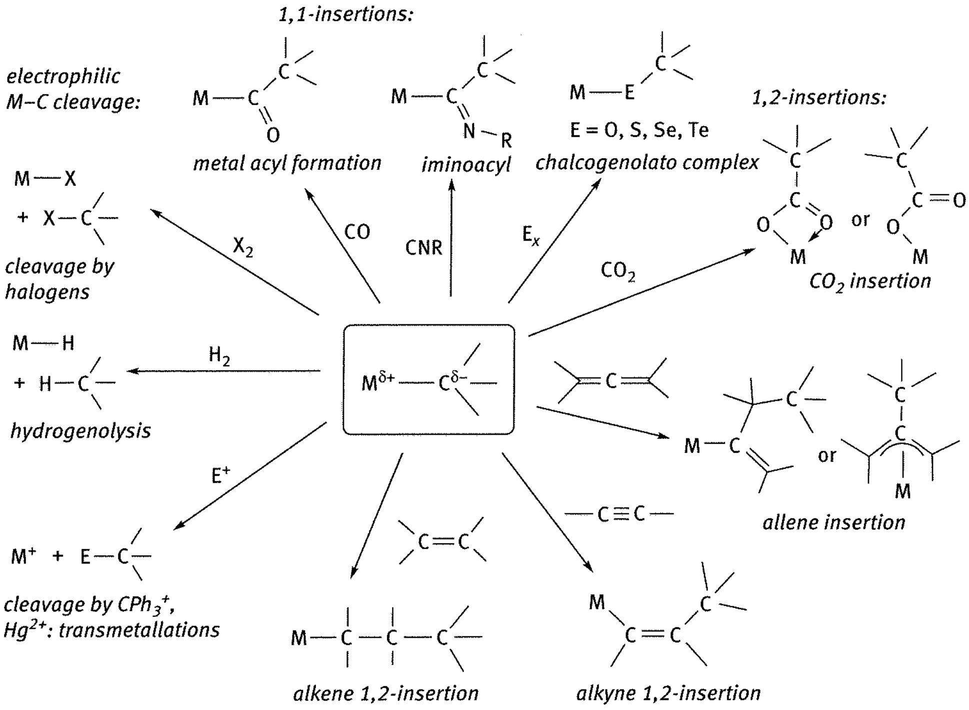
The formation and breaking of metal–alkyl bonds is an integral part of most catalytic reactions. These applications will be discussed in Part 3. Here we will consider typical reactivity patterns of metal alkyl complexes. The reactions can be broadly divided into two types:

(i) reactions of the M–C bond, where the other L- or X-type ligands have a supporting and protecting role, and

(ii) reactions of supporting ligands, leaving the M–C bonds unchanged.

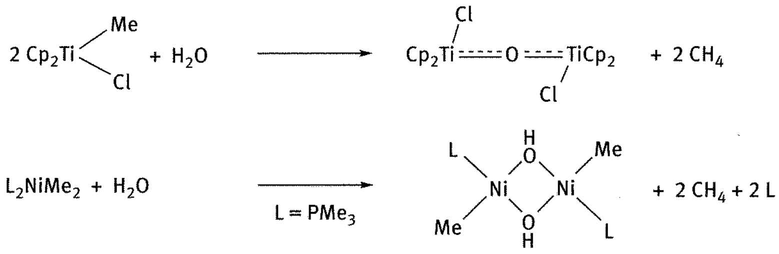
Given the polarity of $M^{\delta+}–C^{\delta-}$ bonds, they tend to be susceptible to **electrophilic attack**. The electrophile can be ***external***, in the simplest case H^+, or ***internal***, where the electrophile may be an unsaturated ligand with an acceptor orbital coordinated in *cis* position to the M–C bond. This arrangement leads to migratory insertion.

The susceptibility towards H^+ attack depends on the nature and oxidation state of the metal and on the electronegativity difference between metal and carbon. Thus, early transition metal alkyls tend to be hydrolytically sensitive, while alkyls of platinum or gold are usually water stable. Electron-deficient metal alkyls, especially those in Groups 3–5, frequently undergo σ-bond metathesis, e.g. with H_2 (cf. Section 2.10.2).



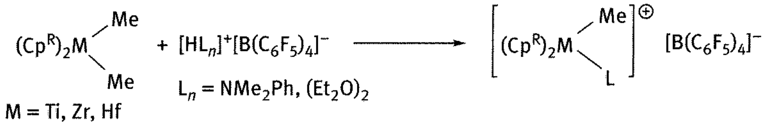
2.11.4.1 M–C Bond Protonolysis

The reaction with sources of H^+, most commonly water, proceeds easily with early transition metal alkyl complexes with less than 18 electrons. The hydrolysis of $Cp_2Ti(Me)Cl$, for example, leads to an oxo-bridged binuclear complex; the Ti–O–Ti bridge is linear because of π-bonding of the oxygen lone pairs to vacant Ti orbitals. Reactive, electron-rich first row metal alkyls may also be prone to hydrolysis.



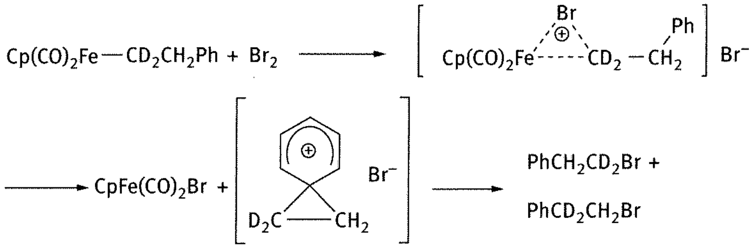
The reaction of electron-deficient metal alkyls with phenols proceeds stepwise as a mild route to mono- and bis-aryloxides (provided the aryls are sufficiently bulky to prevent the formation of polymeric aryloxide-bridged coordination polymers). Ammonium salts are stabilized Brønsted acids and give cationic metal alkyls. This reaction is used in particular with Group 4 metallocene dialkyls; if the anion is very weakly coordinating, as is the case with $[B(C_6F_5)_4]^-$, cationic metallocene complexes result which are highly active catalysts for olefin polymerization. In the case of $[HNMe_2Ph]^+$ salts the aniline by-product coordinates only weakly to the metal centre and can be displaced by the olefin substrate.

$$Zr(CH_2Ph)_4 \xrightarrow[-\,\text{toluene}]{Ar'OH} (Ar'O)Zr(CH_2Ph)_3 \xrightarrow[-\,\text{toluene}]{Ar'OH} (Ar'O)_2Zr(CH_2Ph)_2$$



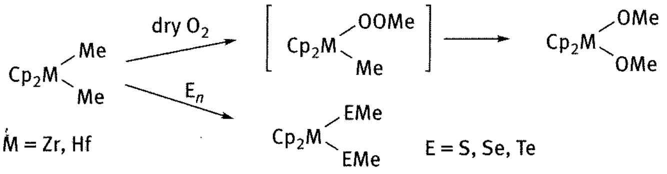
2.11.4.2 Cleavage by Halogens

Halogens (X_2) are frequently used to cleave metal–carbon bonds to give alkyl halides. Bromine and iodine are commonly used. The mechanism of this reaction in aprotic solvents involves electrophilic attack by Br^+, and it has been demonstrated that the bromination of $CpFe(CO)_2R$ ($R = CD_2CH_2Ph$) proceeds via a cyclic carbocation intermediate which generates equal proportions of the two possible alkyl bromide products.



2.11.4.3 Chalcogen Insertions

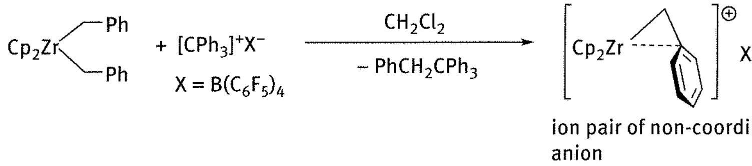
The M–C bonds of electropositive metals react with oxygen, sulfur, selenium, and tellurium under insertion to give the corresponding metal chalcogenolato complexes $L_nM–ER$. The rate of reaction decreases in the order O > S > Se > Te. The insertion of O_2 into M–C bonds probably proceeds via the peroxide, M–O–O–R.



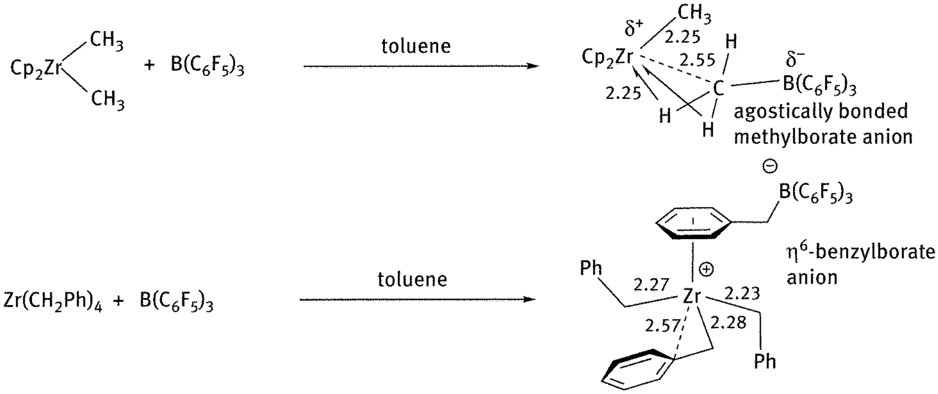
2.11.4.4 Cleavage by Lewis Acids

Lewis acidic compounds like BX_3, as well as carbocations CR_3^+, react with metal alkyls under alkyl anion abstraction. This reaction is most widely applied for the generation of electron-deficient cationic metal complexes as catalysts for the polymerization of 1-alkenes (Section 3.7.2.1). There are three types of products, where (i) an alkyl ligand has been removed completely and an ion pair is formed, (ii) the Lewis acid forms an alkyl bridge, or (iii) a benzyl ligand is abstracted which can act as π-ligand in a zwitterionic complex.

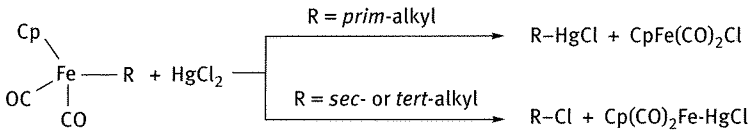
alkyl abstraction with ion pair formation



Lewis acid attack and zwitterion formation

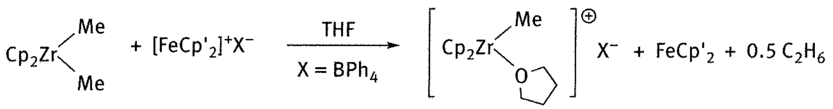


Metal–carbon σ-bonds are also susceptible to attack by electrophilic metal ions such as Hg^{2+}. With 18 VE complexes such as $CpFe(CO)_2R$, two pathways have been observed, leading either to alkyl transfer to Hg, or formation of alkyl halides and Fe–Hg bonds. In protic solvents and if R is a primary alkyl, transmetallation to Hg^{2+} is favoured. In aprotic solvents and with secondary or tertiary alkyls, alkyl halides are formed, probably via the corresponding carbocations.



2.11.4.5 Cleavage by Oxidation

The selective cleavage of M–C bonds is also possible by 1-electron oxidation of metal alkyls with $[Cp'_2Fe]^+$ ($Cp' = Cp, C_5H_4Me$). An alkyl radical $R^\bullet$ is formed which dimerizes to R–R:

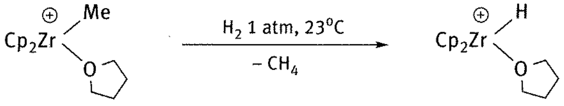


2.11.4.6 Hydrogenolysis of M–C Bonds

The reaction of metal alkyls with H_2 leads to M–C bond cleavage and formation of metal hydrides. Early transition metals and lanthanides react with H_2 by a σ-bond metathesis mechanism. This reaction is used to limit the molecular weight of polyethylene produced with Ti or Zr catalysts. Electronically unsaturated cationic metal alkyls such as $[Cp_2ZrR(L)]^+$ undergo hydrogenolysis very rapidly under ambient conditions, while neutral alkyls Cp_2ZrR_2 usually require H_2 pressure. This is a clean route to metal hydrides. Late transition metal complexes react with H_2 via an oxidative addition–reductive elimination pathway, a key step in hydrogenation and hydroformylation reactions catalysed by such metal complexes.

For hydroformylation, see Section 3.4.1.

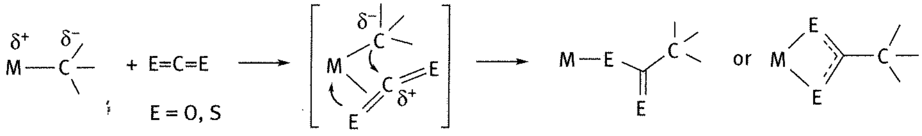
$$Cp^*_2ZrMe_2 \xrightarrow[-\,2\,CH_4]{H_2\ \text{pressure}} Cp^*_2ZrH_2 + 2\,CH_4$$



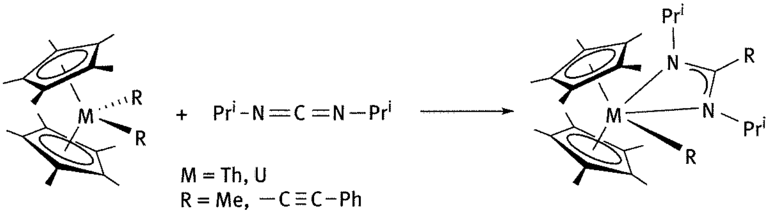
$$(OC)_4Co{-}R \xrightarrow{H_2\ \text{pressure}} (OC)_4Co{-}H + R{-}H$$

2.11.4.7 Insertion of Electrophilic Heterocumulenes

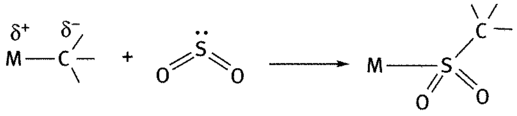
CO_2 is the simplest representative of heterocumulenes X=Y=Z which insert into M–C bonds. Depending on the availability of coordination sites, mono- or bidentate bonding modes may result. COS and CS_2 react similarly, to give mono- and dithiocarboxylate complexes, respectively.



Less common is the insertion of carbodiimides, R–N=C=N–R, into M–alkyl bonds, to give amidinato complexes. Amidinato ligands $[R'C(NR)_2]^-$ are usually prepared by reacting carbodiimides with lithium or magnesium alkyls, but a number of insertions into transition metal, lanthanide, and actinide metal bonds have also been observed, for example:

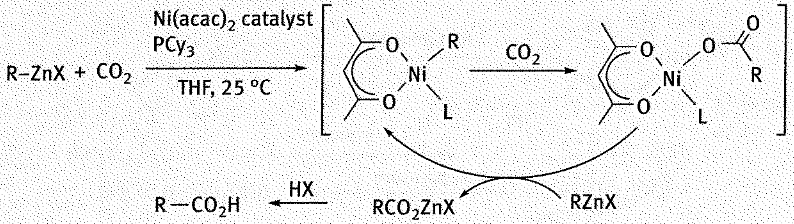


SO_2 inserts similarly to give S-bonded metal complexes. The S atom is tetrahedral.

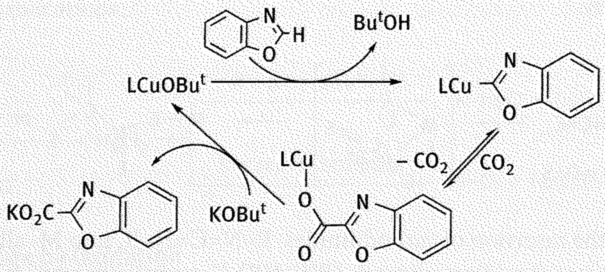


Box 2.11.4.7 CO_2 utilization in synthesis

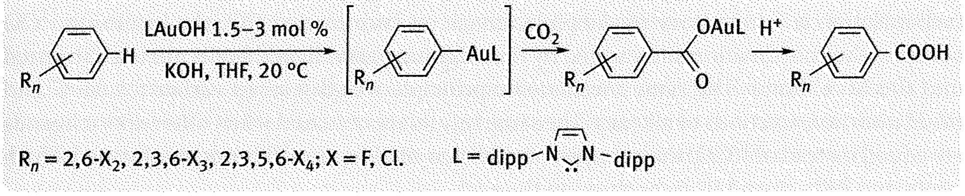
Since CO_2 is a waste product and a cheap starting material, numerous systems for CO_2 utilization have been developed. Many of these are catalytic and involve the insertion of CO_2 into M–C bonds, for example:



Similar CO_2 insertion reactions of Main Group alkyl or aryl compounds leading to carboxylic acids use rhodium, palladium, or copper catalysts. For example, Cs[R–BF(OR′)$_2$] reacts with catalytic amounts of a CuI/ligand mixture to give Cu(I) alkyls and alkenyls Cu–R which insert CO_2 to give Cu(OC(O)R) species. Transalkylation to borate followed by treatment with acid generates RCO_2H. The insertion into the transition metal–carbon bond kinetically outperforms the direct reaction of the Main Group compound with CO_2.



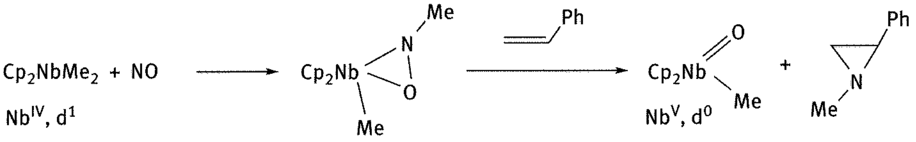
C–H acidic aromatic substrates can be activated by sufficiently basic metal complexes to give M-aryl intermediates which insert CO_2, to convert arenes into carboxylic acids. Metal *t*-butoxides and gold hydroxides stabilized by strongly electron donating N-heterocyclic carbene ligands are able to react with such activated C–H bonds in acid/base fashion to give the corresponding metal aryls, which then insert CO_2:



R_n = 2,6-X_2, 2,3,6-X_3, 2,3,5,6-X_4; X = F, Cl. L = dipp–N⌒N–dipp

2.11.4.8 Insertion of NO

Nitric oxide is a radical. It reacts with diamagnetic metal alkyl complexes usually by double insertion, whereas complexes carrying an unpaired electron give diamagnetic mono-insertion products. These compounds may react further under transfer of the nitrene (N–R) moiety to suitable acceptor substrates to give aziridines.

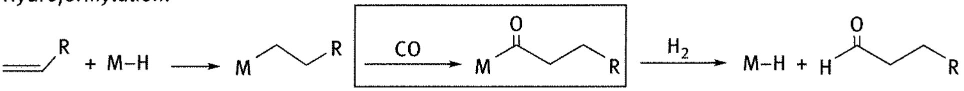


2.11.4.9 Insertion of CO

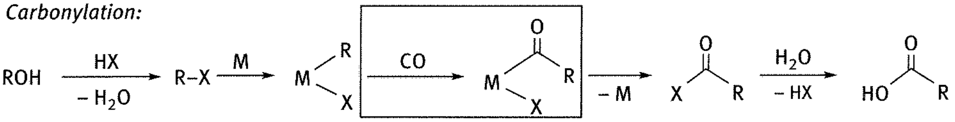
The insertion of CO into M–alkyl bonds leads to acyl complexes, M–C(O)–R. This is one of the most widely applied and industrially important reactions of metal alkyls, and is the basis of catalytic alkene hydroformylation and carbonylation reactions.

For industrial processes involving CO insertions, see Chapter 3.4

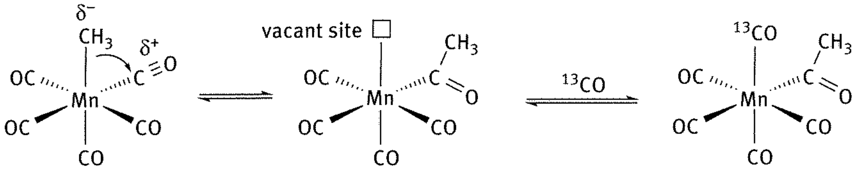
Hydroformylation:



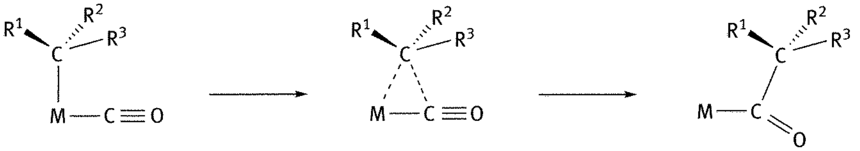
Carbonylation:



Mechanistic principles. The mechanism of these CO reactions has been the subject of many investigations. Manganese(I) carbonyl complexes are convenient because (as d^6 complexes) they form stable octahedral products and are stereochemically rigid. Treatment of Me–Mn(CO)$_5$ with CO under pressure gives MeC(O)–Mn(CO)$_5$. This could arise either by migration of the methyl ligand to a coordinated CO in *cis* position, or by direct insertion of external CO into the Mn–Me bond. Reactions with ^{13}C-labelled CO have demonstrated that carbonylation is a migratory nucleophilic attack on coordinated CO: the incoming ^{13}CO occupies the coordination site vacated by the migrating alkyl ligand but is not itself inserted into the M–C bond. The same mechanistic principle was discussed earlier for M–C and M–H insertion reactions of alkenes. The same results are obtained when other donor ligands are added instead of ^{13}CO; for example, on addition of PPh$_3$ an acyl product is formed which contains a PPh$_3$ ligand in *cis* position to the acyl.



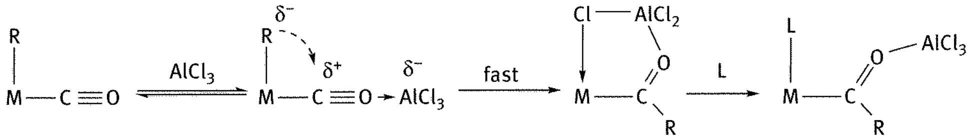
If the alkyl ligand is chiral, the migration step proceeds with retention of configuration:



The reaction is reversible: on heating MeC(O)Mn(CO)$_5$ under vacuum, a CO ligand—again *cis* to the acyl group—dissociates and allows the methyl ligand to migrate back to the metal.

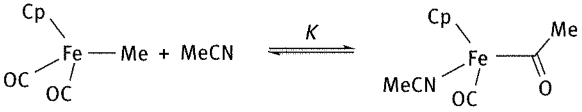
The process is general: the 'insertion' of an unsaturated substrate into an M–C σ-bond constitutes an ***intramolecular nucleophilic attack*** on an electrophilic ligand. However, alkene and alkyne insertions lack the reversibility of the CO insertion.

Acceleration of CO insertions. The insertion of CO is greatly accelerated by the presence of **Lewis acids** (BF$_3$, AlCl$_3$). The Lewis acid can coordinate to the O-terminus of a CO ligand, thereby increasing its polarity, and it can also stabilize the acyl product by forming an even more stable adduct with the acyl-oxygen. The intermediate may also be stabilized if a metal halide Lewis acid coordinates to the site vacated by the migrated alkyl ligand:

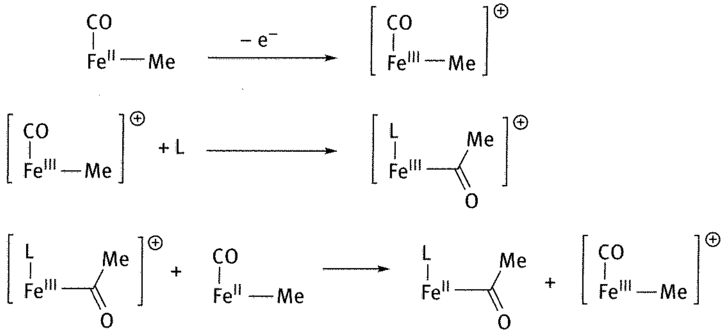


Insertion reactions (as well as de-insertions) of kinetically stable octahedral d^6 complexes proceed relatively slowly since any geometric changes incur a cost in terms of reduced ligand field stabilization energy. The rate of insertion can however be very substantially accelerated by **electron transfer catalysis**. For example, oxidation of a d^6 ion to d^5 removes this kinetic barrier, and insertion can take place readily. This step is then followed by 1-electron transfer to restore the original d^6 configuration and give a stable product. The addition of trace amounts of an oxidizing (or a reducing) agent or electrochemical oxidation is sometimes applied to enhance ligand exchange reactions.

The effect of a change in d-electron configuration can be seen for example in the CO insertions of $CpFe(CO)_2Me$. Given that the Cp ligand occupies three coordination sites, this is an effectively octahedral d^6 complex. In acetonitrile there is the equilibrium:



On 1-electron oxidation the rate of the forward reaction of this equilibrium (and therefore the value of the equilibrium constant K) is increased by a factor of 10^{11}. The electron transfer process is therefore:

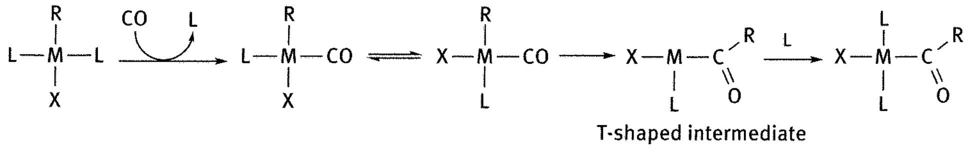


CO insertion in CO-free metal alkyl complexes. The insertion of CO into CO-free, square-planar d^8 metal alkyl complexes $L_2M(R)(X)$ (M = Ni, Pd, Pt) can follow several pathways: (i) displacement of one of the phosphine ligands by CO; (ii) addition of CO to give a five-coordinate complex, and (iii) displacement of the anion X^-. The latter two pathways may be adopted in cases where substitution of L is unfavourable, as in complexes with chelating phosphines L^L. Dissociation of the anion is favoured where the anion is weakly coordinating. Polar solvents may also favour a pathway via ionic intermediates.

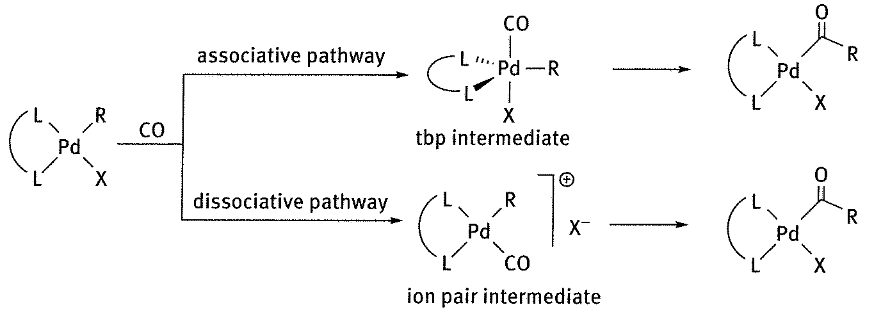
The reaction pathway via displacement of L *cis* to the alkyl R is the most facile. Square-planar *trans*-complexes usually require an X/L isomerization, so that L is *trans* to R to labilize the M–C bond and thus accelerate the migration to CO. Which of these competing pathways is followed depends very much on the metal and the ligands involved. Whereas

Pt(II) complexes $L_2Pt(R)Cl$ tend to follow the *dissociative* pathway, CO insertion into Rh(I) alkyls $R–Rh(CO)(PPh_3)_2$ proceeds by *association* of CO, via the 18 VE intermediate $R–Rh(CO)_2(PPh_3)_2$.

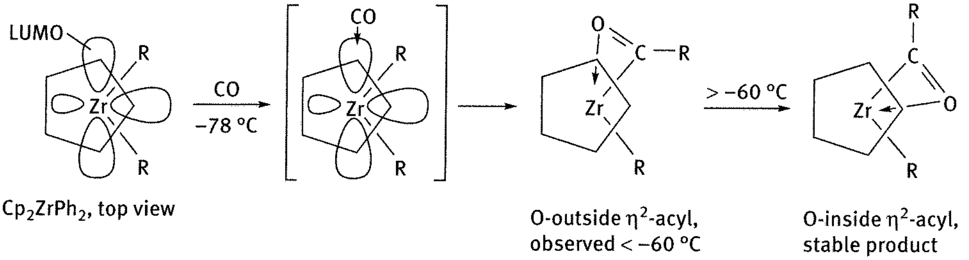
CO insertion by displacement of L:



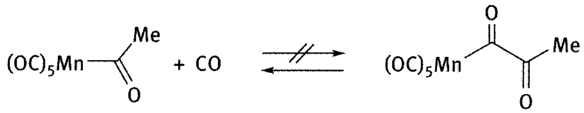
CO insertion without displacement of L:



The reaction of CO with 16 VE metallocene dialkyl complexes takes advantage of the presence of an energetically accessible LUMO, to which CO can coordinate. In the case of the reaction of CO with $CpZrPh_2$ it could be shown that initially the 'O-outside' isomer is formed, which isomerizes subsequently to the thermodynamically preferred 'O-inside' structure, made possible by coordination of an oxygen lone pair to the LUMO.

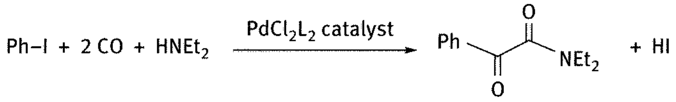


Double carbonylation. In principle, one CO insertion into an M–alkyl bond could be followed by another, to give α-keto-acyl complexes $L_nM–C(O)–C(O)–R$, possibly as a route to such desirable targets as α, β-diketones and α-keto acids. However, this process is thermodynamically disfavoured. α-Keto-acyl complexes can be prepared by other routes, such as the reaction of MeC(O)C(O)Cl with $[Mn(CO)_5]^-$; they are thermally unstable and readily eliminate CO to give acyl complexes:

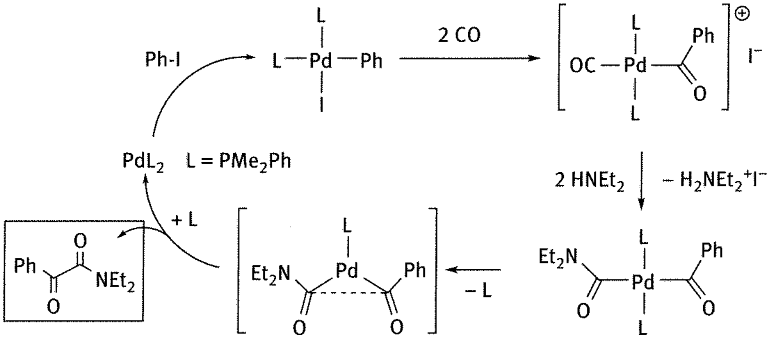


Forward reaction:
$\Delta G \geq +17.5$ kJ mol^{-1}
$\Delta G^{\ddagger} \geq +130$ kJ mol^{-1}

In spite of this, products of what amounts to a double carbonylation have been found, as in the palladium-catalysed formation of α-keto benzoic amides:



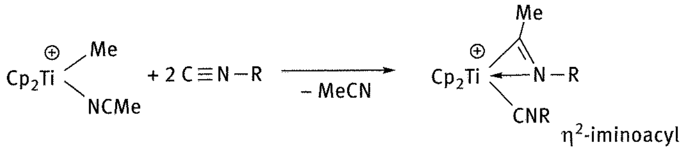
However, it could be shown that products of this type are the result of reductive coupling of two different CO insertion products, –C(O)Ph and –C(O)NEt$_2$. The first is formed by CO insertion into a Pd–Ph bond, the second by nucleophilic attack by HNEt$_2$ on a coordinated CO in a cationic complex:

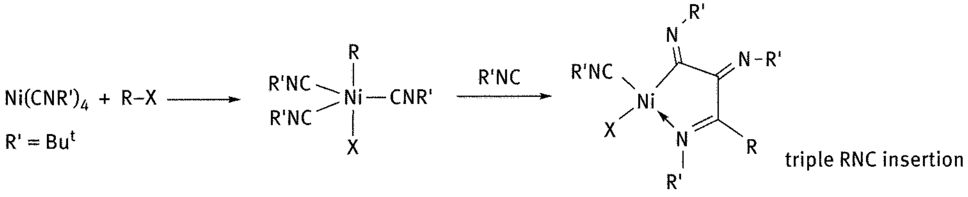


Double carbonylation of metal dialkyls of oxophilic metals, like zirconium or thorium, has been shown to lead to C–C coupling. Such reductive CO coupling reactions are likely to be involved in the generation of hydrocarbons from CO/H$_2$ mixtures (synthesis gas) in the Fischer–Tropsch process.

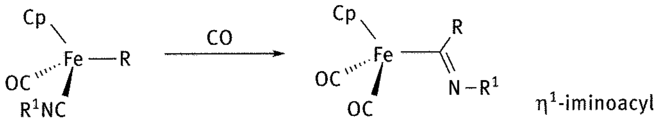
2.11.4.10 Insertion of Isocyanides

The insertion of isocyanides R–N≡C is mechanistically closely analogous to that of CO (see Section 2.4.8). However, isocyanides are stronger σ-donors and weaker π-acceptors than CO and, in contrast to CO, multiple insertions are not energetically disfavoured. In line with the stronger donor character, η^2-coordination of the insertion products is more frequently found for iminoacyls than for acyls.





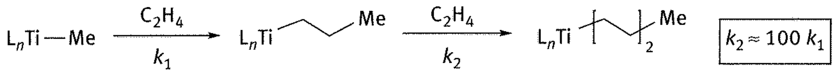
Where there is a competition between CO and RNC insertion, formation of the iminoacyl prevails.



2.11.4.11 Insertion of Alkenes

The insertion of alkenes into M–C σ-bonds proceeds less readily than the insertion of alkenes into M–H bonds, and relatively few examples are found of well-defined alkene insertion products, in spite of the fact that the conversion of a C=C double bond into two C–C single bonds is **exothermic by about 20 kcal mol^{-1}**. The main reason for this is the much higher kinetic barrier of insertions into M–C vs. M–H bonds.

There is also a significant variation in the rates of insertion into M–R (R = Me, Et, etc.) bonds. For the ethylene oligomerization system Cp_2TiRCl / AlR_2Cl (R = Me, Et, Pr^n) it could be shown that the insertion of ethylene into the Ti–Me bond was over 100 times slower than into Ti–Et and Ti–Pr^n bonds.



$\boxed{k_2 \approx 100\, k_1}$

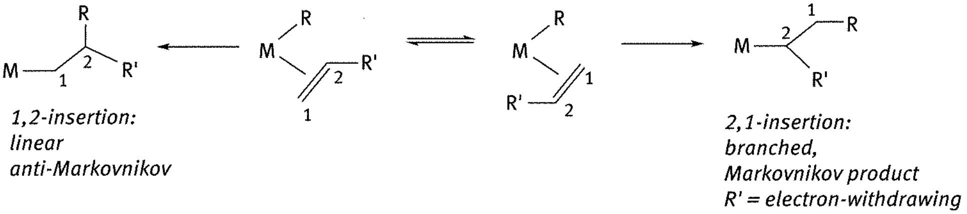
For alkene polymerization processes, see Chapter 3.7.

The result of this difference is that in most such systems a small fraction of Ti–Me bonds in an activated complex will consume all the available alkene monomer, while most of the initial methyl complex remains unreacted. This makes it difficult to isolate well-defined alkene mono-insertion products. Another factor that affects the general synthetic usefulness of alkene insertions is the ease with which an insertion product can undergo β-H elimination: after one of two insertions an alkene product is extruded, with the thermodynamically favourable formation of a metal hydride, so that insertions often lead simply to olefin dimerizations.

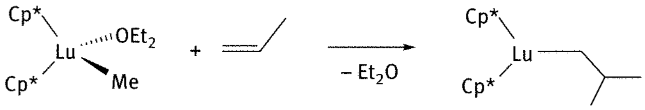
Of course, alkene insertion into M–C bonds is the basis of olefin polymerization processes and a large worldwide industry: given the right electronic and steric conditions multiple alkene insertions can be very rapid. In polymerization catalysts, β-H elimination is suppressed either by electronic or, more often, steric factors.

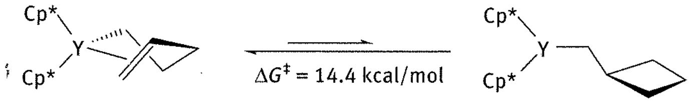
The mechanistic principles of alkene 'insertion' resemble those of the reaction of CO with M–C bonds: it is another example of a migration of a nucleophilic ligand to an electrophilic unsaturated substrate coordinated in the *cis* position. The process is assisted by the asymmetry and polarity induced into the C=C bond on coordination: whereas ethylene has no dipole moment and is quite unreactive towards nucleophiles and electrophiles, coordination leads to the accumulation of a partial positive charge on the β-C atom which facilitates **migratory insertion**:

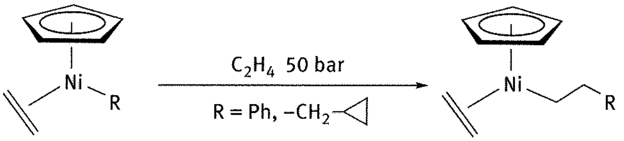
The insertion of substituted alkenes can in principle lead to two regioisomers: a *branched* alkyl (**2,1-insertion**; Markovnikov product), or a *primary* alkyl (**1,2-insertion**, anti-Markovnikov product). In most cases (R′ = alkyl substituent) the anti-Markovnikov product is formed, leading to a linear primary alkyl. On the other hand, electron-withdrawing substituents R′ (e.g. R′ = Ph) stabilize the negative charge on the anionic carbon atom and favour the formation of a branched alkyl:



Well-defined alkene insertion products have for example been obtained for Group 3 as well as some Group 10 complexes. For metals with d^0 configuration, the alkene binding energy is low, ca. 12–13 kcal mol^{-1}.

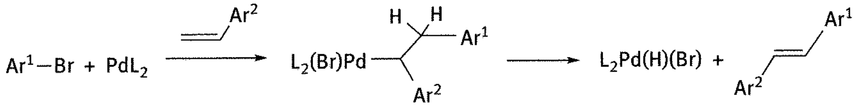




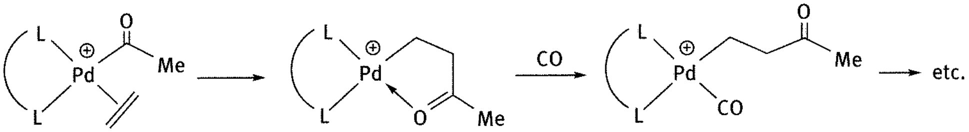


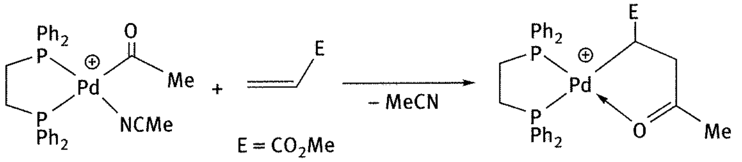
For Heck arylation, see Section 3.6.4.

Alkene insertion into a metal–aryl bond is a key step in the palladium-catalysed Heck *vinylation of aryl halides*, known as the ***Heck reaction***:



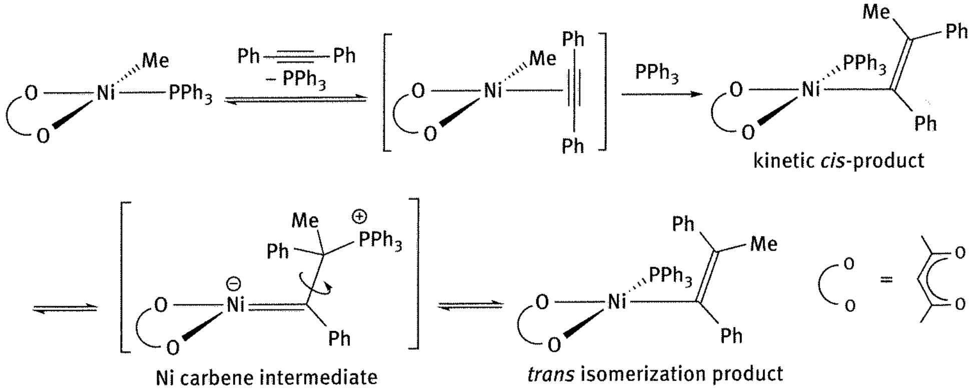
Alkene insertions into M-acyl bonds. The insertion of alkenes into M–C(O)R bonds is relevant for the copolymerization of 1-alkenes with CO. The reaction is catalysed by palladium complexes. At low temperatures and with chelating ligands (such as phenanthroline or chelating diphosphines) the reaction can be monitored by NMR spectroscopy. Insertion activation barriers $\Delta G^{\ddagger}$ of only about 15 kcal mol^{-1} were found. Activated olefins like methylacrylate also insert to give isolable products. The C=O function of the acyl ligand stabilizes the insertion product by chelate formation.



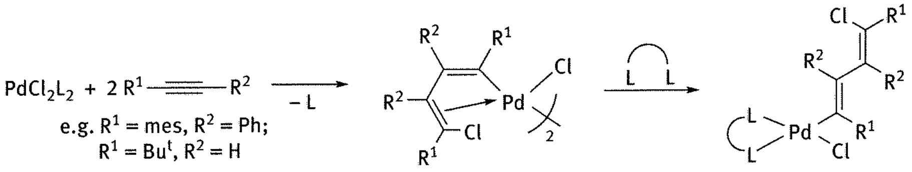


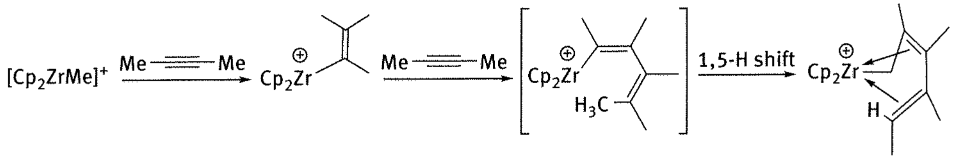
2.11.4.12 Insertion of Alkynes

Carbon–carbon triple bonds are highly reactive, and a reduction in bond order to double or single bonds is thermodynamically favourable. Consequently, alkynes undergo a number of single and multiple insertion reactions. This leads to the carbometallation of the alkyne. The insertion product shows *cis* stereochemistry (kinetic product), although in some cases subsequent isomerization can take place (most probably via a zwitterionic carbene intermediate) to give metal vinyls with *trans* geometry.



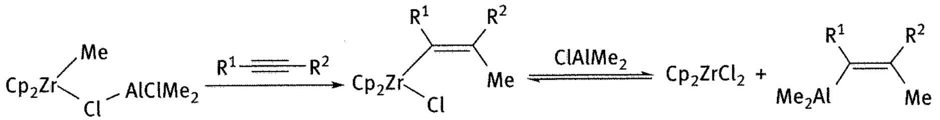
Multiple alkyne insertions have also been observed. The resulting dienyl ligand may act as 1-, 3-, or 5-electron donor, depending on the electron demand of the metal centre.

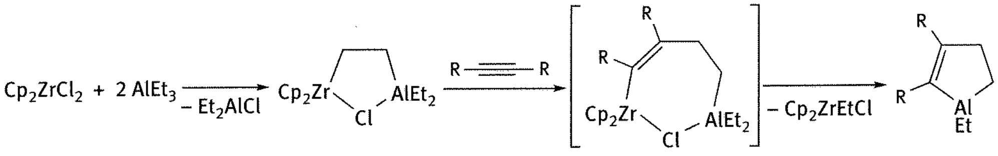




Alkyne insertions into Zr–C bonds are the key mechanistic step in Negishi-type alkyne carboalumination reactions:

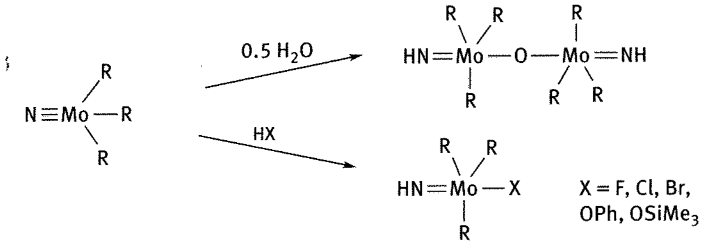
Nobel Prize 2010 for metal catalysed C–C coupling reactions: R. F. Heck, E. Negishi, A. Suzuki

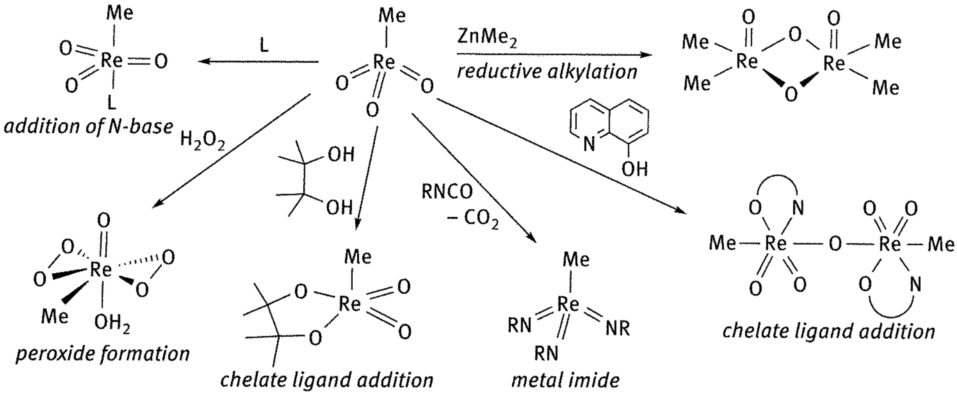




2.11.4.13 Reactions of Metal Alkyls With Non-Innocent Ligands

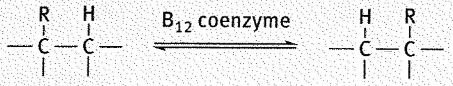
The reactions outlined in the previous sections concerned the transformations of M–C bonds. However, there are cases where the metal-alkyl bond is not the most reactive part of a metal complex, and where other ligands show reactivity while the M–C σ-bond remains intact. This is mainly the case for high oxidation state metal alkyl oxides and nitrides. For example, the polarity of the M=O and M≡N bonds is such that the heteroatoms are the preferred place for protonation. This is illustrated in the following diagram for alkyl complexes of molybdenum and rhenium. The reaction of terminal oxo complexes with organic isocyanates R–N=C=O is particularly interesting as an entry into metal imido complexes.





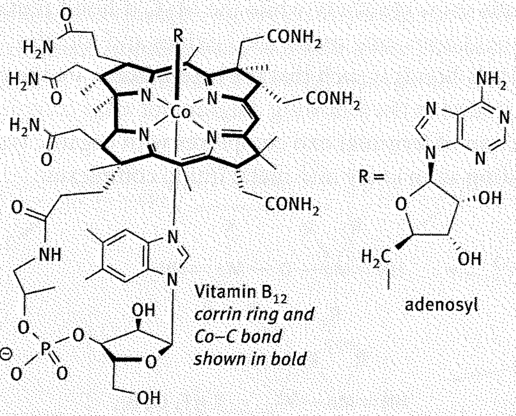
Box 2.11.4.12 Transition metal alkyl complexes *in vivo*

Transition metal-alkyl bonds, particularly of common and abundant metals like iron, are generally too reactive to survive in the aqueous environment or in living systems. There are however some notable exceptions where Nature takes advantage of the reactivity of M–C bonds to catalyse specific and life-essential reactions. Co(III) (d^6) is kinetically inert and forms stable octahedral complexes. Alkyl complexes of Co(III) are therefore able to survive under physiological conditions. Biology utilizes cobalt complexes bound to a macrocyclic tetrapyrrolato (so-called ***corrin***) ring system and which contain a metal-alkyl bond: Vitamin B_{12}, also known as **cobalamine**. The alkyl ligand may be adenosyl or methyl. The adenosyl derivative of cobalamine catalyses 1,2-alkyl shift exchange reactions and is involved in folic acid formation.

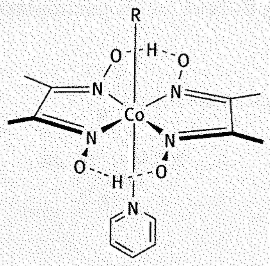


The consequences of vitamin B_{12} deficiency are pernicious anaemia and megaloblastosis.

Adenosyl-B_{12}:

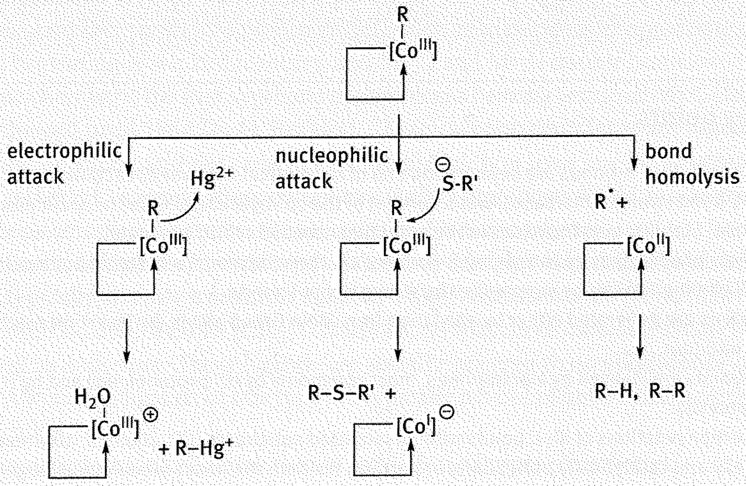


Key features of the chemistry of vitamin B_{12} can be conveniently modelled using simple Co(III) glyoximato complexes, which have similar chemical and redox properties:

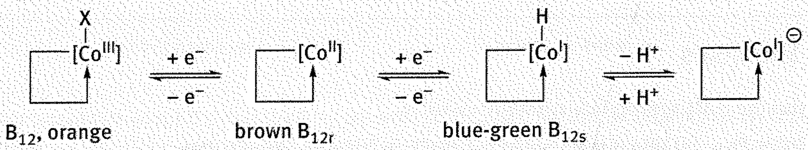


The Co–CH_3 form, methylcobalamine, catalyses methyl group exchange between molecules. Electrophilic metal ions are capable of reacting with methylcobalamine by methyl transfer. By this mechanism soil bacteria are able to generate $MeHg^+$ ions, through which mercury can be introduced into the food chain.

The Co–C bond in cobalamine can be cleaved by electrophiles, nucleophiles or by photolytic bond homolysis. The unsaturated macrocyclic ring helps to stabilize a number of oxidation states, and the systems can be reduced in a sequence of steps.

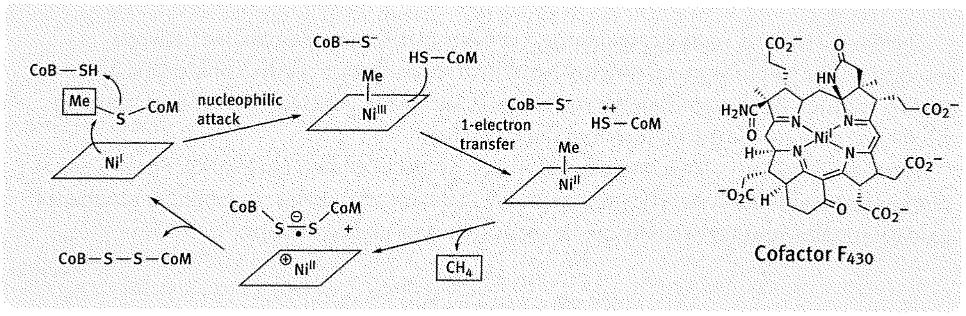


Hydroxycobalamine (R = OH, B_{12b}) and methyl cobalamine are reduced by hydrogen to give a Co(II) complex, B_{12r}. Further reduction gives the blue-green, extremely air-sensitive B_{12s}, which contains Co(I) and reacts both as metal hydride and as a very strong nucleophile (stronger than $SnMe_3^-$, 'super-nucleophile').



The B_{12s} form readily undergoes oxidative addition reactions with alkyl halides and also inserts unsaturated substrates into the Co–H bond, to give a wide variety of functionalized Co alkyl, vinyl, and alkynyl derivatives.

The existence of metal–alkyl bonds has also been demonstrated for another metal-containing enzyme system, methyl-coenzyme M reductase (MCR), albeit as an unstable intermediate. This enzyme system is found in anaerobic archaea bacteria; the enzyme catalyses the terminal step in the generation of methane. In this process, coenzyme B (CoBSH) acts as the 2-electron donor to reduce methyl-coenzyme M (methyl-SCoM) to form methane and the heterodisulfide, CoBS–SCoM. The active site of MCR contains a redox-active cofactor, **coenzyme F_{430}**, a yellow, highly reduced, tetrapyrrolate macrocycle containing a Ni(I) centre (MCR_{red1}). Spectroscopic studies have provided support for a mechanism for MCR that involves **methyl-Ni(III)** and an organic radical as intermediates:



Key points

Complexes with M–C σ-bonds are key components of most metal-catalysed reactions.

The M–C bond strength increases with s-content of the sp^x-hybridized C, in the order alkyl < vinyl, aryl < alkynyl. Stability also increases in the order first < second < third row metal.

Complexes of alkyl ligands containing β-H atoms are thermodynamically stable but kinetically labile. β-H elimination can be suppressed by strong donor ligands.

Metal alkyls are generated either by alkylation from Main Group alkyls, by insertion reactions or oxidative addition.

M–C σ-bonds are cleaved by electrophiles, most commonly by H^+ (protonolysis) and by H_2 (hydrogenolysis).

The insertion reactions of M–C bonds with unsaturated substrates (CO, alkenes, alkynes) are synthetically and catalytically particularly important; they are the bases of numerous large-scale industrial processes. The mechanistic principle is intramolecular nucleophilic attack on an unsaturated ligand coordinated *cis* to the alkyl ligand and is best described as migratory insertion.

In electronically unsaturated complexes, alkyl ligands may adopt unusual bonding modes such as α-, β-, or γ-agostic bonding.

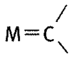
Exercises

1. Devise the most appropriate synthetic routes to

   (i) $Zr(CH_2Ph)_4$; (ii) $TiBr_3(CH_2Ph)$; (iii) $Cp_2TiMeCl$; (iv) $(Me_3P)_2ClNi–C(O)Me$.
2. Both $TiPr^i_4$ and $Ti(1\text{-norbornyl})_4$ contain six β-H atoms per alkyl ligand and have the same electron count. Explain why, in spite of this similarity, $TiPr^i_4$ is very unstable whereas $Ti(1\text{-norbornyl})_4$ is an isolable compound.
3. The mono-alkyl $TiEtCl_3$ is unstable but an isolable complex is obtained on adding the diphosphine $1,2\text{-}C_2H_4(PMe_2)_2$ (dmpe). Discuss the alkyl bonding in this compound.
4. Suggest appropriate synthetic routes that lead selectively to

   (i) $Cp(CO)(^{13}CO)Fe–C(O)CH_3$ and (ii) $Cp(CO)_2Fe–^{13}C(O)CH_3$ and (iii) $Cp(CO)_2Fe–C(O)^{13}CH_3$.
5. Suggest the expected product of the reaction of 2-phenylpyridine with $PdCl_2$ and show the reaction mechanism.
6. The reaction of $[Cp_2YCl]_2$ with $NaAlMe_4$ gives a hydrocarbon-soluble compound **A**. Treatment of **A** with pyridine gives **B**. Measurements by freezing point depression in benzene give the molecular weight of **B** as 450±40, and the elemental analysis shows that it contains no nitrogen. Adding a little THF to **B** gives **C**. Identify **A**, **B**, and **C**, give the chemical equations and explain the structures of the products.

2.12 Alkylidene Complexes

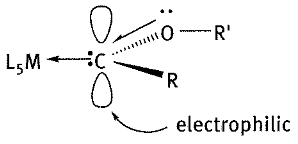


Carbenes, :CR_2, are 2-electron donors like CO or phosphines. Unlike those ligands, most carbenes are, however, highly reactive unstable species, and their use as ligands therefore requires very different synthetic strategies from those of other 2-electron donor ligands. The bonding characteristics of carbenes, and in particular the stable and isolable N-heterocyclic carbenes, have been discussed in Section 2.4.3.

