

