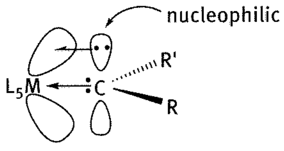
Whereas complexes with M–C σ-bonds date back to the origins of organometallic chemistry at the beginning of the 20th century, and M=O and M=N double bonds are well known in inorganic chemistry, the first synthesis of complexes bearing terminal M=C double bonds was not achieved until 1964 (E. O. Fischer). These carbene complexes are based on metals in low oxidation states, and the carbenes are stabilized by at least one heteroatom such as O or N. The carbene C-atom in these complexes is electrophilic and able to add nucleophiles. These carbene complexes have become known as '***Fischer carbenes***'.

About ten years later a different type of carbene complex was discovered, in which the metal was typically an early transition metal in a high oxidation state (R. R. Schrock). These carbenes could be described as $[CR_2]^{2-}$ dianions, so that these carbenes could be regarded as π- as well as σ-donors. These ligands are usually referred to as **alkylidenes** or '***Schrock carbenes***'. Alkylidene ligands of this type are typically devoid of heteroatoms with lone pairs (R, R′ = H, alkyl, or silyl).

The systematic term 'alkylidenes' is now applied to all types of carbenes.

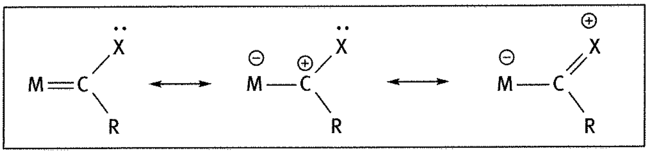


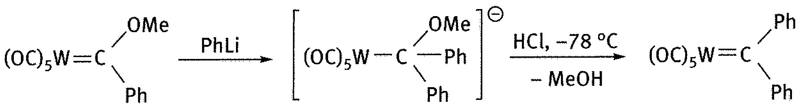
'Fischer carbene'



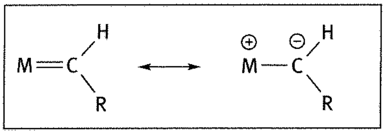
'Schrock carbene'

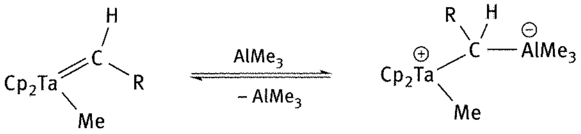
Fischer carbenes can be described by several resonance forms, which show the role of the heteroatom as electron pair donor, as well as the partial positive charge on the carbene-C atom. This explains the reactivity of such carbene complexes with nucleophiles, e.g. the addition of R^- on treatment with LiR:





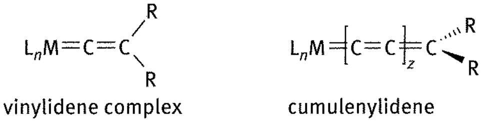
This contrasts with the polarity of alkylidenes of d^0 metals which act as bases and form adducts with Lewis acids:





The formation of M–C multiple bonds is particularly pronounced for metals which are also known to form M–E and M–M multiple bonds, most notably Nb, Ta, Cr, Mo, W, and Re. Alkylidene complexes of Ru are widely used in synthesis. Carbene complexes now play an important role in fine chemical synthesis as well as olefin metathesis, ring-closing metathesis (RCM), and ring-opening metathesis polymerization (ROMP).

In addition, extension of the C=C motif gives rise to vinylidene and cumulenylidene complexes. Note that the π-systems of neighbouring C=C double bonds are perpendicular to one another.



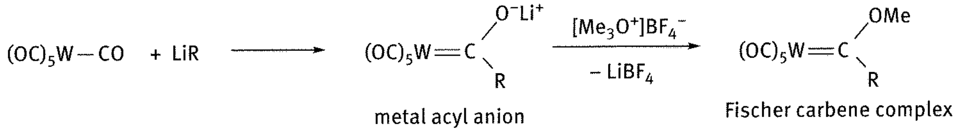
Box 2.12 NMR spectroscopy of metal carbenes

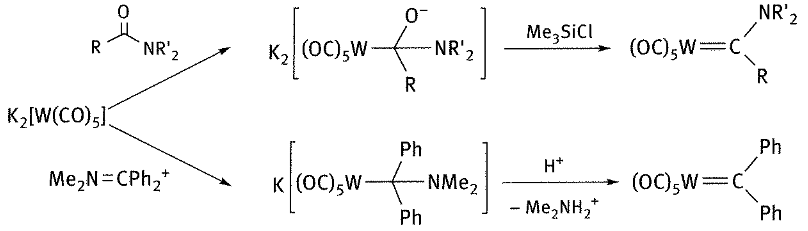
Irrespective of the electrophilic or nucleophilic character of the carbene-C, the ^{13}C NMR resonances of carbenes of the Fischer and Schrock types are typically observed at low field, at δ 290–365 ppm for O-substituted Fischer carbenes and 240–330 ppm for Schrock carbenes (relative to $SiMe_4$). *N*-donor substituents lead to a shift to higher field. The ^1H NMR resonance of alkylidenes M=CHR is found at low field, δ 10–20 ppm, although α-agostic interactions with this H atom may produce a shift to as high as 3 ppm.

2.12.1 **Synthesis of Alkylidene Complexes**

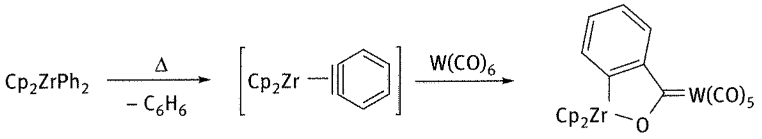
2.12.1.1 Synthesis of alkylidene complexes in low oxidation states: Fischer carbenes

From metal carbonyls. The first carbene complexes of this type were obtained by the reaction of $W(CO)_6$ with lithium alkyls:

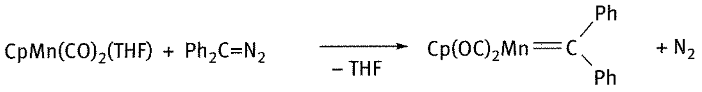


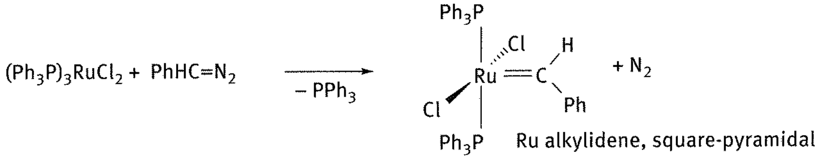


The role of LiR can also be fulfilled by reactive species such as zirconocene benzyne intermediates which are trapped by metal carbonyls to give binuclear carbenes:

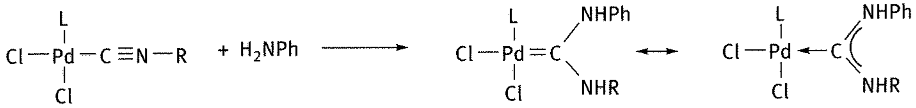


From diazoalkanes:

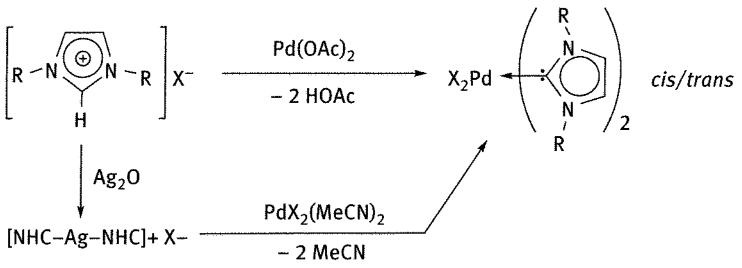




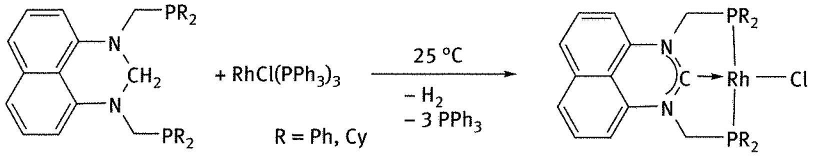
From isocyanides: Amines add to isocyanides to give open N-stabilized carbenes (acyclic diaminocarbenes, ADCs).



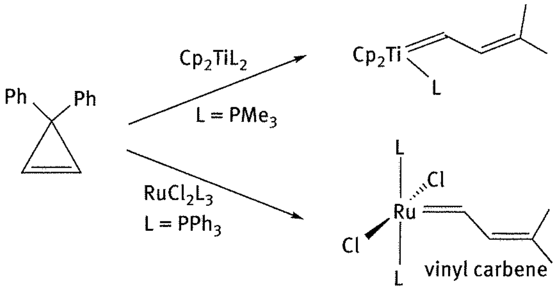
From imidazolium salts: NHC complexes can be made from pre-prepared N-heterocyclic carbenes, or from metal halides and imidazolium salts in the presence of base (here: OAc^-). Labile silver NHC complexes are frequently used as carbene transfer agents and storage forms of carbenes, particularly when the carbenes are prone to dimerization (e.g. R = Me).

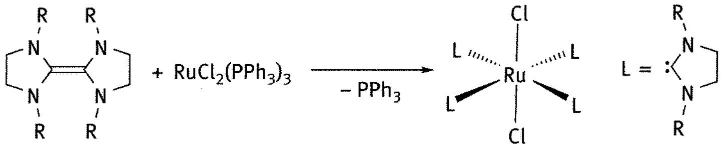


Under sterically favourable conditions, the formation of NHC-type carbene complexes has also been observed by double C–H activation of a heterocyclic alkane precursor. The rigidity of the pincer ligand system shown in the following schematic helps to facilitate this reaction.

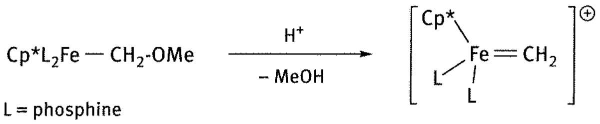


From activated olefins:

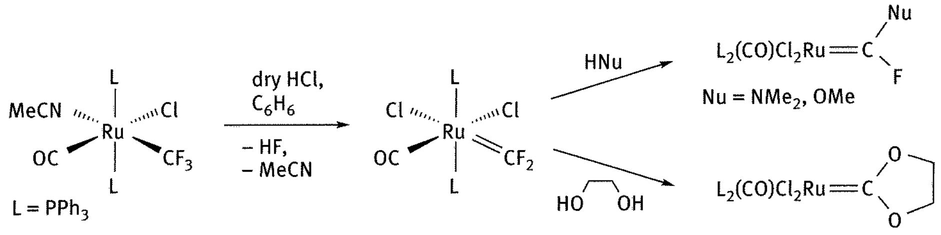




From heteroatom-substituted alkyls complexes:

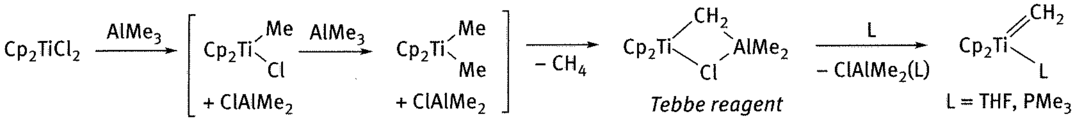


Dihalocarbenes: The carbenes CX_2 (X = F, Cl, Br, I) are highly reactive species but can be stabilized in the coordination sphere of a metal. $L_nM{=}CX_2$ complexes give rise to numerous other carbene complexes by halide substitution.

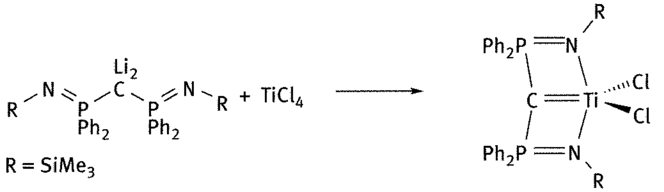


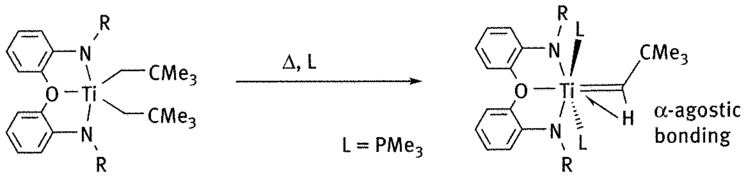
2.12.1.2 Synthesis of Alkylidene Complexes in High Oxidation States (d^0)

Group 4 complexes form few alkylidenes. However, the reaction of Cp_2TiCl_2 with $AlMe_3$ leads to the formation of a Ti-CH_2 complex, stabilized by complexation to Me_2AlCl, which has become important in synthetic applications and is known as the *Tebbe reagent*. It reacts with carbonyls, $R_2C{=}O$, to give olefins by O/CH_2 exchange.

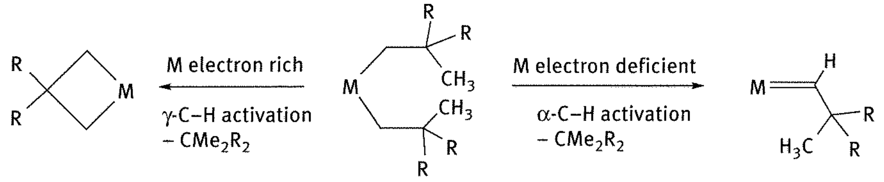


With rigid, bulky ligands well-defined Ti alkylidenes are accessible, for example:

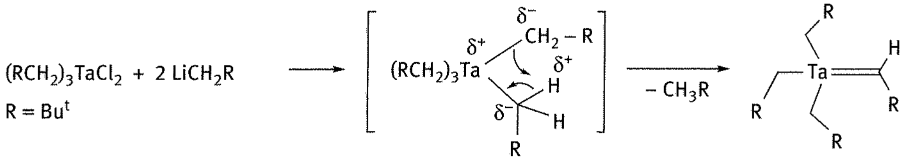


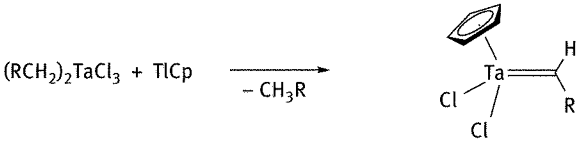


Alkylidene complexes are significantly more common in Groups 5 and 6. Whereas the alkylation of $TaCl_5$ with MeLi gives $TaMe_5$, it is not possible to accommodate five alkyl ligands if these are sterically more demanding. Whereas electron-rich noble metal complexes under similar sterically congested conditions tend to form metallacycles by γ-C–H activation, early transition metals undergo α-H abstraction to give M=CHR species.

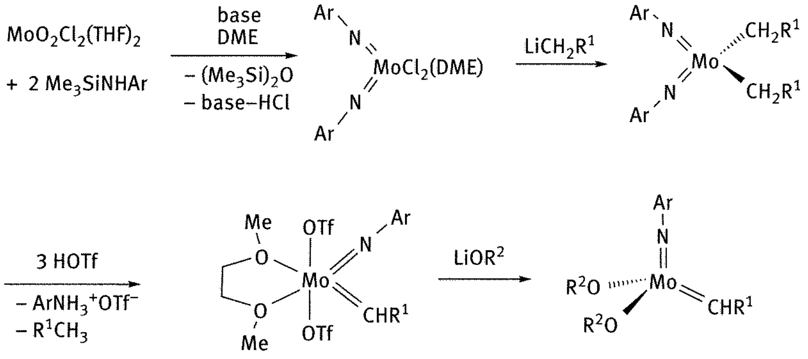


From sterically hindered alkyls. A typical reaction leading to Group 5 alkylidenes is the alkylation of tantalum alkyl halides with bulky alkyls like neopentyl lithium:

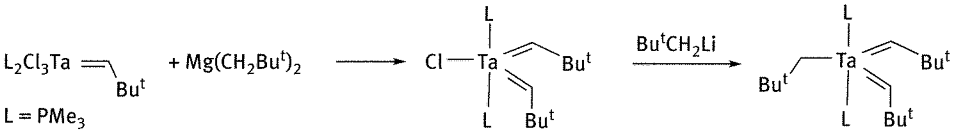




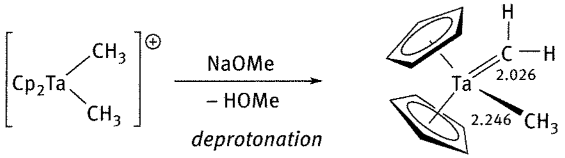
Molybdenum alkylidene complexes stabilized by bulky imido ligands are particularly important as catalysts for olefin metathesis reactions. The reaction principle is the same: steric hindrance in the ligand environment favours α-H elimination to give the alkylidene via an alkyl intermediate.

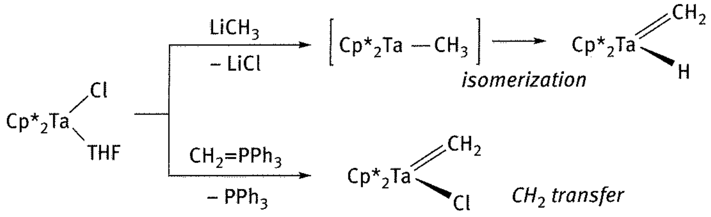


Complexes with more than one alkylidene ligand are similarly accessible:



Other methods involve ***deprotonation, C–H isomerization, and methylene transfer***, all of which have been shown to lead to M=CH_2 complexes:

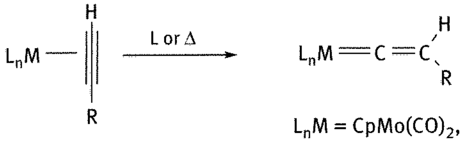




2.12.1.3 Vinylidene Complexes

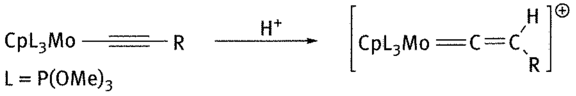
Vinylidene complexes and higher cumulenylidenes contain two or more mutually perpendicular π-systems. They are closely related to alkyne and alkynyl complexes, and these types of complexes are often found to be interconvertible.

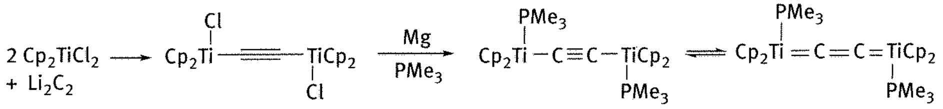
From alkyne complexes:



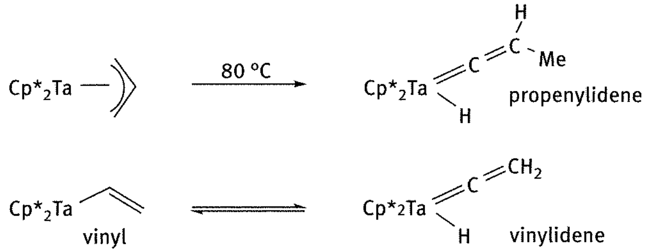
$L_nM = CpMo(CO)_2$, $(P^\wedge P)_2Re$, L_2RhCl, $[CpRu(CO)_2]^+$, etc.

From alkynyl complexes:



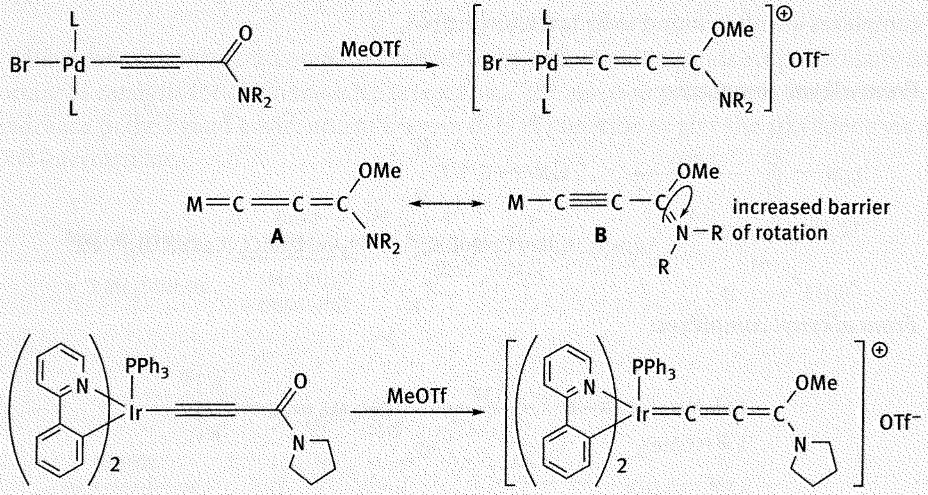


By C–H activation: For tantalum in particular, the formation of a metal–carbon double bond is energetically favourable, not least since this enables lower valent complexes to assume a higher oxidation state. The reactions shown in the following scheme amount to oxidative additions of C–H bonds, where Ta(III) precursors are either converted to Ta(V) species, or an equilibrium between these two states is established. The propenylidene complex shown in the following diagram is formed by β-H elimination from the allyl, whereas in the rearrangement of the vinyl complex α-H elimination is favoured over β-H abstraction.



Box 2.12.1.2 Alkynyl–allenylidene rearrangements

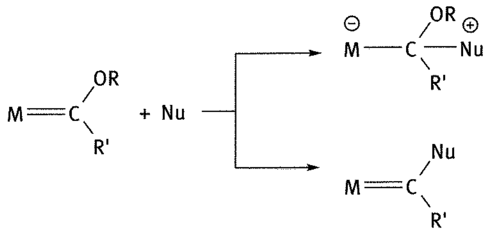
Alkynyl complexes may also be converted to **allenylidenes** by electrophilic attack on a suitable substituent. The examples in the following diagram contain an NR_2 substituent which allows the barrier of rotation about the C(sp^2)–N bond to be measured. The results suggest a significant contribution of the alkynyl-immonium resonance form, **B,** to the bonding in cationic allenylidene complexes. The iridium(III) allenylidene complex shows phosphorescence on excitation with UV light, another member of the large family of iridium-based light-emitting materials.



2.12.2 Reactivity of Alkylidene Complexes

2.12.2.1 Reactions of Fischer Carbenes

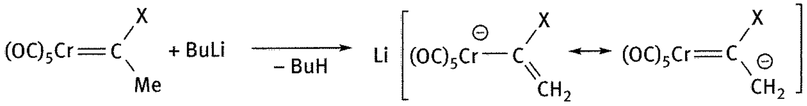
Nucleophilic carbene complexes of the Fischer type show primarily two kinds of reactions: **nucleophilic substitutions** at the carbene-C and **carbene transfer** (cyclopropanation).



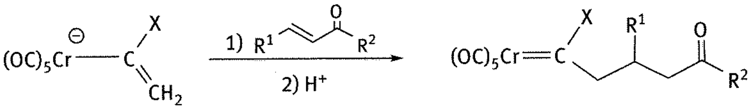
Addition to C: Nu = *tert*-amine

Substitution:
Nu = OH, NR_2, NHR,
alkyl, aryl, SR'

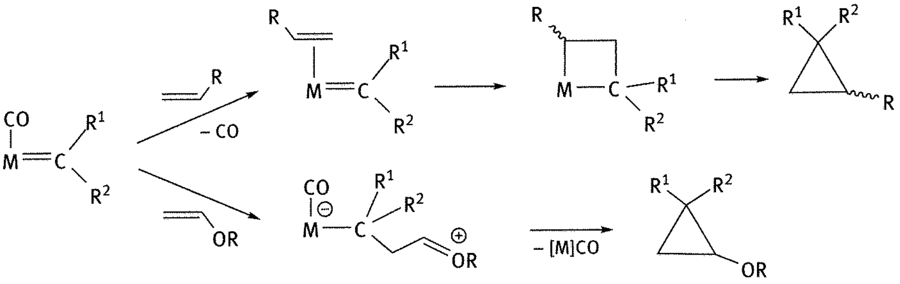
Lithium alkyls may also deprotonate methyl-substituted carbenes to give nucleophilic metal carbonyl enolate anions:



For example, the enolate adds to conjugated enones in 1,4-fashion:

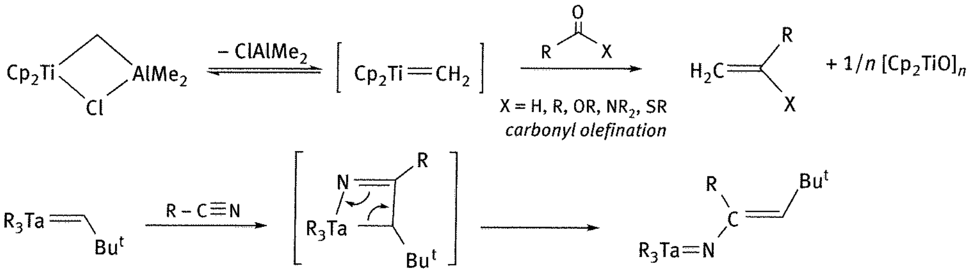


Cyclopropanation of olefins may occur by loss of a CO ligand via a metallacyclobutane intermediate, or by attack on the carbene-C by electron-rich alkenes such as vinyl ethers. Cyclopropanations tend to be slow for classical Fischer-carbene complexes, but are faster for cationic iron carbenes such as $[CpL_2Fe{=}CHR]^+$ where the carbene lacks the heteroatom substituent; the positive charge makes such complexes more prone to nucleophilic attack.



2.12.2.2 Reactions of d^0 Alkylidene Complexes

Alkylidene complexes of early transition metals (d^0) can act like Wittig reagents and convert C=O functions into olefins. Other hetero-alkenes and -alkynes (such as nitriles) also give products where the M=C bond is replaced by M–heteroatom bonds.

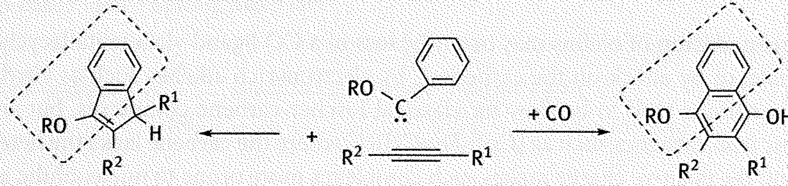


Metathesis, from Greek 'μεταθεση' = to change position.

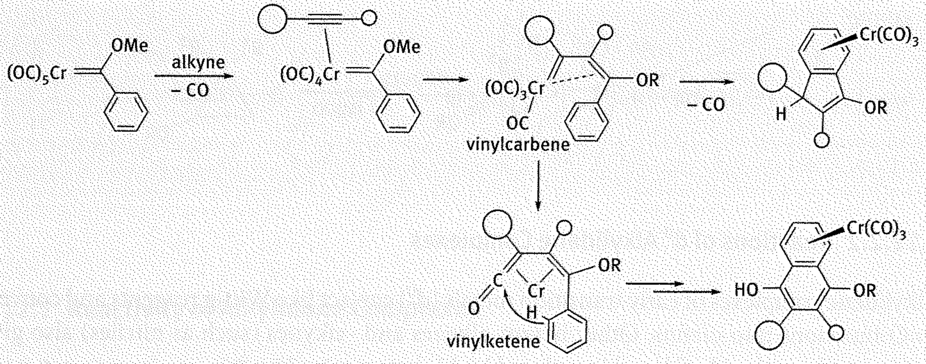
More important however are [2+2] cycloadditions to give metallacyclobutanes: the basis of olefin metathesis reactions. An early example of this type of reactivity was the Tebbe reagent.

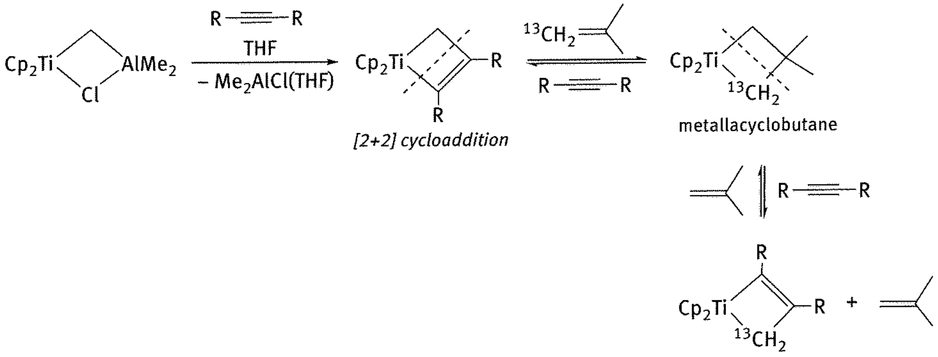
Box 2.12.2.1 The Dötz reaction

Aryl-substituted Fischer carbenes may be combined with disubstituted alkynes and CO in a stoichiometric reaction to generate OH- and OR-substituted five- and six-membered ring systems. The reaction principle is the attack of an alkyne ligand *cis* to the carbene.

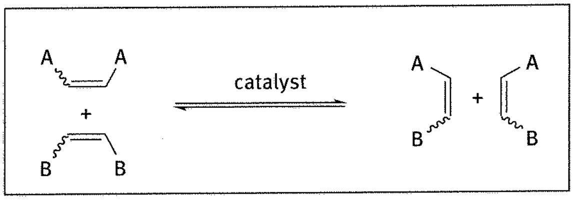


The arrangement of substituents R^1, R^2 is sterically controlled. The reaction proceeds most probably via vinylcarbene (for 5-rings) and vinylketene intermediates (after CO insertion, for 6-rings). The Dötz reaction generates 1,4-hydroquinones and quinones and has been used for the synthesis of natural products, steroids, and antibiotics.



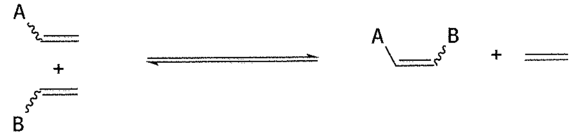


Metallacyclobutane formation through [2+2] cycloaddition is the key reactivity pattern of d^0 Mo and W imido alkylidene complexes (Schrock metathesis catalysts), as well as of Ru(II) alkylidenes (Grubbs catalysts, Section 2.12.2.2). The latter are particularly in demand in organic synthesis due to their stability towards air, moisture, and most functional groups. The principle is the exchange of the two halves of an alkene:

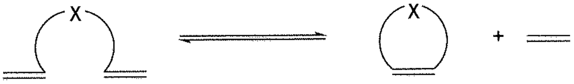


This reaction can be used to join different unsaturated molecules, split molecules, and form rings and polymers. The main reaction types are:

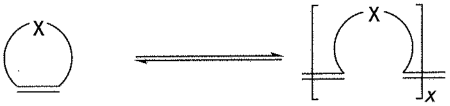
cross-metathesis:



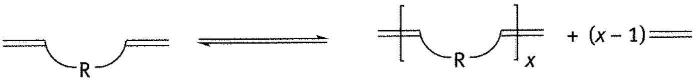
ring-closing
metathesis, RCM



ring-opening metathesis
polymerization, ROMP



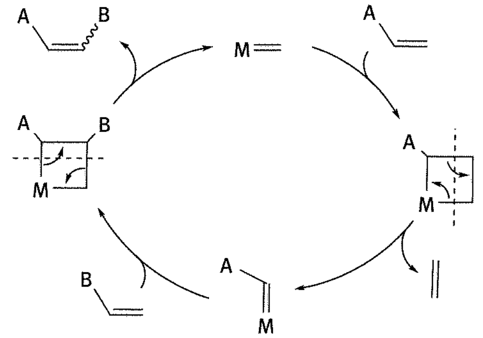
acyclic diene metathesis
polymerization, ADMET



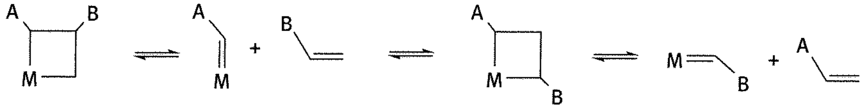
Cross-metathesis is used, for example, to cleave high molecular weight internal alkenes by applying ethylene pressure. Ring-closing metathesis is driven to completion by removal of the volatile ethylene by-product, while ROMP is typically driven by the release of ring strain.

The reaction intermediates alternate between metal alkylidene and metallacyclobutane structures, either of which can be catalyst resting states (***Chauvin mechanism***). There are no obvious termination pathways (unless impurities are present), and the polymerization reactions with well-defined metal alkylidene catalysts are therefore living (i.e. they assume a resting state once the olefinic substrate is consumed and the complexes become active again on addition of further substrate). Termination can be achieved by adding electrophiles X=Y, such as an aldehyde which converts M=C into M=O bonds. The general catalytic cycle for the olefin metathesis process if therefore given by:

Nobel Prize 2005 to Y. Chauvin, R. R. Schrock and R. H. Grubbs for their work on olefin metathesis



Various members of this catalytic cycle have been isolated. The steps in the simplified mechanism shown here are reversible. The process is accompanied by side reactions in which metallacycles are formed with the substituents in 1,3-positions, which do not lead to productive olefin metathesis:



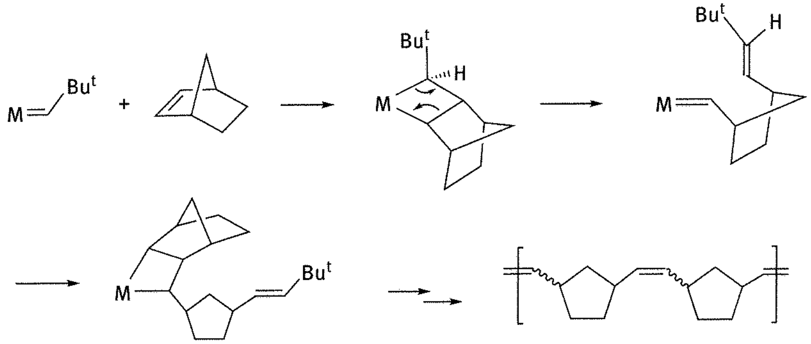
SHOP process: see Section 3.7.3

Olefin metathesis was discovered in the 1950s, and a variety of catalysts were used long before the actual mechanism of this reaction became clear. These were mixed-component catalysts such as $WCl_6/SnMe_4$ mixtures. In the Shell Higher Olefin Process (SHOP), ethylene is oligomerized by soluble nickel catalysts, with the aim of producing terminal mid-range alkenes suitable for the production of detergent alcohols (C_{10}–C_{18}). The unwanted lighter and heavier oligomer fractions are converted into the desired products using a heterogeneous MoO_3/Al_2O_3 metathesis catalyst.

$$C_4\text{–}C_8 \text{ alkenes} + C_{20+} \text{ alkenes} \xrightarrow{MoO_3/Al_2O_3} C_{10}\text{–}C_{18} \text{ alkenes}$$

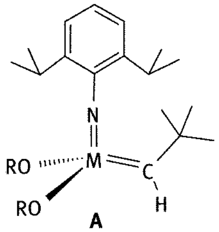
The first examples of single-component metathesis catalysts were Cp_2Ti metallacyclobutanes. Well-defined Mo and W complexes catalyse the living polymerization of cyclic alkenes such as norbornene. Living polymerizations are characterized by the fact that all polymer chains have the same lengths (i.e. the polydispersity $\overline{M}_w/\overline{M}_n$ is close to 1).

The process is exemplified by the ring-opening metathesis polymerization (ROMP) of norbornene:



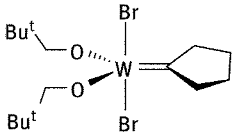
cis or *trans* polymer isotactic, syndiotactic, or atactic orientation of 5-rings

Bulky substituents on the imido-N as well as bulky alkoxide ligands are important design features of these catalysts; their reactivity was found to increase with the electron-withdrawing character of the alkoxide ligands. Some tungsten complexes (e.g. **B**) tolerate ester groups. The Mo complexes are advantageous because of their high reactivity. The alkylidene ligand can adopt two orientations: the major *syn*-isomer, with the Bu^t group pointing towards the imide, and the minor *anti*-isomer. As often happens in catalysis, the minor, higher energy isomer is more reactive (by a factor of about 10^4 in ROMP reactions).

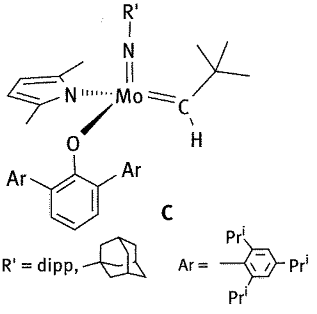


A

M = Mo, W
R = CMe_3, $CMe(CF_3)_2$, aryl

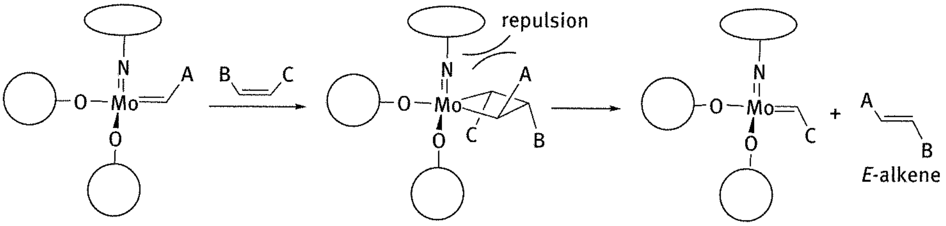


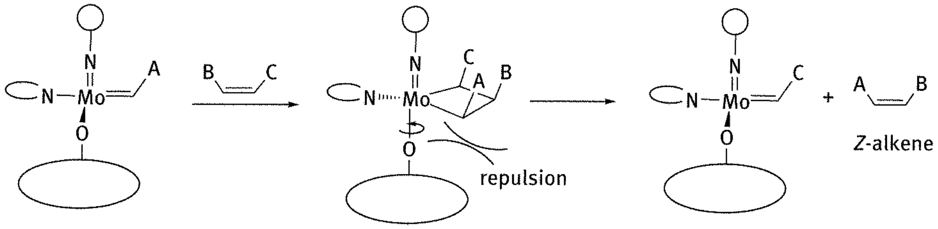
B



C

The orientation of the alkylidene substituent and of the substituents in the metallacyclobutane after alkene addition are responsible for the stereocontrol of the process and determine the microstructures of the resulting ROMP polymers. Whereas the formation of *E*- (*trans*) alkenes is thermodynamically favoured, small substituents on the imido ligand and very large aryloxides, as in structure **C** shown in the previous diagram, favour the formation of *Z*- (*cis*) olefins:

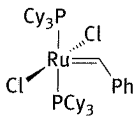




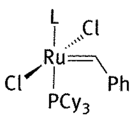
2.12.2.3 Ruthenium Carbene Complexes

Ruthenium complexes $L_2Cl_2Ru{=}CHR$ (L = donor ligand) form a large family of alkene metathesis complexes, which are widely used in organic synthetic applications due to their stability to moisture and their tolerance of functional groups. Several types have been developed. While the PPh_3 derivatives show only modest activity, compounds with L = PCy_3 are much more reactive. These complexes have square-pyramidal structure, and for high activity one ligand L has to dissociate; this is facilitated by the *trans*-influence of strong donors like PCy_3. The remaining L has a stabilizing function. Even more active systems are obtained if this phosphine is replaced by a stronger donor, such as an N-heterocyclic carbene. These classes of complexes have become known as Grubbs I and II type catalysts, respectively. The Grubbs II catalyst has very high ROMP activity for norbornene, but does not give good control over polymer molecular weight and molecular weight distribution. This problem is addressed in Grubbs III complexes, which contain a strong NHC donor combined with labile bromopyridine ligands and give living polymers with narrow polydispersities.

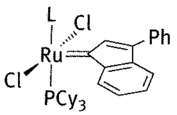
Another type of catalyst is based on benzylidene ligands with *ortho*-ether substituents (reported independently by Hoveyda and Blechert). These are stable complexes in which the OR substituent acts as a hemilabile ligand. The catalyst is re-formed at the end of the metathesis reaction, so that catalyst recycling is facilitated.



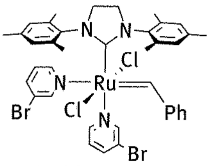
Grubbs 1st generation



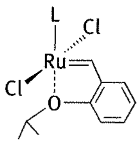
Grubbs 2nd generation



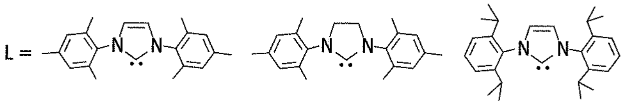
Ru indenylidene



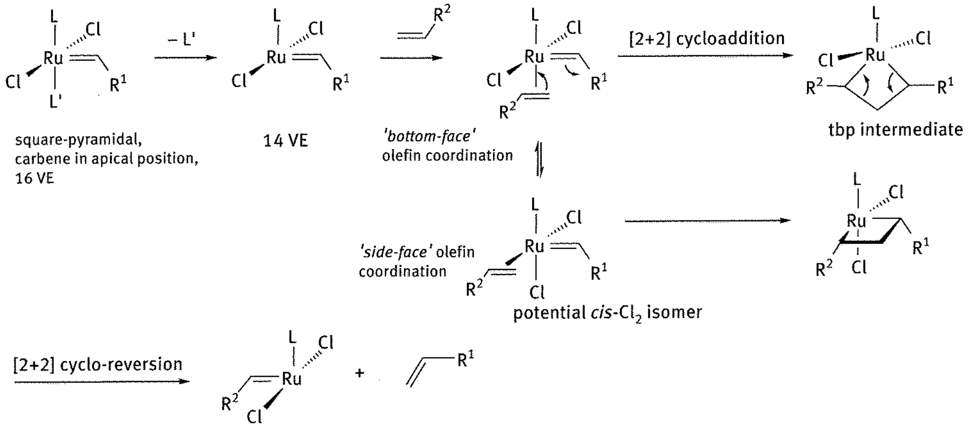
Grubbs 3rd generation



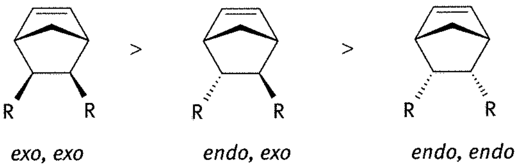
Hoveyda, Blechert



The reaction with olefins follows the [2+2] cycloaddition pathway shown in Section 2.12.2.2 for d^0 complexes. It is likely that this step proceeds via a trigonal-bipyramidal structure (keeping in mind that trigonal-bipyramidal and square-pyramidal isomers are typically close in energy). The precise stereochemistry of the intermediates and transition states will be influenced by the ligands and the reaction medium.



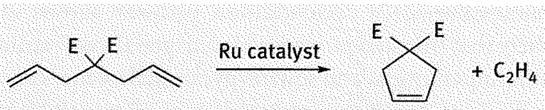
The reactivity of catalysts and olefinic substrates is strongly subject to steric influences. For ring-opening polymerization with norbornenes, the reactivity decreases in the sequence:

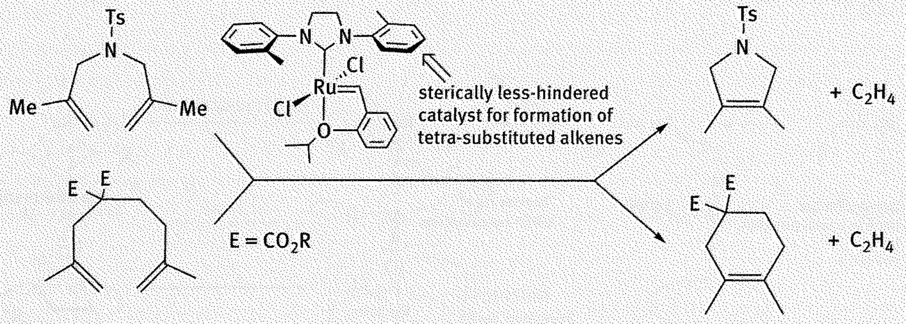


Box 2.12.2.3 Applications of olefin metathesis

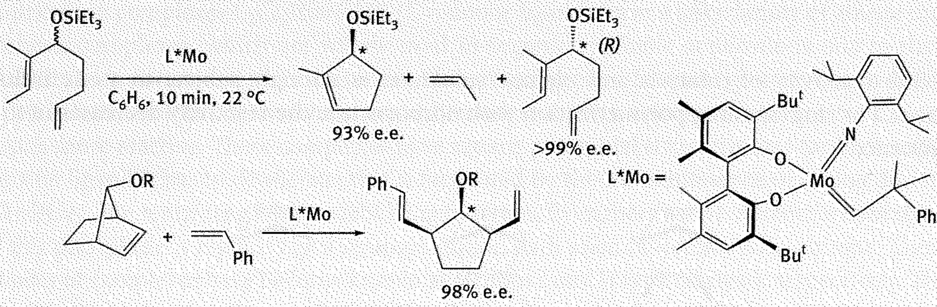
Olefin metathesis has many applications in synthesis and polymer chemistry. Some examples are illustrated in the following diagram.

Ring-closing metathesis (RCM). The formation of 5-membered rings from terminal alkenes is favoured, with the elimination of ethylene. Tetra-substituted alkenes are usually difficult to synthesize but can be made by a C=C metathesis coupling step, depending on a suitably tailored catalyst structure.

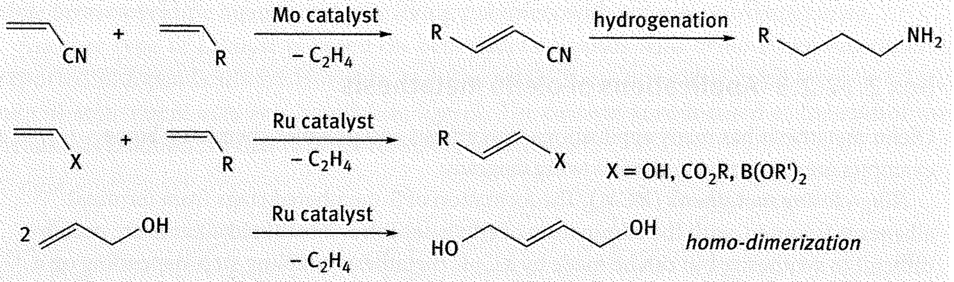




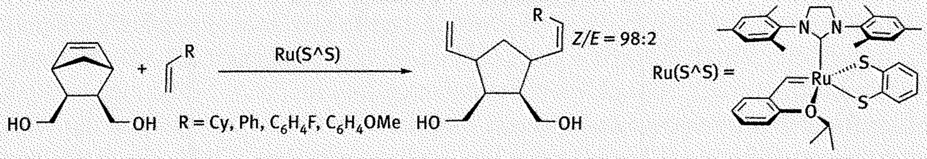
With chiral catalysts enantioselectivity may be achieved, i.e. only one of the two enantiomers reacts. The RCM example shown here illustrates this principle, with the *(S)* enantiomer reacting 58 times faster than the *(R)*. (The reaction is accompanied by about 40% of dimer formation through coupling of the terminal C=C bonds.)

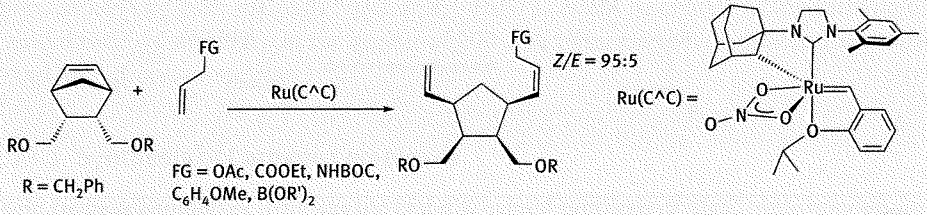


Cross-metathesis (CM) is a means of generating selectively functionalized internal alkenes including nitriles, alcohols, and esters, for example:

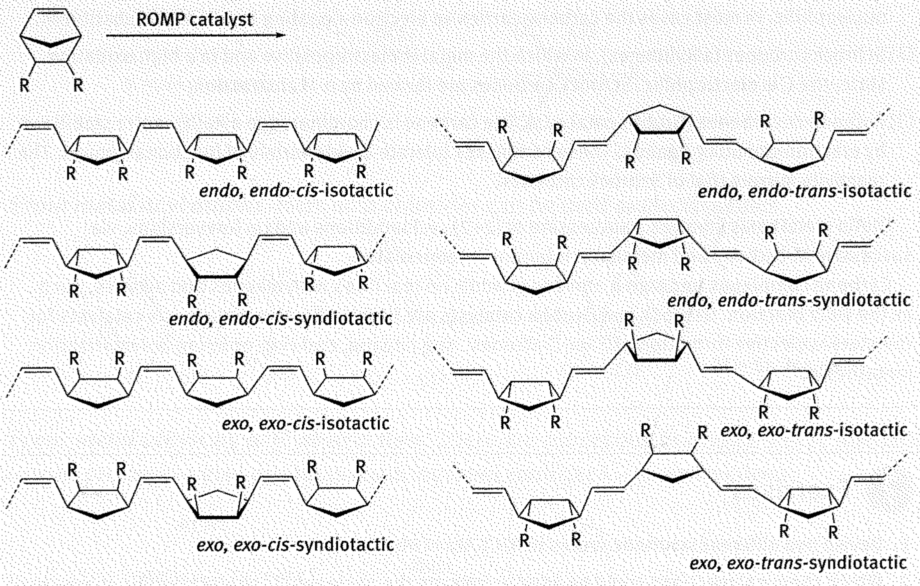


Whereas formation of *trans (E-)*-alkenes is thermodynamically favoured, for many syntheses *cis (Z-)*-alkenes are required. In these cases the catalyst must produce the kinetic product and prevent subsequent ΔH-driven isomerization. Once again, this is achieved by tailoring the ligand structure of the catalyst:

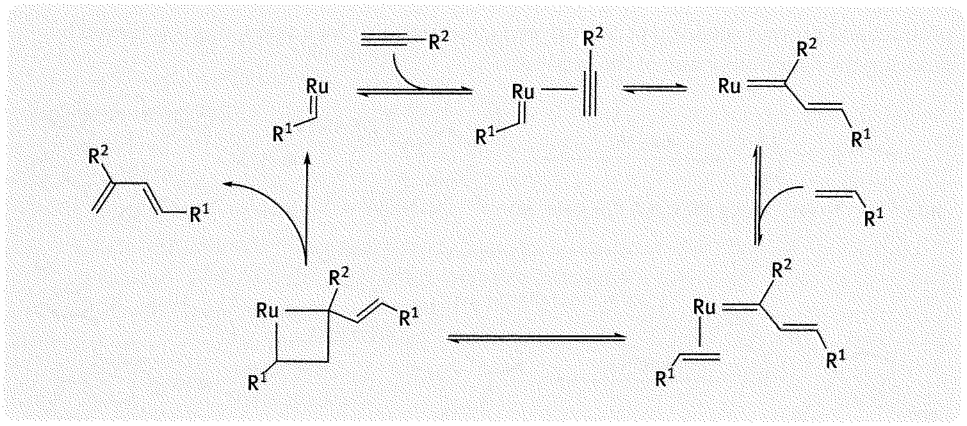




Ring-opening metathesis polymerization (ROMP) with selected catalysts gives a range of polymers with different microstructures, and consequently different material properties. R can be varied widely, including amino acid and peptide residues:



Enyne metathesis. Ruthenium carbene complexes react with alkynes under insertion to give dienylidene derivatives. This reaction can be used to combine alkenes and alkynes to give conjugated dienes:



Key points

Carbene complexes form three types:

(1) Fischer carbenes, in which the carbene is coordinated to a low-valent metal and the C is nucleophilic. In most cases the carbene carries an electron-donating heteroatom substituent.

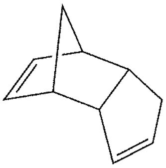
(2) Schrock carbenes (alkylidenes), in which the metal is electropositive and in a high oxidation state; the C is electrophilic. Schrock carbenes are formed by α-H abstraction.

(3) Ruthenium carbenes (Grubbs catalysts). The carbene is coordinated to a Ru(II) centre stabilized by electron-donating ligands. These complexes tolerate a wide variety of functional groups. The reactivity mirrors that of Schrock carbenes.

Olefin metathesis involves a succession of [2+2] cycloadditions and cycloreversions, via successive M-carbene and metallacyclobutane intermediates.

Carbene complexes undergo a number of addition reactions with alkenes and alkynes, such as the Dötz reaction. Schrock and Grubbs catalysts are highly effective metathesis catalysts for the stereoselective formation of *E*- or *Z*-alkenes, ring closing, and ring-opening polymerization metathesis.

Dicyclopentadiene =



Exercises

1. Devise two different synthetic routes to $(OC)_5Mo{=}CPh_2$.
2. Which chemical reactions could be used to indicate the nucleophilic or electrophilic character of (i) $(OC)_5Cr{=}CPh(OMe)$ and (ii) $Cp_2TaMe(CH_2)$?
3. How many products can be formed if a mixture of $R^1CH{=}CHR^2$ and $R^3CH{=}CHR^4$ is subjected to olefin metathesis?
4. A ring-opening polymerization of a cyclic olefin gives initially a living polymer with narrow molecular weight distribution. However, over time a broadening of the polydispersity is observed. Account for this observation.
5. Which polymers are obtained in the ROMP of dicyclopentadiene?
6. What is the product of the enyne metathesis of 1-octen-7-yne?

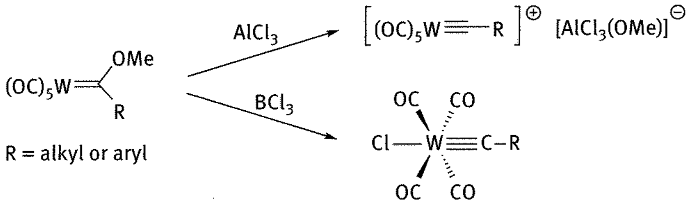
2.13 Complexes with M≡C Triple bonds: Carbynes

M≡C –

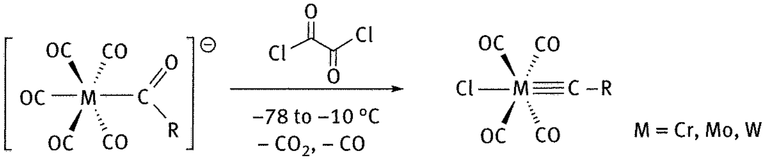
Complexes containing M≡C triple bonds $L_nM{\equiv}C{-}R$ are referred to as carbyne or alkylidyne complexes. The CR fragment could be considered as a trianion, $[CR]^{3-}$, similar to alkylidenes, or as a cation, $[CR]^+$, in analogy to linear nitrosyl ligands. The cationic formulation is more in keeping with its electron-acceptor capacity and susceptibility towards nucleophilic attack. The M≡C bond consists of a σ- and two π-bonds. The bond distances are very short, in keeping with the high bond order. The ^{13}C NMR resonance of the carbyne-C is found downfield of $SiMe_4$, in the region of 200–350 ppm. Carbyne complexes are mostly found for Group 5–7 metals.

2.13.1 Synthesis of Carbyne Complexes

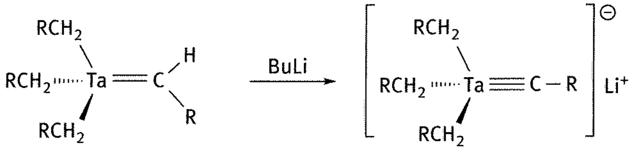
From carbene complexes. This was the first discovered synthesis of M≡C triple bonded compounds, in an attempt to generate halide-substituted carbene complexes.

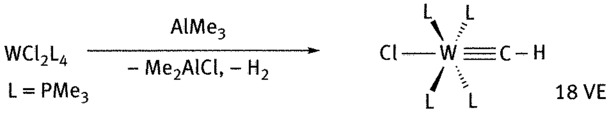


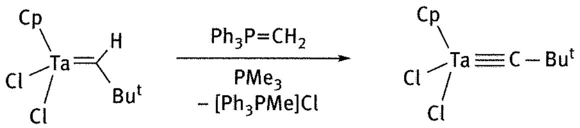
From metal acyl anions. Here acid chlorides can be used as electrophiles.



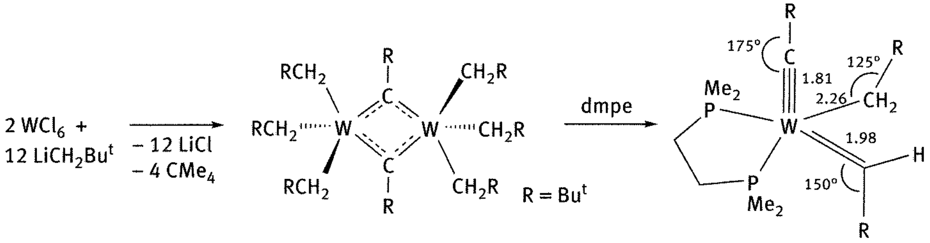
From metal alkyls by α-H abstraction. There are numerous examples where alkylation reactions proceed to give products resulting from multiple C–H abstractions.



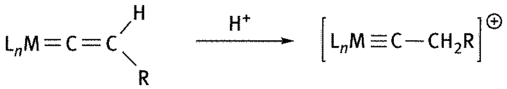




Depending on the alkyl group the reactions may lead to bridging carbyne complexes $[(RCH_2)_nM(\mu\text{-}CR)]_2$ ($n = 2$, M = Nb, Ta, Re; $n = 3$, M = Mo, W; R = Bu^t, SiMe$_3$). The carbyne bridges may be cleaved by donor ligands. The mononuclear tungsten carbyne shown in the following diagram contains all three types of M-C linkages.

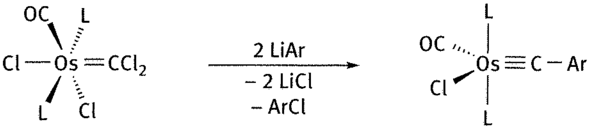


From vinylidenes:



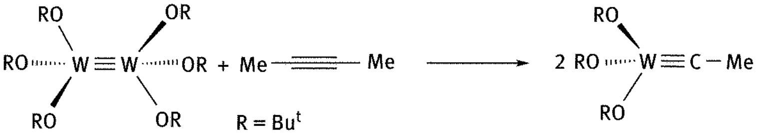
L_nM = e.g. $ReCl(Me_2PC_2H_4PMe_2)_2$, $IrCl(PPr^i_3)_2$

From dihalocarbenes:



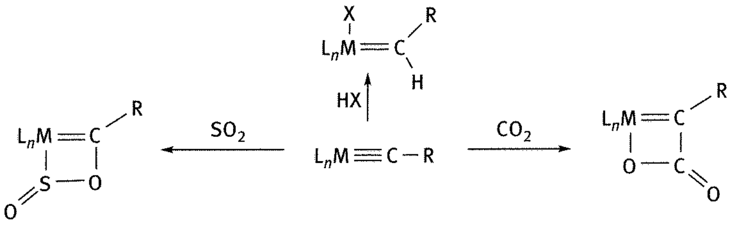
L = PPh$_3$, Ar = *o*-tolyl

By M–M bond cleavage. Electron-deficient Group 6 complexes with M≡M triple bonds undergo metathesis-like reactions with alkynes to give metal carbynes:

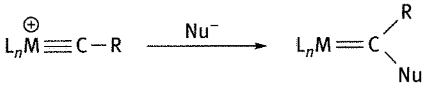


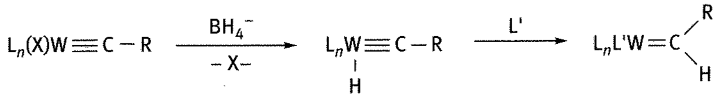
2.13.2 Reactions of Carbyne Complexes

With electrophiles. In analogy to metal alkyls, one might expect carbyne complexes to be susceptible to attack by electrophiles. Carbynes can indeed be protonated to give carbenes, and they undergo addition reactions with electrophiles such as CO_2 and SO_2.

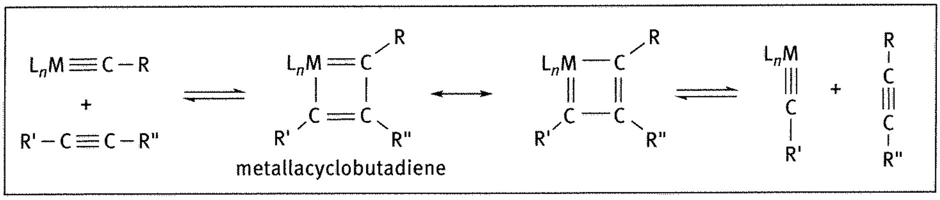


With nucleophiles. 18 VE carbyne complexes react on the carbyne-C atom, less electron-rich complexes primarily on the metal.



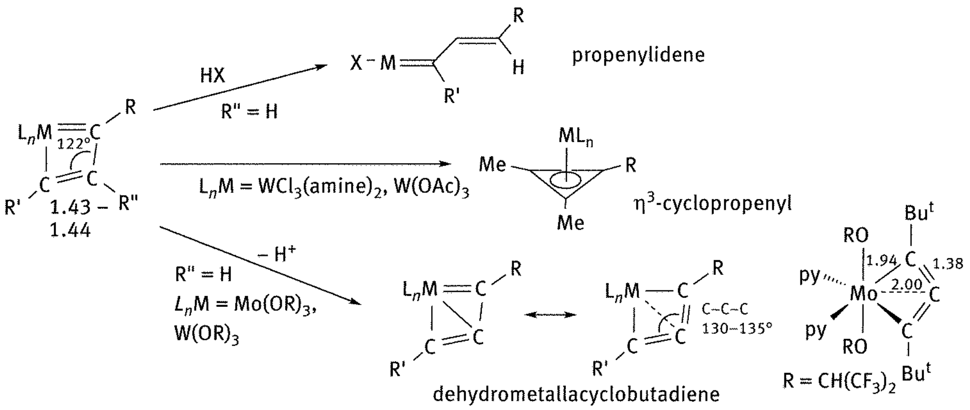


Alkyne metathesis. The most important reaction of carbyne (alkylidyne) complexes is the metathesis of alkynes. The reaction proceeds along similar lines to alkene metathesis, via a MC_3 4-membered ring intermediate:

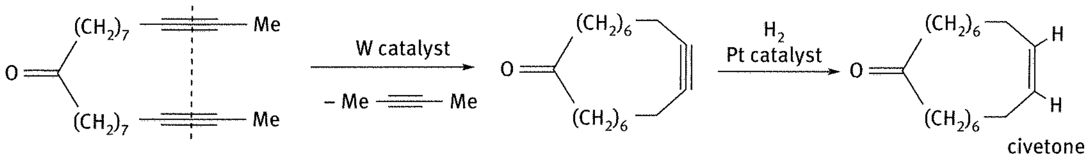


The metallacyclobutadiene intermediate is isolable in some cases and has been structurally characterized. The C–C bond length is similar to that in benzene [e.g. 1.43 and 1.44 Å in $Et_3C_3W(OR)_3$ ($R = CH(CF_3)_2$)].

Apart from the productive sequence shown here, metallacyclobutadiene has been found to undergo side reactions which are associated with catalyst deactivation, including the formation of cyclopropenyl complexes. With terminal acetylenes, deprotonation has been observed to give isolable MC_3R_2 complexes with a ***dehydrometallacyclobutadiene*** ring. The formation of these products explains the difficulty of metathesis reactions with terminal alkynes.



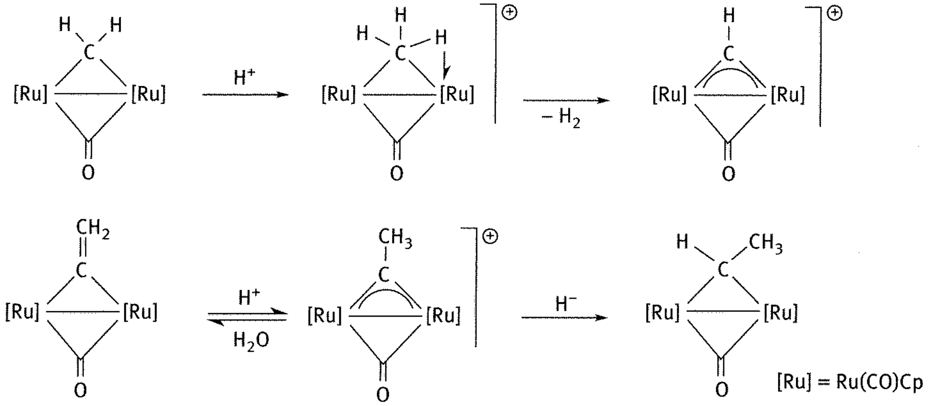
Alkyne metathesis is a useful method for ring closure. Since H_2 delivery to such a C≡C triple bond in a subsequent hydrogenation step usually proceeds with *syn* addition, the sequence is equivalent to the formation of *cis*-alkenes. This principle has been applied, for example in the synthesis of civetone, a perfume ingredient:



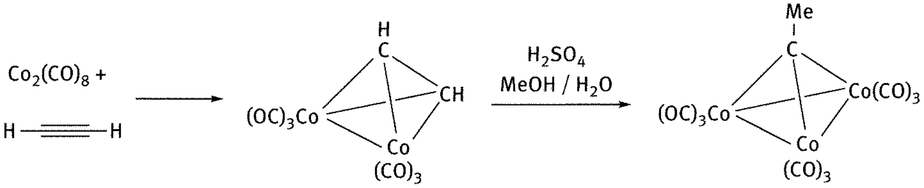
2.13.3 Bridging Carbene and Carbyne Complexes

Fischer–Tropsch process: see Section 2.5.2.

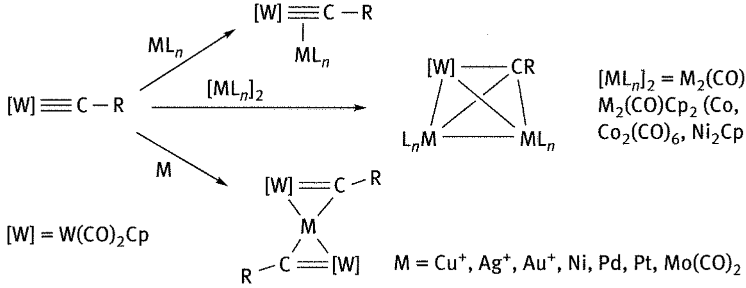
Carbene and carbyne ligands can bridge two or more metal centres. Complexes of this kind have been primarily investigated in connection with understanding the intermediates and reaction patterns of the ***Fischer–Tropsch*** reaction. In such compounds, bridging alkyls, carbenes, and carbynes proved to be interconvertible by successive additions of H⁺ and H⁻. Heterogeneous ruthenium catalysts are used for the FT process, and organometallic Ru complexes demonstrate steps in the alkane formation pathway.



Cobalt carbonyl clusters with triply-bridging carbyne ligands can be generated from acetylenes. They represent numerous such metal carbonyl clusters where the analogy between cluster chemistry and the surface of heterogeneous catalysts is evident.



Bridging carbynes can be produced from alkyl species, or by the addition of coordinatively unsaturated metal centres to M≡CR complexes. In this respect the $L_nM{\equiv}CR$ molecule coordinates like an alkyne.



$[ML_n]_2 = M_2(CO)_4Cp_2$ (Mo, W)
$M_2(CO)Cp_2$ (Co, Rh, Ir)
$Co_2(CO)_6$, $Ni_2Cp'_2$

[W] = $W(CO)_2Cp$

M = Cu^+, Ag^+, Au^+, Ni, Pd, Pt, $Mo(CO)_2$

Key points

Complexes $L_nM{\equiv}C{-}R$ are referred to as carbyne or alkylidyne complexes.

The CR fragment can be considered a trianion $[CR]^{3-}$ or a cation, $[CR]^+$. The cationic formulation is more in keeping with its electron-acceptor capacity and susceptibility towards nucleophilic attack.

Carbyne and carbene complexes are in principle interconvertible.

Carbyne complexes are mostly found for Group 5–7 metals.

Some Mo, W carbyne complexes undergo metathesis exchange with alkynes. This reaction can be used for ring closure to give cyclic alkynes.

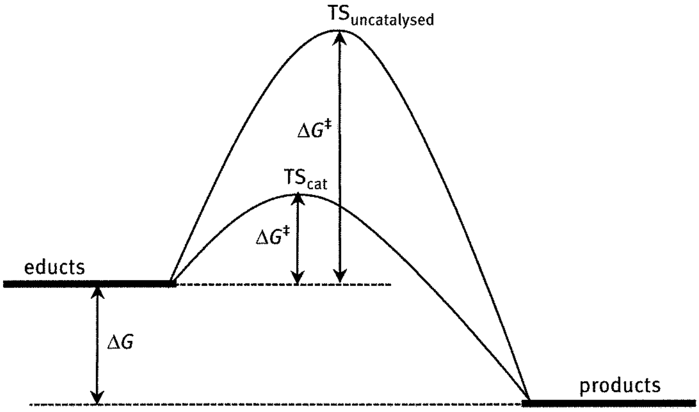
Exercises

1. Describe a synthetic route to $PhC{\equiv}Cr(CO)_4Br$.
2. What are the products of alkyne metathesis of (i) cyclooctyne; (ii) 2,10-dodecadiyne.

3

Homogeneous Catalysis with Organometallic Transition Metal Complexes

Catalysis is a means of accelerating chemical reactions by lowering the activation energy barrier ($\Delta G^{\ddagger}$). Catalysis is therefore a **kinetic, not a thermodynamic phenomenon**, and relates to the energy and structure of the **transition state (TS)**. Microscopic reversibility of the reaction pathway means that educts and products are, in principle, in equilibrium (even if this equilibrium is ideally strongly in favour of the products). Lowering $\Delta G^{\ddagger}$ accelerates the rate with which this equilibrium is reached and the product formed, but a catalyst cannot shift the position of this equilibrium or alter the overall energy gain (ΔG) of the reaction. In its simplest form, catalysed and uncatalysed reactions show the following energy profile:



The Eyring equation relates the rate of a reaction—here k_{cat} of the catalysed transformation—to the activation energy $\Delta G^{\ddagger}{}_{\text{cat}}$:

$$k_{cat} = \left(k_B T / h\right) \exp(-\Delta G^{\ddagger}_{cat} / RT)$$

where T = temperature (in K), k_{B} = Boltzmann constant, h = Planck's constant, R = gas constant.

A catalyst is neither generated nor consumed in the reaction it catalyses. The chemical species after completion of the catalytic cycle must therefore be identical (or closely equivalent) to the species at the start of the cycle, and each cycle starts with the catalyst–substrate interaction. This differentiates a catalyst from an initiator, which is involved in the first step only (initiator-substrate reaction), where it is typically consumed and takes no further part in the reaction.

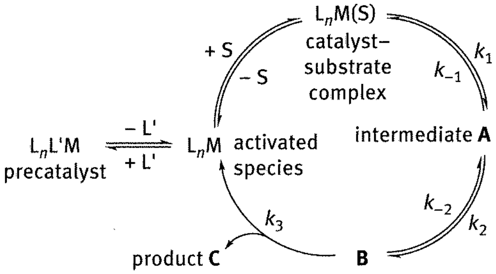
Catalysis provides a means of achieving high product selectivity, minimizing waste by-products by improving atom-efficiency, and cutting down the number of reaction steps required for product synthesis. Catalytic processes are therefore of major importance, and are capable of drastically reducing the energy and raw material consumption of chemical reactions.

Catalysis can be achieved in many ways and by many reagents. In the simplest case, protons can catalyse reactions, e.g. esterification, while in others simple Lewis acids are involved, such as $AlCl_3$. Where C–C and C–X bonds are made or broken, metals are frequently involved, and this is the area where knowledge of organometallic reaction pathways has the most impact. Detailed understanding of the reaction mechanisms and the factors that limit turnover rates is key to designing more highly effective catalysts, and has in many cases led to dramatic improvements in catalyst productivity. Here, we are primarily concerned with the mechanistic principles of reactions catalysed by homogeneous organometallic catalysts. In homogeneous systems both substrate and catalyst are present in the same phase, i.e. in solution. Similar reaction pathways operate in many heterogeneous catalysts, but here the investigation of intermediates and mechanisms at solid/liquid and solid/gas interfaces is much more difficult and is outside the scope of the present text. Heterogeneous catalysts are typically applied in large scale gas phase reactions and offer the advantage of easy separation from the product and long lifetimes. By contrast, homogeneous catalysts are typified by mild reaction conditions and high product selectivity.

3.1 General Considerations

A catalytic cycle involves several steps: formation of a catalytic species capable of binding the substrate, followed by a series of steps leading to the product while regenerating the catalytic species.

It is important to define what is meant by 'catalyst'. The succession of steps in a catalytic cycle implies that several species are involved in the catalytic process—one cannot say that any one of them is 'the' catalyst. Very often, however, the term catalyst is applied to the storage form of the complex that is added to the reaction. Strictly speaking these are pre-catalysts, which require some sort of activation step(s) to become active. Usually this activation step is ligand dissociation to give a coordinatively unsaturated species that is capable of forming an association equilibrium with the substrate. The substrate may associate and dissociate many times before a transformative step takes place. A simple catalytic cycle can therefore be represented by:

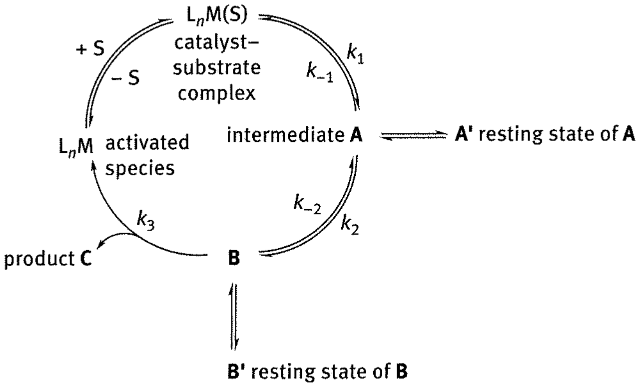


Any one of the rate constants leading to the product, k_1, k_2, k_3 could be rate determining. The turnover frequency is therefore given by the step with the lowest k value, the rate-limiting step. This is the rate that is accessible by reaction kinetic measurements.

Note that rate constants are indicated by lower-case k, whereas upper-case K is used for equilibrium constants: $K_1 = k_1/k_{-1}$

There are cases where the product **C** is the local rather than a global minimum structure. In such cases a second catalytic reaction may ensue, such as an isomerization to a follow-on product **D**. Compound **C** would be the **kinetic product** while **D** is the more stable **thermodynamic product**, and the **C**/**D** ratio will be given by the energy difference between the two (providing none is removed from the equilibrium). If a product is poorly soluble or volatile, so that it can be removed during the reaction, the process becomes irreversible.

As stated, the success of catalysis depends on the structure of the transition state, not the ground state precursors. **The concentration of the transition state is zero**, i.e. such transient species are not directly detectable. The question then arises of how such mechanisms can be investigated. The practice, although frequently adopted, of determining the ground state structures of pre-catalysts (usually solid state) and discussing the steric or conformational features in terms of their relevance to catalysis is rarely helpful. However, in many instances there are **resting states**, which are structurally related to the TS and can be observed. These resting states may be catalytic intermediates (**A** or **B** in the present case), or they may be species **A′** or **B′** in equilibrium with **A** or **B**. The catalytic cycle may then be represented as:



The species **A′** or **B′** are in principle spectroscopically observable and allow conclusions to be drawn about the likely structures of **A** and **B**.

Apart from spectroscopic identification of intermediates and resting states, insight into the mechanisms of catalytic reactions is provided by kinetic methods. A typical **rate law** for catalysed reactions is **first order** in both catalyst (C) and substrate (S) (i.e. k is a second-order rate constant):

$$-d(S)/dt = k[C][S]$$

If [S] is so large that in effect it does not change during the reaction, the process is said to be pseudo-first order. This facilitates the determination of the reaction order in [C]:

$$-d(S)/dt = k_{obs}[C]$$

The determination of the reaction orders for both [C] and [S] should precede any kinetic investigation.

There are also cases where second order dependence on the substrate or broken orders $[C]^a[S]^b$ ($a \neq b \neq 1$) have been reported. In such cases equilibria are involved which may not have been recognized. A detailed discussion of catalysis reaction kinetics is beyond the scope of this text.

In some cases the resting state of the catalytic cycle is the substrate adduct itself, $L_nM(S)$. In such a case the concentration $[L_nM(S)]$ is constant and the reaction becomes independent (**zero-order**) of the substrate concentration [S] (saturation conditions).

When devising reaction mechanisms based on kinetic measurements, it must be borne in mind that kinetics provide information on the ***composition of the transition state****, but not on the manner in which this composition was arrived at. This means there may be various alternative pathways for TS formation, but these are kinetically indistinguishable.*

Dissociative and associative mechanisms. Chemical processes including catalytic transformations are often described as dissociative or associative pathways. In such descriptions the role of the solvent is typically neglected. While dissociative pathways play a role in gas phase processes, in solution phase catalysis truly vacant coordination sites are not created and ligands do not simply dissociate. Rather, ligand 'dissociation' is a process where a ligand has been displaced by a solvent molecule—so that strictly speaking this is an associative process. In homogeneous catalysis, the solvent plays a major role in stabilizing transition states and intermediates and can influence the course of the reaction (e.g. by stabilizing or destabilizing charged or polarized TS structures).

The processes considered here will deal with transition metal catalysts (as well as some cases of rare earth compounds). This is because the chemistry of these elements involves d-orbitals, which offer sufficient symmetry options to provide facile kinetic pathways for catalysis. Although for Lewis acid catalysis Main Group compounds are typically used, p- and s-orbitals are not optimal for most catalytic transformations.

Several catalytic reactions have been described in previous sections where they seemed more appropriate. This part outlines briefly several major catalytic reactions, the general mechanistic aspects, and some applications.

3.2 Key Reaction Steps in Homogeneous Catalysis

Homogeneous catalytic reactions with organometallic catalysts contain a limited number of fundamental reactions which may be combined to construct plausible, self-consistent catalytic cycles. These key steps are:

(1) catalyst activation;
(2) substrate coordination;
(3) oxidative addition;
(4) reductive elimination;
(5) nucleophilic attack on substrate;
(6) product dissociation/substitution.

3.2.1 Catalyst Activation

Catalyst activation converts a coordinatively saturated, storable catalyst precursor into a coordinatively unsaturated species. This can be achieved in various ways:

L dissociation

By dissociation of a ligand L. In the simplest case catalyst activation may be ligand dissociation. Bulky, moderately strongly bonded ligands like PPh_3 often dissociate in this way.

$$MX_mL_n \rightleftharpoons MX_mL_{n-1} + L$$

It is often necessary to shift the equilibrium in favour of the coordinatively unsaturated species. This can be done by a substance that scavenges the ligand L.

$$MX_mL_n + M' \rightleftharpoons MX_mL_{n-1} + M'{-}L$$

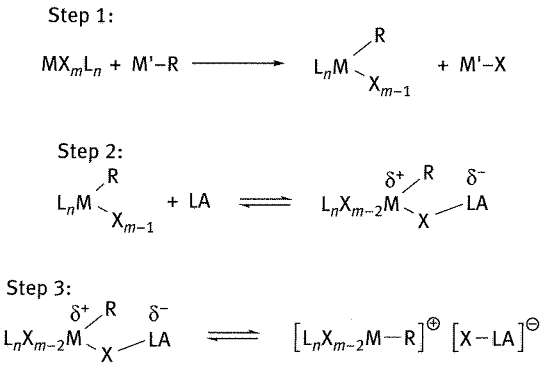
For example, adding $Ni(COD)_2$ to phosphine complexes of metals like rhodium is sometimes used to assist with the removal of PPh_3. $Ni(COD)_2$ is transformed into $Ni(COD)(PPh_3)_2$ or $Ni(PPh_3)_{3,4}$, with COD as non-competitive side product.

X abstraction

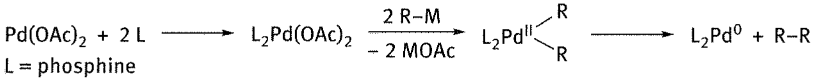
By Lewis acids. Of course, suitable choice of reagent (such as adding a strong Lewis acid LA) can also lead to abstraction of X instead of L:

$$MX_mL_n + LA \rightleftharpoons [MX_{m-1}L_n]^+ [X{-}LA]^-$$

Some catalyst activation processes involve more than one reaction. For example, in order to achieve catalysis, it may be necessary (1) to convert a stable metal halide complex MX_mL_n into a compound containing a metal-alkyl bond, and (2) to convert this product into a coordinatively unsaturated species. In some cases the product thus formed is a resting state (in which case it may be isolable or spectroscopically identifiable) which is (3) in equilibrium with the active species. This dissociation equilibrium may be assisted by the solvent, or by the substrate which displaces the bound anion (by an associative interchange I_A mechanism) to enter the catalytic cycle.

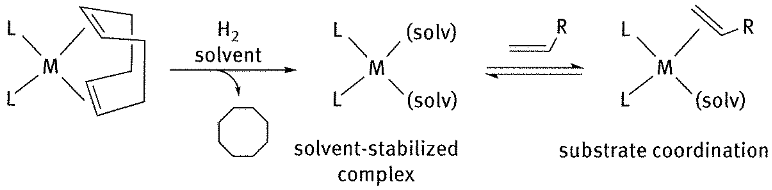


By reductive elimination. In the presence of alkylating agents, a metal dialkyl (or diaryl) may be generated which is prone to reductive elimination. This generates a coordinatively unsaturated metal species in an oxidation state two units below the precursor complex. This form of activation is common for palladium.



$$\underset{L = \text{phosphine}}{Pd(OAc)_2 + 2\,L} \longrightarrow L_2Pd(OAc)_2 \xrightarrow[-\,2\,MOAc]{2\,R\text{–}M} L_2Pd^{II}R_2 \longrightarrow L_2Pd^0 + R\text{–}R$$

By hydrogenation. In the specific case of hydrogenation catalysis, the precursor complex is frequently an olefin complex, such as 1,5-cyclooctadiene. In such a case the place-holder ligand is removed by hydrogenation, to generate a solvent-stabilized intermediate, for example:



Substrate Coordination

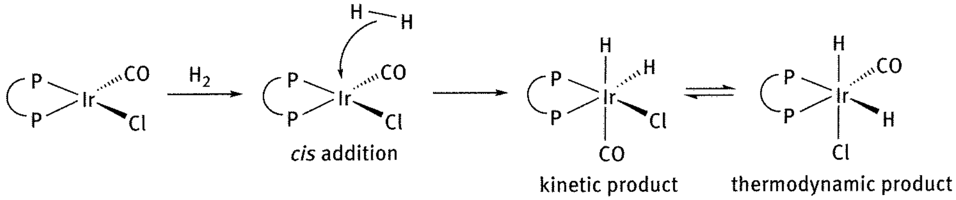
The substrate in most cases will be an alkene or an alkyne, but may also be a saturated hydrocarbon, ether, or ester. In any case, it needs to occupy a coordination site. Very often the substrate will displace a solvent molecule; substrate association is therefore a ligand substitution reaction. However, since the solvent concentration is 1 by definition, this is not apparent in the kinetics.

3.2.2 **Oxidative Addition**

Many catalytic cycles involve changes in the oxidation state of the metal, when reaction partners A–B are introduced that are sufficiently electron accepting and possess a bond that is weak enough to be cleaved under the given reaction conditions. Since A and B, as ligands with a higher electronegativity than the metal, are formally ascribed negative charges, in such a process the metal changes its oxidation state by two units. For transition metals, the d-electron count is reduced by two.

Oxidative addition delivers two potentially reactive ligands A and B in ***cis* position** to one another.

There may be subsequent ligand rearrangement to a thermodynamically more stable isomer, for example:



Reagents that are frequently introduced into the catalytic cycle by an oxidative addition reaction are H_2, for hydrogenation and hydroformylation reactions, and more generally a range of H–X molecules, notably HX = $HSiR_3$ (*hydrosilylation*), HCN (*hydrocyanation*). Other oxidative addition substrates are alkyl halides R–X (e.g. MeI in methanol carbonylation to acetic acid, Section 3.4.2.1), as well as benzyl, vinyl, and aryl halides R′–X (for *C–C cross-coupling reactions*, see Chapter 3.6).

For completeness it is worth mentioning that oxidative addition may not always lead to complete bond scission. For example, O_2 adds to Pt(0) to give the O_2 complexes which show a reduced O–O bond order:

Oxidative addition:

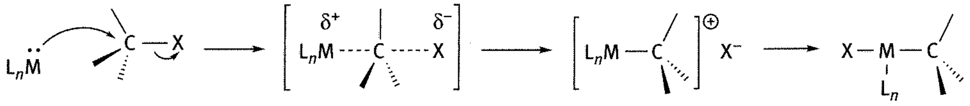
- Requires a coordinatively unsaturated metal centre ML_n and is accelerated if this metal centre has energetically high-lying, occupied d-orbitals. This is the case if the ligands L are strong donors.
- Is favoured by sterically bulky ligands which support low coordination numbers and therefore coordinative unsaturation; this increases the reactivity towards small molecules such as H_2 and HX. On the other hand, the donor strength and bulkiness must not be pushed to the extent that the oxidative addition product becomes an energy sink: in such a case the reaction would stop and the catalytic cycle could not be closed.
- Is common for **16 VE square-planar complexes** of metals with d^8 and d^{10} electron counts: ML_3 (M = Ni, Pd, Pt), XML_3 [M = Rh, Ir, such as the well-known Vaska's complex, $IrCl(CO)(PPh_3)_2$].
- Is limited by the stability of the higher metal oxidation state. For example, whereas Pt(II) may undergo oxidative addition to Pt(IV), the analogous oxidation of Ni(II) to Ni(IV) is not energetically accessible under most catalytic conditions.

- Becomes more favourable down a metal triad, in the sequence **first** < **second** < **third** row transition metal, following the general trend in the stabilities of the higher oxidation state.

Oxidative addition may involve more than one metal centre, as for example in the reaction of H_2 with $[Co(CN)_5]^{3-}$; the resulting $[HCo(CN)_5]^{3-}$ anion is a water-soluble hydrogenation catalyst.

$$2\,[\mathrm{Co^{II}(CN)_5}]^{3-} + \mathrm{H_2} \longrightarrow [\mathrm{Co\cdots H_2\cdots Co}] \longrightarrow 2\,[\mathrm{HCo^{III}(CN)_5}]^{3-}$$

The occurrence of oxidative addition says little about the detailed mechanism of the reaction. While in most catalytic reactions the product appears to be formed by a concerted process, S_N2 and 1-electron-transfer (radical) pathways are also occasionally observed. Polar media favour polar transition states, such as those involved in S_N2 reactions:



3.2.3 **Reductive Elimination**

The reverse of oxidative addition is reductive elimination. It generates a metal fragment in an oxidation state two units lower and is frequently the terminating reaction of a catalytic cycle.

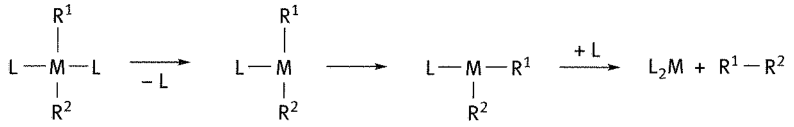
The trends that favour reductive elimination are the opposite to those of oxidative addition.

Reductive elimination:

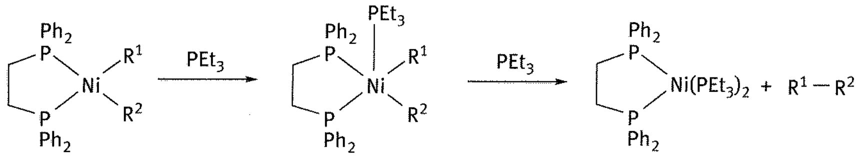
- Is most facile for first row transition metals, since these form the least stable M–C bonds and are smaller, so steric pressure is most pronounced;
- Requires the two ligands R^1 and R^2 to be in *cis* position;
- Is favoured by steric crowding and high coordination numbers, so that the reaction can be induced by additional ligands L;
- Proceeds faster for electron-poor complexes (which are more easily reduced) than for electron-rich ones;
- Is most facile if one of the ligands is H;
- Is favoured for metals where the low oxidation state is energetically readily accessible. Reductive elimination for late transition metals (high d-electron count) is facile whereas for early transition metals, with their high-lying d-orbitals, high oxidation states and d^0 configuration are preferred;

- Is faster for complexes with **odd coordination numbers**: 3- or 5- coordinate > 4- or 6-coordinate.

Since the ligands forming the C–C or C–X bonds must be *cis* to one another, *trans* complexes must undergo an isomerization step:

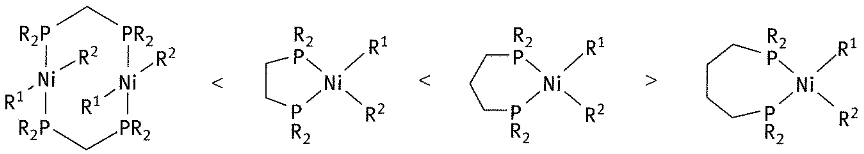


Apart from this dissociation and isomerization sequence, the addition of donor ligands can also accelerate reductive elimination. Note that in either case intermediates with an odd coordination number are generated.



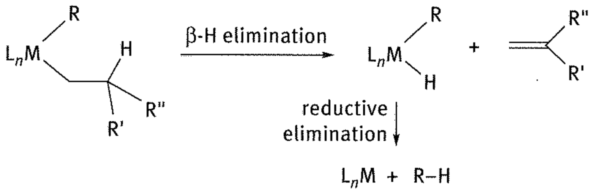
Reductive elimination from complexes with chelating ligands depends on the size and stability of the chelate rings. In Ni-catalysed C–C coupling reactions, for example, 5-rings are too stable, while rings with 7-membered rings and higher are too flexible.

elimination rate:



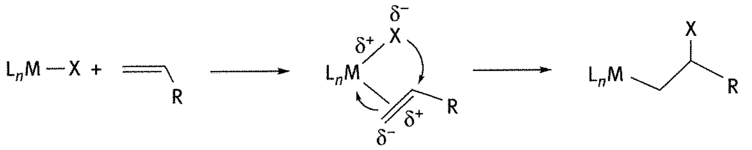
While there are many instances where reductive elimination reactions are induced by light irradiation (e.g. the formation of coordinatively unsaturated metal compounds L_nM from the corresponding L_nMH_2 dihydrides), photolysis is rarely applied to catalytic systems.

Reductive elimination from **metal alkyl hydrides to give R–H** is particularly facile and is the final reaction step in hydrogenation and hydroformylation reactions. Reductive elimination involving alkyls with β-H atoms is sometimes preceded by **β-H elimination**, so that a 1:1 mixture of saturated and unsaturated products results:



3.2.4 Nucleophilic Attack on Coordinated Substrates

Having bound a neutral unsaturated substrate as well as a nucleophilic anionic ligand X, the next productive step for a catalytically active complex is the transfer of X to the neutral substrate. This generates a new C–X bond. In the most important catalytic reactions, the neutral unsaturated substrate is CO or an alkene. The reaction constitutes an intramolecular nucleophilic attack on a coordinated ligand; it is the basis of hydrogenations, olefin polymerizations, HX addition reactions, and carbonylations. For unsaturated substrates with no or little polarity, the success of nucleophilic attack depends on the induction of polarity on coordination:



Alkynes and dienes react similarly, giving metal vinyl and allyl products, respectively. X may be H, alkyl, aryl, amide, OH, or OR. As with oxidative addition and reductive elimination reactions, the two ligands must occupy *cis* coordination sites.

The nucleophilic attack on coordinated CO ('CO insertions') has been discussed in Section 2.5.3.3 and particularly in Section 2.11.4.9.

In the following chapters, some important homogeneously catalysed reactions will be presented, with emphasis on reactions that have gained importance in industrial processes. The catalytic cycles illustrate the principal reaction steps. While the reaction mechanisms presented will be self-consistent and follow the mechanistic principles outlined in the preceding discussion, it is often possible to construct equally plausible alternative reaction sequences and catalytic cycles. In such cases only detailed mechanistic investigations can provide arguments in favour of one or the other.

Key points

Catalysis accelerates the transformation of a substrate via a sequence of intermediates, which lead to product formation and regeneration of the catalyst. The turnover frequency is limited by the slowest of these steps. The catalyst is not consumed.

A catalyst lowers the activation barrier but does not alter ground state energies and equilibrium positions.

Kinetics provide information about the transition state (TS) composition. A TS is not observable and its concentration is zero.

Kinetics do not provide information on the pathways by which the TS is reached.

Homogeneous catalytic cycles consist of a number of key steps: (i) substrate coordination; (ii) oxidative addition; (iii) nucleophilic attack on substrate; (iv) reductive elimination.

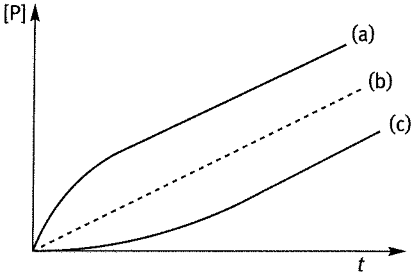
Catalysts are usually introduced as stable storage forms (pre-catalysts). Catalyst activation leads to coordinatively and electronically unsaturated species.

Exercises

1. A chemical reaction in the presence of a catalyst is 1000 times faster than the uncatalysed reaction. What is the difference in energy barriers in these two cases?
2. Many catalytic reactions have an initiation period, during which the catalyst concentration increases. This reaction phase therefore operates under non-steady-state conditions. It can be shown that in such cases the formation of a product P from a substrate S in the presence of catalyst C follows the rate law:

   $$d[P]/dt = k_p[S][C] + (k_i - k_p)[S][C]\exp(-k_i[S]t)$$

   Three different substrates give the following three conversion vs. time curves (a), (b), and (c). What do these curves tell us concerning the kinetic behaviour of the catalyst? In each case, determine the initial and the steady-state slopes of the reactions and identify which information these slopes provide.



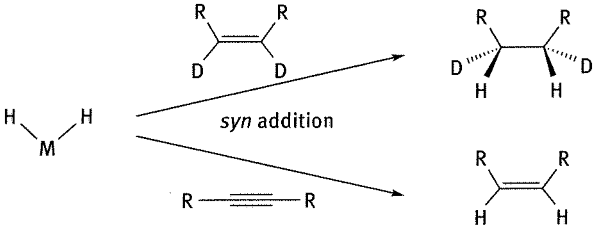
3.3 Catalytic H–H and H–X Additions

3.3.1 Hydrogenation

3.3.1.1 General Hydrogenation Catalysis

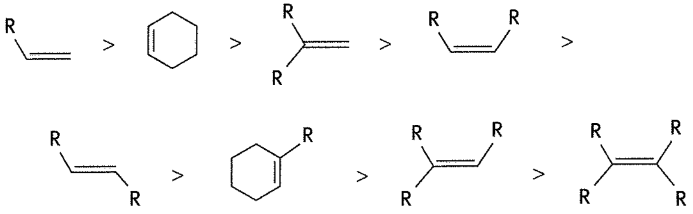
The catalytic hydrogenation of unsaturated organic substrates is a widely applicable reaction. The most important of these is the hydrogenation of alkenes. Hydrogenation is a *structure-insensitive* reaction that can be carried out with heterogeneous as well as homogeneous catalysts. In some cases metal nanoparticles are involved. An early application of hydrogenation catalysis was the partial hydrogenation of doubly unsaturated vegetable oils with heterogeneous nickel catalysts, to give saturated and mono-unsaturated derivatives of butter-like consistency for the production of margarine.

During the hydrogenation step, H_2 is added to the same π-face of unsaturated substrates (***syn* addition**); in the hydrogenation of C≡C triple bonds this generates *cis*-alkenes as primary products.



This stereoselectivity implies a concerted H-transfer mechanism. There are instances where *trans*-hydrogenation products are formed; in such cases a radical mechanism is involved or there is a subsequent isomerization step to the more stable *trans* product.

The general reactivity of alkenes towards hydrogenation decreases with increasing substitution of the C=C bond:



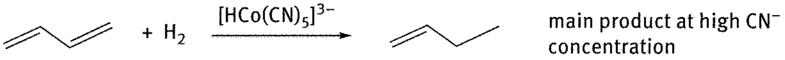
The first homogeneous hydrogenation catalysts were based on first row metal complexes such as $HCo(CO)_4$ or nickel cyanide, which were unstable and required high H_2 pressure. Compounds of second and third row metals offer much more convenient handling and higher activity and stability. The most widely applicable homogeneous hydrogenation

Table 3.3.1 Relative activity of some homogeneous catalysts for 1-hexene hydrogenation

Catalyst precursor	Temp. [°C]	Relative rates
$RhCl(PPh_3)_3$	0	1
$RhCl(PPh_3)_3$	25	11
$Ru(H)Cl(PPh_3)_3$	25	150
$[Rh(COD)(PR_3)_2]^+$	0	70
$[Ir(COD)(py)(PCy_3)]^+$	0	110

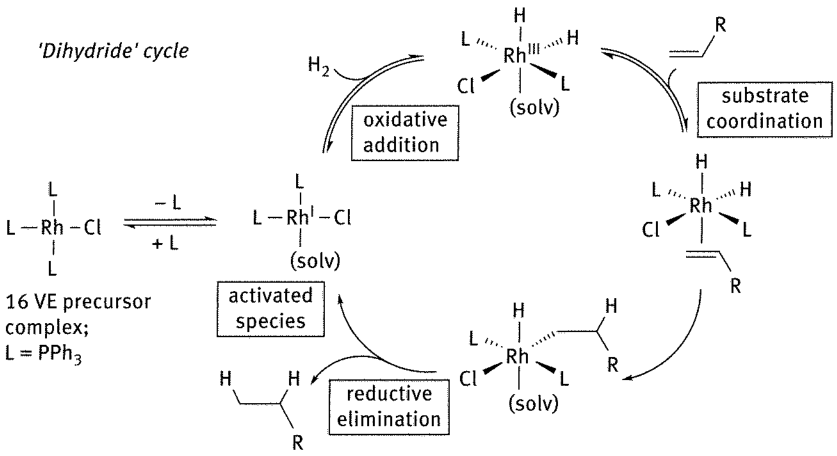
catalysts are based on noble metal phosphine complexes, not least because of their tolerance to air, water, and functional groups. Best known among these is $RhCl(PPh_3)_3$, also known as **Wilkinson's catalyst**. This catalyst is highly selective for terminal alkenes, i.e. the sterically least hindered C=C bond in a molecule. $Ru(H)Cl(PPh_3)_3$ also reduces terminal C=C bonds and is even more active. Cationic complexes like $[M(COD)L_2]^+$ (M = Rh, Ir; L = phosphine) are also highly active (Table 3.3.1); here, as a first step, the COD ligand is hydrogenated to provide two coordination sites for substrate binding. $[Ir(COD)(py)(PCy_3)]^+$ even hydrogenates tetra-substituted internal alkenes such as tetramethylethylene, which the neutral Rh and Ru PPh_3 complexes will not touch.

Another class of catalysts are water-soluble cyano complexes, notably $[HCo(CN)_5]^{3-}$. This catalyst is selective for the **hydrogenation of conjugated dienes** to alkenes. It also hydrogenates conjugated enones.

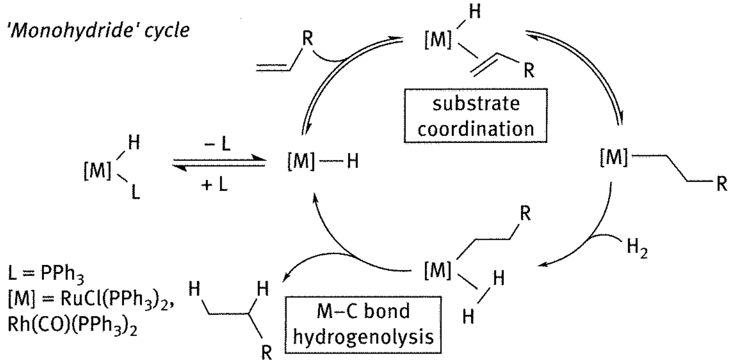


The mechanism of catalytic hydrogenation illustrates several of the key reaction steps that constitute a catalytic cycle. At least two variants exist: one where oxidative addition of H_2 precedes alkene coordination, and one where alkene coordination comes first. The latter tends to be favoured with substituted alkenes and if cationic Rh catalysts $[L_2Rh(solvent)_2]^+$ are used, which have two coordination sites.

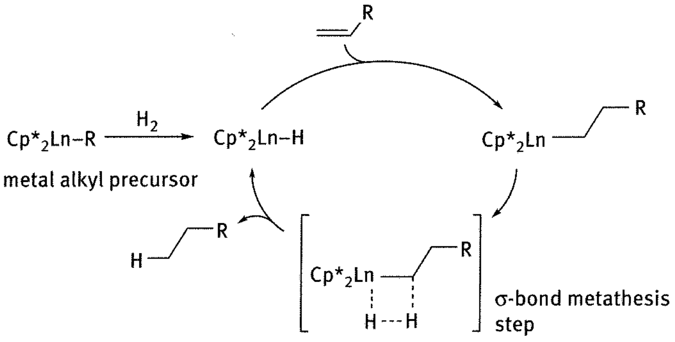
These catalysts are inhibited by the addition of excess phosphine. Loss of phosphine from $RhCl(PPh_3)_3$ gives an equilibrium concentration of a T-shaped three-coordinate 14 VE intermediate (stabilized by solvent) that undergoes oxidative addition of H_2 10^4 times faster than the four-coordinate precursor complex. This is therefore the entry into the catalytic cycle. In this cycle rhodium oscillates between Rh(I) (d^8, square-planar) and Rh(III) (d^6, octahedral) species.



The cycle shown in the diagram above applies to **dihydride** complexes L_nMH_2. Catalysts like $Ru(H)Cl(PPh_3)_3$, where one hydride is already present in the precursor, follow a slightly different '**monohydride**' cycle. The product is released by M–C bond hydrogenolysis, which may involve either oxidative addition of H_2 (likely for Rh^I) or a process akin to σ-bond metathesis (more likely for Ru^{II}). Since the acidity of H_2 increases drastically on coordination (see Section 2.10.1), H^+ transfer to the alkyl ligand is plausible to give the alkane product.

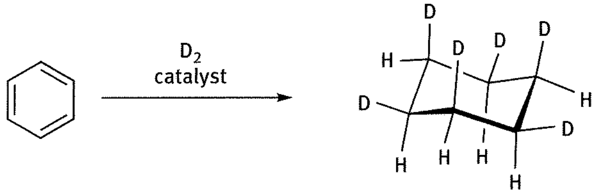


A different type of hydrogenation catalysts is based on bis-Cp lanthanide complexes. The precursors in this case are alkyls, preferably mononuclear ones like $Cp^*{}_2MCH(SiMe_3)_2$, which under H_2 are converted to in situ generated $Cp^*{}_2MH$ (M = e.g. La, Nd). These complexes are extremely active for the hydrogenation of 1-alkenes. However, they do not tolerate functional groups and are very sensitive to air and moisture. The mechanism differs from the one outlined for Rh, since the lanthanide is in oxidation state +III and unable to react with H_2 under oxidative addition. Here, σ-bond metathesis is observed to release the product:

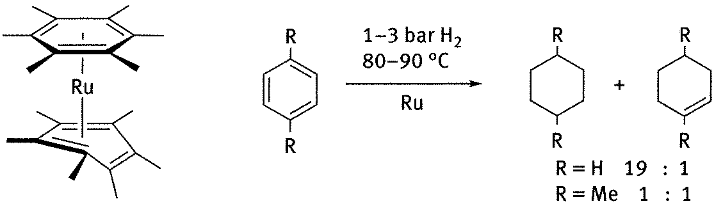


3.3.1.2 Arene Hydrogenation

The hydrogenation of arenes is considerably more difficult than that of alkenes and alkynes. Arene hydrogenation is of interest in the context of coal liquefaction, i.e. the production of liquid fuel from coal. Heterogeneous and surface supported molecular catalysts have been found to be effective. For homogeneous systems, many metals from niobium and tantalum to ruthenium and rhodium are active. A key feature is that the hydrogen is delivered stereoselectively to one π-face of the arene only, so that in deuterations one isomer results:

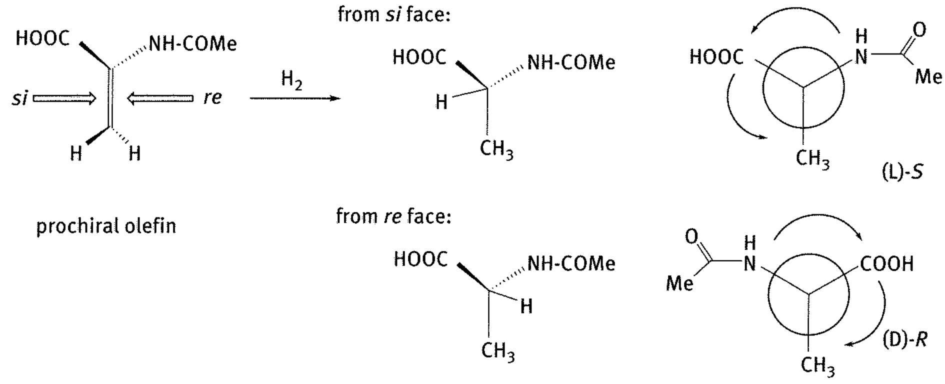


Catalyst precursors that hydrogenate arenes under mild conditions are, for example, (η^3-allyl)Co[$P(OR)_3$]$_3$, [$L_2Rh(\mu\text{-}H)$]$_2$ {L = $P(OPr^i)_3$}, and $Ru(C_6Me_6)_2$. The latter is a fluxional complex with one η^6 and one η^4-bound C_6Me_6 ligand (see Section 2.9.1.1); it hydrogenates arenes to a mixture of cyclohexanes and cyclohexenes:



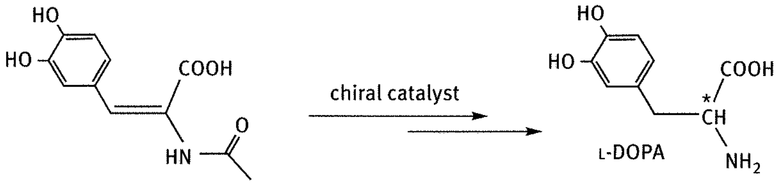
3.3.1.3 Asymmetric Hydrogenation

Substituted olefins are prochiral, i.e. they have π-faces that can be approached from opposite sites, and consequently delivery of H_2 to one side or the other results in enantiomeric products.

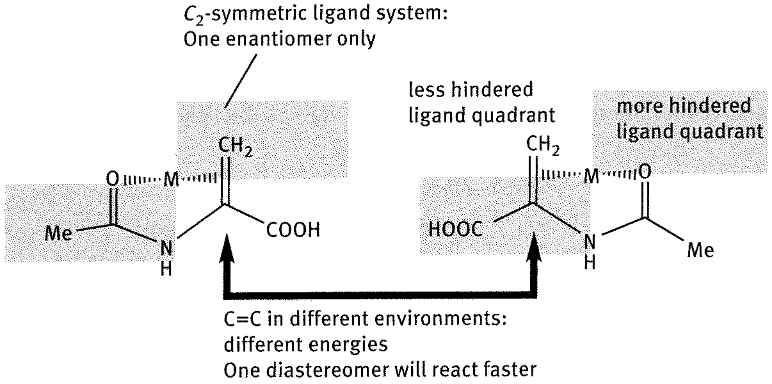


Asymmetric hydrogenation is a convenient way of generating chiral compounds, e.g. in medicines where only one enantiomer is active. One of the first applications was the synthesis of L-dihydroxyphenylalanine (L-DOPA), an amino acid required for the treatment of Parkinson's disease. The precursor is a cinnamic acid derivative with an acyl protected NH_2 group.

Asymmetric hydrogenation: Nobel Prize 2001 to W. S. Knowles and R. Noyori.



The first asymmetric catalysts were based on chiral phosphines where the P atom was the centre of chirality. However, the synthesis of such compounds is laborious. It was subsequently recognized that provided the preferred ligand conformation generates a C_2 symmetric ligand framework, chiral information is transferred from the ligand to the catalytically active site. Cationic Rh complexes of chelating chiral phosphines proved particularly effective for enantio-differentiation. Importantly, the cinnamic acid substrate binds in chelate fashion: both the C=C and the C=O bond of the acyl protecting group are involved. With the ligand imposing a C_2-symmetric complex geometry, coordination of the two C=C π-faces generates two diastereomers that are sufficiently different in energy to give high enantioselectivity. Enantiomeric excesses of >90% are now routine.

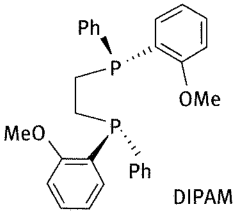

C_2-symmetric ligand system:
One enantiomer only

less hindered ligand quadrant

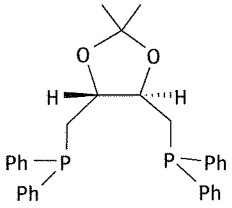
more hindered ligand quadrant

C=C in different environments:
different energies
One diastereomer will react faster

The key to high enantioselectivity is therefore the construction of a stereo-differentiating ligand environment. A large number of suitable ligands have been synthesized. The DIPAMP ligand (W. S. Knowles) was developed for Monsanto's L-DOPA synthesis; it contains two chiral P atoms. Much more common are ligands where the chiral centres are incorporated in the bridge, as in DIOP (H. Kagan), one of the first and most successful examples of this type.

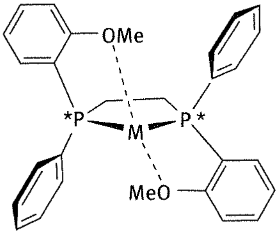


DIPAMP
95% e.e. for L-DOPA synthesis

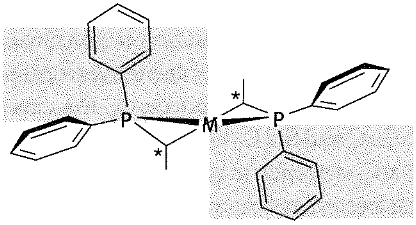


(*R*, *R*)-DIOP

In ligands with chiral bridges, the chiral information is translated by the conformation of the P-aryl substituents, which create sterically hindered and unhindered quadrants in the coordination sphere and thus impose C_2 symmetry:

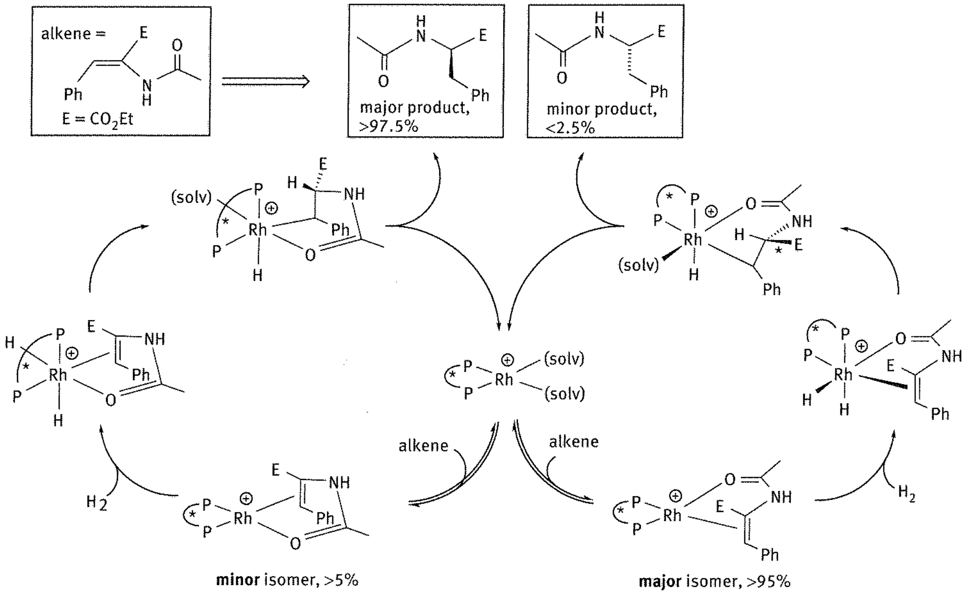


DIPAMP:
Chiral centres directly attached to the metal
Possible conformational influence of aryl



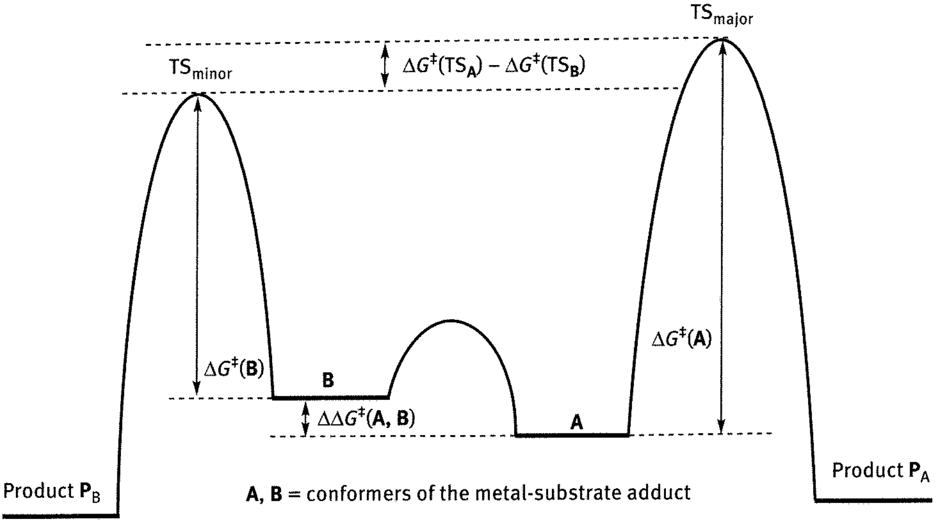
Chiral bridge:
Locked in one conformation
Translates into C_2-symmetric geometry around M
Shaded areas indicate crowded ligand quadrant

The asymmetric hydrogenation of amidocinnamate derivatives proceeds by a chelating 'olefin-first' dihydrogen mechanism. There are two interconverting catalyst–substrate diastereomers. It was initially surprising that the minor diastereomer gives rise to the major product isomer. This arises because in the next step, the oxidative addition of H_2, the energetically slightly higher-lying minor isomer experiences a lower activation barrier than the more stable isomer. The two diastereomers lead to two different transition states for H_2 addition, and since catalysis is a kinetic phenomenon, it is the energy difference between these transition states (and not between the spectroscopically detectable precursor complexes) that controls the enantioselectivity of product formation.

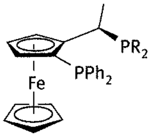


The energy profile of such a situation illustrates this behaviour: there is a rapid equilibrium between the two diastereomeric catalyst–substrate adducts **A** (major) and **B** (minor), with the further reaction (oxidative addition of H_2) to the less stable adduct **B** being favoured.

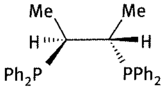
This is a general principle in catalysis: in cases where the educt exists as two conformers **A** and **B,** which exchange more rapidly than the subsequent formation of the products $\mathbf{P}_A$ and $\mathbf{P}_B$, the $\mathbf{P}_A/\mathbf{P}_B$ ratio is **determined by the energy difference of the two transition states** $\Delta\Delta G^{\ddagger}$ **(A,B)** $= \Delta G^{\ddagger}(TS_A) - \Delta G^{\ddagger}(TS_B)$, not by the difference in activation energies $\Delta G^{\ddagger}$**(A)** $-$ $\Delta G^{\ddagger}$**(B)**. This has become known as the ***Curtin–Hammett Principle.***



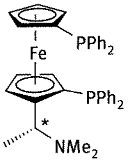
Numerous ligand systems have been developed for asymmetric hydrogenations, in an effort both to widen the range of substrates (asymmetric hydrogenation of unfunctionalized alkenes is challenging) and to achieve high enantiomeric purity. Some examples:



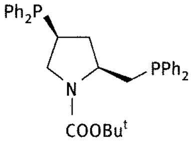
(R)-(S)-Josiphos: R = Cy
(R)-(S)-Xyliphos: R = 3,5-$Me_2C_6H_3$



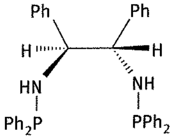
CHIRAPHOS



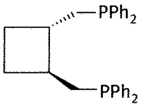
BPPFA

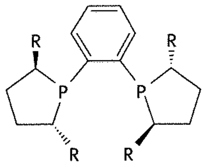


(*S,S*)-BPPM

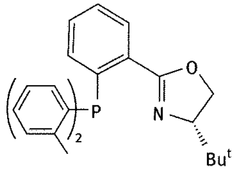


phosphinamide ligand
94% e.e.



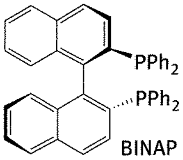


(*S,S*)-DuPHOS

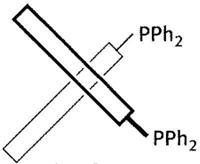


PHOX

A particularly successful ligand is BINAP (R. Noyori), an axially chiral chelating phosphine that owes its enantio-discrimination to the fact that the two naphthyl-halves are unable to interconvert by rotation about the connecting C–C bond due to steric hindrance.



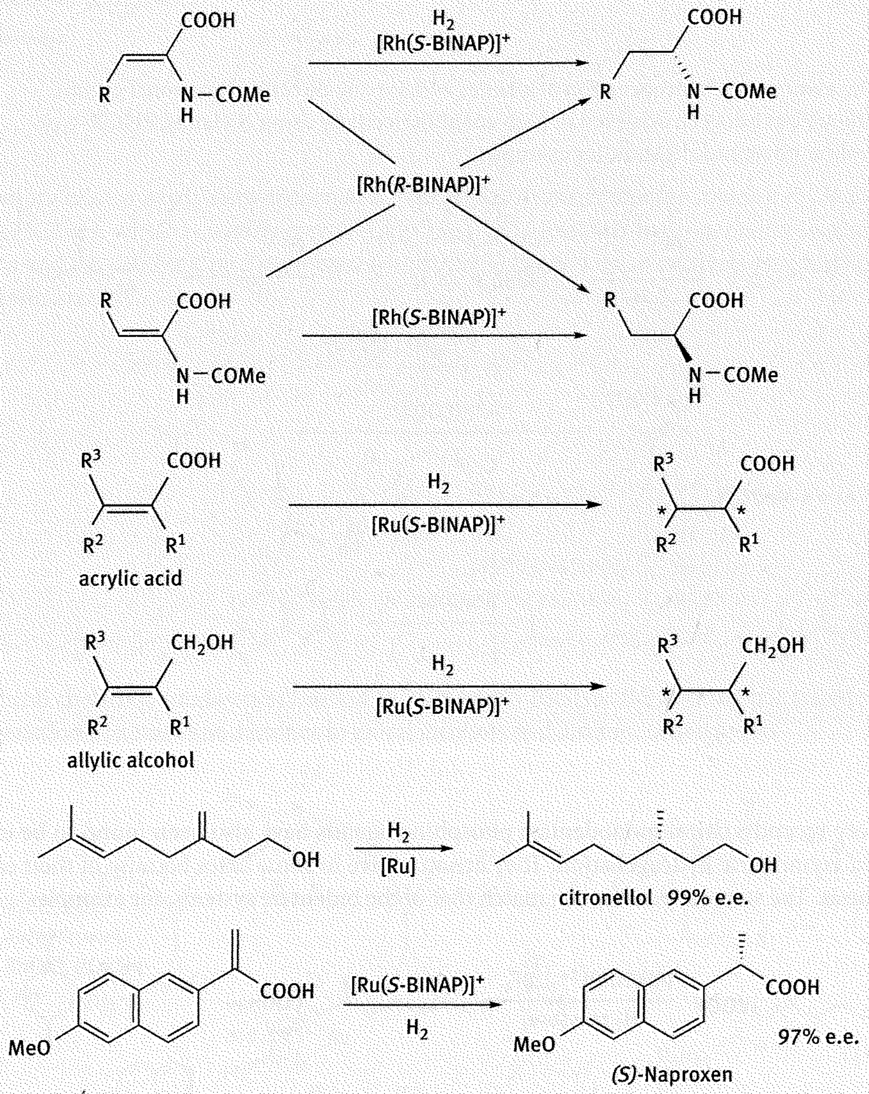
BINAP



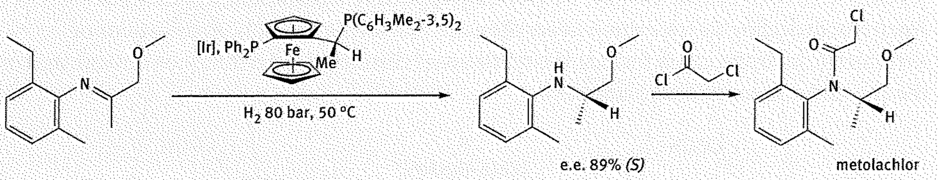
view from top

Box 3.3.1.3 Applications of asymmetric hydrogenations

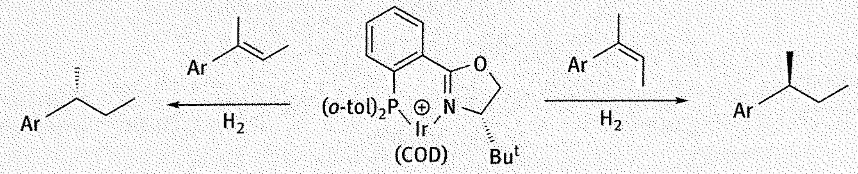
Rh and Ru BINAP complexes have been widely applied to enantioselective catalytic reactions, including the reduction of acrylic acids and allylic alcohols. Applications of asymmetric hydrogenation include the synthesis of citronellol, a perfume constituent, and of the anti-inflammatory drug Naproxen.

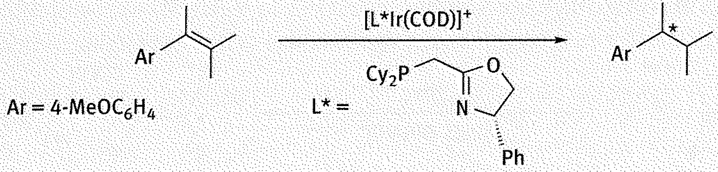


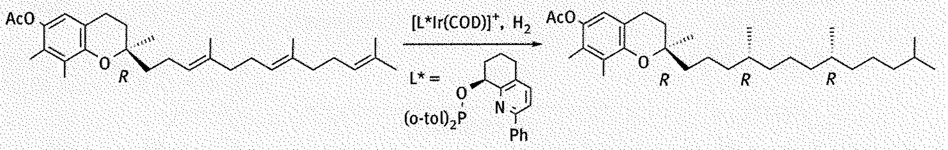
Another important application is the asymmetric imine hydrogenation in the synthesis of metolachlor, a widely used herbicide:



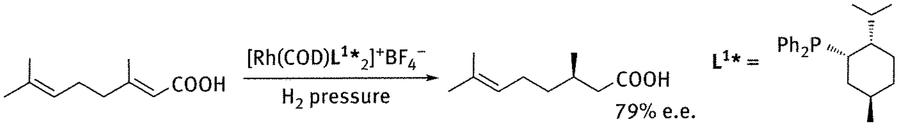
The asymmetric hydrogenation of alkenes *without* any directing functional groups is difficult but has been achieved in high enantioselectivity using chelating PHOX-type oxazoline-phosphine ligands, for example:

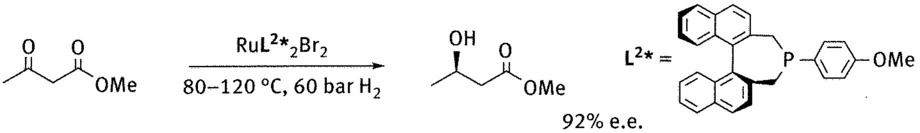






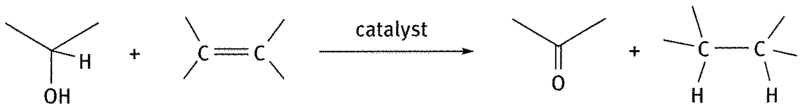
More recently, chiral monodentate phosphine ligands have also been found to be effective in asymmetric hydrogenation. They are attractive in some cases because of their easier synthesis. The stereoselectivity can match that of the bidentate systems, for example:



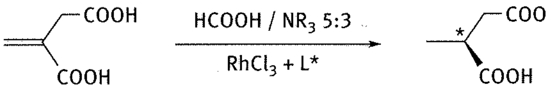


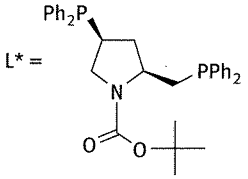
3.3.1.4 Transfer Hydrogenation

Most hydrogenations require hydrogen, often under pressure. An alternative is transfer hydrogenation, where an alcohol solvent is used as the H_2 source. Since such hydrogenations do not require the use of hazardous hydrogen gas or pressure, they are particularly convenient for laboratory scale reactions. The reaction is driven to the right by using the H-source in excess or as solvent.



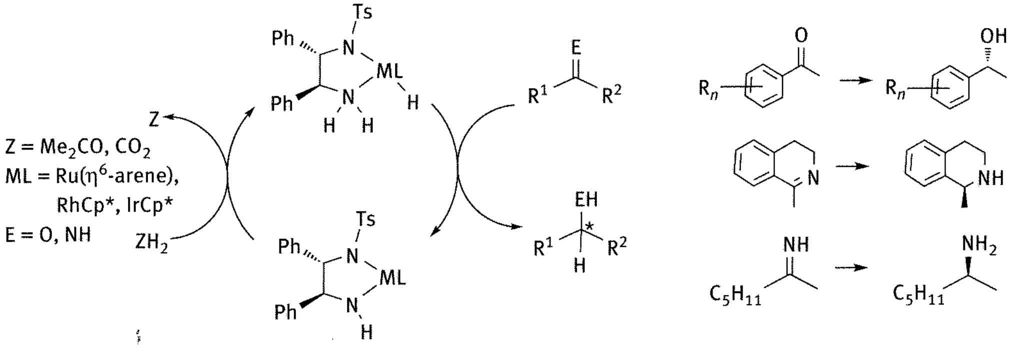
Isopropanol is easily dehydrogenated to acetone. Another storage form of H_2 is formic acid, HCO_2H, which is readily converted to $H_2 + CO_2$. Transfer hydrogenation is catalysed by Ru and Rh catalysts, and partnered with suitable ligands these catalysts give high enantiomeric excesses.





NR_3	e.e. %
NEt_3	82
(*R*)-Ph(Me)$CHNH_2$	80
(*S*)-Ph(Me)$CHNH_2$	99.5 !

Chiral chelating amido complexes of Ru, Rh, and Ir catalyse the asymmetric transfer hydrogenation of ketones and imines to chiral alcohols and amines, respectively.

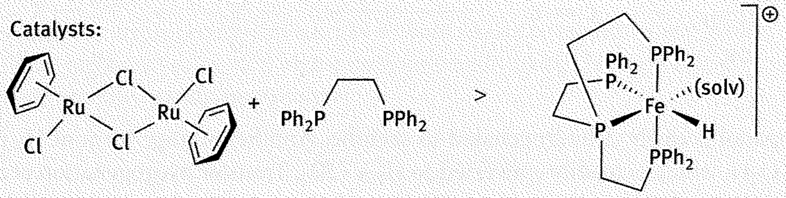


Box 3.3.1.4 Hydrogen storage molecules and H_2 release

The ability to cleave substrates like formic acid into CO_2 and H_2 also implies that such compounds can be used as H_2 storage media for energy generation in fuel cells. Of a variety of catalysts, Ru and Fe complexes supported by chelating phosphines have proved particularly effective for the release of H_2 from formic acid under mild conditions:

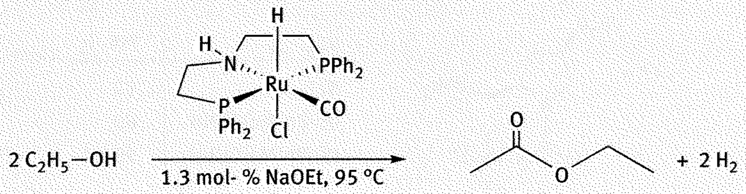
$$HCO_2H \xrightarrow[20\text{–}80\ °C]{\text{catalyst}} CO_2 + H_2$$

Catalysts:



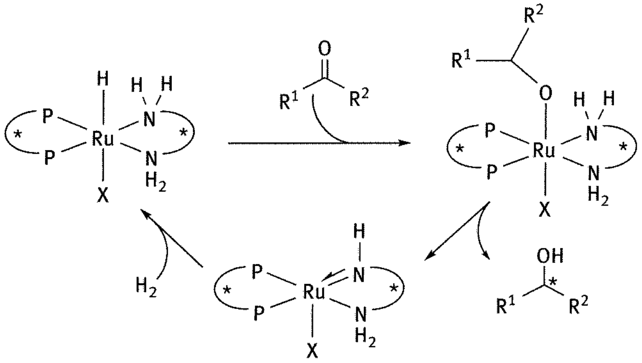
The reverse reaction, the hydrogenation of CO_2 to formic acid, is catalysed by a similar polydentate complex, $[P(o\text{-}C_6H_4PPh_2)_3FeH(H_2)]^+$ under 30–70 bar pressure.

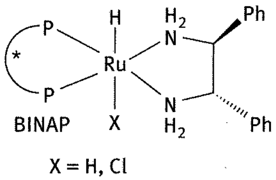
Chelating phosphine complexes of Ru are also effective in the dehydrogenative coupling of ethanol to ethyl acetate. The reaction is co-catalysed by NaOEt and requires only very low catalysts loadings.

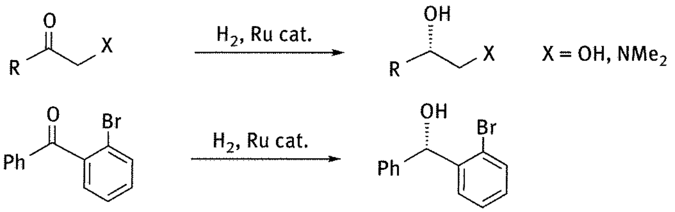


3.3.1.5 Outer-Sphere Hydrogenation of Ketones

Rather remarkably, it was found that polar substrates like ketones can be effectively hydrogenated with Ru catalysts containing chiral chelating primary amines. The substrate is thought to be bound via H bonds to the amine, and reduction takes place without the usual oxidative addition / insertion / reductive elimination sequence on the metal. The addition of base assists with the heterolytic cleavage of H_2 in the Ru hydride regeneration reaction.

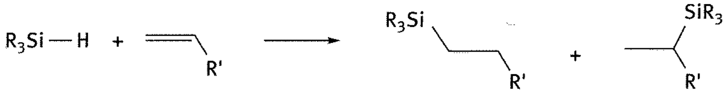




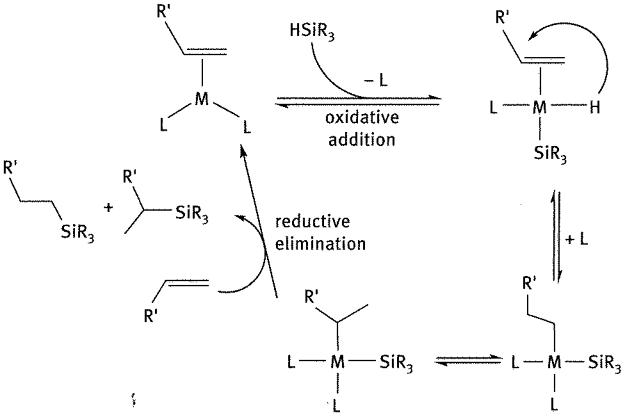


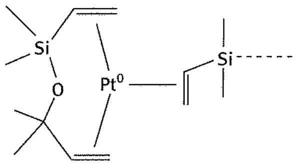
3.3.2 **Hydrosilylation**

The hydrosilylation of unsaturated substrates is used in applications ranging from fine chemical synthesis to cross-linking to give polymer coatings for surface treatments. The asymmetric hydrosilylation of ketones is an alternative to asymmetric hydrogenation to give chiral alcohols. The mechanism of hydrosilylation resembles in principle that of hydrogenation, except that the addition of Si–H to C=C bonds gives two products, in Markovnikov and anti-Markovnikov fashion:



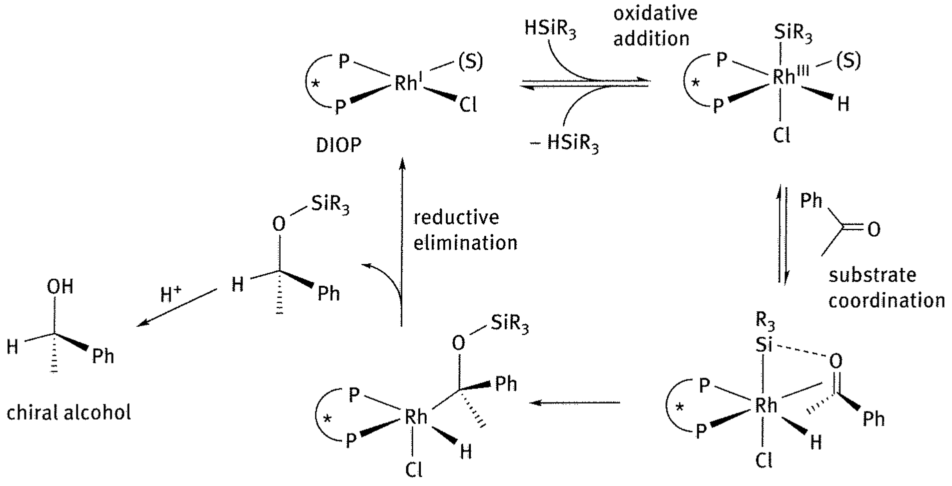
Platinum catalysts are highly effective and give extremely high turnover numbers, often at elevated temperatures. Chloroplatinic acid, $H_2Pt^{IV}Cl_6{\cdot}xH_2O$ (Speier's catalyst) has been used industrially; another is a Pt(0) adduct of vinyl siloxanes (Karstedt's catalyst). Under the reducing conditions of hydrosilylation, the active species is Pt(0). Ni, Pd, and Rh complexes such as $RhH(CO)(PPh_3)_3$ are also active for the hydrosilylation of C=C and C=O bonds.



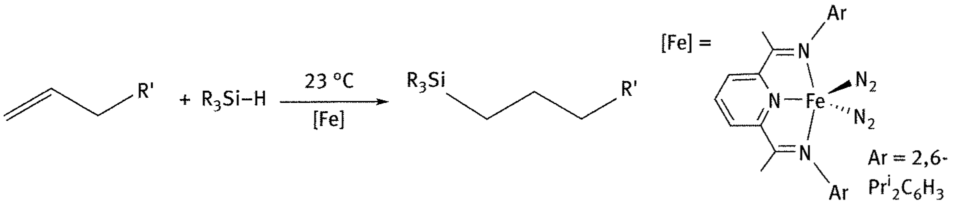


Karstedt's catalyst

The asymmetric hydrosilylation of ketones closely follows the pathway outlined for hydrogenation. Suitable enantioselective ligands are chelating diphosphines, like DIOP.

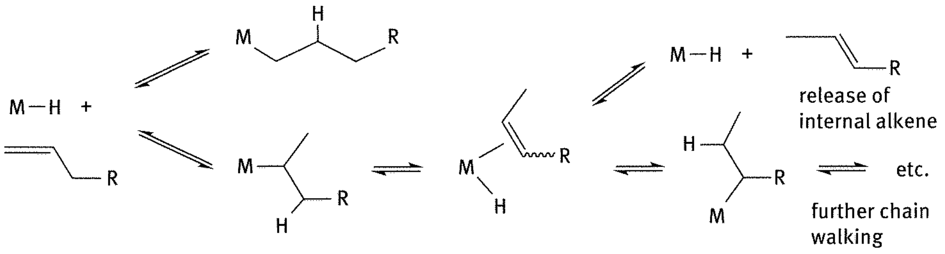


More recently, iron(0) catalysts have also been found to be highly active for the anti-Markovnikov hydrosilylation of alkenes:

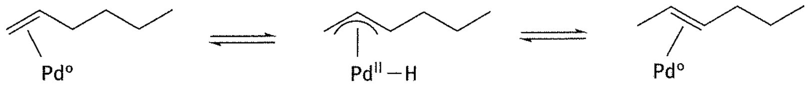


3.3.3 **Isomerizations**

Metal hydride complexes capable of catalyzing C=C bond hydrogenations can also lead to C=C bond isomerizations, if instead of the second H-transfer step, β-H elimination occurs. Terminal C=C bonds can therefore be converted into less reactive internal ones. If, however, the terminal alkene is trapped by forming a metal complex or a subsequent reaction, internal alkenes can be isomerized to give terminally functionalized products.

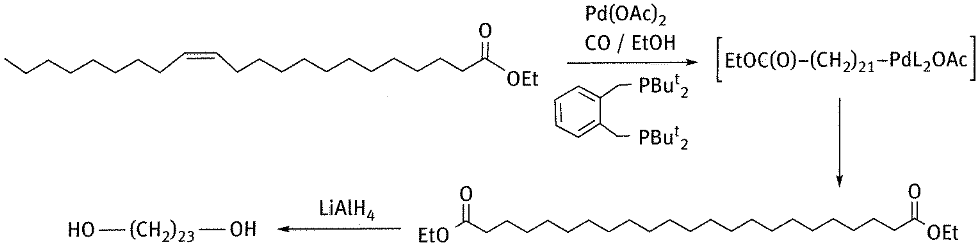


Metals not carrying a hydride ligand, such as Pd(0) complexes, can isomerize olefins via π-allyl intermediates:

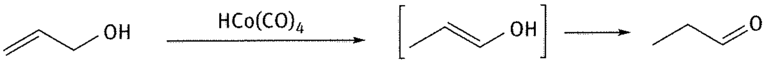


Such reaction sequences enable some metal complexes to shift from one C atom to another, a process referred to as **'chain walking'**.

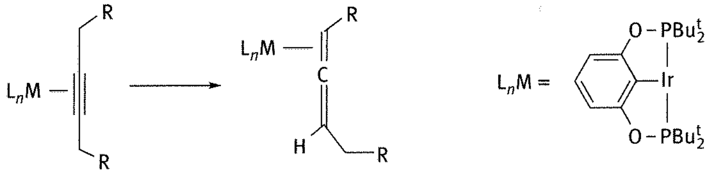
In hydrogenation catalysis, the formation of less reactive, internal olefins may lead to undesirable side products and lower yields; in other applications, isomerization is a desirable process. For example, the formation of primary alkyls from internal alkenes and Schwartz' reagent Cp_2ZrHCl has been mentioned (cf. metallocene hydrides, Section 2.8.2.3). Another example of favourable C=C bond isomerization and trapping of the most reactive isomerization product by a subsequent reaction is the palladium-catalysed carbonylation of a derivative of rape seed oil, which is turned into a long-chain diol for polyester applications:



Hydridocobalt carbonyl catalyses the isomerization of allyl alcohol to acetaldehyde, via Markovnikov-type insertion:



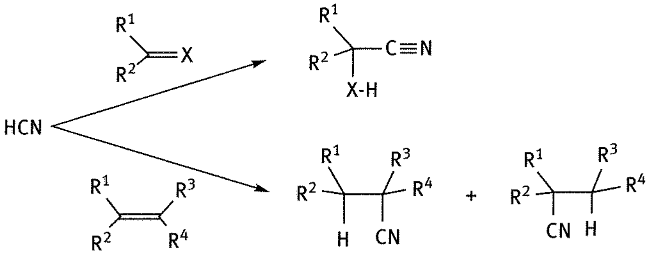
The isomerization of internal alkynes has also been observed and can lead to synthetically useful allenes:



3.3.4 Hydrocyanation

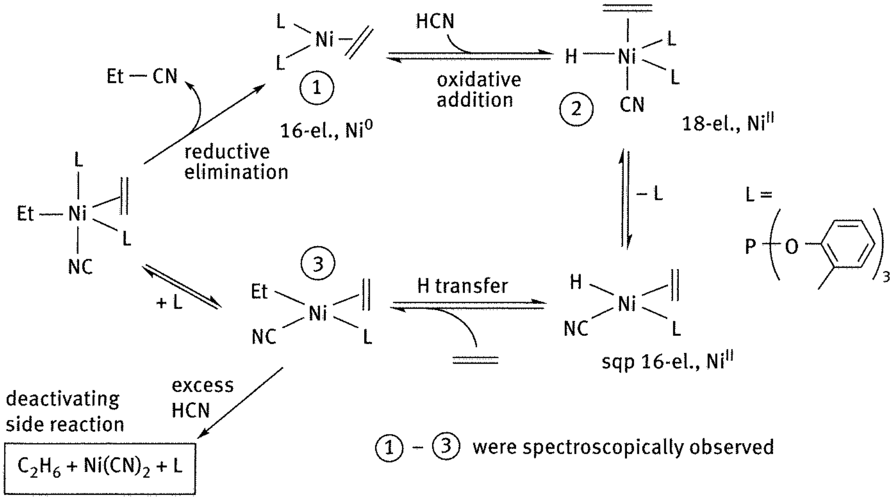
The addition of HCN to C–C double and triple bonds creates a new C–C bond and at the same time introduces functional groups into the product: –CN, –C=NR, –CHO, –C(O)NH$_2$, –COOH, or –CH$_2$NH$_2$. Nickel catalysts have proved most successful. A large scale application of hydrocyanation is the conversion of butadiene into 1,4-adiponitrile, the reduction of which to 1,6-diaminohexane ('hexamethylenediamine') gives a precursor for nylon-6,6. In the laboratory, HCN addition has found less use because of the toxicity of HCN, although in some cases acetone cyanohydrin, $Me_2C(CN)OH$, can be used as the HCN source.

Like other HX additions to C=C, both Markovnikov and anti-Markovnikov products are obtained:

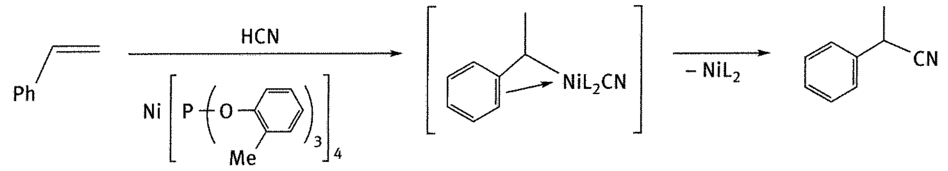


Regarding catalyst design, the main problem is that HCN is acidic and CN^- is a very strong ligand, so that catalyst deactivation due to formation of stable and poorly soluble metal cyanide salts is to be expected. Since HCN oxidative addition would be aggravated by electron-rich donor ligands, soluble catalysts require ligands that are bulky (to restrict coordination numbers) as well as adequately electron withdrawing to make oxidative addition products sufficiently labile for further reactions. Phosphites $P(OR)_3$ fit these requirements. A Lewis acidic co-catalyst is also required.

The mechanism of the hydrocyanation of ethylene has been studied in some detail and illustrates the key steps:



Styrene and other aryl-substituted alkenes react readily. Since they give branched compounds, there is potential for the generation of chiral hydrocyanation products.



Diene hydrocyanation. The majority of the world's adiponitrile [$NC(CH_2)_4CN$] is produced by butadiene hydrocyanation. The reaction proceeds in the following stages:

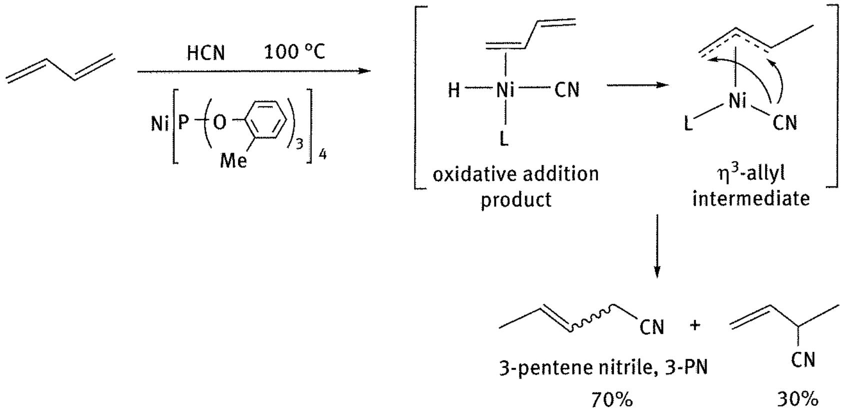
(1) the addition of HCN to 1,3-butadiene to a mixture of C_5 products, catalysed by a nickel phosphite complex;

(2) isomerization of the C_5-nitriles to linear 4-pentene nitrile, catalysed by a Ni / Lewis acid catalyst;

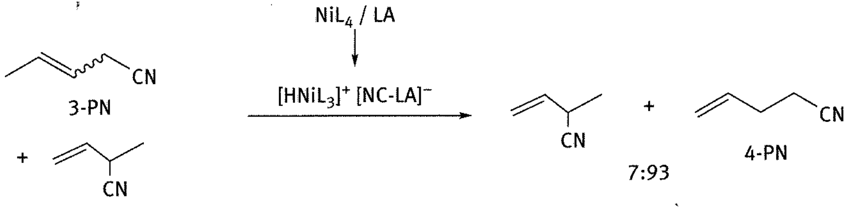
(3) second HCN addition, catalysed again by a Ni / Lewis acid catalyst.

The Lewis acid binds to CN, making the Ni–CN moiety more labile and generating [LA–CN]$^-$ anions. Typical Lewis acid additives are $ZnCl_2$ and in particular BPh_3, which increases the selectivity to adiponitrile (ADN) to >90%.

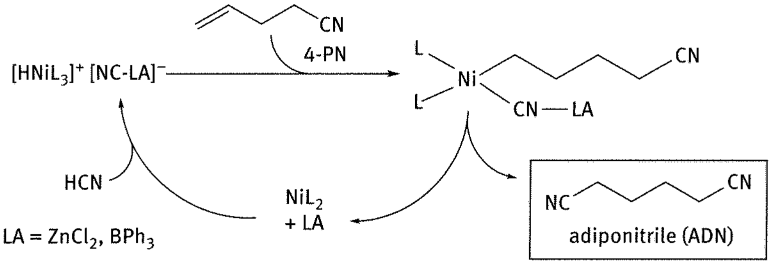
Step 1: Oxidative addition of HCN to the relatively electron-poor Ni(0) phosphite complex generates a nickel hydride, which inserts the butadiene to give an η^3-allyl intermediate. As is typical for π-allyl reactions, intramolecular nucleophilic attack can occur on C-1 and C-3, giving a linear and a branched isomer. For adiponitrile production the branched isomer is unwanted.



Step 2: Isomerization of branched to linear nitrile and double bond shift from 3-pentene nitrile (3-PN) to 4-PN are catalysed by a cationic nickel hydride. 4-PN is needed for the second HCN addition.

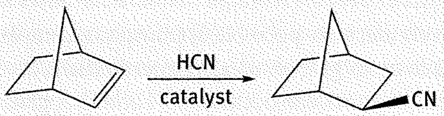


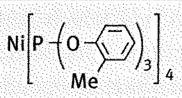
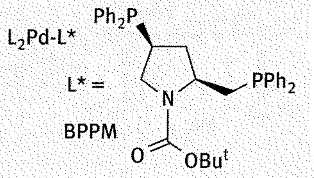
Step 3: Generation of a more acidic, cationic nickel hydride paired with a weakly coordinating anionic Lewis adduct. Insertion of 4-PN gives a terminal nickel alkyl, and reductive elimination generates ADN and closes the cycle.



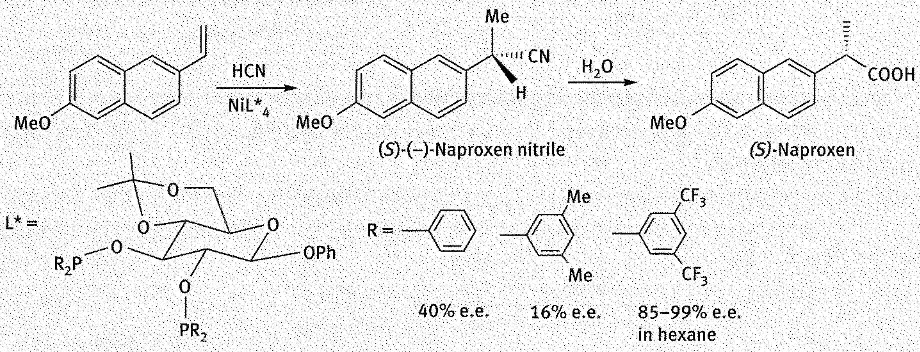
Box 3.3.4 Applications of asymmetric hydrocyanation

Norbornene adds HCN stereoselectively and with chiral ligands gives enantioselectivity, for example:



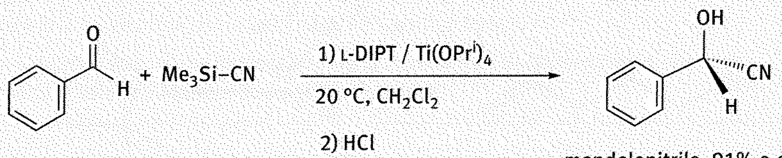
Catalyst:	Yield
	77%
$Pd[P(OPh)_3]_4$	83%
	68% 20% e.e.

Asymmetric hydrocyanation also provides an alternative route to the analgesic drug Naproxen (see also Section 3.3.1.3). The reaction is very sensitive to the steric and electronic characteristics of the chiral ligand—a sugar phosphinite derivative in this case—as well as to the solvent. The highest e.e. is obtained in hexane.

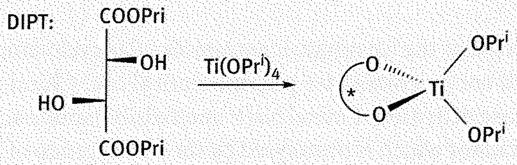


Hydrocyanation of aldehydes and ketones.

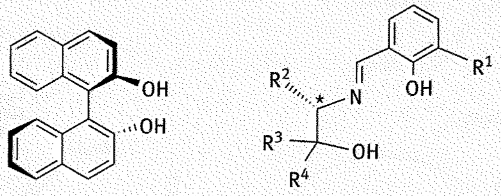
The hydrocyanation of aldehydes and ketones requires different catalysts: a Lewis acid metal complex. Chiral Lewis acids give enantioselectivity; they can be generated in situ by reacting metal alkoxides such as $Ti(OPr^i)_4$ with chiral diols.

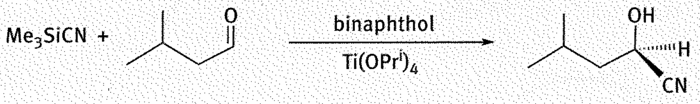


mandelonitrile, 91% e.e.



Other chiral chelates:

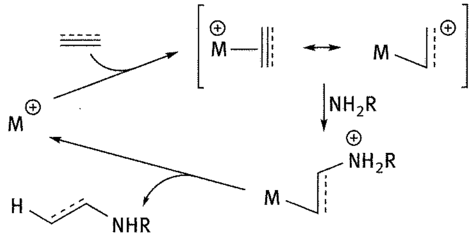




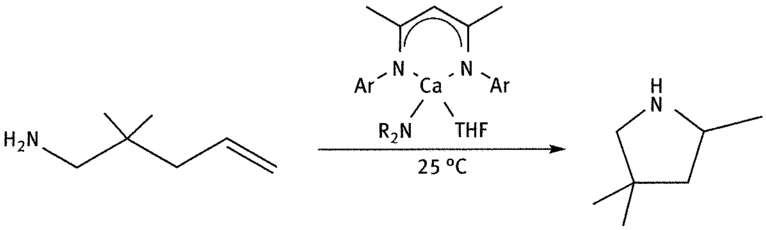
up to 82% e.e.

3.3.5 Hydroamination

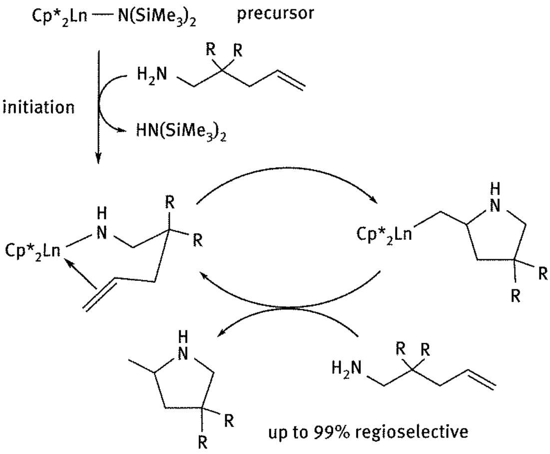
The addition of an H–N bond across C–C double and triple bonds is called hydroamination. The reaction is catalysed by a number of Lewis acidic metal centres and can be carried out intramolecularly to give cyclic amines, or intermolecularly to introduce –NHR functions. The general catalytic cycle for the intermolecular hydroamination of alkenes and alkynes is shown in the following diagram. The key step is the nucleophilic attack on a metal alkyl or metal vinyl intermediate.

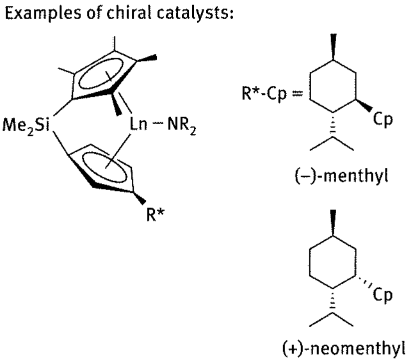


Many metal complexes can be used. Bis-Cp lanthanide complexes are powerful catalysts, while Pd, Pt, Rh, and cationic gold(I) complexes are more tolerant of functional groups. Calcium amide complexes have also been found to be effective:



Many applications are directed at the asymmetric intramolecular cycloamination to give 5-ring amines, many of which are precursors for pharmaceutical use. Chiral lanthanocene complexes achieve good stereoselectivities. A metal bis(trimethylsilyl)amide acts as convenient, hydrocarbon-soluble precursor which is protolysed by the $-NH_2$ group of the substrate.





Key points

Hydrogenation is the catalysed addition of H_2 to unsaturated substrates. H_2 is usually delivered in *syn* fashion.

Hydrogenation is catalysed by a large variety of metal centres, electron-rich and electron-deficient. Ru, Rh, and Pd are most widely applied. The reaction can follow a dihydride and a monohydride mechanism. Non-oxidizable lanthanide catalysts involve a σ-bond metathesis step.

Asymmetric hydrogenation is of particular synthetic importance. It operates by generating a C_2 symmetric ligand framework. Most chiral chelating phosphines transfer chiral information via the conformation of their P-substituents.

The addition of HX ($X = SiR_3$, CN, NR_2) leads, respectively, to hydrosilylation, hydrocyanation, and hydroamination.

HX additions to C=C give Markovnikov and anti-Markovnikov products.

The hydrocyanation of butadiene to adiponitrile is the industrially most important HCN reaction.

Lewis acid catalysts are effective for the hydrocyanation of ketones and alkene and alkyne hydroaminations.

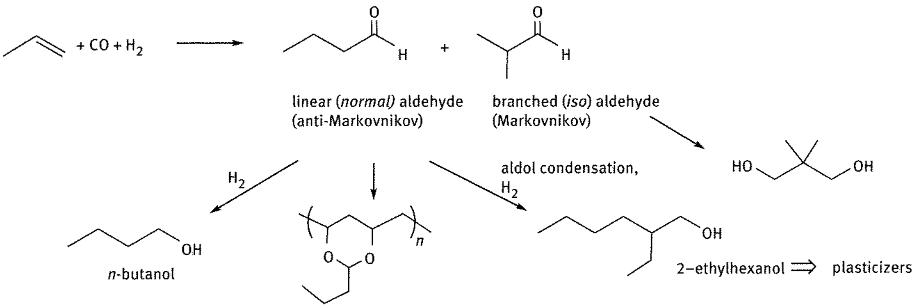
Exercises

1. Which π-face of *Z*-acetamido cinnamic esters (*re* or *si*) leads to the desired L-DOPA on hydrogenation?
2. Calculate the energy difference in the formation of D- and L-DOPA (at $T = 298$ K) that would correspond to an enantiomeric excess of (i) 90% and (ii) 99%.
3. Draw a catalytic cycle for the hydrocyanation of styrene with Ni catalysts. Why does this preferentially lead to a Markovnikov addition product?

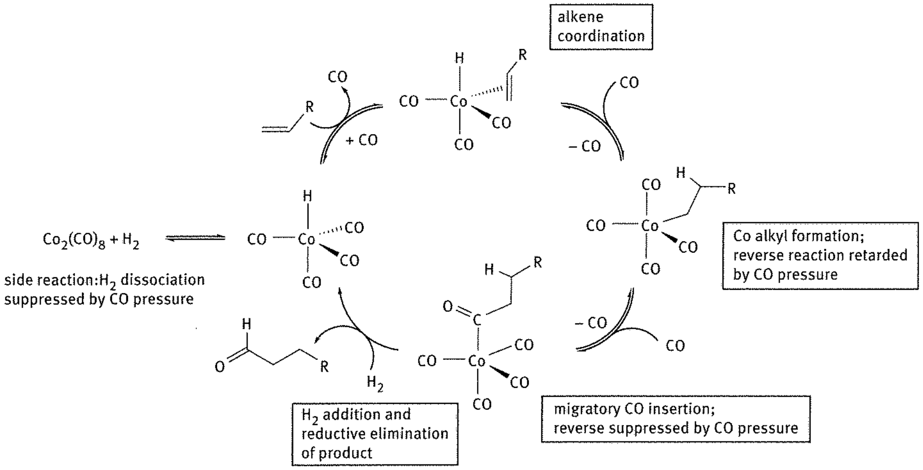
3.4 Catalytic Carbonylations

3.4.1 Hydroformylation

Hydroformylation, also known as the '**oxo reaction**', is the reaction of terminal alkenes with a mixture of CO and H_2 (synthesis gas) to extend the carbon chain by one C atom and introduce a formyl functional group. Hydroformylation is a large-scale industrial process, dominated by the hydroformylation of propene to *n*-butanal, to produce a number of essential commodity chemicals such as alcohols, diols, and carboxylic acids. The hydroformylation of long-chain alkenes is the basis for the production of detergent alcohols. Another major outlet is the production of dioctyl phthalate, 1,2-$C_6H_4(CO_2C_8H_{17})_2$, a plasticizer for PVC.



The first hydroformylation catalysts were based on $HCo(CO)_4$ and this is still a widely used catalyst. The cobalt catalyst demonstrates the key steps of this reaction. Each is in principle reversible. CO competes with the alkene for a coordination site and retards substrate association, but at the same time higher [CO] drives the reaction forward and prevents H_2 elimination from $HCo(CO)_4$ and formation of inactive $Co_2(CO)_8$. Increasing CO pressure also increases the linear:branched (*n*:*iso*) ratio of the product (to ca. 4.4:1 at 90 bar).

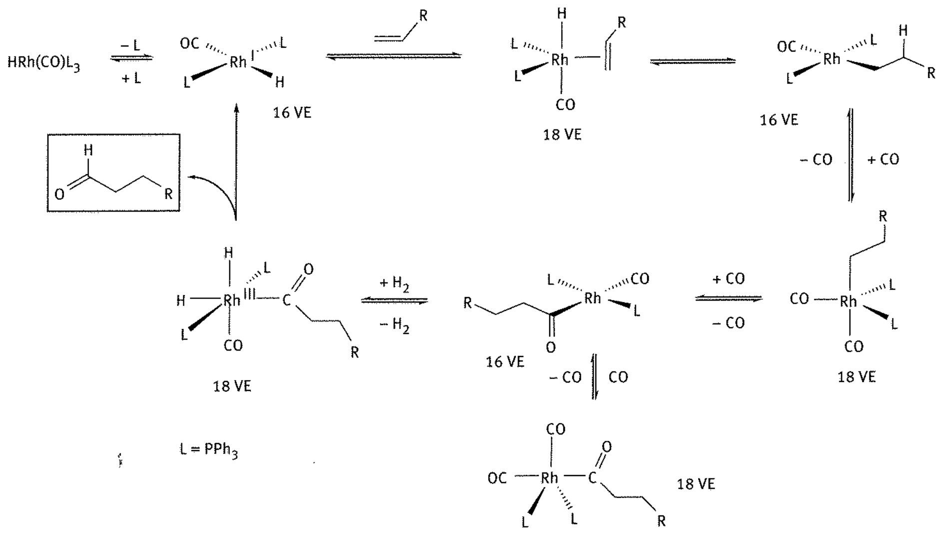


The reaction rate is proportional to $[\text{alkene}][CO]^{-1}$, i.e. the process is retarded by CO since CO dissociation is required to generate the active species. In order to achieve acceptable rates, the reaction has to be conducted at elevated temperatures, 110–180 °C. At such temperatures, cobalt carbonyls decompose unless there is sufficiently high CO pressure. The Co-catalysed process therefore requires both high temperatures and high pressures (ca. 200–300 bar for H_2 and CO combined), and while cobalt is a cheap catalyst, conducting large scale reactions under high pressure requires expensive reactors.

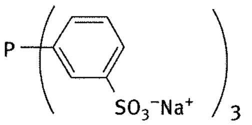
The addition of a trialkylphosphine stabilizes the catalyst against decomposition, so that the pressure can be dropped to 50–100 bar, while the temperature can be increased for faster turnovers. However, since trialkylphosphines greatly increase the hydridic character of the hydride ligand, $HCo(CO)_3(PR_3)$ is a much stronger hydrogenation catalyst, so that the aldehyde product is reduced to the alcohol. The alkene can also be hydrogenated, to give unwanted alkane side products. Overall the hydroformylation with phosphine-modified cobalt catalysts is an order of magnitude slower than with $HCo(CO)_4$; however, the *n*/*iso* ratio is higher. PBu^n_3 gives about 90% linear products as a 1:1 mixture of aldehyde and alcohol.

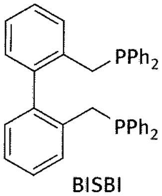
By contrast to the forcing conditions required for Co catalysts, **rhodium complexes** operate even at ambient conditions. Suitable precursors are $Rh(CO)_2(acac)$ and, more specifically, Wilkinson's $HRh(CO)(PPh_3)_3$. Dissociation of a PPh_3 ligand is facile. The resulting 16 VE $HRh(CO)(PPh_3)_2$ readily coordinates olefins, produces no hydrogenation or C=C isomerization by-products, and gives high selectivity for linear aldehydes (*n*/*iso* ≈ 20:1 at 25 °C, 1 bar). For these reasons rhodium catalysts have become dominant in industrial processes.

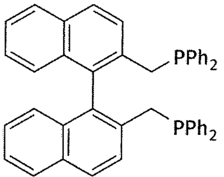
In order to prevent the formation of less selective $HRh(CO)_{3-x}(PPh_3)_x$ species ($x = 0, 1$), an excess of PPh_3 is beneficial for commercial applications. The Rh hydroformylation cycle is closely analogous to the cobalt reaction. In contrast to trigonal-bipyramidal 18 VE Co intermediates, the Rh cycle is thought to involve both square-planar 16 VE and tbp 18 VE Rh(I) intermediates.

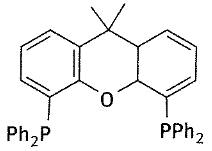


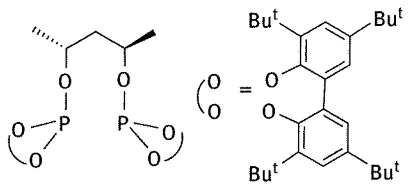
A number of bis-phosphine ligand systems have been developed to generate more *n*-selective or more active catalysts. Hydroformylation processes in water have also been developed, based on rhodium complexes of water-soluble phosphines, such as sulfonated PPh_3. These, too, have led to industrial applications.

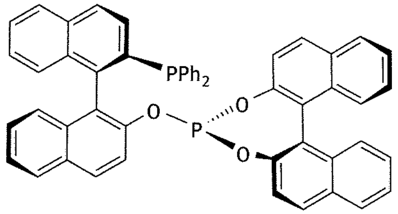

highly water-soluble PAr_3


BISBI

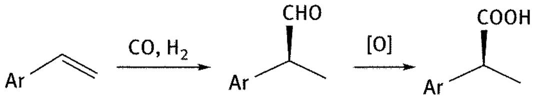

Naphos

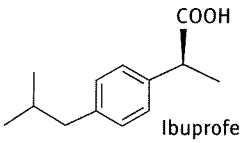

Xantphos

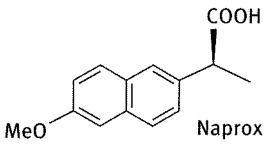



(*R,R*)-BINAPHOS

Chiral phosphite ligands have been developed for the asymmetric hydroformylation of vinyl arenes. For example, enantioselective hydroformylation followed by oxidation is an alternative route to the analgesics Ibuprofen and Naproxen.




Ibuprofen

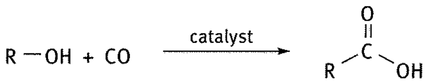

Naproxen

3.4.2 Carbonylation Reactions

Carbonylations insert a CO into a C–X bond. The typical catalysts are late transition metals, mainly second row transition elements. This is a general and atom-efficient route to carboxylic acids and esters. Alcohols, alkenes, and alkynes can be utilized as starting materials.

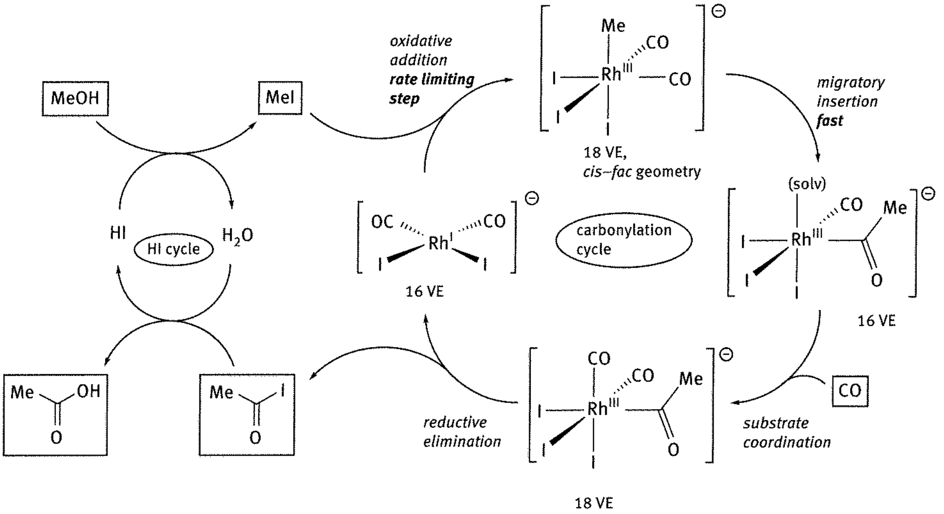
3.4.2.1 Alcohol Carbonylations

The carbonylation of alcohols leads to the production of carboxylic acids:


$$R{-}OH + CO \xrightarrow{\text{catalyst}} RC(=O)OH$$

The industrial process involves the conversion of **methanol to acetic acid**. Since the only feedstocks for this are CO and H_2, it can rely equally well on coal, petroleum, or natural gas as carbon sources. Like hydroformylation, this process was first discovered using cobalt catalysts. However, rhodium proved to be ~10^4 times more active, and operates at much lower CO pressures (30–40 bar for Rh vs. 500–700 bar for Co) and at lower temperatures (180 vs. 230 °C). Rhodium catalysts are the basis of the so-called **Monsanto acetic acid process.**

The process involves two reaction cycles: (i) the conversion of methanol to iodomethane, and (ii) the carbonylation cycle.

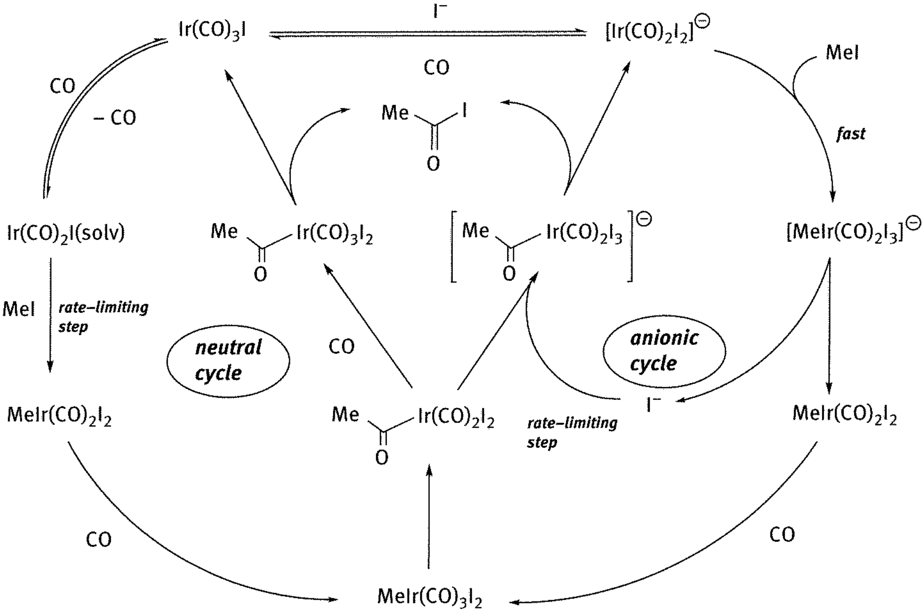


The process requires both a metal and iodide. HI converts methanol to methyl iodide. The oxidative addition of MeI to the *cis*-$[RhI_2(CO)_2]^-$ anion is the rate-limiting step; the reaction is therefore independent of the CO concentration. The Rh(III) methyl thus formed is converted to the metal acetyl complex, which undergoes reductive elimination of acetyl iodide, MeC(O)I. In a separate cycle, this primary product is hydrolysed to acetic acid and HI.

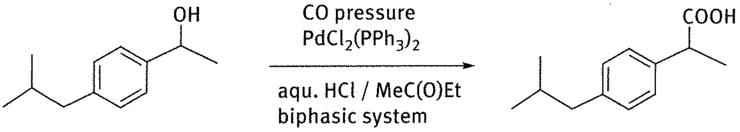
The original Rh-based process required relatively high concentrations of water to reactivate any catalyst lost through precipitation of RhI_3 and formation of $[RhI_4(CO)_2]^-$. However, in the presence of water rhodium can catalyse an undesirable side reaction, the water-gas shift (WGS): $CO + H_2O \rightarrow CO_2 + H_2$ (which lowers selectivity by methane formation). High water concentrations also imply high concentrations of HI, which is highly corrosive and leads to engineering problems. These problems can be reduced by using LiI and similar additives as iodide source. This allows the water concentration to be reduced while maintaining overall rates (*Celanese Acid Optimization Technology*).

An alternative to the rhodium catalyst is **the iridium-catalysed methanol carbonylation**, commercialized by BP (‘**Cativa Process**’). Highest activities are obtained with a ruthenium-based promoter, although simple iodide salts such as ZnI_2 are also effective. The major advantage is that this process can be operated at low water concentrations (5 % w/w water compared to 8–10% for rhodium). The Ir catalyst is more stable and does not lead to precipitation of inactive IrI_3, and the water-gas shift reaction is reduced. This is a rare case where a third-row transition metal catalyst outperforms a second-row metal.

The catalytic cycle for the Ir-based reaction is more complex. At low iodide and water concentrations, a neutral species, $Ir(CO)I_3$ is the resting state. As was the case for Rh, the oxidative addition of MeI is rate determining. At higher iodide concentrations, on the other hand, anionic species predominate, and the carbonyl insertion of $[Ir(CO)_2I_3Me]^-$ to the acyl complex becomes rate determining, via iodide dissociation. By contrast, the oxidative addition of MeI to $[Ir(CO)_2I_2]^-$ is facile, about 100 times faster than with $[Rh(CO)_2I_2]^-$. The negative charge strongly favours MeI addition.

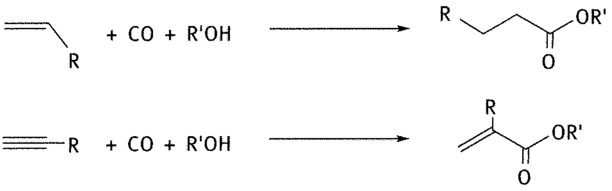


Apart from these large industrial processes, there are numerous applications of carbonylation reactions to fine chemical synthesis, usually using palladium catalysts. Prominent examples are carbonylations as alternative routes to the pharmaceuticals Ibuprofen and Naproxen. Similar carbonylations are achieved using vinylarenes as starting materials, with Pd catalysts under acidic conditions.



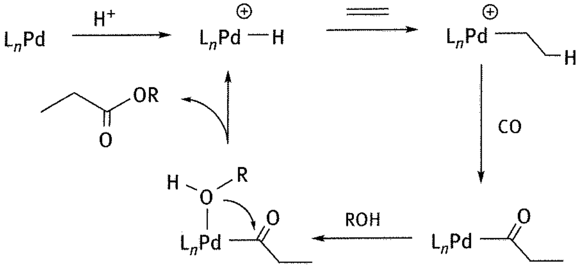
3.4.2.2 Alkene and Alkyne Carbonylations

Alkenes and alkynes can be carbonylated to give carboxylic acids and esters.

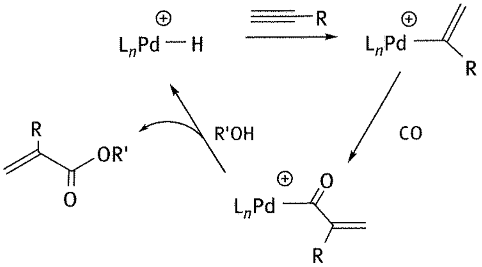


Palladium catalysts are most commonly used. The key reaction step is the formation of a Pd–C bond. This can be achieved using alkenes and alkynes under acidic conditions. Similarly, aryl halides that are capable of oxidative addition to palladium give carbonylation products. The reaction is most frequently used to give esters, using CO and alcohols (***hydroesterification***).

There are several mechanistic possibilities to explain C=C carbonylations and hydroesterifications. The preferred mechanism, supported by spectroscopic detection of the relevant intermediates in some cases (including L = PPh_3), envisages protonation of Pd under acidic conditions to generate a hydride which inserts the unsaturated substrate (*hydride mechanism*). The rate-limiting step is usually the alcoholysis of the Pd-acyl intermediate:

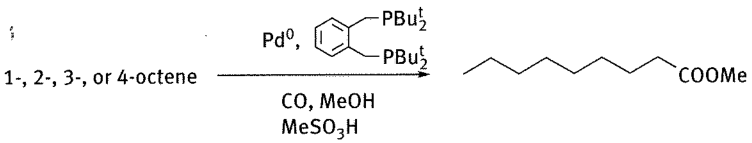


The analogous carbonylation of alkynes involves Pd-vinyl species, preferably with the substituent R in α-position. The product is an α-substituted acrylate ester:

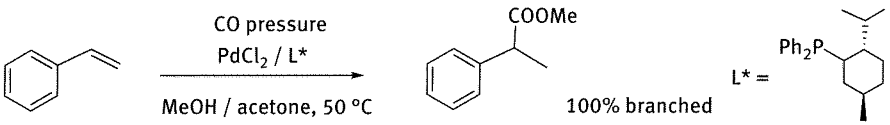


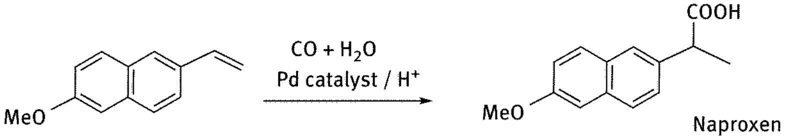
The first such alkyne hydroesterifications were carried out by W. Reppe (BASF) in the 1940s using $Ni(CO)_4$ (production of methyl methacrylate); however, catalysts based on $Pd(OAc)_2$ / 2-pyridyl-PPh_2 mixtures were found to be much more active.

With internal aliphatic alkenes the reaction is often preceded by C=C bond isomerization, resulting in terminal esters.

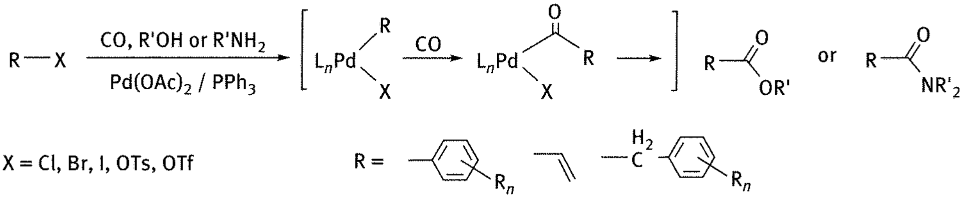


The hydroesterification of vinylarenes gives the branched products with very high regioselectivity. With chiral phosphine ligands these carbonylations give chiral products, although they do not reach the high enantioselectivities of asymmetric hydrogenations.

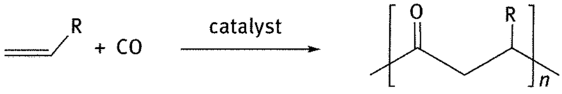




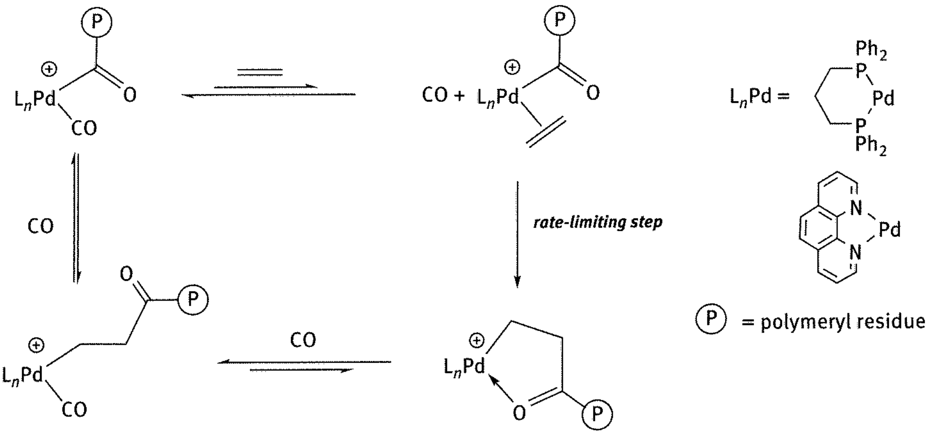
Carbonylation of organic halides. The carbonylation of activated organic halides proceeds in a similar way, again using palladium catalysts in most cases. Since the oxidative addition step is usually rate limiting, the reactivity decreases with increasing C–X bond strength; for this reason using the generally very unreactive (but cheap) aryl chlorides requires catalysts activated by bulky, strongly electron donating trialkylphosphines. This is a general route to carboxylic esters and amides:



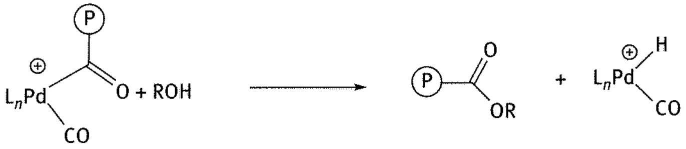
CO/alkene copolymerizations. The alternating copolymerization of CO with alkenes gives polyketones.



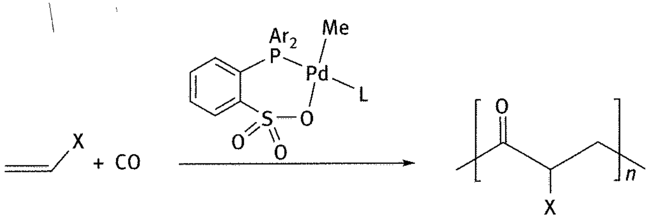
The copolymerization of CO with ethylene was first discovered in the 1940s using $Ni(CN)_2$ catalysts (well before the metal-catalysed ethylene polymerization), although palladium catalysts are much more active. Polyketones have tough, nylon-like properties that make them desirable for engineering applications, and the product was produced commercially for some years. Palladium catalysts with bidentate phosphines or phenanthroline ligands give alternating copolymers. The chemoselectivity is dictated, on the one hand, by the thermodynamically unfavourable insertion of CO in the Pd–acyl bond, and on the other by the higher rate of CO vs. C_2H_4 insertion into a Pd–alkyl bond. The mechanism is closely related to the carbonylation and hydroesterification of alkenes and involves a five-membered metal acyl-chelate ring that acts as resting state (at low [CO]).



Termination:



With other ligands, notably Ar_2P-*o*-$C_6H_4SO_3^-$, non-alternating ethylene/CO copolymers are obtained, i.e. products where CO insertion is followed by one or more ethylene insertions. Again Pd complexes are the most active catalysts. This anionic sulphonated phosphine also allows the alternating copolymerization of CO with polar functionalized alkenes CH_2=CHX (X = COOMe, COOH, OAc, CN, F, $CONR_2$):



Key points

Hydroformylation is the addition of CO and H_2 to alkenes to give aldehydes. After olefin polymerization this is the second-largest industrial process based on organometallic catalysts.

Co catalysts require high pressures and temperatures.

Rhodium catalysts work under milder conditions and give higher selectivity for linear aldehydes.

Alcohol carbonylation is a process for the production of carboxylic acids. The carbonylation of methanol to acetic acid is catalysed by rhodium (Monsanto process) or iridium (BP Cativa process). The carbonylation cycle is coupled with a water/HI cycle.

Hydroesterification is the addition of CO and alcohols to alkenes and alkynes, to give carboxylic esters.

Palladium catalysts are most commonly used.

With suitable ligands, palladium complexes are also the catalysts of choice for the alternating co-polymerization of CO and 1-alkenes to give polyketones.

Exercises

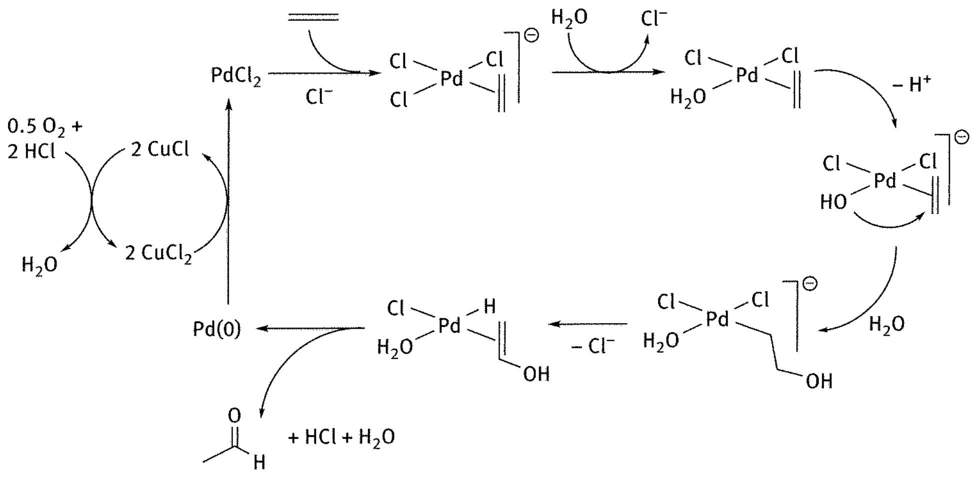
1. Explain the role of PBu^n_3 in Co catalysed hydroformylation. Why is this ligand not used in the Rh-catalysed process?
2. What is the consequence of high PPh_3 concentrations in the Rh-catalysed hydroformylation reactions? Explain the effect.
3. Show the main reaction steps for the conversion of 3-hexene into 1-heptanal.
4. Explain the differences in rate-limiting steps in the Rh and the Ir catalysed carbonylation of methanol. In particular, what are the reasons for the different reactivities of the iodo anions $[MI_2(CO)_2]^-$ (M = Rh, Ir)?
5. Draw catalytic cycles for the Pd-catalysed carbonylation of (i) styrene; (ii) iodobenzene. Why is the addition of base beneficial in this case?

3.5 Alkene Oxidations

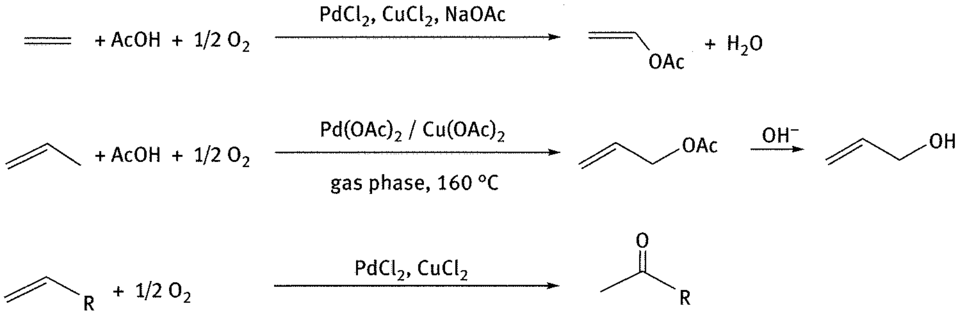
The oxidation of 1-alkenes is a route to aldehydes, ketones, as well as vinyl and allylic acetate and ethers. The oxidation of ethylene to acetaldehyde is an industrial process; most of the product is oxidized to acetic acid, as an alternative to methanol carbonylation (**Wacker process**). The process is catalysed by $PdCl_2$ / $CuCl_2$ mixtures in an aqueous solvent in the presence of HCl. The process can be described by a sequence of reactions:

$$\begin{array}{rcl}
C_2H_4 + PdCl_2 + H_2O & \longrightarrow & CH_3CHO + Pd(0) + 2\,HCl \\
Pd(0) + 2\,CuCl_2 & \longrightarrow & PdCl_2 + 2\,CuCl \\
2\,CuCl + 1/2\,O_2 + 2\,HCl & \longrightarrow & 2\,CuCl_2 + H_2O \\
\hline
\text{Overall: } C_2H_4 + 1/2\,O_2 & \longrightarrow & CH_3CHO
\end{array}$$

The mechanism has been studied intensively and the detailed steps seem to depend on the reaction conditions. They all have in common the formation of a Pd–CH_2CH_2–OH intermediate, by either intramolecular or intermolecular nucleophilic attack by OH^- on a coordinated ethylene ligand. This intermediate undergoes β-H elimination to give vinyl alcohol, which isomerizes to acetaldehyde.



Ethylene oxidations in the presence of acetic acid give vinyl acetate, while the oxidation of propene leads to allyl alcohol:



Key points

The oxidation of ethylene by Pd(II)/Cu(II) catalysts is known as the Wacker process. It gives acetaldehyde which is oxidized to acetic acid.

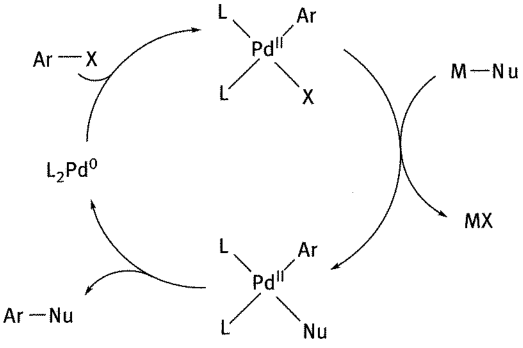
Pd/Cu catalysts oxidize alkenes to aldehydes or, in the presence of carboxylic acids, to vinyl acetates.

Oxidation of the alkyl substituents in alkenes CH_2=CHR in the presence of carboxylic acids leads to allylic esters; otherwise the products are ketones.

3.6 Coupling Reactions

C–C and C–N coupling reactions represent very versatile protocols in organic synthesis. In most cases these reactions are catalysed by palladium, not least because of the tolerance of this metal to moisture and functional groups. Most of these reactions involve C–C bond formation to an arene derivative, and depending on the coupling partners, these reactions have become known by a number of different names. However, they follow very similar catalytic mechanisms. Key to catalysis is the oxidative addition of the arene reaction partner Ar–X to a suitably reactive Pd(0) species (X = halide or tosylate, or occasionally H). The success of this step is strongly dependent on the type of ligands bonded to palladium. Less basic phosphines like PPh_3 are less successful here, while bulky di- and tri-alkyl phosphines enable even the very unreactive aryl chlorides to be utilized. The general catalytic cycle is based on the familiar key steps of oxidative addition, nucleophilic attack, and reductive elimination:

Nobel Prize 2010 to R.F. Heck, A. Suzuki and E. Negishi for catalytic C–C coupling methodology

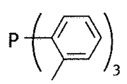


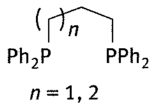
M–Nu	Coupling reaction
$R{-}B(OH)_2$	*Suzuki–Miyaura*
$R{-}SnR'_3$	*Stille*
R–ZnX	*Negishi*
R–MgX	*Kumada*
R–C≡CH / CuI	*Sonogashira*
$R{-}SiR'_3$	*Hiyama*
HNR'_2	*Buchwald–Hartwig*
$Zn(CN)_2$, $K_4[Fe(CN)_6]$	*Cyanation*

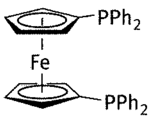
The reactions can be catalysed by generating the catalyst in situ, e.g. by combining $Pd(OAc)_2$ or $Pd_2(dba)_3$ and the appropriate ligand, although superior results have sometimes been found with pre-formed complexes PdL_2, many of which are now commercially available. Bulky, strongly donating phosphines, both monodentate and bidentate, as well as N-heterocyclic carbenes are widely used, for example:

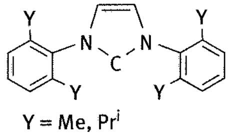
For $Pd_2(dba)_3$, see Section 2.6.1.1.

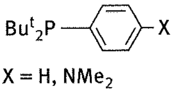
PR_3
R = Bu^t, Cy

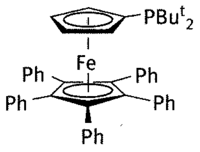


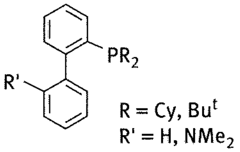


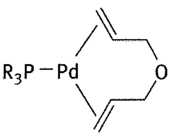








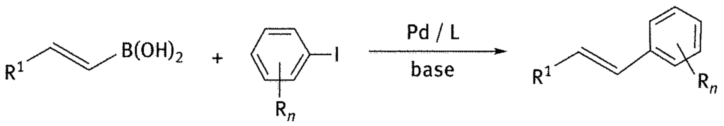




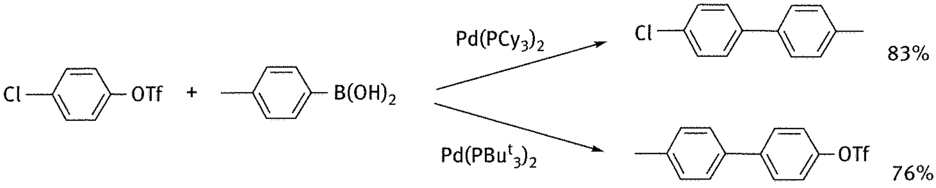
There are several storage forms for the catalyst, either as Pd(0) or Pd(II) complexes. Cyclometallated Pd(II) compounds are convenient and thermally stable catalyst precursors, but require a reductive elimination step to generate the active species.

3.6.1 C–C Cross-Coupling Reactions

Some combinations of transition metals and nucleophiles are better than others; e.g. Ni catalysts often work well with Grignard reagents, whereas for Pd less basic and more covalent Main Group components are more successful. Coupling reactions with boronic acids Ar–$B(OH)_2$ are particularly popular since these reagents tolerate most functional groups and are not water-sensitive. The addition of some water as well as base is usually required for boronic acid coupling; OH^- assists with substitution of X^- and the reductive elimination step. A very wide range of boronic acids is commercially available, including vinyl boron reagents.

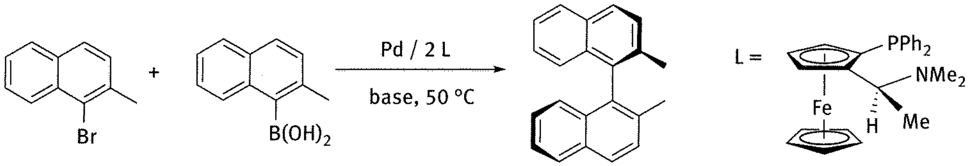


The phosphine may dictate the chemoselectivity:

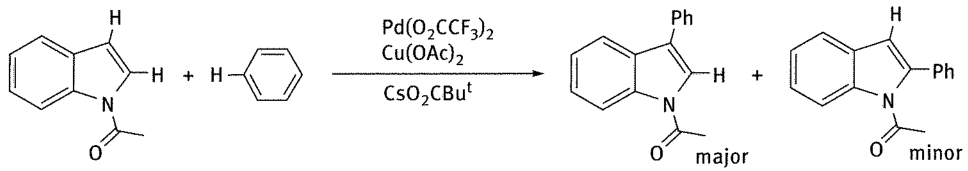


The Stille coupling involves tin reagents which, although tolerant of functional groups and water, are toxic. A non-toxic alternative are zinc reagents which are easily prepared by transmetallation from the Grignard reagents, e.g. with anhydrous $ZnCl_2$ which is soluble in dry Et_2O.

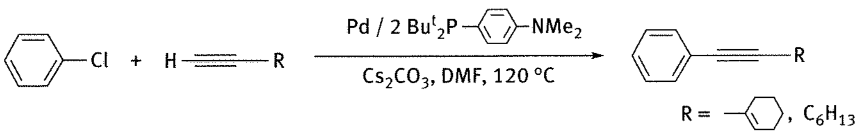
In the presence of chiral ligands C–C coupling reactions can be conducted enantioselectively. An example is the synthesis of axially chiral binaphthyls:



C–H coupling. With electron-rich arenes, the direct C–C coupling by oxidative activation of C–H bonds has also been realized, assisted by microwave heating. An organometallic nucleophile is not required.

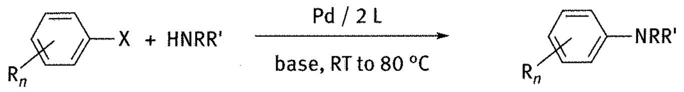


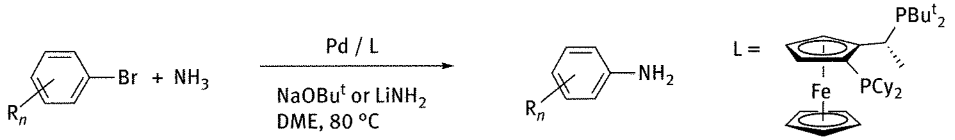
The coupling of aryls to acetylenes usually involves the addition of catalytic quantities of CuI and a base (NEt_3 or piperidine, for example) to generate the copper acetylides *in situ*. However, variants free of copper and amine additives have also been developed, such as:



3.6.2 C–N Cross-Coupling Reactions

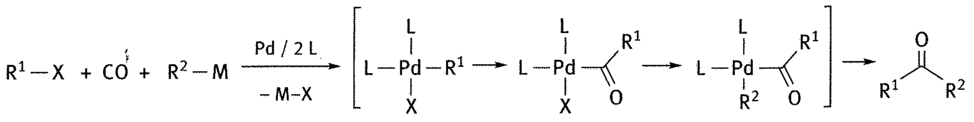
The arylation of amines is possible with Pd complexes of a variety of bulky, electron-rich phosphines, but also chelating PPh_2 derivatives such as dppf, BINAP, and Xantphos (***Buchwald–Hartwig amination***). Again the reaction sequence is initiated by oxidative addition of the aryl halide, followed by substitution of the halide ligand by the amine nucleophile, followed by reductive elimination of the product.

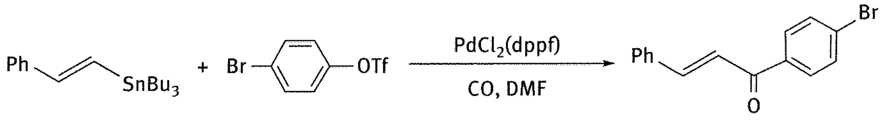




3.6.3 Coupling Reactions with Carbonylation

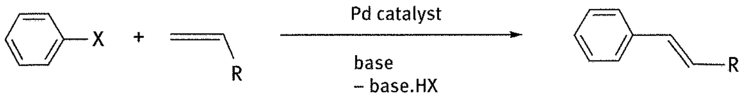
Following the formation of a Pd–C bond by oxidative addition of an aryl or vinyl halide, CO insertion reactions may take place before the product is released. Under such conditions ketones are formed:



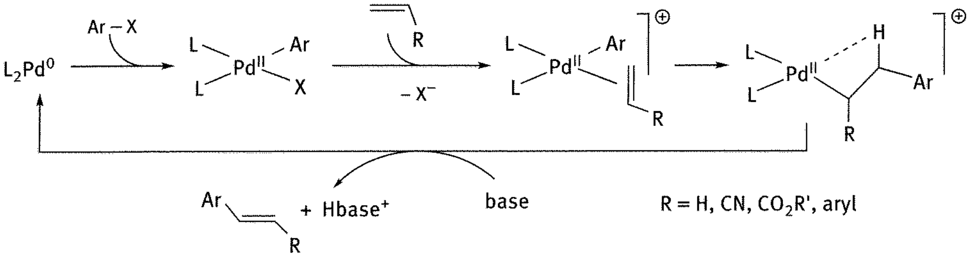


3.6.4 Heck Arylations

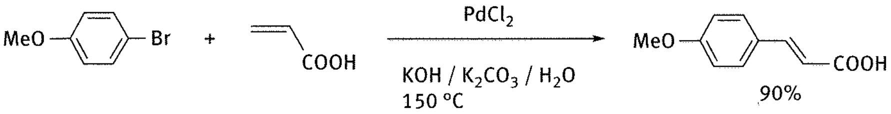
The insertion of an olefin into Pd-aryl bonds can lead to alkene arylation. This C–C coupling method has become known as the ***Heck reaction***. It is a widely applicable method for coupling aryl or vinyl halides (or triflates) with activated olefins such as styrene or acrylates.



Since these alkenes carry an electron-withdrawing substituent, the insertion proceeds preferentially with 2,1-regiochemistry since the substituent stabilizes the branched Pd-alkyl species, so that 1,2-disubstituted olefins are formed.



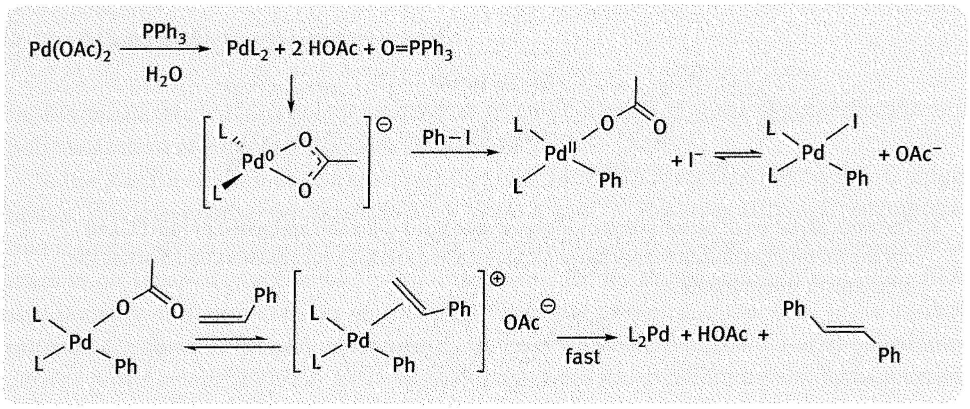
The coupling of acrylic acid with aryl bromides is a route to cinnamic acid derivatives. It is catalysed by palladium without the need for supporting ligands:



Box 3.6.4 Mechanistic aspects of the Heck reaction

The oxidative addition of PhI + $Pd(0)L_2$ gives an isolable product, $L_2Pd(Ph)I$ (L = PPh_3). This does not, however, react with styrene. On the other hand, the reaction with styrene proceeds readily if mixtures of $Pd(OAc)_2$ + $2PPh_3$ + PhI are used.

The reason is that under such conditions PPh_3 is a reducing agent, while acetate acts as a chelating ligand and gives an anionic Pd(0) species. This will readily add PhI to form Ph–Pd(II). The iodide is partially displaced by acetate, which, as a labile anion, can itself be displaced by styrene. The result is the formation of kinetically relevant concentrations of a cationic alkene complex with the correct stereochemistry for alkene insertion:



Key points

The formation of C–C bonds from two different molecules in the presence of metal catalysts is called C–C cross-coupling. The reaction is typically catalysed by nickel and particularly palladium complexes.

Aryl, vinyl, and benzyl halides can be coupled with organometallic reagents M–R, where M = Mg, Al, Zn, Si, Hg, or B.

Coupling reactions with boronic acids RB(OH)$_2$ are synthetically particularly important (*Suzuki–Miyaura coupling*).

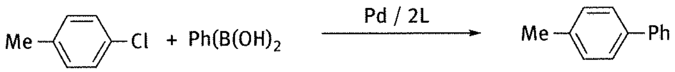
Coupling reactions involve the oxidative addition of R–X as the first step, generating a metal–C bond.

The *Heck reaction* involves the insertion of an alkene into the Pd–aryl bond to give arylated *trans*-alkenes.

Pd–aryl intermediates can also be coupled with *prim*- and *sec*-amines to give aryl amines (*Buchwald–Hartwig* amination).

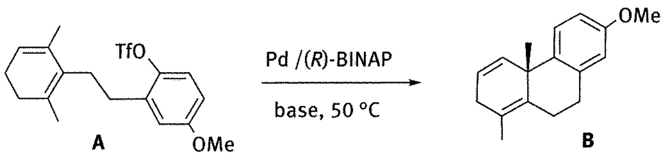
Exercises

1. Explain why in the reaction

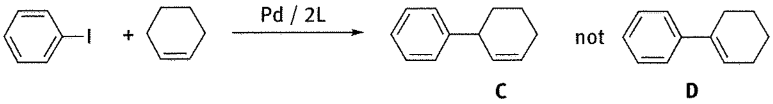


different ligands L give the coupling product in the following yields (%): L = PPh$_3$ (0); dppf (0); PCy$_3$ (75); PBu$^t_3$ (86).

2. Show the mechanistic steps for the transformation of **A** into **B**. Although **A** contains two C=C bonds, product **B** is formed selectively. Give your reasons.



3. The Heck arylation of cyclohexene by iodobenzene gives the non-conjugated product **C** and not the thermodynamically expected conjugated alkene **D**. Give your reasons and discuss the mechanistic intermediates.



3.7 Alkene Polymerizations

In this chapter we will discuss the polymerization of 1-alkenes. For the oligomerization and polymerization of conjugated dienes, see Section 2.7.1.3.

In the polymerization of ethylene, one C=C double bond is replaced by two C–C single bonds. This is an **exothermic** process ($\Delta G \approx -20$ kcal mol^{-1}). However, although polymerization is thermodynamically favourable, polymerization cannot proceed spontaneously since there is no kinetically accessible reaction pathway. Under drastic conditions (1000–3000 atm pressure and temperatures of 150–230 °C) in the presence of traces of O_2 as radical initiator, ethylene can be polymerized to a soft, highly branched material, the so-called low-density polyethylene (**LDPE**). This material is light and has excellent insulating properties, which makes it suitable for electrical insulation applications; it still constitutes about 20% of total world polyethylene (PE) production.

The polymerization of 1-alkenes under less forcing conditions requires a catalyst and metal alkyl activators. Several conditions must be fulfilled for a metal to be an active alkene polymerization catalyst:

(1) As explained in Section 2.6.1.2, the alkene must be able to coordinate to the metal, and this coordination must induce polarity in the C=C bond.
(2) There must be no significant back-bonding, i.e. the metal must not have high-lying occupied d-orbitals.
(3) The catalyst must be sufficiently Lewis acidic to form at least transient adducts with alkenes.
(4) The catalyst must possess two sterically accessible coordination sites *cis* to one another.
(5) The catalyst must contain a metal–alkyl bond.
(6) The rate of β-H elimination (or β-H transfer to monomer) of the alkyl (polymeryl) ligand must be slow compared to the rate of alkene insertion into the M–C σ-bond.

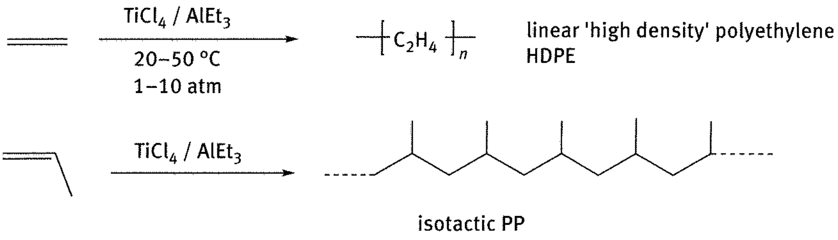
The production of polyethylene and polypropylene is probably the world's largest-scale application of organometallic chemistry, with an estimated combined output of about 100–150 million tons of polymers annually worldwide (2012). Applications include numerous products of daily life, such as packaging materials, tubes and pipes, bags, bottles, household goods, toys, carpets, ropes, but also car bumpers, fuel tanks, and even bullet-proof vests. In the last 2–3 decades, catalyst development has significantly expanded the range of polyolefin-based materials.

3.7.1 Ziegler Catalysts

Nobel Prize 1963 to K. Ziegler and G. Natta for the discovery of ethylene and stereoselective propene polymerization catalysis.

3.7.1.1 Catalyst Composition

The first effective ethylene polymerization catalyst to be discovered was a mixture of $TiCl_4$ and $AlEt_3$ (**Ziegler catalyst**). The polymer this produced was linear and much less branched than LDPE; it contained a high degree of crystallinity and has become known as **high-density polyethylene** (**HDPE**). The same catalyst also polymerizes propene stereoselectively to give **isotactic polypropylene** (**i-PP**).



Although it is now known that under such conditions monomeric $TiCl_4$ is reduced to give finely divided crystallites of polymeric $[TiCl_3]_x$, and the catalyst is therefore heterogeneous, the reaction mechanism nevertheless follows organometallic reaction principles, which also apply to the homogeneous polymerization catalysts discussed in the following section. Subsequently, highly effective heterogeneous Ziegler catalysts were developed by ball-milling $TiCl_3$ with $MgCl_2$; both these metal chlorides have solid state layer structures and intercalate to give a material with a high concentration of surface defects. It is on these coordinatively unsaturated surface defect sites that catalysis takes place. These catalysts can be further improved by adding various organic additives; details are beyond the scope of this text.

Apart from titanium-based Ziegler catalysts, chromium salts supported on silica represent another important class of ethylene polymerization catalysts (**Phillips catalysts**). These heterogeneous Cr catalysts produce a very linear high molecular weight polyethylene with very few methyl side chains. As a consequence, this material is hard and rigid and mainly used for structural applications such as water pipes. Mechanistically, the Cr catalysts are less well understood than the titanium system.

Box 3.7.1 Polymers and polymer structure

Whereas most catalytic reactions produce small target molecules of well-defined structures and properties, polymerization catalysts can convert a simple starting material like ethylene or propylene into a multitude of products with very different physical and materials properties, suitable for many different applications. The challenge to the catalytic chemist is to translate the demands of engineers and polymer processors for desirable material properties into the design of catalysts capable of achieving these properties. The main parameters are:

(1) ***Polymer molecular weight***. For example, low molecular weight PE (e.g. MW 10^4–10^5 g/mol) tends to form brittle films and has low tensile strength; even lower MW gives

waxes. By contrast, PE with molecular weights of well over 10^6 g/mol (**UHMWPE** = ultra-high molecular weight polyethylene) can be formed into high tensile strength fibres for mountaineering ropes and bullet-proof vests. The usefulness and commercial success of a polymer therefore strongly depends on the molecular weight.

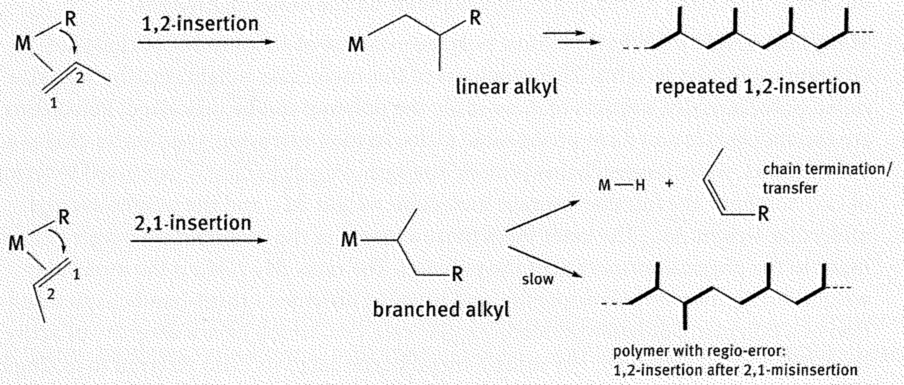
(2) ***Molecular weight distribution***. Most polymers consist of an assembly of chains of different molecular weights. The broadness of this molecular weight distribution, also called polydispersity, impacts on how easily the polymer can be processed. Polyolefins are thermoplastics and form processable melts. In melt extrusion, the shorter chains act as lubricants, while longer chains provide strength. Polydispersity is expressed in terms of two numbers: the number-average molecular weight $\overline{M}_n$, and the weight-average molecular weight $\overline{M}_w$. The latter takes more account of the contribution longer chains make to the physical properties of the polymer. The ratio $\overline{M}_w / \overline{M}_n$ is the molecular weight distribution or polydispersity, and its value provides a short-hand characterization of a polymer. For heterogeneous Ziegler catalysts, which have a diversity of active sites, $\overline{M}_w / \overline{M}_n$ is around 5. For soluble metallocene catalysts (also referred to as single-site catalysts) the value is ~2. So-called 'living' polymerizations have no chain termination and all active centres produce polymer chains of the same length; the $\overline{M}_w / \overline{M}_n$ value is therefore close to 1.

(3) ***Branching***. Polyethylene can be free of branches ('polymethylene': linear, highly crystalline, rigid) or have long-chain and short-chain (mostly methyl) branches. Branching reduces the van der Waals interactions between chains and creates amorphous, flexible polymers. Long-chain branches increase the strength in the melt and are useful for extrusion processing into films, for packaging applications. Information on branching can be gathered from infrared and NMR spectra, as well as from polymer rheology. Adding co-monomers like 1-hexene and 1-octene generates PE with controlled degrees of branching (linear low-density PE, or **LLDPE**); this is an area where metallocene-type catalysts excel.

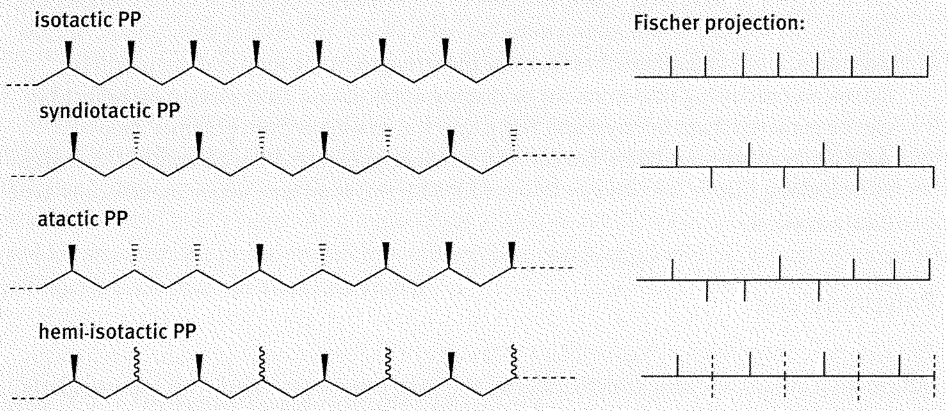
Polypropylene

The structure of a polymer chain is like a videotape of its formation: it provides mechanistic information about the chain growth process, and each error is recorded. This is particularly obvious for polypropylene.

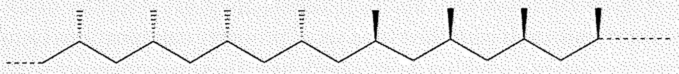
The polymerization of propene is more complicated than of ethylene, since the methyl substituents along the chain can adopt many different relative orientations. The most important isomer is ***isotactic*** polypropylene (**i-PP**); it has high tensile strength and a melting point that increases with stereoregularity (up to 165 °C). Ropes made from stretched i-PP fibres are stronger weight-for-weight than steel ropes. By contrast, atactic PP (**a-PP**), with irregular Me orientations, is soft and much less useful. There are therefore many different forms of polypropylenes, each with their own set of property combinations (tensile strength, toughness, impact resistance, melting point, elasticity). These polymers are generated by monomer insertion with 1,2-regiochemistry; there is of course the possibility of stereo-errors, as well as the incorporation of a monomer 'the wrong way round' (regio-error by 2,1-insertion).



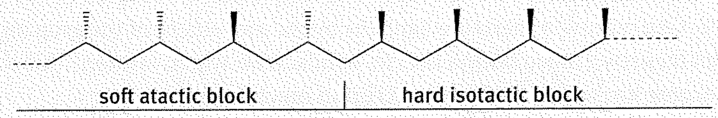
This leads to a family of compositionally identical polymers which exhibit very different properties, from extremely strong fibres to rubber-like elastomers and waxes.

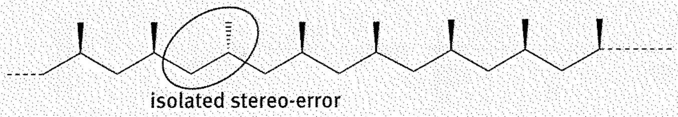


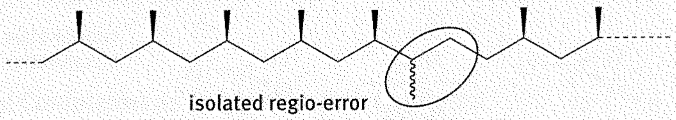
There is also the possibility of building polymer chains that consist of blocks of polymers with different characteristics, and of incorporating regio-errors, e.g. to convert a tough polymer with a high concentration of crystalline domains and high melting point into a soft, amorphous elastomer.



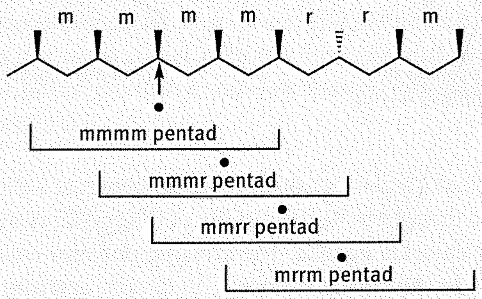
isotactic blocks







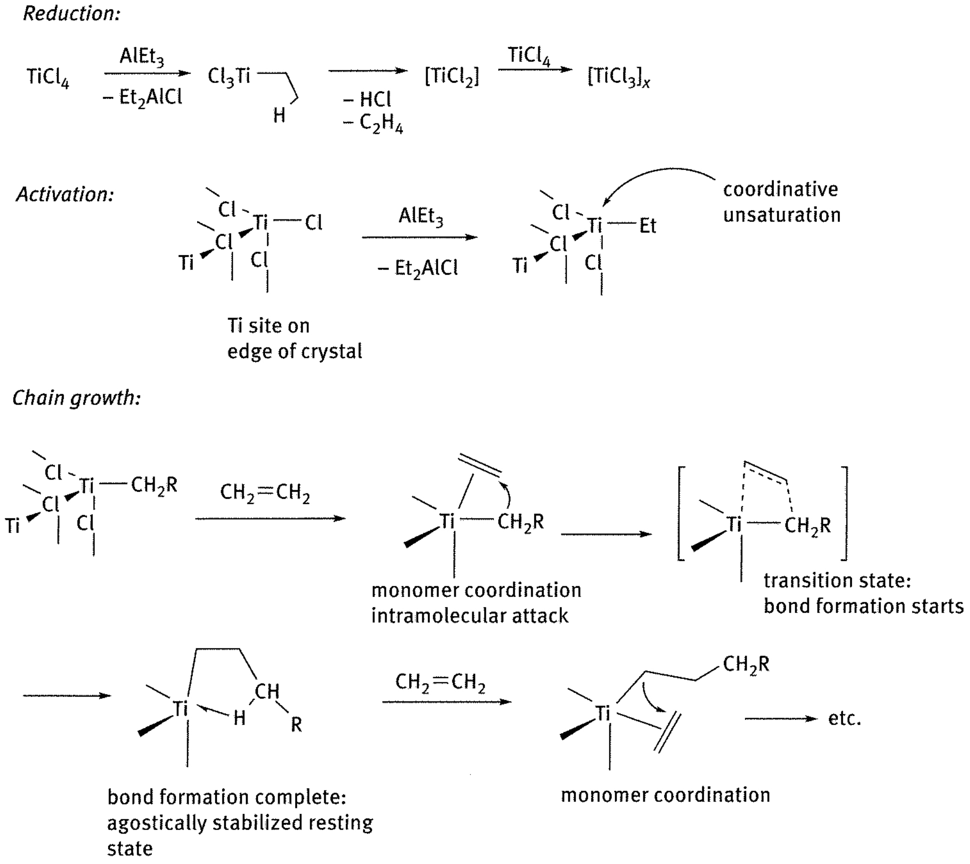
PP microstructure. For polypropylene, very detailed information has been obtained by ^{13}C NMR spectroscopy. The chemical shift of a given methyl side chain is sensitive to its nearest neighbours and their relative orientation. With high-field NMR spectrometers the influence of at least the nearest two other methyl groups to the left and the right of the observed Me substituent can be determined (i.e. the segment structure of five methyl groups, 'pentad level'). In favourable cases the structure over a segment with 7 or 9 methyl groups can be resolved (heptad or nonad level). In polypropylene, every second C atom is chiral. The methyl substituents on these C atoms can be in either a *meso* (*m*) or *rac* (*r* = *racemo*) relationship to one another (*racemus* (Latin) = bunch of grapes, referring to grape acid where *rac* and *meso* isomers were first identified). The structure of PP can therefore be described by *m* or *r* diads. Several of these combined give the pentad structure, e.g. *mmmm* for an isotactic pentad. Highly isotactic PP may display an *mmmm* pentad intensity of >90%, with the remaining Me signals spread over other types of pentads.



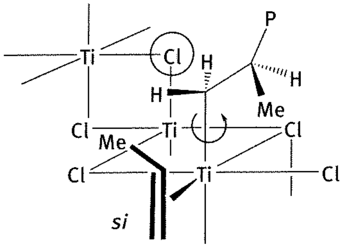
The distribution of pentads is a measure of the stereo- and regioselectivity of a given catalyst.

3.7.1.2 Mechanism of Ziegler Catalysts

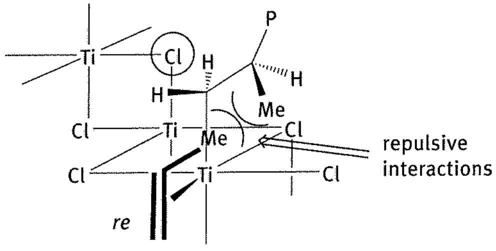
The key for polymerization catalysis, from the point of view of mechanistic understanding, is the formation of a Ti–alkyl bond on the edges and corners of the $[TiCl_3]_x$ crystals, by alkylation of a coordinatively unsaturated Ti–Cl site by $AlEt_3$. This is followed by ethylene coordination and intramolecular nucleophilic attack by the ethyl ligand on the alkene. Alkyl migration to the alkene vacates a *cis* coordination site, which is occupied by the next monomer molecule. Chain growth therefore happens by the movement of the growing polymeryl chain between these two coordination sites in 'windscreen-wiper' fashion. This chain growth model has become known as the **Cossée–Arlman mechanism**.



Fortunately the original Ziegler catalyst proved to generate i-PP with excellent stereoregularity. The reason is thought to be the rigidity of the crystal surface structure and steric hindrance provided by chloride ligands. The growing polymer chain is forced into a specific orientation relative to the crystal surface. This in turn determines the coordination of propene, a prochiral alkene, in such a way as to minimize steric interactions between the polymeryl chain and the methyl substituent of propene. With the chain orientation shown in the following diagram, this is the case if the *si* face of propene coordinates, whereas coordination from the opposite face encounters steric interactions with the β-Me group on the chain. This small repulsive interaction is enough to ensure that successive propene molecules always bind via the same π-face, leading to an isotactic polymer.



favoured conformation



disfavoured conformation

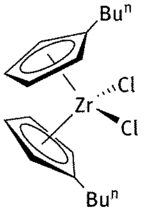
3.7.2 Metal Complexes as Polymerization Catalysts

Whereas detailed mechanistic information on heterogeneous polymerization catalysts is difficult to obtain, soluble catalysts suffer no such drawbacks. Since these are coordination complexes, their ligand environment can be tailored to optimize performance in terms of activity, polymer molecular weight, co-monomer incorporation, and stereoselectivity. The polymer molecular weight distribution is usually much narrower than that obtained with heterogeneous catalysts ($\overline{M}_w/\overline{M}_n \approx 2\text{–}3$), since all active sites are identical.

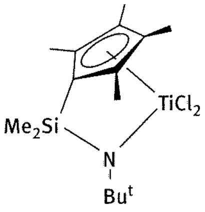
Early studies focussed on Group 4 metallocenes Cp_2MCl_2 as catalyst precursors, mainly M = Ti and Zr. Attempts were initially made to activate these with $AlEt_3$ or Et_2AlCl, and although they showed some activity, they were far from competitive with Ziegler catalysts. This changed when it was found that a hydrolysis product of $AlMe_3$, called **methylaluminoxane** (**MAO**, see Section 1.5.2.3), activated Cp_2ZrCl_2 to give catalysts with excellent ethylene polymerization activities. The structure of MAO, an amorphous, toluene soluble glassy substance, is a matter of conjecture, but it remains the industrially preferred activator for metallocene catalysts, both in solution and for silica-supported catalysts for solvent-free gas phase polymerizations.

With few exceptions, for convenience catalysts are generated in situ from stable metal halide precursors and an aluminium alkyl activator. Some representative catalyst precursors for ethylene polymerization are:

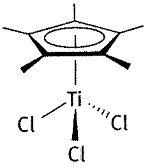
For the synthesis of Group 4 metallocene complexes, see Section 2.8.2.1.



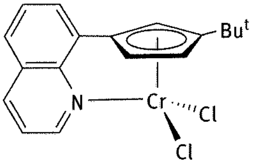
Zirconocene catalyst, high PE activity, standard for PE



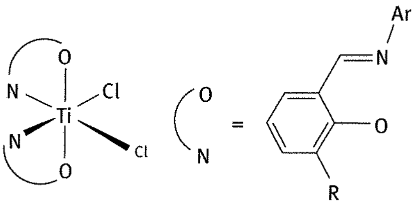
'Constrained-geometry' catalyst (CGC). The more open structure gives very high activity and high comonomer incorporation.



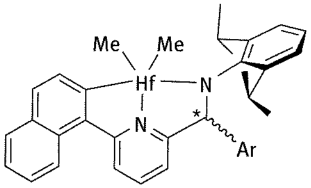
Ti half-sandwich complex, best for syndiotactic styrene polymerization



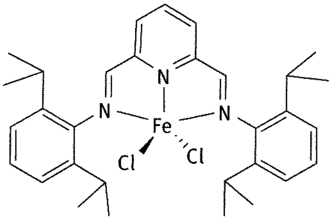
Cr catalyst, capable of producing UHMWPE



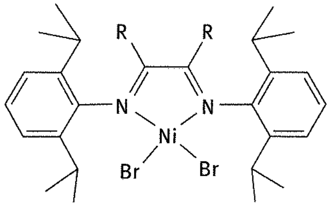
'Post-metallocene' Ti catalyst, with a highly variable N^O chelate with bulky Ar and R, for ethylene homo-and copolymerizations.



Hf catalysts for ethylene / 1-alkene copolymerizations for high-temperature solution phase processes (Dow). An example of a catalyst discovered by high-throughput technology.



Iron catalyst,
highly active for ethylene polymerization.
The sterically hindered N-aryl substituents prevent chain transfer.



Nickel catalyst, gives highly branched soft PE by 'chain walking'.

The catalysts shown here all have high ethylene polymerization activity. The so-called 'constrained-geometry' titanium catalysts (CGC), which contain a chelating Cp-amido ligand, are particularly effective for incorporating 1-alkenes (hexene, octene) to give copolymers with controlled amounts of evenly distributed branching. This is an area where soluble catalysts excel: whereas heterogeneous Ziegler catalysts usually give mixtures of high molecular weight chains with low co-monomers content and low molecular weight components of high co-monomer incorporation, metallocene catalysts, by contrast, are able to produce homogeneous, high molecular weight copolymers with improved properties.

3.7.2.1 Catalyst Activation and Active Species

The activation of metal halide precursor complexes consists of two steps:

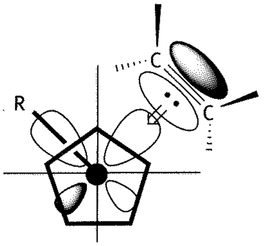
(i) **alkylation**, i.e. the substitution of at least one halide by an alkyl ligand;

(ii) creation of a **vacant coordination site**. This involves abstraction of an anionic ligand by a Lewis acidic activator (there are also rare cases where a neutral catalytically active species is generated by abstraction of a phosphine ligand).

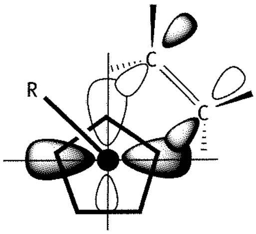
The most important class of soluble catalysts are based on Group 4 metallocenes. Here, the active species is a cationic 14-electron species, $[Cp_2M{-}R]^+$. Other types of metal halide precursors show an analogous chemistry.

As was shown in Section 2.8.2.2, a 14 VE metallocene cation $[Cp_2M{-}R]^+$ has a vacant d-orbital d_σ, capable of accepting electron density from the π-orbital of an olefin. There is also a d_π orbital of the correct symmetry to overlap with the π^* orbital of the C=C bond.

However, if M is a d^0 metal such as Ti, Zr, or Hf, this orbital is not occupied and there is no back-bonding stabilization, which would strongly retard any subsequent reaction. The same holds for neutral lanthanide complexes Cp_2LnR. This contrasts with isostructural d^2 complexes such as $Cp_2NbEt(\eta^2\text{-}C_2H_4)$, where strong back-bonding blocks any alkene insertion.

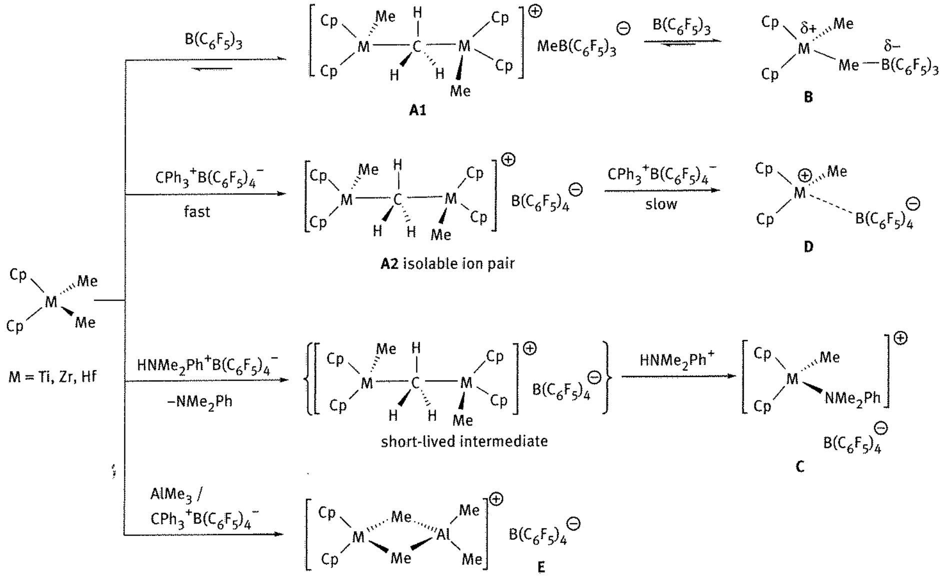


d_σ acceptor orbital
for alkene binding



Orbital of d_π symmetry.
Absence of back-bonding for d^0 systems

Alkylation is achieved most commonly by adding aluminium alkyls like $AlMe_3$ (a constituent of MAO) or $AlBu^i_3$. Alternatively, pre-formed metal alkyl complexes can be used. The second step requires a strong Lewis acid or a Brønsted acid, paired with an anion that is so weakly nucleophilic that it does not out-compete the olefin monomer for a coordination site on the metal. Commonly used so-called 'non-coordinating' anions like BF_4^-, PF_6^-, BPh_4^- or the triflate anion ($CF_3SO_3^-$) do not give active catalysts since they bind to metals far too strongly. Perfluoroarylborates, on the other hand, give extremely active catalysts. Activation can be achieved using a neutral Lewis acid like $B(C_6F_5)_3$ or CPh_3^+ (trityl) or $HNMe_2Ph^+$ salts of $[B(C_6F_5)_4]^-$ or related tetraarylborate anions. The process has been studied in detail using metal methyl complexes:



These processes are spectroscopically observable. It is evident that high-energy 14 VE cationic species are not detected but are stabilized in a number of ways:

(i) by reacting with a neutral Cp_2MMe_2 molecule to give homo-binuclear outer-sphere ion pairs (OSIPs) of structures **A1** and **A2**;

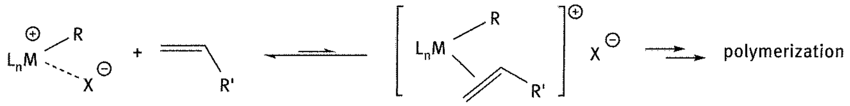
(ii) by forming inner-sphere ion pairs (ISIPs) of type **B** with the more coordinating $[MeB(C_6F_5)_3]^-$ anion;

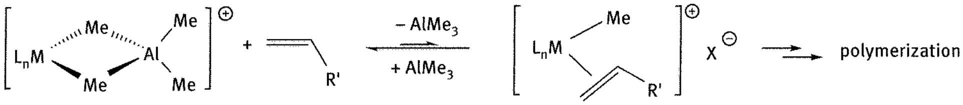
(iii) by forming aniline adducts **C** if aniline is the by-product;

(iv) by forming an ion pair **D**;

(v) by adduct formation with $AlMe_3$, to give a heterobinuclear ion pair **E**.

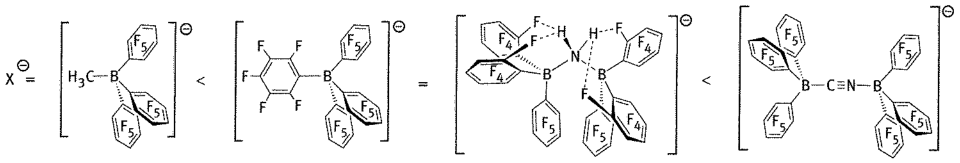
Importantly, in the presence of alkene monomer these various associated ion pairs are in equilibrium with the propagating species:





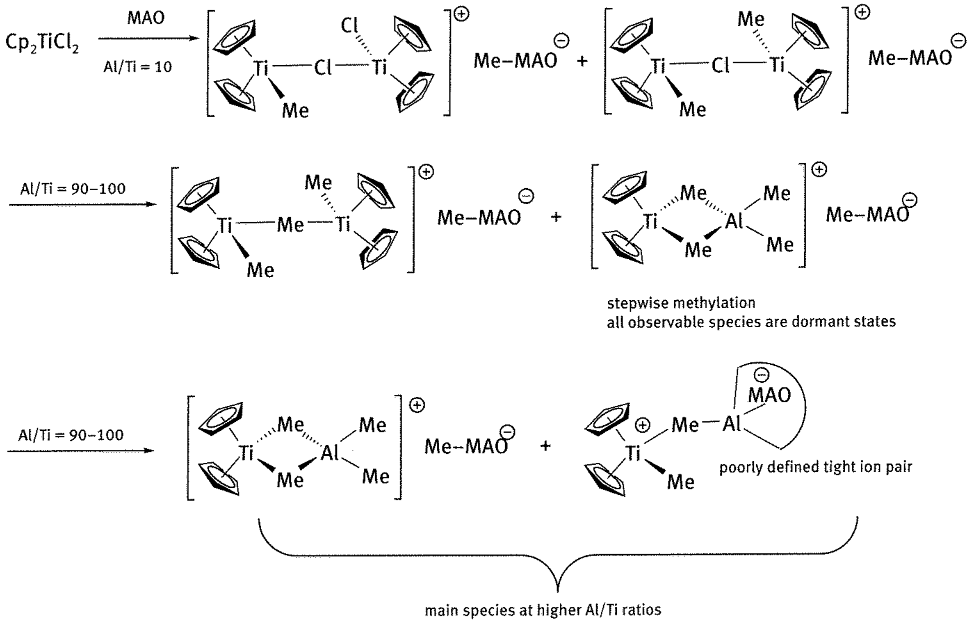
Starting with Group 4 metal dihalides L_nMCl_2, very high alkene polymerization activities can also be obtained using an $AlBu^{i}_{3}$ / $CPh_3^+[B(C_6F_5)_4]^-$ mixture as activator.

Distributing the negative charge of an anion over as large a volume as possible reduces the ability of this anion to coordinate to the catalytically active site, and the polymerization activity increases as a consequence. One method for increasing the size of the anion is to bridge two borate centres (e.g. with CN or NH_2). Accordingly, the activity of a given catalyst ion pair $[L_nM{-}R]^+X^-$ increases in the series:



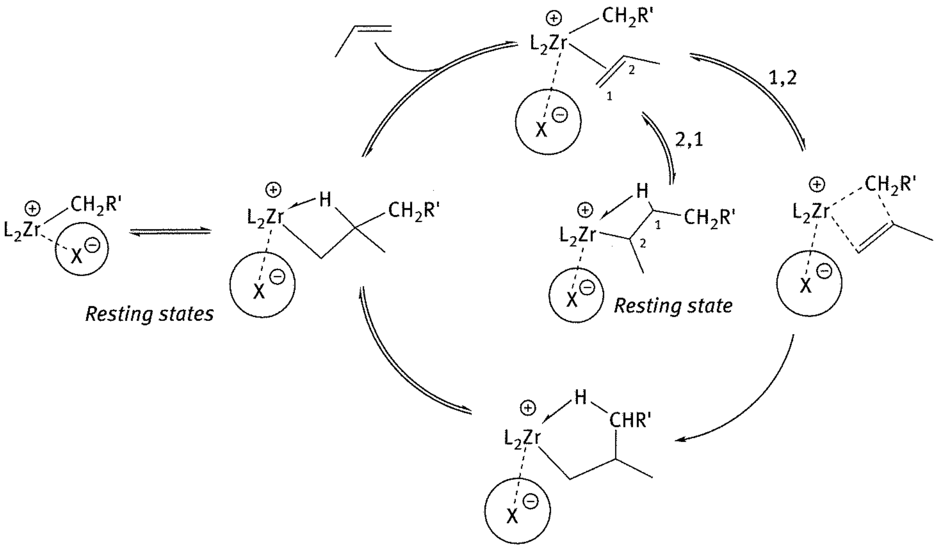
Catalyst activation with MAO. Methylaluminoxane (MAO) acts both as an alkylating agent and as the source of the counter-anion. MAO is a mixture of oligomeric species $[MeAlO]_n$ together with associated and free $AlMe_3$; the average composition is typically $[Me_{1.4-1.5}AlO_{0.80-0-75}]_n$. Recent studies suggest that MAO consists of species with an average molecular weight of around 1800 g mol^{-1} and about 30 Al atoms, $(MeAlO)_n(AlMe_3)_m$, with $n \approx 23$ and $m \approx 7$ for the primary component. Because MAO is a poorly-defined mixture of different species, and because only a small fraction of these oligomeric species are capable of activating a catalyst, high Al/metal ratios have to be applied for high activity, typically 1000–3000:1.

The alkylation of metallocene dichloride pre-catalysts with MAO proceeds stepwise, via chloro-bridged cationic complexes which are alkylated much faster than neutral complexes. At sufficiently high Al/M ratios the onset of polymerization activity corresponds to the formation of both a heterobinuclear $AlMe_3$ adduct and of another, poorly characterized ion pair, $[Cp_2MMe^+\cdots\cdots Me\text{–}MAO^-]$. It is also plausible that MAO acts as a source for the highly reactive and Lewis acidic $AlMe_2^+$ cation, which in turn can abstract a chloride or a methyl ligand from the metallocene to generate a catalytically active cationic metallocene species.



3.7.2.2 Alkene Polymerization Reactions

General polymerization cycle. Alkene polymerization proceeds by intramolecular nucleophilic attack of the growing polymeryl chain on the coordinated monomer. The process is a 1,2-insertion step, as shown in the following diagram for propene. With metallocene catalysts, which are typically non-living, there are several resting states, such as agostically stabilized ion pairs as well as products of 2,1-misinsertion, which give branched alkyls and are slow to react with further monomer for steric reasons. These resting states mean that in most polymerization catalysts only 10–20% of the total metal species are actively engaged in chain growth at any one time. Dormant and active species are in equilibrium, so that all metal centres can carry a polymeryl chain.



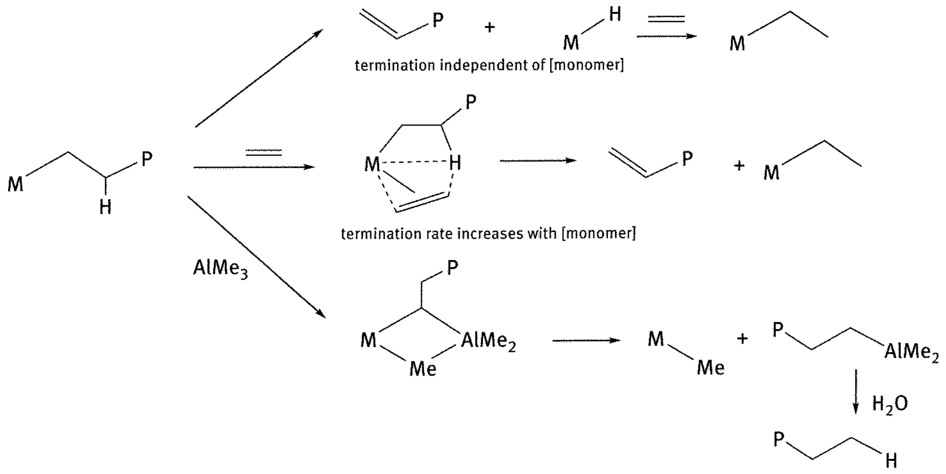
Alkene polymerizations follow the rate law:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{C}][\mathrm{M}]$$

where M = monomer, C = catalyst, and k_p = propagation rate constant. Higher-order dependence on [M] is sometimes found; this is indicative of unrecognized equilibria such as incomplete initiation. The degree of polymerization is given by the ratio of the rate constants for propagation and chain termination, $k_\mathrm{p}/k_\mathrm{t}$. In many instances these rates are strongly dependent on steric factors.

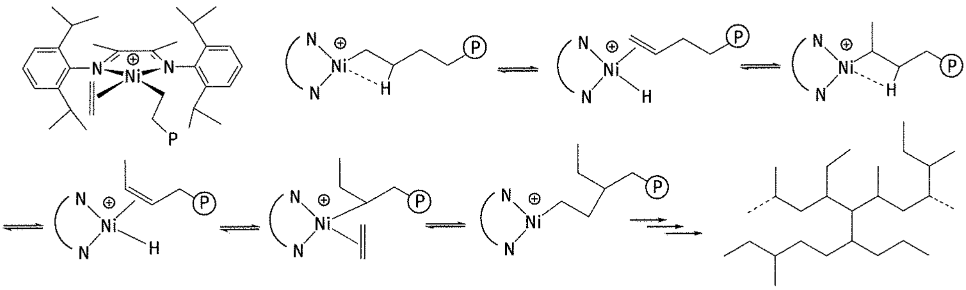
Propene polymerizations with high activity metallocene catalysts can produce in excess of 10^8 g PP $\mathrm{mol}_{(\mathrm{catalyst})}^{-1}\ \mathrm{h}^{-1}\ \mathrm{bar}^{-1}$, with about 10^4–10^5 monomer insertions per second which, in the case of propene, proceed with high regio- and stereoselectivity.

Chain transfer. Chain transfer proceeds at a slower rate k_t, which is typically 2–3 orders of magnitude smaller than the rate of propagation. In 1-alkene polymerizations chain transfer has three primary pathways: β-H transfer to the metal, β-H transfer to monomer (the energetically preferred pathway in most cases), and, if $\mathrm{AlR_3}$ is present, chain transfer to aluminium. The first two pathways generate terminally unsaturated polymers, while transfer to Al gives, after hydrolytic workup, a completely saturated polymer. This latter pathway is common in MAO-activated polymerizations. It has been found that both the catalyst activity and the polymer molecular weight are controlled by the $\mathrm{AlMe_3}$ concentration in these systems.

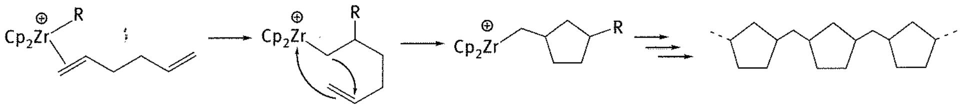

termination independent of [monomer]

termination rate increases with [monomer]

'***Chain walking***'. Suppression of k_t by sterically highly hindered N-aryl substituents is the key to success with nickel diazadiene catalysts: enclosing the active site with bulky Pr^i substituents reduces the rate of chain transfer. Here, β-H elimination becomes competitive with monomer insertion, so that chain growth is frequently interrupted by elimination/re-insertion reactions, which allow the metal to 'chain-walk' and initiate numerous side branches. The resulting polymer therefore resembles radical-generated LDPE.

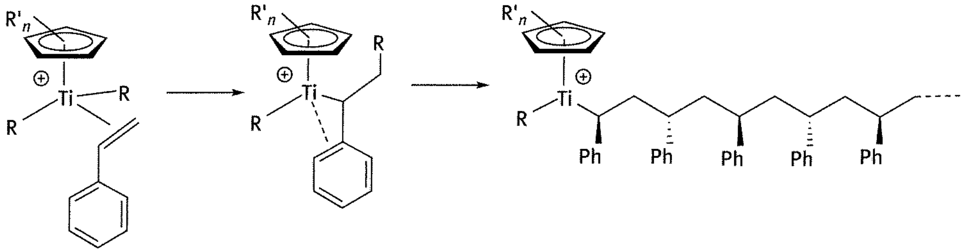


Cyclopolymerization. Non-conjugated dienes undergo insertion in 1,2-fashion. The insertion of the second C=C bond tends to be faster than insertion of a new monomer, so that a cycle is formed, as in the case of 1,5-hexadiene. Since each 5-ring has potentially two chiral C atoms and rings can be mutually *cis* and *trans* as well as isotactic and syndiotactic, with suitable ligands many different stereoisomers can be produced.



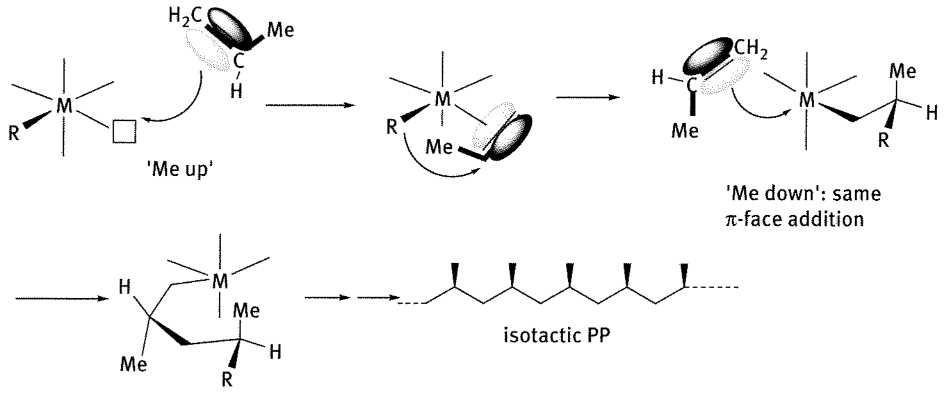
Styrene is also polymerized by anionic, cationic, and radical mechanisms; these give the much more soluble atactic polymer.

Styrene polymerization. Unlike most other alkene insertions, the polymerization of styrene catalysed by Ti mono-Cp complexes involves chain propagation by 2,1-insertion, since the α-phenyl substituent helps to delocalize the negative charge on the metal-bound C atom, and there is some π-interaction with the metal. This polymerization produces syndiotactic polystyrene (**s-PS**).

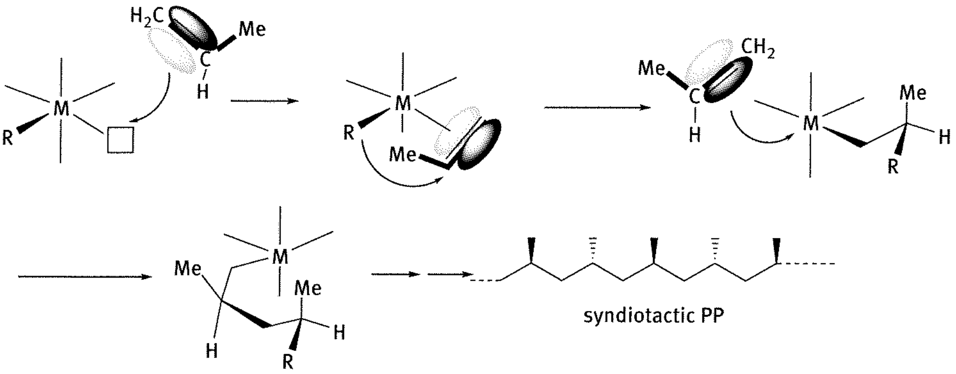


3.7.2.3 Stereoselective Polymerization

1-Alkenes like propene are prochiral. If in successive polymerization steps the alkene coordinates to the metal centre always through the same π-face, an isotactic polymer results.

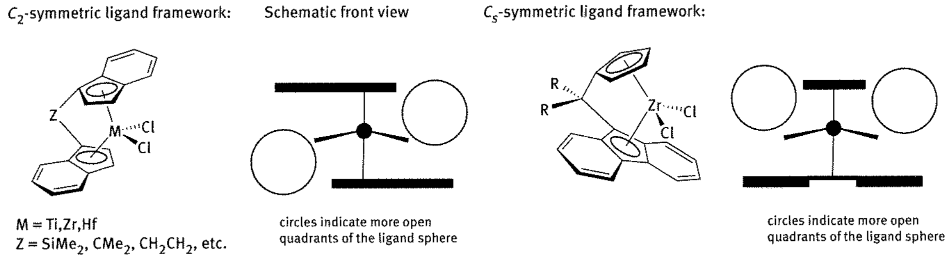


Conversely, if every second monomer binds via the opposite π-face to the first, a syndiotactic polymer is formed:

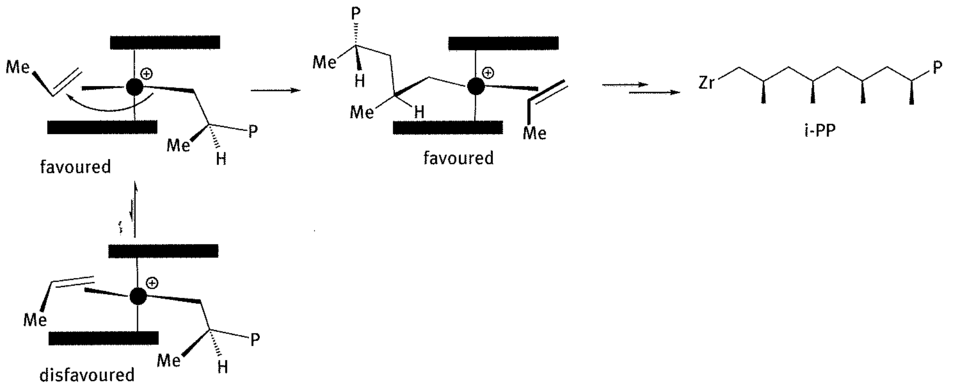


These situations can be realized by appropriate tailoring of the ligand symmetry of coordination catalysts: ligands that impose C_2 symmetry will lead to isotactic polymers, whereas C_s symmetry enforces syndiotactic stereochemistry. For example, connecting the two Cp ligands in a metallocene with a bridging group prevents their rotation, so that C_2- or C_s-symmetric environments result. It is evident, particularly in the schematic view, that the C_2- symmetric ligand creates diagonally related less and more crowded quadrants in the coordination sphere of the complex, whereas the C_s- symmetric complex has a mirror plane and less crowded quadrants on the 'upper' side of the ligand. This ligand geometry controls the conformation of the growing polymer chain, and this conformation in turn determines which π-face of a prochiral olefin will coordinate preferentially.

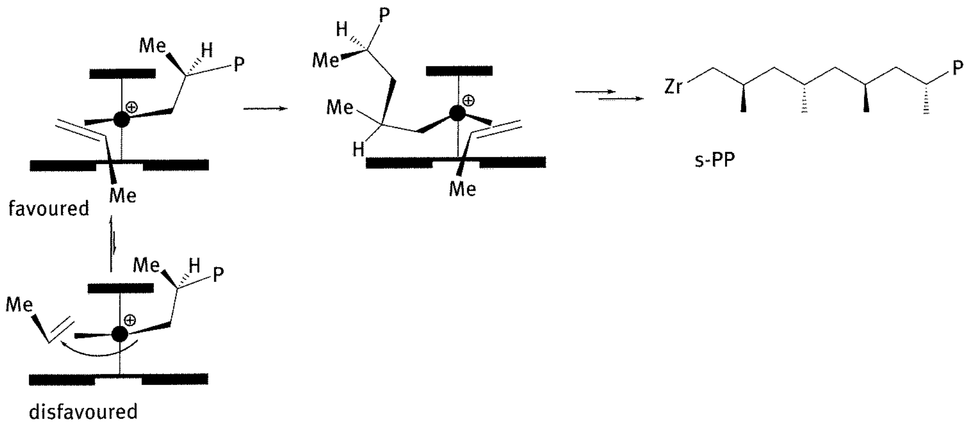
The synthesis of *ansa*-metallocenes of the type $Z(1\text{-Ind})_2MCl_2$ can lead to two types of products: the C_2-symmetric complex shown in the following diagram, which exists as a racemic mixture of two enantiomers as indicated by the prefix *rac*, and its *meso* isomer. The latter has much lower activity and is not stereoselective.



In the C_2- symmetric *ansa*-metallocene, the methyl substituents of propene, for example, will be directed into one less hindered quadrant, while the growing polymer chain occupies the other. Since the chain growth involves migration of the polymeryl chain to the coordinated ligand, that site becomes vacant and ready to bind the next monomer, again with the Me group pointing into the less hindered quadrant. Isotactic polypropylene is generated. The polymerizations are conducted in hydrocarbon solvents where these compounds exist as tight ion pairs; the counter-anion must therefore be in the immediate vicinity but does not influence the stereocontrol process.

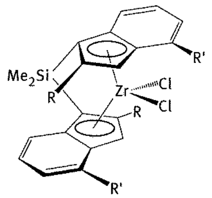


An analogous sequence can be formulated for the C_s- symmetric Cp-fluorenyl catalyst. Here the polymeryl chain always occupies the empty quadrants. The methyl substituent of propene fits neatly into the groove of the fluorenyl ligand moiety, so that stereocontrol is ensured.

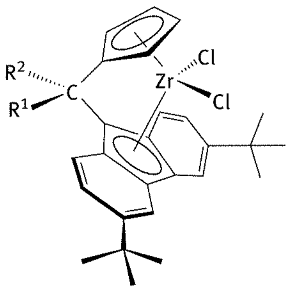


Ligand development allows control of stereoregularity, of 2,1-misinsertion and of chain termination; e.g. an alkyl substituent in 2-position on the C_5 ring of an indenyl ligand greatly increases the molecular weight, and bulky substituents in 4-position increase chain length and tacticity (Table 3.7.2.3). These modifications turn an interesting laboratory observation into a commercially viable product.

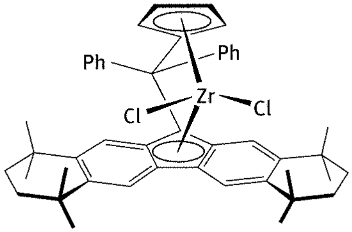
Table 3.7.2.3 Structure–property relationships in iso-specific propene polymerization catalysts

Complex	2-R	4-R′	$\overline{M}_w$	PPmp	*mmmm*%
	H	H	36,000	138 °C	81.7%
	Me	Ph	729,000	157 °C	95.2%
	Me	1-naphthyl	875,000	161 °C	99.1%
	Et	Ph	930,000	162 °C	>99%

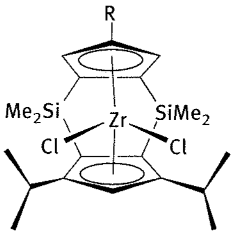
Similar developments have led to highly syndiospecific catalysts. Syndiotactic polypropylene (**s-PP**) is desirable because of its excellent optical transparency (due to small, uniform crystallites), its resistance to γ-radiation and very high impact resistance.



Increased stereoselectivity at higher temperatures

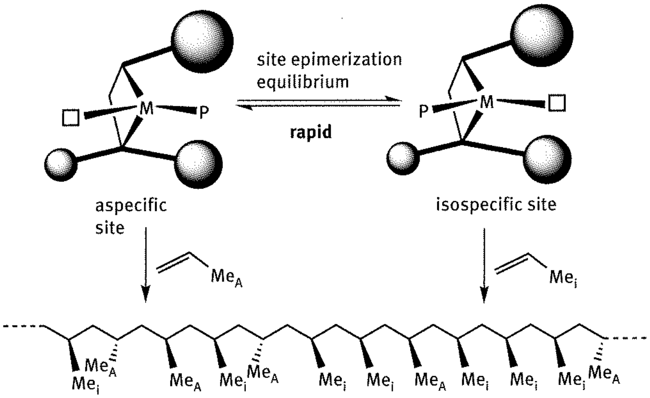


gives the most stereoregular s-PP reported (rrrr > 99%)

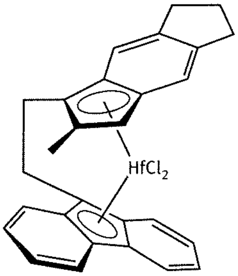


Stereoselectivity: $R = H < Pr^i > SiMe_3$

Yet other ligand structures provide for two very different coordination sites to be involved in propagation, such as one stereoselective and one non-stereoselective site. This is realized by C_1-symmetric catalysts. Swinging of the polymeryl chain from one to the other without monomer incorporation allows for the construction of atactic and tactic blocks, provided this chain swinging is fast compared to the rate of monomer insertion. Although such catalysts seem to give a polymer full of stereo-defects, these polymers can in fact be the most interesting, since they give rubber-like elasticity that is atypical of polypropylene. The Hf complex shown here is an example of a C_1-symmetric metallocene that gives high molecular weight elastomeric PP:



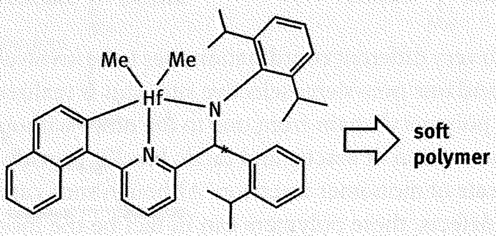
PP with block structure



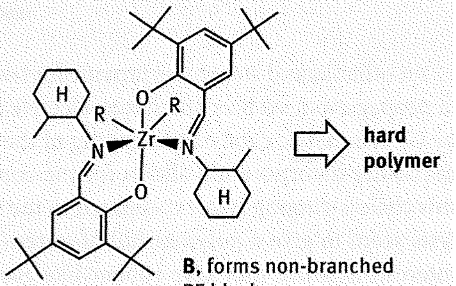
Box 3.7.2.3 Chain-shuttling polymerization

Usually, transfer of a growing polymeryl chain from the catalytic site to a Main Group metal is slow and undesirable. However, this process can also been utilized to construct polymer architectures that cannot be made otherwise, by shuttling the polymer chain between two different catalysts with very different polymerization characteristics.

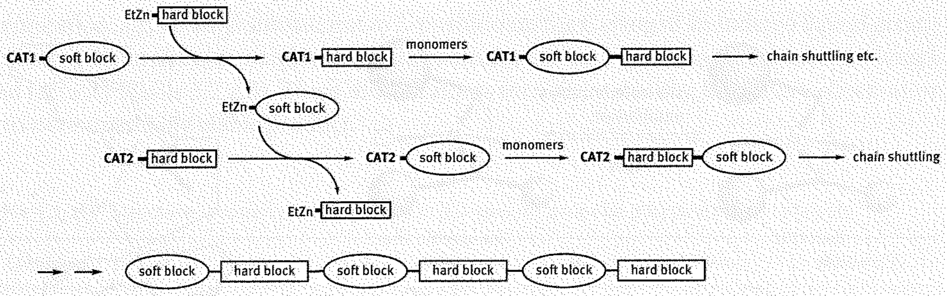
The Hf pyridine complex A gives soft ethylene/1-octene copolymers, whereas the Zr iminophenolate B gives hard, highly crystalline linear polyethylene without octene incorporation. Adding $ZnEt_2$ as chain shuttling agent allows the polymer chains to be exchanged between the two catalysts at a sufficiently slow rate to obtain a polymer with hard-soft-hard block structure. This material has properties that cannot be obtained by the mechanical mixing of hard and soft polymers. In the polymer, the hard and soft domains phase-segregate. If these domains are large enough to be commensurate with the wavelength of light, they refract light like the wing scales of some butterflies and give red or green polyethylene ('photonic polyethylene').



A, good octene incorporation



B, forms non-branched PE blocks

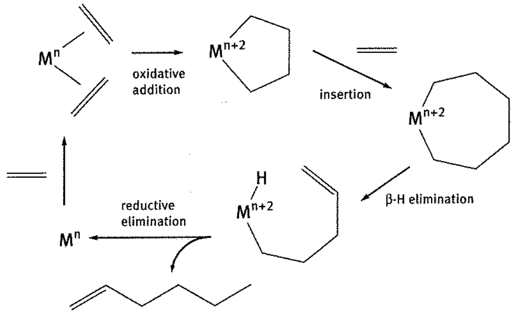


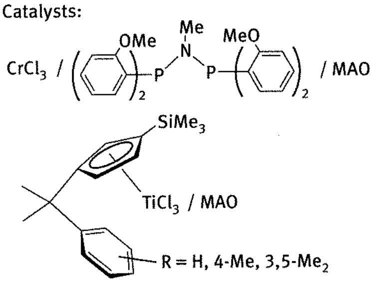
3.7.3 Alkene Oligomerizations

The oligomerization of ethylene is a cheap route to α-olefins. These are valuable as co-monomers (1-hexene, 1-octene) for the production of linear low-density polyethylene (**LLDPE**) for stretchable films and packaging applications, for the production of plasticizers (C_6–C_{10}) or as precursors for surfactant alcohols (C_{12}–C_{20} range).

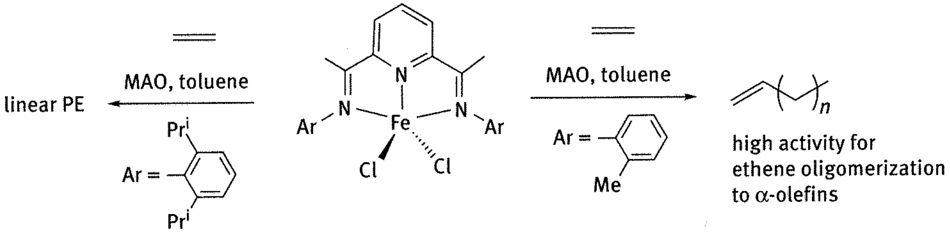
Catalysts can oligomerize ethylene by two mechanisms: (i) the selective trimerization (or even tetramerization) via metallacycles, or (ii) oligomerization to give a statistical Schulz–Flory distribution of 1-alkenes via an insertion mechanism. The reactions are highly dependent on the choice of ligand.

Mono-Cp titanium complexes with pendant benzyl substituents trimerize ethylene to 1-hexene with good selectivity. Similarly, Cr complexes of P–N–P chelate ligands $RN(PAr_2)_2$ show high activity and selectivity, whereas C-bridged diphosphines $CH_2(PAr_2)_2$ have poor activity and are unselective. For both the Ti and Cr complexes the evidence supports a metallacycle mechanism, presumably involving M^{II}/M^{IV} species.

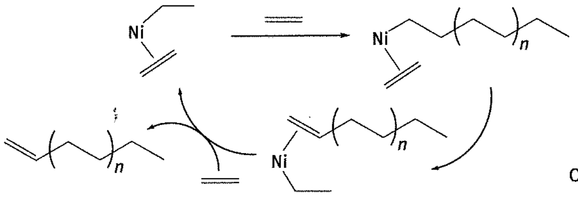


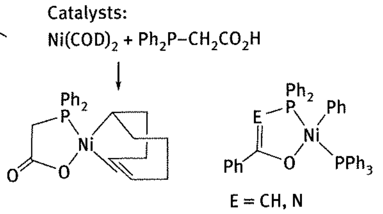


Iron complexes catalyse the polymerization or oligomerization of ethylene, depending on steric factors: bulky N-aryl substituents like 2,6-$Pr^i_2C_6H_3$ give high molecular weight PE, whereas smaller aryls with only one *ortho*-substituent, such as 2-MeC_6H_4, allow faster chain termination and give ethylene oligomers. The process follows an insertion (Cossée–Arlman) mechanism.



The longest-established commercial ethylene oligomerization reaction is the **Shell Higher Olefin Process** (SHOP), catalysed by nickel complexes with chelating phosphines. A range of oligomers is produced by an insertion/β-H elimination sequence. The heavier fraction (>C_{18}) is isomerized to internal alkenes, followed by olefin metathesis with short-length alkenes over heterogeneous MoO_3/Al_2O_3 catalysts to produce more medium-length α-olefins.





Key points

The polymerization of 1-alkenes is catalysed by Lewis acidic metal centres with no or very limited capacity for back-bonding. Catalysts based on $TiCl_3$ activated with aluminium alkyls (Ziegler catalysts) are used commercially for the production of high-density polyethylene (HDPE) and isotactic polypropylene (i-PP). Phillips catalysts (Cr on silica) are also used industrially for linear polyethylene.

Group 4 metallocene, half-sandwich, and N–O chelate complexes are highly active soluble catalysts.

The activation process consists of the formation of a metal–alkyl bond and a vacant coordination site. The polymerization follows an insertion (Cossée–Arlman) mechanism.

The copolymerization of ethylene with higher 1-alkenes gives linear low-density polyethylene (LLDPE).

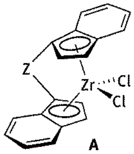
Cr, Fe, Co, and Ni complexes are also active. Nickel catalysts give branched polymers through a 'chain walking' process.

Ligand design controls activity, stereoselectivity, molecular weight, and co-monomer incorporation.

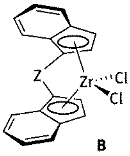
Steric protection of the active site is important to achieve high molecular weights. Sterically less hindered Ti and Ni complexes lead to ethylene oligomerization (SHOP process).

Exercises

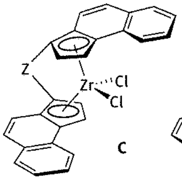
1. Show the likely mechanistic steps in the activation of *rac*-$Me_2Si(Ind)_2ZrCl_2$ with $AlBu^i_3$ / $CPh_3[B(C_6F_5)_4]$.
2. Show the structure of *meso*-$Me_2Si(Ind)_2ZrCl_2$ and explain why propene polymerization with this complex is not stereoselective.
3. Which of the following *ansa*-metallocenes **A–D** is likely to show (a) the highest stereoselectivity in propene polymerizations and (b) the highest polymer molecular weight? State your reasons.



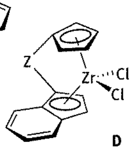
A



B

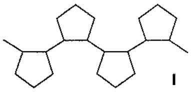


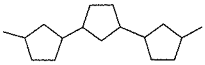
C



D

4. Show the Fischer projections for the following polypropylene pentad structures: *mmmm*, *mrrm*, *rrrr*, *mrmm*. What mechanistic information can be obtained from the observation of *mrrm* and *mrmm* pentads, and why are these not observed in the same polymer?
5. The polymerization of cyclopentene with a zirconocene catalyst was originally thought to produce a polymer of type **I**. However, it was subsequently discovered that in fact the polymer has 1,3-connectivity (**II**). Give the mechanism of the formation of this polymer.

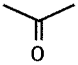

I

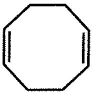
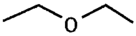
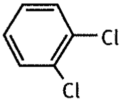
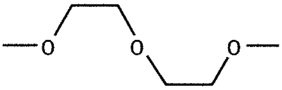
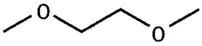
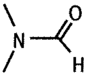

II

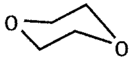
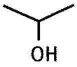
6. With some metallocene catalysts some H_2 is added to control the molecular weight of polyethylene. What type of polymer would result if $PhSiH_3$ was added instead of H_2?

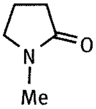
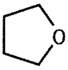
APPENDIX 1

Commonly Used Solvents and Their Properties

Name	Formula	Dielectric constant, ε	Properties, uses
Acetone	$Me_2C{=}O$ 	20.7	Highly polar solvent, good solvent for both lipophilic and ionic compounds, miscible with water in any ratio. Attacked by bases and acids, reacts rapidly with many M–C bonds. Dried with anhydrous K_2CO_3; bp 56 °C, mp −95 °C.
Acetonitrile	$CH_3C{\equiv}N$	37.5	Highly polar, non-protic solvent, misc. water, attacked by bases. Coordinates to Lewis acidic metal centres, often forms isolable complexes. Capable of inserting into M–C bonds. Good solvent for ionic and polar compounds; bp 82 °C, mp −45 °C.
Acetic acid	CH_3COOH	6.20	Acid, pK_a 4.76; bp 118 °C, mp +16 °C.
Benzene	C_6H_6	2.28	Non-polar, higher dissolving power than alkanes, high mp, so not for low-temp. reactions. Long-term exposure to vapours is accumulative and may cause leukaemia; bp 80 °C, mp +5.5 °C.
Chlorobenzene	C_6H_5Cl	5.69	More polar aromatic solvent, higher boiling; bp 131.7 °C, mp −45.2 °C.
Chloroform	$CHCl_3$	4.81	Moderately polar non-protic solvent, excellent for dissolving non-polar and polar substances, may produce Cl radicals under some conditions, cancer suspect solvent; component of some cough mixtures, vapour may cause drowsiness; bp 61.2 °C, mp −63.5 °C.

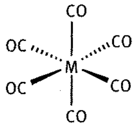
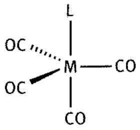
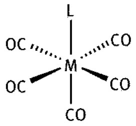
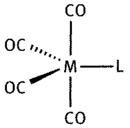
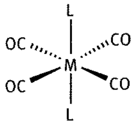
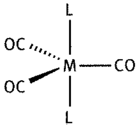
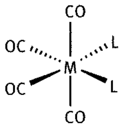
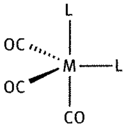
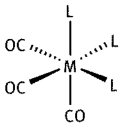
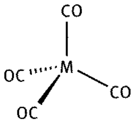
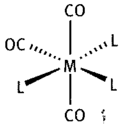
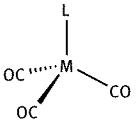
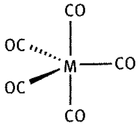
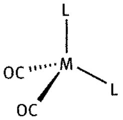
Name	Formula	Dielectric constant, ε	Properties, uses
Cyclohexane	C_6H_{12}	2.02	Non-polar solvent, high mp; bp 80.7 °C, mp +6.5 °C.
Cyclopentane	C_5H_{10}	1.97	Non-polar low boiling solvent, bp 49 °C, mp −94 °C.
1,5-Cyclooctadiene, COD			Commonly used as ligand or reagent; bp 150 °C, mp −69 °C.
Diethyl ether	Et_2O 	4.27	Moderately polar non-protic solvent, coordinates to Lewis acidic metal ions, good solvent for polar organometallic reagents, can take up water and needs drying with Na metal under N_2, highly flammable; bp 34.6 °C, mp −116.3 °C.
1,2-Dichlorobenzene (*o*-dichlorobenzene)	$C_6H_4Cl_2$ 	10.12	High boiling, polar aromatic solvent, used for liquid chromatography, dissolves polyethylene at high temperatures; bp 180 °C, mp −16.7 °C.
Dichloromethane (methylene chloride)	CH_2Cl_2	8.93	Polar non-protic solvent, excellent for dissolving non-polar and some ionic compounds, also used as paint stripper and dry cleaning fluid; bp 40 °C, mp −95.1 °C.
Diglyme		7.23	High boiling potentially chelating ether, good for coordination to alkali ions; bp 162 °C, mp −64 °C.
Dimethoxyethane	$MeOC_2H_4OMe$ 	7.30	High boiling alternative to Et_2O, less prone to polymerization than THF, can form chelate complexes; bp 85 °C, mp −58 °C.
Dimethylformamide, DMF	Me_2NCHO 	36.7	Polar solvent, dissolves ionic compounds, misc. with water, may act as formylating reagent; bp 153 °C, mp −61 °C.

Name	Formula	Dielectric constant, ε	Properties, uses
Dimethyl sulfoxide, DMSO	Me_2SO 	4.7	Moderately polar aprotic solvent, miscible with water, dissolves polar and non-polar compounds, penetrates skin; bp 189 °C, mp +19 °C.
1,4-Dioxane		2.21	High boiling ether, forms insoluble coordination polymers with Mg halides, miscible with water; bp 101.1 °C, mp +11.8 °C
Ethanol	CH_3CH_2OH	24.30	Polar protic solvent, less polar than methanol or water, dissolves ionic compounds; bp 78.2 °C, mp −114.1 °C.
Ethyl acetate	CH_3CO_2Et	6.08	Polar non-protic solvent; bp 77.1 °C, mp −83.8 °C.
Fluorobenzene	C_6H_5F	5.47	Polar, non-coordinating aromatic solvent; bp 84.7 °C, mp −42.2 °C.
n-Heptane	C_7H_{16}	1.92	Non-polar saturated hydrocarbon, used when higher boiling than hexane is needed; bp 98.5 °C, mp −91 °C.
n-Hexane	C_6H_{14}	1.89	Non-polar saturated hydrocarbon, dissolves substances with no or very low dipole moment, good for separation from salt by-products; bp 68.7 °C, mp −94 °C.
Light petroleum	C_nH_{2n+2}, $n \approx 6$	ca. 1.9	Saturated hydrocarbons, mainly mixture of C6 isomers; bp range 40–60 °C, non-polar, non-protic, dissolves compounds with no or only small dipole moments, does not dissolve salt by-products.
Isopropanol	Me_2CHOH 	18.3	Polar protic solvent, less polar than MeOH, misc. water, used for base baths for cleaning flasks and low temperature mixtures; bp 82.5 °C, mp −89 °C
Methanol	CH_3OH	32.63	Polar protic solvent, misc. water, dissolves ionic compounds, reacts with M–C bonds; bp 65 °C, mp −98 °C.

Name	Formula	Dielectric constant, ε	Properties, uses
Methylcyclohexane		2.02	Non-polar solvent with very wide liquid range, suitable for low temperature reactions; bp 101 °C, mp −126.3 °C.
N-Methylpyrrolidone, NMP		32.0	Polar aprotic solvent, miscible with water, dissolves polar and non-polar compounds; bp 202 °C, mp −24 °C.
n-Pentane	C_5H_{12}	1.84	Non-polar, low boiling solvent, suitable for low temperature reactions; bp 36 °C, mp −130 °C.
Pyridine	C_5H_5N	13.26	Strongly coordinating aromatic solvent, basic, hygroscopic, miscible with water, forms stable complexes with metal ions; bp 115 °C, mp −41.7 °C
Tetrahydrofuran (THF)	C_4H_8O, 	7.52	Polar non-protic solvent, coordinates very well to Lewis acidic metal centres and often forms isolable complexes, excellent solvent for ionic compounds, miscible with water in any ratio. Dry with Na metal or Na/benzophenone under N2; bp 66 °C, mp −108.4 °C.
Toluene	$C_6H_5CH_3$	2.38	Aromatic non-polar solvent, with higher dissolving power for non-polar substances than alkanes; bp 110.6 °C, mp −94.9 °C.

APPENDIX 2

Number and Symmetry of Infrared-Active Vibrations of Metal Carbonyl Complexes

Complex	Symmetry	Number of IR bands (mode)	Complex	Symmetry	Number of IR bands (mode)
	O_h	1 (T_{1u})		C_{3v}	3 ($2A_1 + E$)
	C_{4v}	3 ($2A_1 + E$)		C_{2v}	4 ($2A_1 + B_1 + B_2$)
	D_{4h}	1 (E_u)		D_{3h}	1 (E')
	C_{2v}	4 ($2A_1 + B_1 + B_2$)		C_s	3 ($2A' + A''$)
	*fac*- $L_3M(CO)_3$ C_{3v}	2 ($A_1 + E$)		T_d	1 (T_2)
	*mer*- $L_3M(CO)_3$ C_{2v}	3 ($2A_1 + B_2$)		C_{3v}	2 ($A_1 + E$)
	D_{3h}	2 ($A_2'' + E$)		C_{2v}	2 ($A_1 + B_1$)

APPENDIX 3

Answers to Exercises

Chapter 1.1

1. Order according to increasing polarity of the M–C bonds: $ZnMe_2$, LiMe, $MgMe_2$, BMe_3, $SiMe_4$.

   Use EN scale p. 6: $BMe_3 < SiMe_4 < ZnMe_2 < MgMe_2 <$ LiMe.

2. Draw the structures of the compounds shown in question 1 and determine the electron counts of the metal centres. Which of them achieve an electron octet?

   BMe_3 trigonal-planar, 6 electrons in valence shell; $SiMe_4$ tetrahedral, 8 el.; $ZnMe_2$ linear, sp hybrid, $d^{10}(sp)^4$; $MgMe_2$ 2e3c bonded polymer, 4 el.; LiMe cube with triply-bridging Me, 2e4c bonding, 2 el. per Li. Only $SiMe_4$ has an electron octet.

3. Why are $C_5H_5^-$ (Cp^-) and benzene said to be isoelectronic?

   Both contain 6 π-electrons (Hückel 4n+2 rule).

Chapter 1.2

1. Show how lithium reagents can be made from lithium metal. Which solvent should be used? Give the chemical equations.

   $R–X + 2\ Li \rightarrow LiR + LiX$. Li reagents are usually generated in hydrocarbons, except LiMe which is not soluble.

2. Does BuLi react with iodobenzene, and if so, how? Give the chemical equation and show the mechanism in detail.

   BuLi undergoes alkyl–aryl exchange via an intermediate with 2e3c-type bridging aryl and alkyl ligands.

   $Ph–I + BuLi \rightarrow LiPh + BuI$. Ligand exchange is possible because of vacant orbitals on Li^+.

3. Butyllithium is a hexamer $[RLi]_6$ in hexane but a dimer when tetramethylethylene diamine ($Me_2N–C_2H_4–NMe_2$, TMEDA) is added. What is the structure of the product? Does the lithium ion achieve an octet electron configuration?

   TMEDA is capable of delivering two electron pairs to each Li^+. Therefore the electron-deficient cluster structure of $(BuLi)_6$ is broken down to give a butyl-bridged dimer with 1 TMEDA per Li. The last Bu^- anion is not displaced because of strong electrostatic attraction to Li^+ cation. Each Li is tetrahedrally coordinated, 6 el.

4. Show how sodium hydride reacts with cyclopentadiene. Show structures and equations. Does the product contain ionic or covalent metal-carbon bonds? Which solvent should be used, and why? Give your reasons.

   $NaH + C_5H_6 \rightarrow Na^+C_5H_5^- + H_2$. Ionic product, stabilized by non-protic solvents that coordinate well to Na^+, such as THF.

Chapter 1.3

1. Show how $PhCH_2Cl$ reacts to give a Grignard reagent. Which solvent should be used, and why?

   R–Cl reacts with a magnesium atom on the surface of an Mg crystal. The process goes via a polar transition state and is stabilized by polar ether solvents, as is the product. Benzyl chloride contains an activated C–Cl bond in benzylic position which is particularly susceptible to nucleophilic attack, here by Mg:

   $PhCH_2Cl + Mg + 2\ Et_2O \rightarrow PhCH_2MgCl(OEt_2)_2$

2. What are the oxidation states of Mg before and after formation of the Grignard reagent? What type of reaction is this?

   0 and +II, so this is an oxidative addition.

3. Draw the mechanistic steps involved in the Schlenk equilibrium.

   See p. 21–22.

4. How can the Schlenk equilibrium be used for the preparation of magnesium dialkyls?

   Adding 1,4-dioxane gives insoluble $MgX_2(dioxane)_n$ which precipitates and thereby removes itself from the reaction equilibrium. The halide-free magnesium dialkyl stays in solution and can be separated.

5. What type of bonding is present in $[MgPh_2]_n$?

   2e3c like Li and Al aryls. Infinite chain, each $MgPh_2$ link perpendicular to its neighbour.

6. Which structure would you expect for CpMgBr and why?

   In Et_2O, a dimer with η^5-bound Cp and bridging Br. With more strongly coordinating solvents the bridge may be cleaved.

Chapter 1.4

1. Show synthetic routes to $ZnMe_2$ and $[ZnMe_4]^-$ and give balanced chemical equations.

   $3\ Zn(OAc)_2 + Al_2Me_6 \rightarrow 3\ ZnMe_2 + 2\ Al(OAc)_3$

   $ZnMe_2 + 2\ LiMe \rightarrow Li_2[ZnMe_4]$ (linear to tetrahedral).

2. Why is $ZnEt_2$ a monomer but EtZnCl a polymer?

   Each alkyl ligand has a strong positive inductive (+I) effect and makes the metal centre more electron rich. This pushes up the energy levels of acceptor orbitals and reduces Lewis acidity in Et_2Zn. The metal centre in EtZnCl on the other hand is a much stronger Lewis acid, and each Zn will bind to three Cl^- anions to give a tetrahedral coordination geometry.

3. Draw the mechanism and intermediates for the mercuration of benzene with mercury(II) acetate.

   See p. 34 for details.

4. What is the structure of $Zn(C_5Me_5)_2$, and why does the ^1H NMR spectrum at room temperature show only one signal?

   In the solid, one Cp* is pentahapto, one monohapto. Both ligands undergo rapid 1,2-metallotropic shifts, which generates a time-averaged signal for 10 equivalent Me substituents.

5. What is a 'Reformatsky reagent'?

   Bromomethylcarboxylic esters oxidatively add to zinc metal to give zinc alkyls carrying a functional group, to give a product known as the Reformatsky reagent. It adds to organic carbonyl compounds in the fashion of a Grignard reagent.

6. How can mercury compounds be useful for the preparation of di-Grignard reagents?

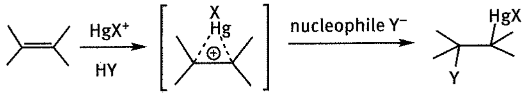
   Electron-rich arenes can be attacked twice by electrophilic mercury compounds such as $Hg(O_2CCF_3)_2$, to give dimercurated products. Transmetallation of these with $MgBr_2$ is a selective route to aromatic di-Grignard reagents (cf. Section 1.4.3).

$$H{-}R{-}H + HgX_2 \longrightarrow XHg{-}R{-}HgX + 2\ HX$$

$$XHg{-}R{-}HgX + MgBr_2 \longrightarrow BrMg{-}R{-}MgBr + 2\ HgXBr$$

7. What is 'solvomercuration'? Give the reaction scheme and intermediates.

   Electron-rich alkenes can react with electrophilic mercury salts HgX_2 in a reactive solvent HY to add HgX and Y across the C=C double bond, via a cyclic cationic intermediate. This addition of both mercury and a nucleophile Y to a double bond has become known as solvomercuration.



Chapter 1.5

1. Discuss the structures of (a) Al_2Me_6 and (b) $Al_2Cl_2Me_4$, and show which orbitals interact to form the bridges. What is the electron configuration of Al in each case?

   See details in Chapter 1.1, p. 5. 2e3c bonding in Al_2Me_6, and octet configuration in $[Me_2AlCl]_2$, with each Cl contributing three electrons.

2. Show the mechanism and reaction product of the hydroboration of 1-hexene with 9-BBN.

   9-BBN is a monoborane $[R_2BH]_2$, see p. 40. Cleavage in ether into monomeric $R_2BH(OEt_2)$ is necessary for reactivity. It adds to the C=C bond of 1-hexene in anti-Markovnikov sense, to give R_2B-1-hexyl.

3. How does $AlMe_3$ react with $B(C_6F_5)_3$, showing the structures of the intermediates and the end product.

   Ligand exchange via 2e3c-intermediates. Since one component of the equilibrium, BMe_3, is very volatile and easy to remove, the equilibrium is shifted to the product $Al(C_6F_5)_3$.

4. Show all reaction steps of the reaction of $GaMe_3$ with AsH_3, comment on the intermediates and the end product.

   Stepwise thermal protolysis, eliminates methane:

   $GaMe_3 + AsH_3 \rightarrow Me_2GaAsH_2 + CH_4$

   $Me_2GaAsH_2 \rightarrow MeGaAsH + CH_4$

   $MeGaAsH \rightarrow GaAs + CH_4$

   The intermediates Me_2GaAsH_2 and MeGaAsH oligomerize, which can give rise to side reactions in the gas phase. The reaction kinetics must be controlled for the reaction to happen on the target surface.

5. What is meant by the 'Aufbau' reaction and how does it work?

   Successive insertion of ethylene into Al–H and Al–C bonds, to give Al with long alkyl chains, $Al\{(C_2H_4)_nH\}_3$ where n = about 4–10. First step in the synthesis of surfactant alcohols. Initial reaction step is the formation of an ethylene adduct of AlH_3, followed by H-transfer ('ethylene insertion').

6. Why does $Ph(Cl)B{-}NMe_2$ show two methyl signals in the ^1H NMR spectrum at room temperature?

   The B–N bond shows strong double bond character due to π-donation of electron pair on N into vacant p-orbital on B, see p. 42.

Chapter 1.6

1. Show two routes for the synthesis of Me_3SiCl.

   Rochow process: Si + 3 MeCl, oxidative addition, gives product mixture that needs to be separated

   Also cleavage of Si_2Me_6 by halogens.

   The alkylation with Grignard reagents is not successful since it does not proceed cleanly and separation from ether is difficult.

2. The ^1H NMR spectrum of Me_3SiCp at −10 °C shows four signals in the ratio 1:2:2:9. On warming to 130 °C the spectrum is simplified and shows only two signals in the ratio 5:9. Explain this observation.

   At low temperature 1,2-metallotropic shift of $SiMe_3$ to all Cp carbons is slow on the NMR time scale but fast on heating.

3. Ph_3SnBr reacts with sodium metal in a 1:1 molar ratio to give **A**. Product **A** reacts with two further equivalents of Na to give **B**. Show the chemical equations and products.

   $2\ Ph_3SnBr + 2\ Na \rightarrow Ph_3Sn{-}SnPh_3$ (**A**) + 2 NaBr

   $Ph_3Sn{-}SnPh_3 + 2\ Na \rightarrow 2\ Na^+SnPh_3^-$ (**B**) pyramidal, Sn(II).

4. Al_2Me_6 reacts readily with water and oxygen but $SiMe_4$ and $SnMe_4$ do not. Explain this observation.

   Lack of low-lying vacant orbitals on Si and Sn, and low polarity of the Si–C and Sn–C bonds, even though the Sn–C bond is much weaker than the Al–C bond. The lack of a low energy reaction pathway means the Group 14 compounds are kinetically stabilized against oxidation and hydrolysis.

5. Show why and how stannylenes R_2Sn can act as both Lewis acid and Lewis base.

   R_2Sn has a lone pair but only an electron sextet. It also has a vacant orbital which can bind 2-el. donors.

6. What is a polysiloxane? What are its structure and properties, and what are its applications?

   Hydrolysis product of Me_2SiCl_2, $[-Me_2Si-O-]_x$ polymers, flexible, elastomers with low conformation barriers. Thermally very stable, low flashpoint, chemically inert. Depending on molecular weight and degree of cross-linking, used as silicone oils, rubbers, sealants, gaskets, medical implants.

7. An industrial method for the synthesis of $PbEt_4$ is the alkylation of $PbCl_2$ with $LiAlEt_4$. Only three of the four Et ligands of the aluminate are exchanged, and one of the products is $LiAlEtCl_3$. Give the balanced equation for this process.

   Since Pb(II) is the starting material, the Pb(IV) product must arise by disproportionation of Pb(II) into Pb(IV) and Pb(0). Since each $PbCl_2$ requires two ethyl ligands but each Al delivers three, $PbCl_2$ reacts with $LiAlEt_4$ in a 3:2 molar ratio. The rest is an exercise in balancing equations:

   $6\ PbCl_2 + 4\ LiAlEt_4 \rightarrow 3\ PbEt_4 + 3\ Pb + 4\ LiAlEtCl_3$.

Chapter 2.3

1. Give examples of (i) a metallocene complex, (ii) a half-sandwich complex; (iii) an arene complex.
   - (i) Metallocene complexes contain two η^5-bonded Cp ligands, Cp_2M or Cp_2ML_2, as in Cp_2Fe, Cp_2TiCl_2 or $Cp_2Ti(CO)_2$.
   - (ii) half-sandwich complexes contain one Cp or one η^6-arene ligand, as in $CpTiCl_3$, $CpMn(CO)_3$, or (benzene) $Cr(CO)_3$.
   - (iii) examples are $(\eta^6\text{-}C_6H_6)_2Cr$, $(\eta^6\text{-arene})Cr(CO)_3$, $[(\eta^6\text{-arene})FeCp]^+$.
2. Assign the number of electrons donated to metal centres by the following ligands: (i) hydride; (ii) bridging chloride; (iii) CO; (iv) a phosphine PR_3; (v) ethylene; (vi) 1,3-butadiene; (vii) cycloheptatriene; (viii) cyclopentadienyl.

   (i) 1, (ii) 3, (iii) 2, (iv) 2, (v) 2, (vi) 4, (vii) 7, (viii) 5.
3. What is the electron count of the metal centre in the following complexes: (i) Cp_2Co; (ii) $[Cp_2Co]^+$; (iii) Cp_2Ni; (iv) $CpMn(CO)_3$; (v) $Fe(CO)(1,3\text{-butadiene})_2$; (vi) $Co(NO)(CO)_3$; (vii) $CpNi(\eta^3\text{-allyl})$; (viii) $Ni(C_2H_4)_2(PPh_3)$.

   (i) 19, (ii) 18, (iii) 20, (iv) 18, (v) 18, (vi) 18, (vii) 18, (viii) 16.
4. What are the formal metal oxidation states in the complexes in question 3?

   (i) II, (ii) III, (iii) II, (iv) I, (v) 0, (vi) 0, (vii) II, (viii) 0.

Chapter 2.4

1. Order in sequence of increasing π-acceptor strength: NO^+, $P(OMe)_3$, $N{\equiv}CR$, PBu^t_3, PCl_3, PPh_3, CO, NH_3.

   $NH_3 < N{\equiv}CR < PBu^t_3 < PPh_3, < P(OMe)_3 < PCl_3 < CO < NO^+$.
2. Why are Tolman cone angles calculated using $Ni-PR_3$ complexes and not just for the free phosphines PR_3?

   The C–P–C angles vary little between different phosphines and do not take into account how bulky substituents, such as those in *ortho* position, shield the metal centre.
3. Why can both alkynes and imido ligands be said to act as 4-electron donors? Describe the structural indicators that justify this description.

   Alkynes form many complexes where a 16 or 18 electron count can only be achieved assuming a 4-electron contribution from the alkyne. This leads to a reduction of the R–C–C angle to values as low as 140° and an elongation of the C–C bond, as well as characteristic shifts in the ^{13}C NMR signals.

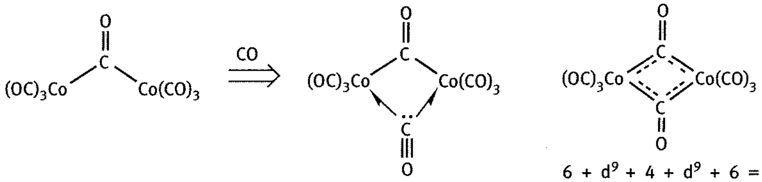
   Imido ligands NR have 4 electrons on N available, including a lone pair which can act as π-donor towards a metal-based acceptor orbital. The result is a shortening of the M–N distance and a linear M–N–R arrangement. For the same reason, metal alkoxides and aryloxides of electron-deficient metal centres are typically close to linear.
4. Explain why the stretching frequency of CO coordinated to strongly electrophilic metal cations is often higher than that of free CO.

   The C-centred lone pair in CO is weakly C–O antibonding. Binding to an electrophile (in the simplest case to H^+) removes this antibonding interaction. Metal cations without other donor ligands are very strong electrophiles and form complexes where the CO ligands act purely as σ-donors. Any occupied d-orbitals are energetically too low to be available for effective back-bonding.

Sections 2.5.1–2.5.2

1. Account for the absence of a Co–Co bond in solid $Co_2(CO)_8 = [(OC)_3Co(\mu\text{-}CO)]_2$. Does this compound obey the 30/34 VE rule?

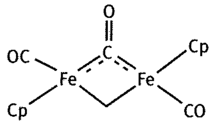
   One can envisage $Co_2(CO)_8$ to consist of two $(OC)_3Co$ moieties that form ketone-like σ-bonds to a bridging CO, giving an electron count of 16 per Co. The lone pair of the second bridging CO can then form an 2-el-3-centre bond. Alternatively, each $Co(CO)_3$ fragment can be considered as a 34 VE binuclear cluster where the two CO ligands form a delocalized 4-electron bridging unit.



$6 + d^9 + 4 + d^9 + 6 = 34$

2. Describe the bonding in $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$.

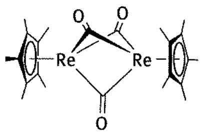
   Here, too, CO acts as a delocalized bridge:



$7 + d^8 + 2{+}2 + d^8 + 7 = 34$

3. Discuss the electron count and bonding in $(Cp^*Re)_2(\mu\text{-}CO)_3$.

   The structure is shown in Section 2.5.3.2. The complex belongs to the 30 VE triple-decker class with delocalized $Re_2(\mu\text{-}CO)_3$ core.



$5 + d^7 + 6 + d^7 + 5 = 30$

4. How many electrons are contributed to cluster bonding by the following fragments: $Fe(CO)_3$, $Mn(CO)_3$, μ-CO, $\mu\text{-}C_4H_4BR$, $\mu\text{-}C_6H_6$, μ-CR, $\mu\text{-}CH_2$.

   $Fe(CO)_3$: $8 + 6 - 12 = 2$; $Mn(CO)_3$: 1; μ-CO: 2; $\mu\text{-}C_4H_4BR$: 4; $\mu\text{-}C_6H_6$: 6; μ-CR: 3; $\mu\text{-}CH_2$: 2.

Sections 2.5.3–2.5.8

1. Metal carbonyl alkyls $R\text{–}M(CO)_x$ insert CO to give the corresponding acyl complexes. By contrast, treating metal carbonyl hydrides $HM(CO)_x$ with CO fails to give the formyl complex, $(CO)_xM\text{–}CHO$. Rationalize this observation.

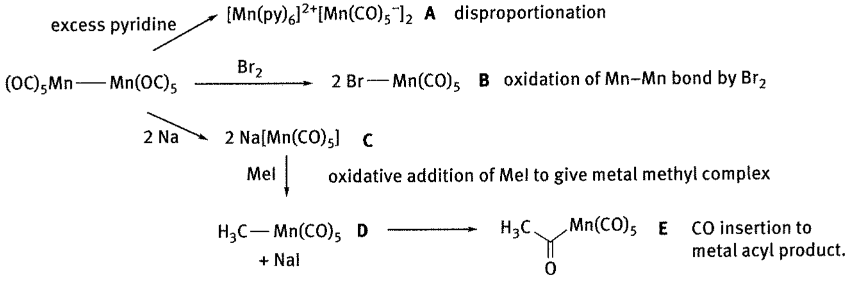
   M–H bonds are stronger than M–C bonds. The formation of M–CHO is endothermic, while CO insertion into metal-alkyl bonds is exothermic: the M–C bond to an electron-withdrawing acyl ligand is stronger than the M–C bond in an electron donating metal alkyl. However, metal formyl complexes can be made by intermolecular hydride attack on a coordinated CO ligand.

2. Irradiating $ClRe(CO)_5$ under an atmosphere of ^{13}CO gives a ^{13}C-containing product. Show the stereochemistry of this reaction.

   CO dissociation takes place *cis* to the Cl ligand, so that ^{13}CO is incorporated in *cis* and not *trans* position.

3. Identify the products and write the chemical equations for the following reactions of $Mn_2(CO)_{10}$:
   - (i) treatment with an excess of pyridine to give product **A**;
   - (ii) reaction with 1 Br_2 to give **B**;
   - (iii) reaction with sodium amalgam to give **C**.
   - (iv) Treatment of product **C** with MeI gives **D** and an inorganic salt. Exposure of **D** to CO gives product **E** which shows C–O stretching modes in the IR spectrum at 2115, 2011, 2003 and 1664 cm^{-1}. Identify products **A–E** and draw the reaction pathways.

   These reactions exemplify (a) disproportionation of Mn(0) into Mn(II) and Mn(–I), driven by effective complexation of Mn^{2+} by pyridine, the cleavage of a metal-metal bond with electrophiles (Br_2) as well as electrons (supplied by Na), followed by oxidative addition to a metal centre with formal oxidation state –I.



4. $PtCl_2(CO)_2$, a carbonyl of a third row M^{II} metal, shows $\nu_{CO} = 2175\ cm^{-1}$. $Cp_2W(CO)_2$, another third row M^{II} carbonyl, shows $\nu_{CO} = 1872$ and $1955\ cm^{-1}$. What do these differences indicate in terms of M–CO bonding?

   The Pt(II) halides are electron-poor, i.e. do not have diffuse high-lying d-orbitals for back-bonding. The Pt(II) CO complex falls into the category of non-classical CO bonding.

   $Cp_2W(CO)_2$ is only apparently a 20 VE compound—it is in fact fluxional with one η^5- and one η^3-bonded Cp. Since W is an early transition metal with high-lying d-orbitals and the complex is electron rich, back-bonding to CO is extensive, lowering the C–O stretching frequency.

5. Why is the rate of CO substitution of $Co_2(CO)_8$ much faster than that of $Ni(CO)_4$, even though the latter has fewer ligands?

   $Co_2(CO)_8$ can dissociate into the 17 VE radical $Co(CO)_4$. Substitution reactions in odd-electron complexes are much faster than in even-electron complexes. $NiCO)_4$, although only 4-coordinate, is an 18 VE species; ligand substitution must involve CO dissociation and therefore has a higher barrier.

6. What is the water-gas shift reaction and how is it catalysed?

   The WGS reaction generates H_2 from CO and water: $CO + H_2O \rightarrow CO_2 + H_2$. It is an equilibrium but the forward reaction is thermodynamically favourable. It is catalysed by many metals, most prominently Fe and Ru, by nucleophilic attack by OH^- on coordinated CO to give surface-bound M-COOH species. These decompose to M–H and CO_2. The M–H species reacts with H^+ to generate H_2.

Chapter 2.6

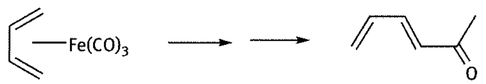
1. Explain why the addition of catalytic amounts of $SnCl_2$ facilitates the synthesis of Zeise's salt $K[PtCl_3(C_2H_4)]$ from $K_2[PtCl_4]$ and ethylene.

   This is an application of the *trans* effect. $SnCl_2$ inserts into the Pt-Cl bond forming Pt-$SnCl_3$ which labilizes the Pt-Cl bond in *trans* position to facilitate its substitution by C_2H_4. The $SnCl_2$ insertion is reversible.

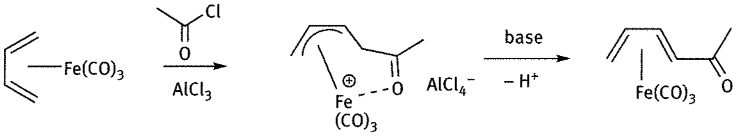
2. Order the following compounds according to increasing rotational barriers of the alkene or alkyne ligands: (i) $(Ph_3P)_2Ni(C_2H_4)$, (ii) $Fe(C_2H_4)(CO)_4$, (iii) $[PtCl_3(C_2H_4)]^-$, (iv) $Cp_2Zr(C_2H_4)(PMe_3$, (v) $Ni(1,5\text{-}COD)_2$, (vi) $(Ph_3P)_2Ni(C_2Ph_2)$. Provide reasons for this ordering.

   The barrier of rotation is a measure of back-bonding which increases from right to left of the Periodic Table with decreasing oxidation state, strength of donor ligands, π-acceptor capacity of alkene/alkyne ligands: $[PtCl_3(C_2H_4)]^- < Ni(1,5\text{-}COD)_2 < (Ph_3P)_2Ni(C_2H_4), < (Ph_3P)_2Ni(C_2Ph_2) < Fe(C_2H_4)(CO)_4, Cp_2Zr(C_2H_4)(PMe_3)$.

3. Show the reaction sequence and intermediates in the transformation



Acylation of (butadiene)Fe(CO)$_3$ with MeC(O)Cl / AlCl$_3$, followed by oxidative removal of the Fe(CO)$_3$ fragment.

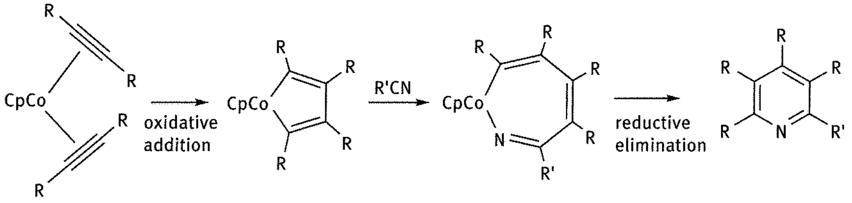


4. Discuss the bonding in Pt(C$_2$Ph$_2$)$_2$. Which electron count best describes the complex, and why is it not planar?

   Pt(0), d^{10}, can assume a trigonal-planar 16 VE geometry with three 2-el. donor ligands, or a tetrahedral 18 VE structure. Alkynes are able to act as 4-el. donors, so that a tetrahedral structure is favoured, which minimizes steric repulsion.

5. Draw the reaction steps and intermediates in the Co(I) catalysed formation of pyridines from internal alkynes and nitriles.

   The reaction is catalysed by CpCo(C$_2$H$_4$)$_2$ and proceeds by C–C coupling of alkynes and nitrile via metallacycles:



Chapter 2.7

1. What is the product of the reaction of [(η^2-C$_3$H$_6$)PdCl$_2$]$_2$ with a base?

   Base deprotonates the propene ligand to eliminate HCl and form [(η^3-allyl)Pd(μ-Cl)]$_2$.

2. Nickel(0) complexes catalyse the dimerization of 1,3-butadiene to 4-vinylcyclohexene (VCH), which can be oxidized to produce styrene. Draw all intermediates of VCH formation and describe each reaction step.

   The reaction sequence is shown in Box 2.7.1. VCH formation is favoured by the presence of L = phosphite. The dimerization of butadiene coordinated to Ni(0) amounts to an oxidative addition to give an η^1,η^3-bis(allyl) complex. The reductive elimination step to VCH is facilitated by coordination of L.

3. Draw the reaction steps and intermediates in the following transformation, mediated by PdCl$_2$ in the presence of a nucleophile HNu:

PdCl$_2$ coordination to the C=C bond is followed by loss of HCl and formation of an (η^3-allyl)Pd intermediate. This is attacked by Nu$^-$ in 3-position to give the product, Pd(0) and Cl$^-$.

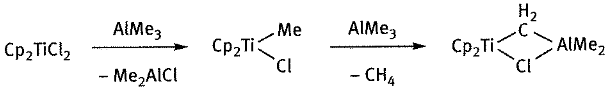
Section 2.8.1

1. Calculate the oxidation state, valence electron count and magnetism of Cp_2V, Cp^*_2TiH, $Cp_2Zr(CO)_2$, Cp_2NbCl_2, $[Cp_2WH_3]^+$, $(C_5H_4Me)_2Mn$, Cp_2Ru, $[Cp_2Ni]^+$, Cp_2Co. Which of these obey the 18-electron rule?

Cp_2V: V(II), 15 VE, high-spin d^3, paramagnetic;
Cp^*_2TiH: Ti(III), 15 VE, d^1, paramagnetic;
$Cp_2Zr(CO)_2$: Zr(II), 18 VE, d^2, diamagnetic;
Cp_2NbCl_2: Nb(IV), 17 VE, d^1, paramagnetic;
$[Cp_2WH_3]^+$: W(VI), 18 VE, d^0, diamagnetic
$(C_5H_4Me)_2Mn$: Mn(II), 17 VE, d^5, paramagnetic;
Cp_2Ru: Ru(II), 18 VE, diamagnetic;
Cp_2Co: Co(II), 19 VE, d^7, paramagnetic.
$[Cp_2Ni]^+$: Ni(III), 19 VE, d^7, paramagnetic;

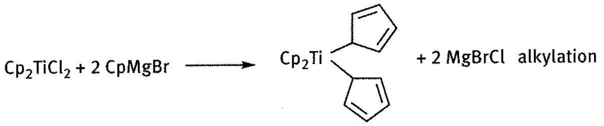
2. Describe the reaction of Cp_2TiCl_2 with $AlMe_3$ and explain the formation of the Tebbe reagent, $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2$. How does this reagent react with ketones $R_2C{=}O$?

The reaction proceeds first with mono-alkylation, followed by C–H activation.



3. Give chemical equations for the following reactions, show the structures of the products and explain these reasons for this reactivity:

(i) $Cp_2TiCl_2 + 2\ CpMgBr$; (ii) $Cp^*_2ZrH_2$ HCl; (iii) $Cp_2WH_2 + HBF_4(OEt_2)$; (iv) $(C_5H_4SiMe_3)_2ZrH_2 + CPh_3^+$; (v) $Cp_2HfCl_2 + 2\ LiEt$; (vi) $Cp_2ZrCl_2 + 2\ EtMgBr$ + 1-hexene; (vii) $[Cp_2ZrMe(THF)]^+$ + 1) H_2 and 2) 1-hexene.



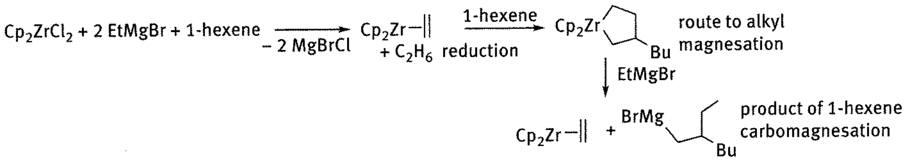
alkylation

$Cp^*_2ZrH_2 + HCl \longrightarrow Cp^*_2ZrHCl + H_2$ protonation of hydridic Zr-H releases H_2

$Cp_2WH_2 + HBF_4(OEt_2) \longrightarrow [Cp_2WH_3]^+BF_4^-$ W is d^2 and acts as base. Electron pair is protonated.

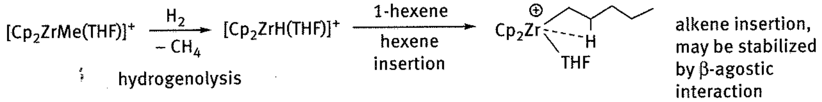
$(C_5H_4SiMe_3)_2ZrH_2 + CPh_3^+ \longrightarrow [\{(C_5H_4SiMe_3)_2Zr\}_2H_3]^+ + HCPh_3$ Example of H^- abstraction by CPh_3^+. The cationic hydride adds neutral Cp'_2ZrH_2 to give dinuclear hydride-bridged cation.

$Cp_2HfCl_2 + 2\ LiEt \longrightarrow Cp_2HfEt_2 + 2\ LiCl$ alkylation. Hf alkyls are relatively stable against β-H elimination and can be isolated.



route to alkyl magnesation

product of 1-hexene carbomagnesation



alkene insertion, may be stabilized by β-agostic interaction

4. Explain the fluxional processes observed in the product of reaction 3(i).

See Section 2.8.1.

5. What is an *ansa*-metallocene and what are the characteristics and applications of this type of compound?

   Ansa-metallocenes are metallocene compounds where the two Cp ligands are connected by a linker. This prevents rotation and changes the tilt angle of the Cp ligands, which in turn influences the frontier orbital energy levels. Ansa-metallocenes are widely applied as polymerization catalysts for 1-alkenes.

Section 2.8.2

1. Give synthetic routes and equations for the synthesis of mono-Cp complexes starting from (i) $TiCl_4$; (ii) $Mo(CO)_6$; (iii) $Fe(CO)_5$; (iv) $[RhCl(C_2H_4)_2]_2$.

   (i) $TiCl_4 + CpSiMe_3 \longrightarrow CpTiCl_3 + Me_3SiCl$ Silyl-Cp as Cp^- equivalent

   (ii) $Mo(CO)_6 + NaCp \longrightarrow Na^+[CpMo(CO)_3]^- + 3\,CO$ CO substitution by Cp^- anion

   (iii) $Fe(CO)_5 + CpH \longrightarrow [CpFe(CO)(\mu\text{-}CO)]_2 + H_2$ CO substitution by Cp; formation of CO-bridged dimer.
   For structure, see Section 2.5.2.

   (iv) $RhCl(C_2H_4)_2]_2 + NaCp \longrightarrow CpRh(C_2H_4)_2]_2 + NaCl$ halide metathesis

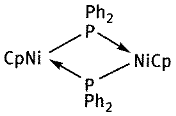
2. Devise synthetic routes to and discuss the structure and bonding of (i) $[CpNi(CO)]_2$; (ii) $CpNi(NO)$; (iii) $[CpNi(PPh_2)]_2$; (iv) $[CpNi(PPh_3)_2]BF_4$; (v) $[CpNi(PEt_3)]_2$.

   (i) $Ni(CO)_4 + Cp_2Ni \longrightarrow [CpNi(\mu\text{-}CO)]_2 + 2\,CO$ Comproportionation of Ni(II) + Ni(0) to 34 VE binuclear Ni(I) compound.

   For discussion of the structure, see Section 2.5.2.

   (ii) $Cp_2Ni + NO \longrightarrow CpNi(NO) + 0.5\,(Cp)_2$ Ni nitrosyl compound, NO as 3-el. donor, 18 VE "pogo stick" structure

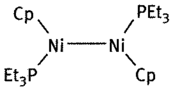
   (iii) $[CpNi(\mu\text{-}CO)]_2 + Ph_2P\text{–}PPh_2 \xrightarrow[-\,CO]{}$



   oxidative addition of P_2Ph_4; 18 VE complex

   (iv) $Cp_2Ni + NiCl_2(PPh_3)_2 \longrightarrow 2\,CpNiCl(PPh_3) \xrightarrow[-\,2\,AgCl]{2\,AgBF_4,\ 2\,PPh_3} 2\,[CpNi(PPh_3)_2]^+BF_4$ cationic 18 VE complex

   (v) $2\,CpNiCl(PEt_3) + 2\,Na \longrightarrow$



   Reduction of Ni(II) chloride with Na
   There are 2 structural possibilities: a Ni(I) dimer with unbridged
   Ni–Ni bond, or formation of Cp bridges.
   In this case a compound with unsupported Ni–Ni bond is formed.

3. Explain why the substitution of ethylene ligands by CO in $(\eta^5\text{-indenyl})Rh(C_2H_4)_2$ is orders of magnitudes faster than in $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$.

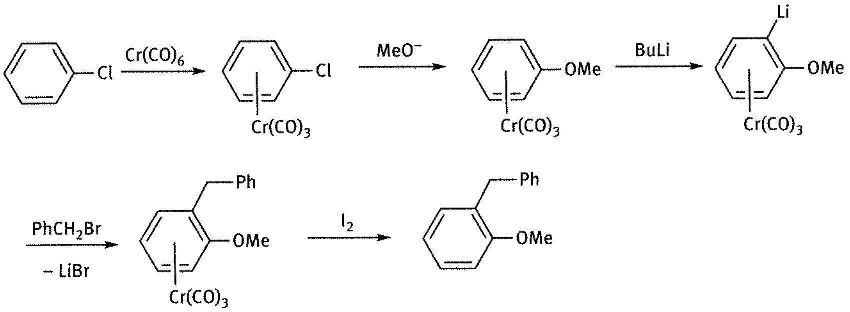
   This is an example of the kinetic effect of $\eta^5 \rightarrow \eta^3$ indenyl slippage: the 16 VE intermediate is accessible only for indenyl.

Chapter 2.9

1. Draw the structures and determine the oxidation states and electron count for (i) $[Cr(C_6H_6)_2]^+$; (ii) $Cr(C_6H_3Me_3)_2$; (iii) $Cr_2(C_6H_3Me_3)_3$; (iv) $(C_7H_7)Mo(CO)_2Br$; (v) $U(C_8H_8)_2$.

   The structures are given in the main text. (i) $[Cr(C_6H_6)_2]^+$: Cr(I), 17 VE. (ii) $Cr(C_6H_3Me_3)_2$: Cr(0), 18 VE. (iii) $Cr_2(C_6H_3Me_3)_3$: Cr(0), 15 VE per Cr, avoiding double-counting of bridging arene. In total a 30 VE binuclear structure. (iv) $(C_7H_7)Mo(CO)_2Br$: could be Mo(0) assuming $C_7H_7^+$, or Mo(IV) assuming $C_7H_7^{3-}$, in either case 18 VE. (v) $U(C_8H_8)_2$: U $s^2d^1f^3 + 2 \times 8 = 22$ VE.

2. Using (arene)$Cr(CO)_3$ synthesis strategies, devise a route for the synthesis of 2-benzylanisole, $MeOC_6H_4$-2-CH_2Ph, from chlorobenzene.



3. Why is the COT ligand planar in CpTi(COT) but non-planar in CpCo(COT)?

   CpTi(COT) contains Ti(III) bound to the aromatic COT^{2-} anion, giving an electron count of 16. In the Co complex coordination to two of the 4 C=C bonds is required to achieve 18 VE, Co(I).

Chapter 2.11

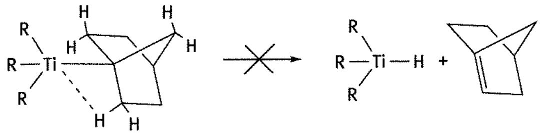
1. Devise the most appropriate synthetic routes to

   (i) $Zr(CH_2Ph)_4$; (ii) $TiBr_3(CH_2Ph)$; (iii) $Cp_2TiMeCl$; (iv) $(Me_3P)_2ClNi\text{-}C(O)Me$.

   (i) $Zr(CH_2Ph)_4$ is prepared by alkylation of $ZrCl_4$ with benzyl Grignard reagent: $ZrCl_4 + 4\ RMgCl \rightarrow ZrR_4 + 4\ MgCl_2$. (ii) Mixed-ligand alkyls like $TiBr_3(CH_2Ph)$ are best prepared by comproportionation: $TiR_4 + 3\ TiBr_4 \rightarrow 4\ RTiBr_3$. (iii) Whereas LiMe gives complete alkylation, $AlMe_3$ is more selective: $Cp_2TiCl_2 + AlMe_3 \rightarrow Cp_2TiMeCl + Me_2AlCl$. (iv) Oxidative addition of MeC(O)Cl to NiL_4 or treatment of $NiMeClL_2$ with one equivalent of CO gives $(Me_3P)_2ClNi\text{–}C(O)Me$.

2. Both $TiPr^i_4$ and Ti(1-norbornyl)$_4$ contain six β-H atoms per alkyl ligand and have the same electron count. Explain why, in spite of this similarity, $TiPr^i_4$ is very unstable whereas Ti(1-norbornyl)$_4$ is an isolable compound.

   Ti(1-norbornyl)$_4$ is a bridgehead alkyl. Although there are 6 β-H atoms, β-H elimination would result in a highly strained bridgehead alkene which makes this decomposition pathway inaccessible. There are no such constraints for $TiPr^i_4$, and β-H elimination is facile.



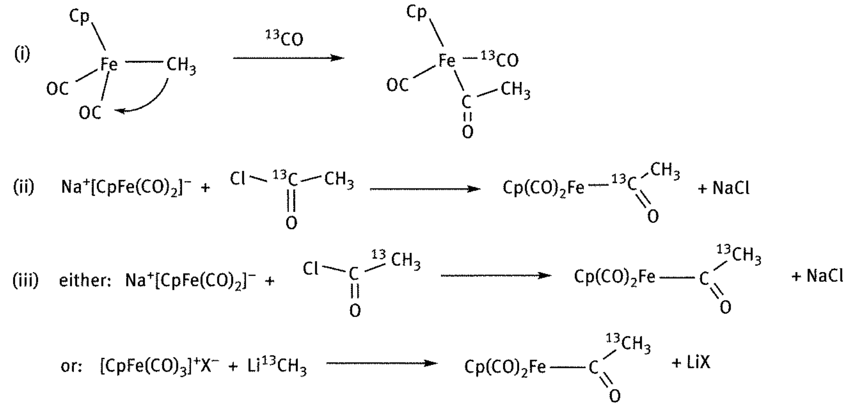
3. The mono-alkyl $TiEtCl_3$ is unstable but an isolable complex is obtained on adding the diphosphine 1,2-$C_2H_4(PMe_2)_2$ (dmpe). Discuss the alkyl bonding in this compound.

   The phosphine addition stabilizes the Ti-alkyl by forming a 6-coordinate complex. However, the metal centre is still electronically unsaturated (12 VE), and there is one C–H bond on the β-carbon of the ethyl ligand agostically bonded to the metal. This bonding is fluxional, i.e. there is exchange between all three methyl H atoms even at −90 °C. This is one of the classical examples of this type of bonding.

4. Suggest appropriate synthetic routes that lead selectively to

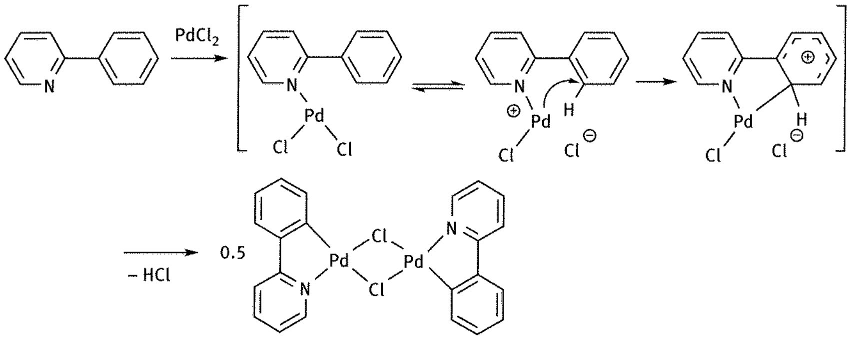
   (i) Cp(CO)(^{13}CO)Fe–C(O)CH$_3$ and (ii) Cp(CO)$_2$Fe–^{13}C(O)CH$_3$ and (iii) Cp(CO)$_2$Fe–C(O)^{13}CH$_3$.

   This question exemplifies (a) the migratory insertion process, (b) oxidative addition and (c) nucleophilic intermolecular attack on a coordinated ligand.



5. Suggest the expected product of the reaction of 2-phenylpyridine with PdCl$_2$ and show the reaction mechanism.

   This is a typical example of *ortho*-metallation, where the pyridine N atom directs the position of electrophilic attack by the Pd^{2+} ion. Chloride acts as base to abstract H$^+$ from the carbocationic intermediate.



6. The reaction of [Cp$_2$YCl]$_2$ with NaAlMe$_4$ gives a hydrocarbon-soluble compound **A**. Treatment of **A** with pyridine gives **B**. Measurements by freezing point depression in benzene give the molecular weight of **B** as 450 ± 40, and the elemental analysis shows that it contains no nitrogen. Adding a little THF to **B** gives **C**. Identify **A**, **B**, and **C**, give the chemical equations and explain the structures of the products.

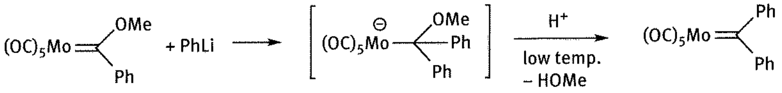
   Alkylation of Cp$_2$YCl (and other related lanthanide complexes) with [AlMe$_4$]$^-$ gives a heterobinuclear complex Cp$_2$Y(μ-Me)AlMe$_2$ (**A**). Treatment with pyridine abstracts AlMe$_3$ as the AlMe$_3$(py) complex, leaving binuclear [Cp$_2$Y(μ-CH$_3$)]$_2$ (**B**). The methyl bridges in both **A** and **B** give 2e3c bonds, akin to Al$_2$Me$_6$. The molecular weight determination shows that **B** is a dimer. THF cleaves the dimer, giving Cp$_2$YMe(THF) (**C**).

Chapter 2.12

1. Devise two different synthetic routes to $(OC)_5Mo{=}CPh_2$.

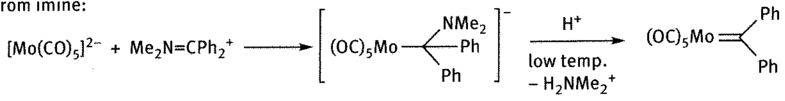
Possible routes:

(i) from carbene precursors:



(ii) from $PhCHN_2$:

(iii) from imine:



2. Which chemical reactions could be used to indicate the nucleophilic or electrophilic character of (i) $(OC)_5Cr{=}CPh(OMe)$ and (ii) $Cp_2TaMe(CH_2)$?

For Fischer type carbenes, the exchange of the carbene substituents is possible by nucleophilic attack, e.g. with lithium alkyls or aryls. By contrast, $Cp_2TaMe(CH_2)$ is made by deprotonation of $[Cp_2TaMe_2]^+$; this reaction is reversible. Similarly, the Ta carbene adds $AlMe_3$ to the carbon, whereas Fischer carbenes $(OC)_5Cr{=}C(OMe)R$ would bind $AlMe_3$ via OMe, not C.

3. How many products can be formed if a mixture of $R^1CH{=}CHR^2$ and $R^3CH{=}CHR^4$ is subjected to olefin metathesis?

In a metathesis reaction, each terminus $R^nCH{=}$ can be combined with every other terminus ($n = 1.....4$).

1 + 1, 2, 3, 4

2 + 2, 3, 4

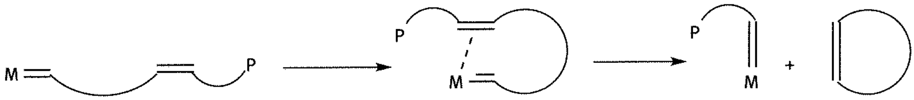
3 + 3, 4

4 + 4

There are therefore ten possible olefin combinations. Each may be formed as the *cis* and *trans* isomers.

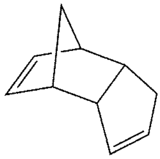
4. A ring-opening polymerization of a cyclic olefin gives initially a living polymer with narrow molecular weight distribution. However, over time a broadening of the polydispersity is observed. Account for this observation.

The polymer of a ROMP reaction contains C=C bonds. Over time the catalyst may 'back-bite' and react with a C=C bond of the polymer chain, extruding a cyclic olefin and starting a new polymer chain. This may occur towards the end of a polymerization reaction, when the monomer is depleted, or with olefins that are not very strained, so that the reactivity of the cyclic monomer differs little from that of the C=C bond of the linear polymer.

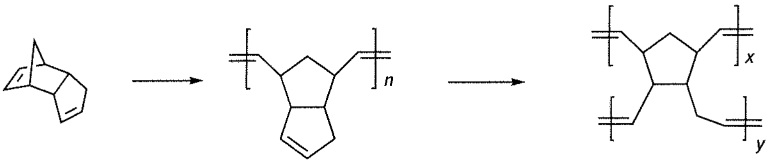


Of course, it is also possible for a M=CHR catalyst terminus to react with a C=C bond of a neighbouring polymer chain. This, too, would result in cleavage of that chain and a degradation of the polymer molecular weight. However, back-biting is kinetically preferred.

5. Which polymers are obtained in the ROMP of dicyclopentadiene?

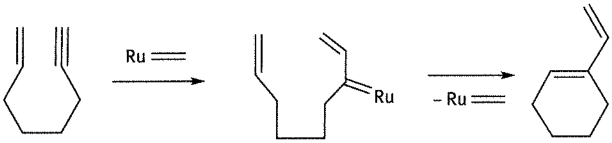


The C=C bond in the bicyclic ring is more strained and more reactive than the second C=C bond and will be opened in the ROMP process. If the catalyst is sufficiently active, and when all more reactive C=C bonds are consumed, the C=C bond in the bicyclic linker may also react:



6. What is the product of the enyne metathesis of 1-octen-7-yne?

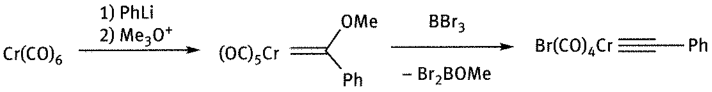
The enyne metathesis of $CH_2{=}CH{-}(CH_2)_4{-}C{\equiv}CH$ leads to ring closure:



Chapter 2.13

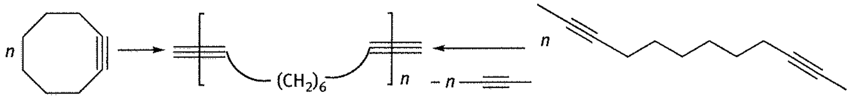
1. Describe a synthetic route to $PhC{\equiv}Cr(CO)_4Br$.

The synthesis proceeds via the Cr carbene complex by the Fischer protocol:



2. What are the products of alkyne metathesis of (i) cyclooctyne; (ii) 2,10-dodecadiyne.

The first is a case of ring-opening metathesis alkyne polymerization. The second is an acyclic alkyne metathesis. Both lead to the same product:



Chapter 3.2

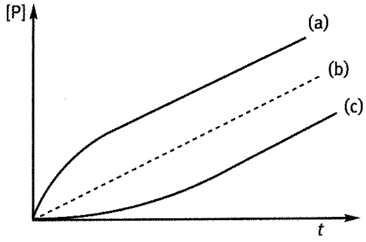
1. A chemical reaction in the presence of a catalyst is 1000 times faster than the uncatalysed reaction. What is the difference in energy barriers in these two cases?

According to the Eyring equation, the difference in activation energies of the two reactions is given by $\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}_{uncat} - \Delta G^{\ddagger}_{cat} = RT\ln(k_{cat}/k_{uncat})$. With $k_{cat}/k_{uncat} = 1000{:}1$, it follows that $\Delta\Delta G^{\ddagger} = 17.1$ kJ/mol (or 4.0 kcal/mol). This is comparable to the rotational barrier in ethane (11.5 kJ/mol). It demonstrates that even very small energy differences lead to drastic increases in reaction rates.

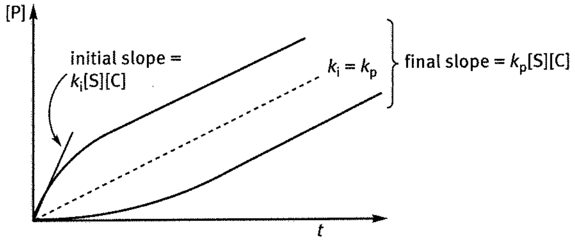
2. Many catalytic reactions have an initiation period, during which the catalyst concentration increases. This reaction phase therefore operates under non-steady-state conditions. It can be shown that in such cases the formation of a product P from a substrate S in the presence of catalyst C follows the rate law:

$$d[P] / dt = k_p [S] [C] + (k_i - k_p) [S] [C] \exp(-k_i [S] t)$$

Three different substrates give the following three conversion *vs.* time curves (a), (b), and (c). What do these curves tell us concerning the kinetic behaviour of the catalyst? In each case, determine the initial and steady-state slopes of the reactions and comment what information these slopes provide.



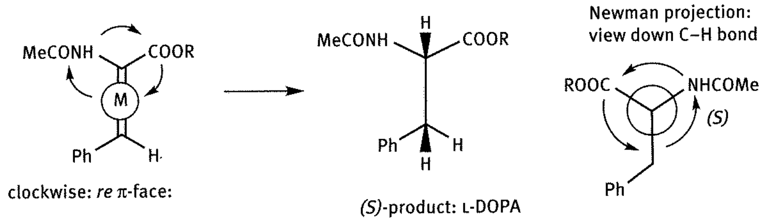
Curves (a) and (c) show the behaviour of a catalyst with an induction or initiation period, characterized by rate constant k_i. In curve (a) the rate of initiation k_i is faster than the rate of propagation k_p (a rare situation), and in (c) $k_i < k_p$, which is the more usual case. In curve (b) $k_i = k_p$, i.e. there is no initiation phase. For the initial phases of curves (a) and (c) one can draw tangents with the slope k_i[S][C]. Under steady-state conditions ($k_i = k_p$) all three curves show a slope k_p[S][C]. Curves (a) and (c) therefore allow both k_i and k_p to be determined.

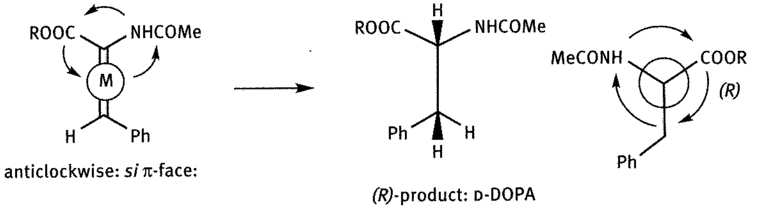


Chapter 3.3

1. Which π-face of *Z*-acetamido cinnamic esters (*re* or *si*) leads to the desired L-DOPA on hydrogenation?

The assignment of *re* or *si* prochirality follows the usual substituent priority rules:





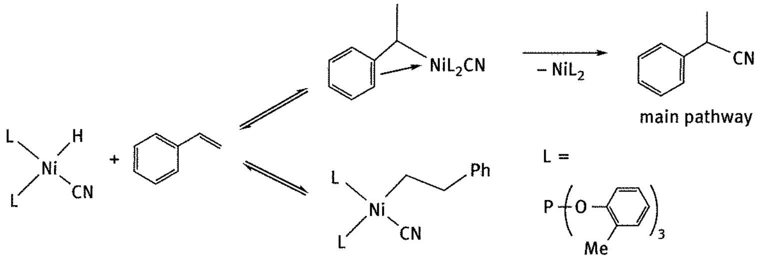
2. Calculate the energy difference in the formation of D- and L-DOPA (at $T = 298$ K) that would correspond to an enantiomeric excess of (i) 90% and (ii) 99%.

   It follows from the Eyring equation that $\Delta\Delta G^{\ddagger}_{L/D} = -RT\ln(r_D/r_L)$. (i) An enantiomeric excess of 90% corresponds to a rate ratio of 95:5. With $T = 298$K and $R = 8.31441$ J/(mol K) it follows: $\Delta\Delta G^{\ddagger}_{L/D} = 7.3$ kJ/mol. (ii) The same calculation gives $\Delta\Delta G^{\ddagger}_{L/D} = 13.1$ kJ/mol.

   As pointed out in Exercise 1 of Chapter 3.2, these energy differences are similar to the rotational barrier of ethane. This means that very small energy differences lead to very high enantiomeric excesses.

3. Draw a catalytic cycle for the hydrocyanation of styrene with Ni catalysts. Why does this preferentially lead to a Markovnikov addition product?

   The entry in the catalytic cycle is again the oxidative addition of HCN to a Ni(0) phosphite complex. This can occur in a Markovnikov and anti-Markovnikov sense. The reaction is reversible. The Markovnikov product is stabilized by π-bonding to the phenyl ring, and this electron delocalization stabilizes this alkyl intermediate, so that the reaction is predominantly channelled towards the branched reductive elimination product.



Chapter 3.4

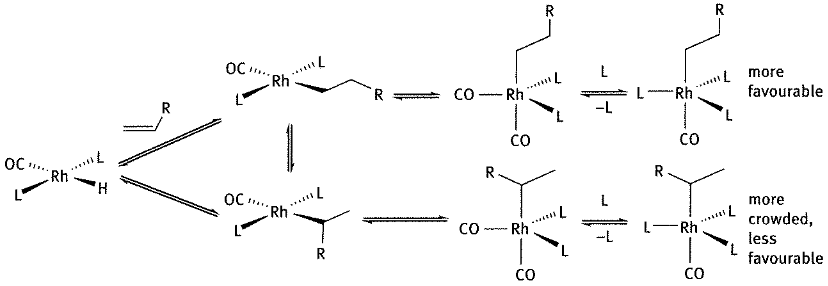
1. Explain the role of PBu$^n_3$ in Co catalysed hydroformylation. Why is this ligand not used in the Rh-catalysed process?

   The metal centre in $HCo(CO)_4$ is comparatively electron-poor due to four electron-withdrawing CO ligands, and the Co–H bond is labile, so that decomposition with H_2 elimination is facile. PBu$^n_3$ coordinates more strongly than CO and allows the CO pressure to be lowered without catalyst decomposition. However, since PBu$^n_3$ is a strong electron donor, the hydride in L_nCoH becomes more hydridic and more strongly reducing, so that aldehyde is reduced to the alcohol.

   None of these effects are required in Rh catalysts, where PPh_3 gives a better balance of coordinative stabilization, ligand dissociation and control of M–H acidity.

2. What is the consequence of high PPh_3 concentrations in the Rh-catalysed hydroformylation reactions? Explain the effect.

   The insertion of an alkene into the Rh–H bond can give linear and branched alkyl complexes. In the presence of high [PPh_3], sterically crowded species prevail in the equilibrium. Branched alkyls are more crowded than linear alkyls. To reduce steric repulsion, the equilibrium is shifted towards the linear Rh alkyl, which leads to a higher selectivity for linear aldehyde.



3. Show the main reaction steps for the conversion of 3-hexene into 1-heptanal.

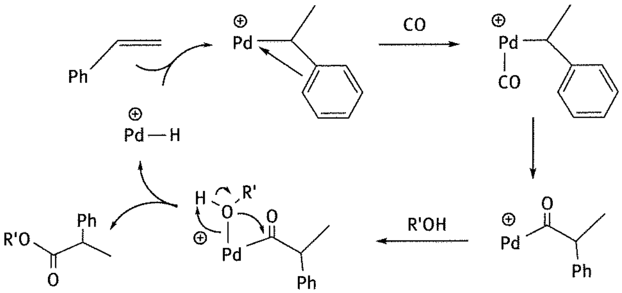
   3-Hexene contains an internal C=C bond. The hydroformylation must therefore be preceded by several isomerization steps. Since hydroformylation catalysts contain Rh–H bonds and are therefore capable of double bond isomerization, the thermodynamically favoured Rh-n-hexyl intermediate is formed prior to CO insertion.

4. Explain the differences in rate-limiting steps in the Rh and the Ir catalysed carbonylation of methanol. In particular, what are the reasons for the different reactivities of the iodo anions $[MI_2(CO)_2]^-$ (M = Rh, Ir)?

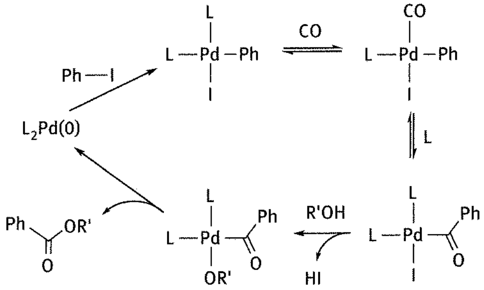
   In the Rh system, oxidative addition of MeI to $[RhI_2(CO)_2]^-$ is rate limiting. Since for third row metals the higher oxidation states are more stable, Ir prefers oxidation state +III. $[IrI_2(CO)_2]^-$ is a stronger nucleophile than $[RhI_2(CO)_2]^-$, and therefore the reaction with MeI is more facile. For the Ir system, the rate-limiting step is therefore elsewhere in the catalytic cycle.

5. Draw catalytic cycles for the Pd-catalysed carbonylation of (i) styrene; (ii) iodobenzene. Why is the addition of base beneficial in this case?

   Styrene carbonylation: assumed to involve Pd(II)–H species:



   The iodobenzene reaction starts with oxidative addition to Pd(0). The reaction produces HI, which needs to be neutralized by base.



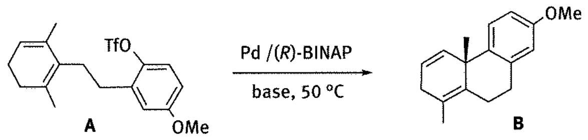
Chapter 3.6

1. Explain why in the reaction

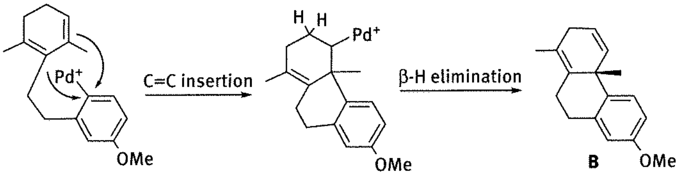
   different ligands L give the coupling product in the following yields (%): L = PPh_3 (0); dppf (0); PCy_3 (75); PBu^t_3 (86).

   The aryl halide is a chlorobenzene derivative which is very unreactive and will undergo oxidative additions only with very electron-rich Pd(0) centres. This is the rate-limiting step. Only trialkylphosphines generate sufficiently reactive metal centres, in the order $PCy_3 < PBu^t_3$.

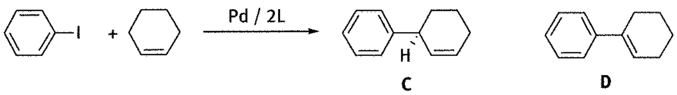
2. Show the mechanistic steps for the transformation of **A** into **B**. Although **A** contains two C=C bonds, product **B** is formed selectively. Give your reasons.



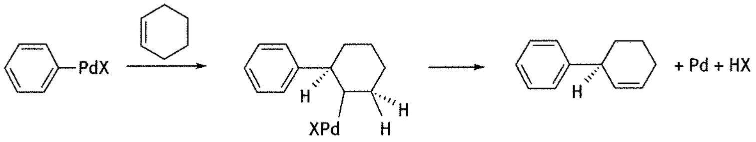
The tosylate oxidatively adds to Pd to give a Pd aryl. Insertion of one or the other of the C=C bonds leads to either 5- or 6-membered rings. Since each C=C bond has two π-faces, there are in principle four possibilities for insertion. Six-ring formation is most favourable:



3. The Heck arylation of cyclohexene by iodobenzene gives the non-conjugated product **C** and not the thermodynamically expected conjugated alkene **D**. Give your reasons and discuss the mechanistic intermediates.



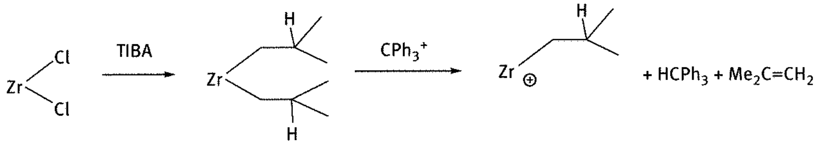
Insertion of cyclohexene into the Ph–Pd bond gives a Pd alkyl as expected. H-H elimination can take place only from periplanar C–H bonds, i.e. C–H bonds that are in the same plane as the Pd–C bond. This precludes elimination of the H atom in α-position to the phenyl ring, so that a conjugated product cannot be formed in this step. It could however be generated by subsequent C=C bond isomerization.



Chapter 3.7

1. Show the likely mechanistic steps in the activation of *rac*-$Me_2Si(Ind)_2ZrCl_2$ with $AlBu^i_3$ / $CPh_3[B(C_6F_5)_4]$.

The activation involves (a) alkylation and (b) alkyl abstraction. With alkyls carrying β-H atoms, the trityl cation usually reacts by abstraction of the kinetically accessible β-H, with alkene elimination, rather than alkyl abstraction. The result is the formation of an ion pair of a 14 VE metallocene alkyl cation.

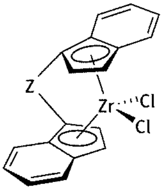


TIBA = $AlBu^i_3$

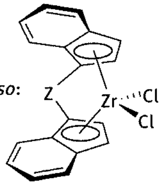
2. Show the structure of *meso*-$Me_2Si(Ind)_2ZrCl_2$ and explain why propene polymerization with this complex is not stereoselective.

   In the meso isomer both indenyl ligand parts point in the same direction. Therefore neither offers stereoselectivity. Approach of the monomer from the indenyl side is hindered, so that monomer binds less readily, with no possibility for preferential orientation of the methyl substituent of propene. The result is a low yield of an atactic polymer.

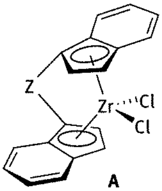
rac:



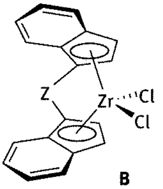
meso:



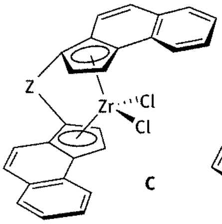
3. Which of the following *ansa*-metallocenes **A–D** is likely to show (a) the highest stereoselectivity in propene polymerizations and (b) the highest polymer molecular weight? State your reasons.



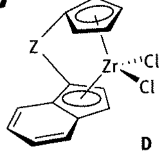
A



B



C

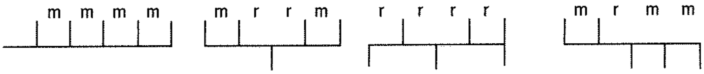


D

   Structure **B** is the *meso* isomer of **A** and has no stereoselectivity. **D** is C_1-symmetric and offers stereo control at only one coordination site. **C** has the most stereoregulating ligand framework. The sequence is therefore **B** < **D** < **A** < **C**, both for stereoregularity and polymer molecular weight.

4. Show the Fischer projections for the following polypropylene pentad structures: *mmmm, mrrm, rrrr, mrmm*. What mechanistic information can be obtained from the observation of mrrm and mrmm pentads, and why are these not observed in the same polymer?

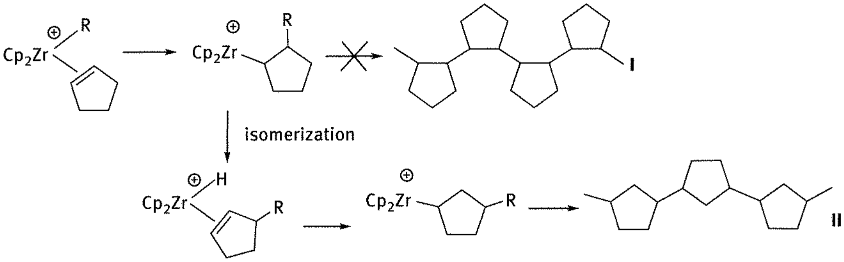
   The Fischer projections are:



   mmmm and *rrrr* correspond to isotactic and syndiotactic PP, respectively. The *mrrm* and *mrmm* pentads are indicative of stereo-errors. The *mrrm* pentad indicates a stereo-error that has been corrected in the next insertion step, as would happen with a stereoselective catalyst, such as a racemic C_2-symmetric *ansa*-metallocene (enantiomorphic site control). The *mrmm* indicates a stereo-error that has not been corrected: the error is propagated. This indicates a catalyst where the stereoselectivity derives from the chirality of the β-C atom of the polymer chain, not the ligand framework (chain end control). Once a misinsertion has occurred, there is no ligand framework to enforce its reversal.

5. The polymerization of cyclopentene with a zirconocene catalyst was originally thought to produce a polymer of type **I**. However, it was subsequently discovered that in fact the polymer has 1,3-connectivity (**II**). Give the mechanism of the formation of this polymer.

   Polymer **I** would follow the normal 1,2-insertion process. A polymer with 1,3-connectivity can only arise if each insertion is followed by an isomerization step, i.e. β-H elimination followed by re-insertion.



6. With some metallocene catalysts some H_2 is added to control the molecular weight of polyethylene. What type of polymer would result if $PhSiH_3$ was added instead of H_2?

   Hydrogen terminates a polymer chain by σ-bond metathesis, i.e. a hydrogenolysis step. This limits the molecular weight and a saturated polymer results. $PhSiH_3$ reacts in principle in a similar way; however, since there are three H functions per Si, three polymer chains can be transferred from the catalyst to the Si atom. The result would be a star-polymer, with a PhSi unit as the bridge: $PhSiR^1R^2R^3$ ($R^{1,2,3}$ = polymer chains).

APPENDIX 4

Further Reading

General Major Reference Works

COMC I: G. Wilkinson, F. G. A. Stone, E. W. Abel (Eds.): *Comprehensive Organometallic Chemistry.* Pergamon, Oxford, 1982.

COMC II: E. W. Abel, F. G. A. Stone, G. Wilkinson (Eds.): *Comprehensive Organometallic Chemistry II.* Elsevier, Oxford, 1995.

COMC III: D. M. P. Mingos, R. H. Crabtree (Eds.): *Comprehensive Organometallic Chemistry III.* Elsevier, Oxford, 2007.

C. H. Elschenbroich: *Organometallics, A Concise Introduction.* 3rd ed. VCH, Weinheim, 2005.

C. Cornils, W. A. Herrmann: *Applied Homogeneous Catalysis with Organometallic Compounds.* Volumes 1 and 2. VCH, Weinheim, 1996.

J. Hartwig: *From Bonding to Catalysis.* University Science Books, Sausalito, 2010.

Part 1 Organometallic Compounds of Main Group Elements

Chapter 1.1

COMC I: M. E. O'Neill, K. Wade: Structural and Bonding Relationships Among Main Group Organometallic Compounds. Vol. 1, p. 1.

Chapter 1.2

COMC I: J. L. Wardell: Alkali Metals. Vol. 1, p. 43.

COMC II: D. S. Wright, M. A. Beswick: Alkali Metals. Vol. 1, p. 1.

COMC III: K. Ruhland-Senge, K. W. Henderson, P. C. Andrews: Alkali Metal Organometallics—Structure and Bonding. Vol. 2, p. 1.

R. E. Mulvey: Avant-garde metalating agents: structural basis of alkali-metal-mediated metalation. *Acc. Chem. Res.* **2009**, *42*, 743.

H. J. Reich: Role of organolithium aggregates and mixed aggregates in organolithium mechanisms. *Chem. Rev.* **2013**, *113*, 7130.

Chapter 1.3

COMC I: W. E. Lindsell: Magnesium, Calcium, Strontium, and Barium. Vol. 1, p. 155.

COMC II: W. E. Lindsell: Magnesium, Calcium, Strontium, and Barium. Vol. 1, p. 57.

COMC III: T. P. Hanusa: Alkaline Earth Organometallics. Vol. 2, p. 67.

H. Ila, O. Baron, A. J. Wagner, P. Knochel: Functionalized magnesium organometallics as versatile intermediates for the synthesis of polyfunctional heterocycles. *Chem. Commun.* **2006**, 583.

T. Satoh: Recent advances in the chemistry of magnesium carbenoids. *Chem. Soc. Rev.* **2007**, *36*, 1561.

P. Knochel, C. Diène: Preparation of functionalized Zn and Mg organometallics. Application to the performance of diastereoselective cross-couplings. *Comptes Rendus Chimie* **2011**, *14*, 842.

Chapter 1.4

COMC I: (a) J. Boersma: Zinc and Cadmium. Vol. 2, p. 823. (b) J. L. Wardell: Mercury. Vol. 2, p. 863. (c) P. J. Craig: Environmental Aspects of Organometallic Chemistry. Vol. 2, p. 979.

COMC II: (a) P. O'Brien: Cadmium and Zinc. Vol. 3, p. 175. (b) A. G. Davies, J. L. Wardell: Mercury. Vol. 3, p. 135.

COMC III: (a) L. Stahl, I. P. Smoliakova: Zinc Organometallics. Vol. 2, p. 309. (b) F. P. Gabbai, C. N. Burress, M. A. Melaimi, T. J. Taylor: Mercury and Cadmium Organometallics. Vol. 2, p. 419.

Chapter 1.5

COMC I: (a) J. D. Odom: Non-Cyclic Three-and Four-Coordinated Boron Compounds. Vol. 1, p. 253. (b) J. J. Eisch: Aluminium. Vol. 1, p. 555. (c) D. G. Tuck: Gallium and Indium. Vol. 1, p. 683. (d) H. Kurosawa: Thallium. Vol. 1, p. 725.

COMC II: (a) C. E. Housecroft: Compounds With Three- and Four Coordinate Boron, Emphasizing Cyclic Systems. Vol. 1, p. 129. (b) J. J. Eisch: Aluminium. Vol. 1, p. 431. (c) M. A. Paver, C. A. Russell, D. S. Wright: Gallium, Indium, and Thallium. Vol. 1, p. 503.

COMC III: (a) A. Mitra, D. A. Atwood: Aluminium Organometallics. Vol. 3, p. 265. (b) S. Schulz: Aluminium, Indium, Gallium, and Thallium. Vol. 3, p. 287.

E. Vedejs et al.: Cationic tricoordinate boron intermediates: Borenium chemistry from the organic perspective. *Chem. Rev.* **2012**, *112*, 4246.

D. W. Stephan, G. Erker: Frustrated Lewis pair chemistry of carbon, nitrogen and sulfur oxides. *Chem Sci.* **2014**, *5*, 2625.

A. Schnepf, H. Schnöckel: Metalloid aluminum and gallium clusters: Element modifications on the molecular scale? *Angew. Chem. Int. Ed.* **2002**, *41*, 3532.

R. A. Fischer et al.: Cyclopentadiene based low-valent Group 13 metal compounds: Ligands in coordination chemistry and link between metal rich molecules and intermetallic materials. *Chem. Rev.* **2012**, *112*, 3136.

J. A. J. Pardoe, A. J. Downs: Development of the chemistry of indium in formal oxidation states lower than +3. *Chem. Rev.* **2007**, *107*, 2.

Z.-L. Shen et al.: Organoindium reagents: The preparation and application in organic synthesis. *Chem. Rev.* **2013**, *113*, 271.

Chapter 1.6

COMC I: (a) D. A. Armitage: Organosilanes. Vol. 2, p. 1. (b) R. West: Organopolysilanes. Vol. 2, p. 365. (c) A. G. Davies: Tin. Vol. 2, p. 519. (d) P. G. Harrison: Lead. Vol. 2, p. 629.

COMC II: (a) D. A. Armitage: Organosilanes. Vol. 2, p. 1. (b) R. West: Organopolysilanes. Vol. 2, p. 77. (c) S. S. Brown, T. C. Kendrick, J. McVie, D. R. Thomas: Silicones. Vol. 2, p. 111. (d) A. G. Davies: Tin. Vol. 2, p. 217. (d) P. G. Harrison: Lead. Vol. 2, p. 305.

COMC III: (a) J. Beckmann: Organopolysilanes. Vol. 3, p. 549. (b) M. H. Mazurek: Silicones. Vol. 3, p. 651. (c) C. S. Weinert: Germanium Organometallics. Vol. 3, p. 699. (d) A. G. Davies: Tin Organometallics. Vol. 3, p. 809. (e) M. Weidenbruch: Lead Organometallics. Vol. 3, p. 885.

S. Nagendran, H. W. Roesky: The chemistry of aluminum(I), silicon(II), and germanium(II). *Organometallics* **2008**, *27*, 457.

T. Müller: Cations of group 14 organometallics. *Adv. Organomet. Chem.* **2005**, *53*, 155.

T. Müller et al.: Synthesis of silylium and germylium ions by a substituent exchange reaction. *Organometallics* **2013**, *32*, 4713.

M. Oestreich et al.: Activation of the Si–B interelement bond: Mechanism, catalysis, and synthesis. *Chem. Rev.* **2013**, *113*, 402.

V. Y. Lee, A. Sekiguchi: Cyclic polyenes of heavy group 14 elements: New generation ligands for transition-metal complexes. *Chem. Soc. Rev.* **2008**, *37*, 1652.

Part 2: Transition Metals

Chapter 2.1

COMC I: D. M. P. Mingos: Bonding of Unsaturated Organic Molecules to Transition Metals. Vol. 3, ch. 19, p. 1.

J. A. M. Simões, J. L. Beauchamp: Transition metal–hydrogen and metal–carbon bond strengths: The keys to catalysis. *Chem. Rev.* **1990**. *90*, 629.

J. C. Green, M. L. H. Green, G. Parkin: The occurrence and representation of three-centre 2-electron bonds in covalent inorganic compounds. *Chem. Commun.* **2012**, *48*, 11481.

E. D. Jemmis, A. R. Pinhas, R. Hoffmann: $Cp_2M_2(CO)_4$—quadruply bridging, doubly bridging, semibridging, or non-bridging? *J. Am. Chem. Soc.* **1980**, *102*, 2576.

Chapter 2.4

Phosphines

C. A. Tolman: Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis. *Chem. Rev.* **1977**, *77*, 313.

A. K. Brisdon, C. J. Herbert: Fluoroalkyl-containing phosphines. *Coord. Chem. Rev.* **2013**, *257*, 880.

M. P. Carroll, P. J. Guiry: P, N ligands in asymmetric catalysis. *Chem. Soc. Rev.* **2014**, *43*, 819.

M. M. Pereira et al.: Synthesis of binaphthyl based phosphine and phosphite ligands. *Chem. Soc. Rev.* **2013**, *42*, 6990.

Carbenes

H. Clavier, S. P. Nolan: Percent buried volume for phosphine and N-heterocyclic carbene ligands: Steric properties in organometallic chemistry. *Chem. Commun.* **2010**, *46*, 841.

A. Collado et al.: Steric and electronic parameters of a bulky yet flexible N-heterocyclic carbene: 1,3-Bis(2,6-bis(1-ethylpropyl)phenyl)imidazol-2-ylidene (IPent). *Organometallics* **2013**, *32*, 3249.

C. Ganter et al.: Determining the π-acceptor properties of N-heterocyclic carbenes by measuring the ^{77}Se NMR chemical shifts of their selenium adducts. *Organometallics* **2013**, *32*, 5269.

M. Albrecht et al.: Piano-stool iron(II) complexes as probes for the bonding of N-heterocyclic carbenes: Indications for π-acceptor ability. *Organometallics* **2006**, *25*, 5648.

R. H. Crabtree et al.: Rhodium and iridium complexes of N-heterocyclic carbenes via transmetalation: Structure and dynamics. *Organometallics* **2003**, *22*, 1663.

F. E. Hahn, M. C. Jahnke: Heterocyclic carbenes: Synthesis and coordination chemistry. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122.

H. DiazVelazquez, F. Verpoort: N-heterocyclic carbene transition metal complexes for catalysis in aqueous media. *Chem. Soc. Rev.* **2012**, *41*, 7032.

O. Kühl: The chemistry of functionalized N-heterocyclic carbenes. *Chem. Soc. Rev.* **2007**, *36*, 592.

H. G. Raubenheimer, S. Cronje: Carbene complexes of gold: preparation, medical application and bonding. *Chem. Soc. Rev.* **2008**, *37*, 1998.

W. Liu, R. Gust: Metal N-heterocyclic carbene complexes as potential antitumor metallodrugs. *Chem. Soc. Rev.* **2013**, *42*, 755.

Pincer ligands

D. Gelman, S. Musa: Coordination versatility of sp^3-hybridized pincer ligands towards ligand–metal cooperative catalysis. *ACS Catal.* **2012**, *2*, 2456.

H. Nishiyama: Synthesis and use of bisoxazolinyl-phenyl pincers. *Chem. Soc. Rev.* **2007**, *36*, 1133.

G. van Koten: Pincer ligands as powerful tools for catalysis in organic synthesis. *J. Organomet. Chem.* **2013**, *730*, 156.

Chapter 2.5

G. Granozzi: Gas phase UV photoelectron spectra and DV-$X\alpha$ calculations of bridged organometallic dimers. *J. Mol. Struct.* **1988**, *173*, 313.

J. C. Green, M. L. H. Green, G. Parkin: The occurrence and representation of three-centre 2-electron bonds in covalent inorganic compounds. *Chem. Commun.* **2012**, *48*, 11481.

H. Willner, F. Aubke: σ-Bonded metal carbonyl cations and their derivatives: Synthesis and structural, spectroscopic, and bonding principles. *Organometallics* **2003**, *22*, 3612.

B. E. Mann: CO-releasing molecules. *Organometallics* **2012**, *31*, 5728.

J. A. Wright, P. J. Turrell, C. J. Pickett: The third hydrogenase: more natural organometallics. *Organometallics* **2010**, *29*, 6146.

[FeFe] hydrogenase: R. Cammack: *Nature* **1999**, *397*, 214; M. W. W. Adams, E. I. Stiefel: *Science* **1998**, *282*, 1842.

Chapter 2.6

Y. Yamamoto: Transition-metal-catalyzed cycloisomerizations of α,ω-dienes. *Chem. Rev.* **2012**, *112*, 4736.

H. Kurosawa et al.: Redox-induced reversible metal assembly through translocation and reversible ligand coupling in tetranuclear metal sandwich frameworks. *Nat. Chem.* **2012**, *4*, 52.

H. Tobita et al.: Iridium and platinum complexes of $Li^+@C_{60}$. *Organometallics* **2014**, *33*, 608.

T. Takahashi et al.: Reaction of zirconacyclopentadienes. *J. Am. Chem. Soc.* **1999**, *121*, 1094 and *J. Am. Chem. Soc.* **2002**, *124*, 1144.

U. Rosenthal et al.: Five-membered titana- and zirconacyclocumulenes: stable 1-metallacyclopenta-2,3,4-trienes. *Organometallics* **2005**, *24*, 456.

U. Rosenthal et al.: Five-membered metallacycles of titanium and zirconium—attractive compounds for organometallic chemistry and catalysis. *Chem. Soc. Rev.* **2007**, *36*, 719.

N. Savjani et al.: Gold(III) olefin complexes. *Angew. Chem. Int. Ed.* **2013**, *52*, 874.

S. I. Lee, N. Chatani: Catalytic skeletal reorganization of enynes through electrophilic activation of alkynes: Double cleavage of C–C double and triple bonds. *Chem. Commun.* **2009**, 371.

A. Fürstner, P. W. Davies: Catalytic carbophilic activation: Catalysis by platinum and gold π-acids. *Angew. Chem. Int. Ed.* **2007**, *46*, 3410.

A. Fürstner: Gold and platinum catalysis—a convenient tool for generating molecular complexity. *Chem. Soc. Rev.* **2009**, *38*, 3208.

I. Braun et al.: Gold catalysis 2.0. *ACS Catalysis* **2013**, *3*, 1902.

B. Heller, M. Hapke: The fascinating construction of pyridine ring systems by transition metal catalysed [2 + 2 + 2] cycloaddition reactions. *Chem. Soc. Rev.* **2007**, *36*, 1085.

A. S. K. Hashmi, M. Rudolph: Gold catalysis in total synthesis. *Chem. Soc. Rev.* **2008**, *37*, 1766.

N. Marion, S. P. Nolan: N-heterocyclic carbenes in gold catalysis. *Chem. Soc. Rev.* **2008**, *37*, 1776.

S. M. Abu Sohel, R.-S. Liu: Carbocyclisation of alkynes with external nucleophiles catalysed by gold, platinum, and other electrophilic metals. *Chem. Soc. Rev.* **2009**, *38*, 2269.

T. J. Brown, R. A. Widenhoefer: Synthesis and equilibrium binding studies of cationic, two-coordinate gold(I) pi-alkyne complexes. *J. Organomet. Chem.* **2011**, *696*, 1216.

A. Corma et al.: Gold-catalyzed carbon–heteroatom bond-forming reactions. *Chem. Rev.* **2011**, *111*, 1657.

X. Fu et al.: Highly efficient synthesis of *cis*-[3]-cumulenic diols via zirconocene-mediated coupling of 1,3-butadiynes with aldehydes. *Organometallics* **2012**, *31*, 531.

R. A. Widenhoefer et al.: Mechanistic analysis of gold(I)-catalyzed intramolecular allene hydroalkoxylation reveals an off-cycle bis(gold) vinyl species and reversible C-O bond formation. *J. Am. Chem. Soc.* **2012**, *134*, 9134.

Y. Yamamoto: Theoretical study on ruthenium-catalyzed hydrocarboxylative dimerization of phenylacetylene with acetic acid. *Organometallics* **2013**, *32*, 5201.

F. Schüth et al.: Catalytic reactions of acetylene: A feedstock for the chemical industry revisited. *Chem. Rev.* **2014**, *114*, 1761.

R. Chinchilla, C. Nájera: Chemicals from alkynes with palladium catalysts. *Chem. Rev.* **2014**, *114*, 1783.

Chapter 2.7

J.-E. Bäckvall et al.: Central versus terminal attack in nucleophilic addition to (π-allyl)palladium complexes. Ligand effects and mechanism. *Organometallics* **1997**, *16*, 1058.

S. Tobisch: Structure–reactivity relationships in the cyclo-oligomerization of 1,3-butadiene catalyzed by zero-valent nickel complexes. *Adv. Organomet. Chem.* **2003**, *49*, 167.

M. Ogasawara et al.: Synthesis, structure, and reactivity of (1,2,3-η^3-butadien-3-yl)palladium complexes. *Organometallics* **2007**, *26*, 5025.

S. Tobisch, R. Taube: Mechanistic insight into the polymerization of butadiene by 'ligand-free' polybutadienyl-nickel(II) complexes: Computational assignment of the true structure of the resting state. *Organometallics* **2008**, *27*, 2159.

P. W. N. M. van Leeuwen et al.: New processes for the selective production of 1-octene. *Coord. Chem. Rev.* **2011**, *255*, 1499.

C. Bruneau et al.: Transition metal catalysed nucleophilic allylic substitution: Activation of allylic alcohols *via* π-allylic species. *Chem. Soc. Rev.* **2012**, *41*, 4467.

S. Schörshusen, J. Heck: Metal-mediated transformations of cyclooctatetraene to novel methylene-bridged, bicyclic compounds. *Organometallics* **2007**, *26*, 5386.

S. E. Lewis et al.: Valuable new cyclohexadiene building blocks from cationic η^5-iron-carbonyl complexes derived from a microbial arene oxidation product. *Chem. Eur. J.* **2012**, *18*, 13480.

Section 2.8.1

Ferrocene: COMC I: A. J. Deeming: Mononuclear iron compounds with η^2-η^6 hydrocarbon ligands. Vol. 4, ch. 31.3.

Cp ligands: P. C. Möhring, N. J. Coville: Group 4 metallocene polymerization catalysts: Quantification of ring substituent steric effects. *Coord. Chem. Rev.* **2006**, *250*, 18.

K. Mach et al.: Synthesis and crystal structures of thermally stable titanocenes. *J. Organomet. Chem.* **2002**, *663*, 134.

R. Layfield: Manganese(II): the black sheep of the organometallic family. *Chem. Soc. Rev.* **2008**, *37*, 1098.

Organic chemistry of MCp^2 and half-sandwich complexes

COMC I: W. E. Watts: The Organic Chemistry of Metal-coordinated Cyclopentadienyl and Arene Ligands. Vol. 8, ch. 59.

S. S. Braga, A. M. S. Silva: A new age for iron: Antitumoral ferrocenes. *Organometallics* **2013**, *32*, 5626.

D. Schaarschmidt, H. Lang: Selective synthesis of planar-chiral ferrocenes. *Organometallics* **2013**, *32*, 5668.

P. Molina et al.: Ferrocene-based small molecules for multichannel molecular recognition of cations and anions. *Eur. J. Inorg. Chem.* **2008**, 3401.

C. Bresner et al.: Selective electrochemical detection of hydrogen fluoride by ambiphilic ferrocene derivatives. *Angew. Chem. Int. Ed.* **2005**, *44*, 3606.

T.D. James et al.: Colorimetric enantioselective recognition of chiral secondary alcohols via hydrogen bonding to a chiral metallocene containing chemosensor. *Chem. Commun.* **2013**, *49*, 8314.

Section 2.8.2

P. Chirik et al.: Dinitrogen complexes of bis(cyclopentadienyl) titanium derivatives: Structural diversity arising from substituent manipulation. *Organometallics* **2009**, *28*, 4079.

K. Strohfeldt, M. Tacke: Bioorganometallic fulvene-derived titanocene anti-cancer drugs. *Chem. Soc. Rev.* **2008**, *37*, 1174.

G. Erker: Using bent metallocenes for stabilizing unusual coordination geometries at carbon. *Chem. Soc. Rev.* **1999**, *28*, 307.

C. E. Zachmanoglou et al.: The electronic influence of ring substituents and *ansa* bridges in zirconocene complexes as probed by infrared spectroscopy, electrochemical, and computational studies. *J. Am. Chem. Soc.* **2002**, *124*, 9525.

E. Negishi: Magical power of transition metals: Past, present, and future (Nobel lecture). *Angew. Chem. Int. Ed.* **2011**, *50*, 6738.

P. Wipt, H. Jahn: Synthetic applications of organochlorozirconocene complexes. *Tetrahedron* **1996**, *52*, 12853.

M. Ephritikhine: Recent advances in organoactinide chemistry as exemplified by cyclopentadienyl compounds. *Organometallics* **2013**, *32*, 2464.

T. Li, S. Kaercher, P. W. Roesky: Synthesis, structure, and reactivity of rare-earth metal complexes containing anionic phosphorus ligands. *Chem. Soc. Rev.* **2014**, *43*, 42.

Single-molecule magnets

R. A. Layfield et al.: A high anisotropic barrier in a sulfur-bridged organodysprosium single-molecule magnet. *Angew. Chem. Int. Ed.* **2012**, *51*, 6976.

S. Gao et al.: Series of lanthanide organometallic single-ion magnets. *Inorg. Chem.* **2012**, *51*, 3079.

Section 2.8.3

R. O. Duthaler, A. Hafner: Chiral titanium complexes for the enantioselective addition of nucleophiles to carbonyl groups. *Chem. Rev.* **1992**, *92*, 807.

W. E. Geiger: 1-Electron electrochemistry of parent piano-stool complexes. *Coord. Chem. Rev.* **2013**, *257*, 1459.

Y. Nibayashi et al.: Design and preparation of molybdenum–dinitrogen complexes. *Chem. Eur. J.* **2013**, *19*, 11874.

G. X. Jin et al.: Stepwise formation of organometallic macrocycles, prisms, and boxes from Ir, Rh, and Ru-based half-sandwich units. *Chem. Soc. Rev.* **2009**, *38*, 3419.

R. Beck, S. A. Johnson: Dinuclear Ni(I)–Ni(I) complexes with syn-facial bridging ligands from Ni(I) precursors of Ni(II)/Ni(0) comproportionation. *Organometallics* **2013**, *32*, 2944.

D. W. Stephan: Olefin polymerization and deactivation pathways of titanium phosphinimide catalysts. *Macromol. Symp.* **2001**, *173*, 105.

B. Ye, N. Cramer: Chiral cyclopentadienyl ligands as stereocontrolling elements in asymmetric C–H functionalization. *Science* **2012**, *338*, 504.

I. N. Michaelides, D. J. Dixon: Catalytic stereoselective semihydrogenation of alkynes to *E*-alkenes. *Angew. Chem. Int. Ed.* **2013**, *52*, 806.

E. B. Bauer: Chiral-at-metal complexes and their catalytic applications in organic synthesis. *Chem. Soc. Rev.* **2012**, *41*, 3153.

R. M. Bullock et al.: An iron complex with pendent amines as a molecular electrocatalyst for oxidation of hydrogen. *Nat. Mater.* **2013**, *5*, 228.

Chapter 2.9

COMC III: D. Zargarian: Nickel–Carbon π-Bonded Complexes. Vol. 8, chapter 3.

A. M. Echavarren et al.: Metal–arene interactions in dialkylbiarylphosphane complexes of copper, silver, and gold. *Chem. Eur. J.* **2010**, *16*, 5324.

C. C. Hartinger, N. Metzler-Nolte, P. J. Dyson: Challenges and opportunities in the development of organometallic anticancer drugs. *Organometallics* **2012**, *31*, 5677.

J. Pérez-Castells et al.: Chromium arene complexes in organic synthesis. *Chem. Soc. Rev.* **2007**, *36*, 1589.

P. Kumar et al.: Half-sandwich arene ruthenium complexes: Synthetic strategies and relevance in catalysis. *Chem. Soc. Rev.* **2014**, *43*, 707.

A. Glöckner, M. Tamm: The organometallic chemistry of cycloheptatrienyl zirconium complexes. *Chem. Soc. Rev.* **2013**, *42*, 128.

U. Richter et al.: Electronic structure of the electron-poor dinuclear organometallic compounds [(CpM)(CpM′)]μ-COT (M, M′ = V, Cr, Fe, Co). *Inorg. Chem.* **1999**, *38*, 77.

M. Murugesu et al.: An organometallic building block approach to produce a multidecker 4f single-molecule magnet. *J. Am. Chem. Soc.* **2013**, *135*, 3502.

M. Ephritikhine et al.: Revisiting the chemistry of the actinocenes $[(\eta^8\text{-}C_8H_8)_2An]$ (An = U, Th) with neutral Lewis bases. *J. Am. Chem. Soc.* **2013**, *135*, 10003.

T. Murahashi et al.: Square tetrapalladium sheet sandwich complexes: Cyclononatetraenyl as a versatile face-capping ligand. *J. Am. Chem. Soc.* **2009**, *131*, 9888.

Chapter 2.10

G. J. Kubas: Fundamentals of H_2 binding and reactivity on transition metals underlying hydrogenase function and H_2 production and storage. *Chem. Rev.* **2007**, *107*, 4152.

G. J. Kubas: *Metal Dihydrogen and Sigma-Bond Complexes: Structure, Theory, and Reactivity.* Kluwer Academic, New York, 2001.

R. Waterman: σ-Bond metathesis: A 30-year retrospective. *Organometallics* **2013**, *32*, 7249.

A. J. Cowan, M. W. George: Formation and reactivity of organometallic alkane complexes. *Coord. Chem. Rev.* **2008**, *252*, 2504.

W. H. Bernskoetter et al.: Characterization of a rhodium(I) σ-methane complex in solution. *Science* **2009**, *326*, 553.

A. S. Weller et al.: Synthesis and characterization of a rhodium(I) σ-alkane complex in the solid state. *Science* **2012**, *337*, 1648.

J. Takaya, N. Iwasawa: Reaction of bis(*o*-phosphinophenyl)silane with M(PPh_3)$_4$ (M = Ni, Pd, Pt). *Dalton Trans.* **2011**, *40*, 881.

A. S. Goldman et al.: Dehydrogenation and related reactions catalyzed by iridium pincer complexes. *Chem. Rev.* **2011**, *111*, 1761.

C. Gunanathan, D. Milstein: Transformations in chemical synthesis: Applications of acceptorless dehydrogenation and related transformations in chemical synthesis. *Science* **2013**, *341*, 249.

M. Etienne, A. S. Weller: Intramolecular C–C agostic complexes: C–C sigma interactions by another name. *Chem. Soc. Rev.* **2014**, *43*, 242.

Chapter 2.11

Alkyls and aryls

G. S. Girolami et al.: Are d^0 ML_6 complexes always octahedral? The X-ray structure of trigonal-prismatic [Li(tmed)]$_2$[$ZrMe_6$]. *J. Am. Chem. Soc.* **1989**, *111*, 4114.

V. Pfennig, K. Seppelt: Crystal and molecular structure of hexamethyltungsten and hexamethylrhenium. *Science* **1996**, *271*, 626.

P. Alemany et al.: Theoretical evidence of persistent chirality in D_3 homoleptic hexacoordinate complexes with monodentate ligands. *Chem. Eur. J.* **2003**, *9*, 1952.

Philip P. Power: Stable two-coordinate, open-shell (d^1–d^9) transition metal complexes. *Chem. Rev.* **2012**, *112*, 3482.

M. Lersch, M. Tilset: Mechanistic aspects of C–H activation by Pt complexes. *Chem. Rev.* **2005**, *105*, 2471.

M. Albrecht: Cyclometalation using d-block transition metals: Fundamental aspects and recent trends. *Chem. Rev.* **2010**, *110*, 576.

K. R. D. Johnson, P. G. Hayes: Cyclometalative C–H bond activation in rare earth and actinide metal complexes. *Chem. Soc. Rev.* **2013**, *42*, 1947.

L. M. Xu et al.: Organopalladium(IV) chemistry. *Chem. Soc. Rev.* **2010**, *39*, 712.

D. Gryko et al.: Vitamin B_{12}: Chemical modifications. *Chem. Soc. Rev.* **2013**, *42*, 6605.

S. W. Ragsdale: Nickel-based enzyme systems. *J. Biol. Chem.* **2009**, *284*, 18571.

W. J. Evans et al.: Insertion of carbodiimides and organic azides into actinide–carbon bonds. *Organometallics* **2009**, *28*, 3350.

L.-P. Liu, G. B. Hammond: Recent advances in the isolation and reactivity of organogold complexes. *Chem. Soc. Rev.* **2012**, *41*, 3129.

P. H. Dixneuf et al.: Ruthenium(II)-catalyzed C–H bond activation and functionalization. *Chem. Rev.* **2012**, *112*, 5879.

L. Ackermann: Carboxylate-assisted transition-metal-catalyzed C–H bond functionalizations: Mechanism and scope. *Chem. Rev.* **2011**, *111*, 1315.

D. V. Partyka: Transmetalation of unsaturated carbon nucleophiles from boron-containing species to the mid to late d-block metals of relevance to catalytic C–X coupling reactions (X = C, F, N, O, Pb, S, Se, Te). *Chem. Rev.* **2011**, *111*, 1529.

Alkynyls

Z. N. Chen et al.: Structures and phosphorescence properties of triphosphine-supported Au_2Ag_2 and Au_8Ag_4 alkynyl cluster complexes. *Organometallics* **2013**, *32*, 5402.

C. Lapinte et al.: Straightforward access to tetrametallic complexes with a square array by oxidative dimerization of organometallic wires. *Organometallics* **2013**, *32*, 5015.

P. Pale et al.: The organic chemistry of silver acetylides. *Chem. Soc. Rev.* **2007**, *36*, 759.

P. J. Low: Twists and turns: Studies of the complexes and properties of bimetallic complexes featuring phenylene ethynylene and related bridging ligands. *Coord. Chem. Rev.* **2013**, *257*, 1507.

C–C bond formation

COMC I: P. M. Maitlis, P. Espinet, M. J. H. Russell: Compounds with Palladium–Carbon σ-Bonds. Vol. 6, chapter 38.4.

COMC III: C. J. Elsevier, M. R. Eberhard: Palladium–Carbon σ-Bonded Complexes. Chapter 8.05.

D. Alberico et al.: Aryl–aryl bond formation by transition-metal-catalyzed direct arylation. *Chem. Rev.* **2007**, *107*, 174.

CO_2 insertion

S. N. Riduan, Y. Zhang: Recent developments in carbon dioxide utilization under mild conditions. *Dalton Trans.* **2010**, *39*, 3347.

A. M. Appel et al.: Frontiers, opportunities, and challenges in biochemical and chemical catalysis of CO_2 fixation. *Chem. Rev.* **2013**, *113*, 6621.

S. W. Ragsdale et al.: Metal centers in the anaerobic microbial metabolism of CO and CO_2. *Metallomics* **2011**, *3*, 797.

Cyclometallated complexes for fluorescence and sensors

J. A. G. Williams: The coordination chemistry of dipyridylbenzene: N-deficient terpyridine or panacea for brightly luminescent metal complexes? *Chem. Soc. Rev.* **2009**, *38*, 1783.

Q. Zhao, F. Li, C. Huang: Phosphorescent chemosensors based on heavy metal complexes. *Chem. Soc. Rev.* **2010**, *39*, 3007.

Y. Chi, P.-T. Chou: Transition-metal phosphors with cyclometalating ligands: Fundamentals and applications. *Chem. Soc. Rev.* **2010**, *39*, 638.

V. W.-W. Yam, K. M.-C. Wong: Luminescent metal complexes of d^6, d^8 and d^{10} transition metal centres. *Chem. Commun.* **2011**, *47*, 11579.

Y. You, W. Nam: Photofunctional triplet excited states of cyclometalated Ir(III) complexes: Beyond electroluminescence. *Chem. Soc. Rev.* **2012**, *41*, 7061.

J. J. Chruma et al.: Near-infrared phosphorescence: Materials and applications. *Chem. Soc. Rev.* **2013**, *42*, 6128.

F. Li et al.: A non-emissive iridium(III) complex that specifically lights-up the nuclei of living cells. *J. Am. Chem. Soc.* **2011**, *133*, 11231–11239.

M. R. Bryce et al.: Dinuclear iridium(III) complexes of cyclometallated fluorenylpyridine ligands as phosphorescent dopants for efficient solution-processed OLEDs. *J. Mater. Chem.* **2012**, *22*, 13529.

W.-Y. Wong, C.-L. Ho: Functional metallophors for effective charge carrier injection/transport: New robust OLED materials with emerging applications. *J. Mater. Chem.* **2009**, *19*, 4457.

Chapter 2.12

COMC II: A. F. Hill: Mononuclear Complexes of Ruthenium and Osmium Containing η^1-Carbon Ligands. Vol. 7, Section 6.2.

R. R. Schrock: Multiple metal–carbon bonds for catalytic metathesis reactions (Nobel lecture). *Angew. Chem. Int. Ed.* **2006**, *45*, 3748.

R. H. Grubbs: Olefin-metathesis catalysts for the preparation of molecules and materials (Nobel lecture). *Angew. Chem. Int. Ed.* **2006**, *45*, 3760.

R. H. Grubbs (ed.): *The Handbook of Metathesis.* Wiley-VCH, Weinheim, 2003.

R. R. Schrock: High oxidation state multiple metal–carbon bonds. *Chem. Rev.* **2002**, *102*, 145.

G. C. Vougioukalakis, R. H. Grubbs: Ruthenium-based heterocyclic carbene-coordinated olefin metathesis catalysts. *Chem. Rev.* **2010**, *110*, 1746.

S. Sutthasupa et al.: Recent advances in ring-opening metathesis polymerization, and application to the synthesis of functional materials. *Polymer J.* **2010**, *42*, 905.

H. Fischer et al.: Bis(allenylidene) complexes of palladium and platinum. *Organometallics* **2010**, *29*, 5154.

H. Fischer et al.: A simple approach to room temperature phosphorescent allenylidene complexes. *Angew. Chem. Int. Ed.* **2012**, *51*, 8030.

J. Heppekausen, A. Fürstner: Rendering Schrock-type molybdenum alkylidene complexes air stable: User-friendly pre-catalysts for alkene metathesis. *Angew. Chem. Int. Ed.* **2011**, *50*, 7829.

A. H. Hoveyda et al.: Readily accessible and easily modifiable Ru-based catalysts for efficient and *Z*-selective ring-opening metathesis polymerization and ring-opening/cross-metathesis. *J. Am. Chem. Soc.* **2013**, *135*, 10258.

S. J. Meek et al.: Catalytic *Z*-selective olefin cross-metathesis for natural product synthesis. *Nature* 2011 *471*, 461.

R. R. Schrock et al.: Synthesis and ROMP chemistry of decafluoroterphenoxide molybdenum imido alkylidene and ethylene complexes. *Organometallics* **2013**, *32*, 2983.

C. Bolm et al.: Ring closing enyne metathesis: A powerful tool for the synthesis of heterocycles. *Chem. Soc. Rev.* **2007**, *36*, 55.

S. Kotha et al.: Advanced approach to polycyclics by a synergistic combination of enyne metathesis and Diels–Alder reaction. *Chem. Soc. Rev.* **2009**, *38*, 2065.

S. Monsaert et al.: Latent olefin metathesis catalysts. *Chem. Soc. Rev.* **2009**, *38*, 3360.

S. Kress, S. Blechert: Asymmetric catalysts for stereocontrolled olefin metathesis reactions. *Chem. Soc. Rev.* **2012**, *41*, 4389.

D. Gillingham, N. Fei: Catalytic X–H insertion reactions based on carbenoids. *Chem. Soc. Rev.* **2013**, *42*, 4918.

Chapter 3.1

B. Cornils, W. A. Herrmann: *Applied Homogeneous Catalysis with Organometallic Compounds. Volume 1: Applications.* VCH, Weinheim, 1996.

C. Bolm et al.: Trace metal impurities in catalysis. *Chem. Soc. Rev.* **2012**, *41*, 979.

M. Gómez-Gallego, M. A. Sierra: Kinetic isotope effects in the study of organometallic reaction mechanisms. *Chem. Rev.* **2011**, *111*, 4857.

Y. Kuninobu, K. Takai: Organic reactions catalyzed by rhenium carbonyl complexes. *Chem. Rev.* **2011**, *111*, 1938.

N. Selander, K. J. Szabó: Catalysis by palladium pincer complexes. *Chem. Rev.* **2011**, *111*, 2048.

P. W. N. M. van Leeuwen et al.: Phosphite-containing ligands for asymmetric catalysis. *Chem. Rev.* **2011**, *111*, 2077.

A. Vidal-Ferran et al.: Phosphine–phosphinite and phosphine–phosphite ligands: Preparation and applications in asymmetric catalysis. *Chem. Rev.* **2011**, *111*, 2119.

F. E. Kühn et al.: Synthesis and application of water-soluble NHC transition-metal complexes. *Angew. Chem. Int. Ed.* **2013**, *52*, 270.

Section 3.3.1

R. H. Morris: Asymmetric hydrogenation, transfer hydrogenation and hydrosilylation of ketones catalysed by iron complexes. *Chem. Soc. Rev.* **2009**, *38*, 2282.

M. Beller et al.: Well-defined iron catalyst for improved hydrogenation of carbon dioxide and bicarbonate. *J. Am. Chem. Soc.* **2012**, *134*, 20701.

A. M. Smith, R. Whyman: Review of methods for the catalytic hydrogenation of carboxamides. *Chem. Rev.* **2014**, *114*, 5477.

Section 3.3.1.3

W. S. Knowles: Asymmetric hydrogenations (Nobel lecture). *Angew. Chem. Int. Ed.* **2002**, *41*, 1998.

R. Noyori: Asymmetric catalysis: Science and opportunities (Nobel lecture). *Angew. Chem. Int. Ed.* **2002**, *41*, 2008.

R. Noyori: Facts are the enemy of truth—reflections on serendipitous discovery and unforeseen developments in asymmetric catalysis. *Angew. Chem. Int. Ed.* **2013**, *52*, 79.

X. Cui, K. Burgess: Catalytic homogeneous asymmetric hydrogenations of largely unfunctionalized alkenes. *Chem. Rev.* **2005**, *105*, 3272.

Y. Zhu, K. Burgess: Filling gaps in asymmetric hydrogenation methods for acyclic stereocontrol: Application to chirons for polyketide-derived natural products. *Acc. Chem. Res.* **2012**, *45*, 1623.

A. Pfaltz et al.: Iridium-catalysed asymmetric hydrogenation of unfunctionalized tetrasubstituted olefins. *Angew. Chem. Int. Ed.* **2007**, *46*, 8274.

A. Pfaltz et al.: Asymmetric hydrogenation of unfunctionalized, purely alkyl-substituted olefins. *Science* **2006**, *311*, 642.

G. Erre et al.: Synthesis and application of chiral monodentate phosphines in asymmetric hydrogenation. *Coord. Chem. Rev.* **2008**, *252*, 471.

M. M. Pereira et al.: Synthesis of binaphthyl based phosphine and phosphite ligands. *Chem. Soc. Rev.* **2013**, *42*, 6990.

Y.-G. Zhou et al.: Homogeneous palladium-catalysed asymmetric hydrogenation. *Chem. Soc. Rev.* **2013**, *42*, 497.

P. Etayo, A. Vidal-Ferran: Rhodium-catalysed asymmetric hydrogenation as a valuable synthetic tool for the preparation of chiral drugs. *Chem. Soc. Rev.* **2013**, *42*, 728.

D. J. Ager et al.: Asymmetric homogeneous hydrogenations at scale. *Chem. Soc. Rev.* **2012**, *41*, 3340.

J. J. Verendel et al.: Asymmetric hydrogenation of olefins using chiral Crabtree-type catalysts: Scope and limitations. *Chem. Rev.* **2014**, *114*, 2130.

Section 3.3.1.4

A. Boddien et al.: Efficient dehydrogenation of formic acid using an iron catalyst. *Science* **2011**, *333*, 1733.

M. Beller et al.: Towards a green process for bulk-scale synthesis of ethyl acetate: Efficient acceptorless dehydrogenation of ethanol. *Angew. Chem. Int. Ed.* **2012**, *51*, 5711.

Section 3.3.2

P. J. Chirik et al.: Iron catalysts for selective anti-Markovnikov alkene hydrosilylation using tertiary silanes. *Science* **2012**, *335*, 567.

M. Wills et al.: Hydrogen generation from formic acid and alcohols using homogeneous catalysts. *Chem. Soc. Rev.* **2010**, *39*, 81.

Section 3.3.3

D. Quinzler, S. Mecking: Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306.

N. Phadke, M. Findlater: Formation of iridium(III) allene complexes via isomerization of internal alkynes. *Organometallics* **2014**, *33*, 16.

M. Beller et al.: Synthesis of heterocycles via palladium-catalyzed carbonylations. *Chem. Rev.* **2013**, *113*, 1.

Section 3.3.5

R. Severin, S. Doye: The catalytic hydroamination of alkynes. *Chem. Soc. Rev.* **2007**, *36*, 1407.

Chapter 3.4

B. Cornils, W. A. Herrmann: *Applied Homogeneous Catalysis with Organometallic Compounds. Volume 1: Applications.* VCH, Weinheim, **1996**, ch. 2, p. 27ff.

H.-W. Bohnen, B. Cornils: Hydroformylation of alkenes: An industrial view of the status and importance. *Adv. Catal.* **2002**, *47*, 1.

M. L. Clarke: Branched selective hydroformylation: A useful tool for organic synthesis. *Curr. Org. Chem.* **2005**, *9*, 701.

R. Franke et al.: Applied hydroformylation. *Chem. Rev.* **2012**, *112*, 5675.

A. Haynes: Catalytic methanol carbonylation. *Adv. Catal.* **2010**, *53*, 1.

R. V. Chaudhari: Homogeneous catalytic carbonylation and hydroformylation for synthesis of industrial chemicals. *Top. Catal.* **2012**, *55*, 439.

A. Nakamura et al.: *o*-Phosphinobenzenesulfonate: A superb ligand for palladium-catalyzed coordination-insertion copolymerization of polar vinyl monomers. *Acc. Chem. Res.* **2013**, *46*, 1438.

Chapter 3.5

S. S. Stahl et al.: Palladium(II)-catalyzed alkene functionalization via nucleopalladation: Stereochemical pathways and enantioselective catalytic applications. *Chem. Rev.* **2011**, *111*, 2981.

Chapter 3.6

A. Suzuki: Cross-coupling reactions of organoboranes: An easy way to construct C–C bonds (Nobel lecture). *Angew. Chem. Int. Ed.* **2011**, *50*, 6722.

E. Negishi: Magical power of transition metals: Past, present, and future (Nobel lecture). *Angew. Chem. Int. Ed.* **2011**, *50*, 6738.

T. J. Colacot et al.: Palladium-catalyzed cross-coupling: A historical contextual perspective to the 2010 Nobel Prize. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062.

T. J. Colacot et al.: Development of preformed Pd catalysts for cross-coupling reactions, beyond the 2010 Nobel Prize. *ACS Catal.* **2012**, *2*, 1147.

D. R. Stuart, K. Fagnou: The catalytic cross-coupling of unactivated arenes. *Science* **2007**, *316*, 1172.

A. Molnár: Efficient, selective, and recyclable palladium catalysts in carbon–carbon coupling reactions. *Chem. Rev.* **2011**, *111*, 2251.

P. W. N. M. van Leeuwen et al.: Bite angle effects of diphosphines in C–C and C–X bond forming cross-coupling reactions. *Chem. Soc. Rev.* **2009**, *38*, 1099.

C. A. Fleckenstein, H. Plenio: Sterically demanding trialkylphosphines for palladium-catalysed cross-coupling reactions—alternatives to PBu^t_3. *Chem. Soc. Rev.* **2010**, *39*, 694.

A. J. J. Lennox, G. C. Lloyd-Jones: Selection of boron reagents for Suzuki–Miyaura coupling. *Chem. Soc. Rev.* **2014**, *43*, 412.

V. B. Phapale, D. J. Cárdenas: Nickel-catalysed Negishi cross-coupling reactions: Scope and mechanisms. *Chem. Soc. Rev.* **2009**, *38*, 1598.

B. M. Rosen et al.: Nickel-catalyzed cross-couplings involving carbon–oxygen bonds. *Chem. Rev.* **2011**, *111*, 1346.

C. Amatore et al.: The triple role of fluoride ions in palladium-catalyzed Suzuki–Miyaura reactions. *Angew. Chem. Int. Ed.* **2012**, *51*, 1379.

L.-C. Campeau, K Fagnou: Applications of and alternatives to π-electron-deficient azine organometallics in metal catalyzed cross-coupling reactions. *Chem. Soc. Rev.* **2007**, *36*, 1058.

A. Minatti, K. Muñiz: Intramolecular aminopalladation of alkenes as a key step to pyrrolidines and related heterocycles. *Chem. Soc. Rev.* **2007**, *36*, 1142.

C. Bruneau et al.: Activation and functionalization of benzylic derivatives by palladium catalysts. *Chem. Soc. Rev.* **2008**, *37*, 290.

M. Carril et al.: Palladium and copper-catalysed arylation reactions in the presence of water, with a focus on carbon–heteroatom bond formation. *Chem. Soc. Rev.* **2008**, *37*, 639.

G. P. McGlacken, L. M. Bateman: Recent advances in aryl–aryl bond formation by direct arylation. *Chem. Soc. Rev.* **2009**, *38*, 2447.

J. A. Ashenhurst: Intermolecular oxidative cross-coupling of arenes. *Chem. Soc. Rev.* **2010**, *39*, 540.

R. Jana et al.: Advances in transition metal (Pd,Ni,Fe)-catalyzed cross-coupling reactions using alkyl-organometallics as reaction partners. *Chem. Rev.* **2011**, *111*, 1417.

Y. Yamamoto: Synthesis of heterocycles *via* transition-metal-catalysed hydroarylation of alkynes. *Chem. Soc. Rev.* **2014**, *43*, 1575.

Y. Luo et al.: Double carbometallation of alkynes: An efficient strategy for the construction of polycycles. *Chem. Soc. Rev.* **2014**, *43*, 834.

M.-L. Louillat, F. W. Patureau: Oxidative C–H amination reactions. *Chem. Soc. Rev.* **2014**, *43*, 901.

F.-S. Han: Transition-metal-catalysed Suzuki–Miyaura cross-coupling reactions: A remarkable advance from palladium to nickel catalysts. *Chem. Soc. Rev.* **2013**, *42*, 5270.

X. Shang, Z.-Q. Liu: Transition metal-catalysed C_{vinyl}–C_{vinyl} bond formation *via* double C_{vinyl}–H bond activation. *Chem. Soc. Rev.* **2013**, *42*, 3253.

D. R. Spring et al.: Palladium-catalysed cross-coupling of organosilicon reagents. *Chem. Soc. Rev.* **2012**, *41*, 1845.

G. Song et al.: C–C, C–O and C–N bond formation *via* rhodium(III)-catalysed oxidative C–H activation. *Chem. Soc. Rev.* **2012**, *41*, 3651.

B. Li, P. H. Dixneuf: sp^2 C–H bond activation in water and catalytic cross-coupling reactions. *Chem. Soc. Rev.* **2013**, *42*, 5744.

J. Magano, J. R. Dunetz: Large-scale applications of transition metal-catalyzed couplings for the synthesis of pharmaceuticals. *Chem. Rev.* **2011**, *111*, 2177.

Section 3.6.4

J. Le Bras, J. Muzart: Intermolecular dehydrogenative Heck reactions. *Chem. Rev.* **2011**, *111*, 1170.

C. S. Yeung, V. M. Dong: Catalytic dehydrogenative cross-coupling: Forming carbon–carbon bonds by oxidizing two carbon–hydrogen bonds. *Chem. Rev.* **2011**, *111*, 1215.

Section 3.7.1

COMC I: P. D. Gavens et al.: Ziegler–Natta Catalysis. Vol. 3, ch. 22.5, p. 476.

Section 3.7.2

COMC III: L. Resconi, J. C. Chadwick, L. Cavallo: Olefin Polymerizations with Group IV Metal Catalysts. Vol. 4, ch. 4.09, p. 1006.

COMC III: T. Fujita, H. Makio: Polymerization of Alkenes. Vol. 11, ch. 11.20, p. 692.

M. Bochmann: The chemistry of catalyst activation: The case of Group 4 polymerization catalysts. *Organometallics* **2010**, *29*, 4711.

F. Ghiotto et al.: Probing the structure of methylalumoxane (MAO) by a combined chemical, spectroscopic, neutron scattering and computational approach. *Organometallics* **2013**, *32*, 3354.

H. Makio et al.: FI catalysts for olefin polymerization—a comprehensive treatment. *Chem. Rev.* **2011**, *111*, 2363.

K. Bryliakov, E. P. Talsi: Frontiers of mechanistic studies of coordination polymerization and oligomerization of alpha-olefins. *Coord. Chem. Rev.* **2012**, *256*, 2994.

J. R. Severn et al.: 'Bound but not gagged' —immobilizing single-site α-olefin polymerization catalysts. *Chem. Rev.* **2005**, *105*, 4073.

F. Ghiotto et al.: Rapid evaluation of catalysts and MAO activators by kinetics: What controls polymer molecular weight and activity in metallocene / MAO catalysts? *Dalton Trans.* **2013**, *42*, 9040.

D. H. Camacho, Z. Guan: Designing late-transition metal catalysts for olefin insertion polymerization and copolymerization. *Chem. Commun.* **2010**, *46*, 7879.

T. Matsugi, T. Fujita: High-performance olefin polymerization catalysts discovered on the basis of a new catalyst design concept. *Chem. Soc. Rev.* **2008**, *37*, 1264.

M. Delferro, T. J. Marks: Multinuclear olefin polymerization catalysts. *Chem. Rev.* **2011**, *111*, 2450.

C. Redshaw, Y. Tang: Tridentate ligands and beyond in group IV metal α-olefin homo-/co-polymerization catalysis. *Chem. Soc. Rev.* **2012**, *41*, 4484.

K. Nomura, S. Zhang: Design of vanadium complex catalysts for precise olefin polymerization. *Chem. Rev.* **2011**, *111*, 2342.

A. Valente et al.: Coordinative chain transfer polymerization. *Chem. Rev.* **2013**, *113*, 3836.

Section 3.7.3

S. Tobisch, T. Ziegler: Catalytic linear oligomerization of ethylene to higher α-olefins: Insight into the origin of the selective generation of 1-hexene promoted by a cationic cyclopentadienyl-arene titanium active catalyst. *Organometallics* **2003**, *22*, 5392.

T. Agapie: Selective ethylene oligomerization: Recent advances in chromium catalysis and mechanistic investigations. *Coord. Chem. Rev.* **2011**, *255*, 861.

D. S. McGuinness: Olefin oligomerization via metallacycles: Dimerization, trimerization, tetramerization, and beyond. *Chem. Rev.* **2011**, *111*, 2321.

Index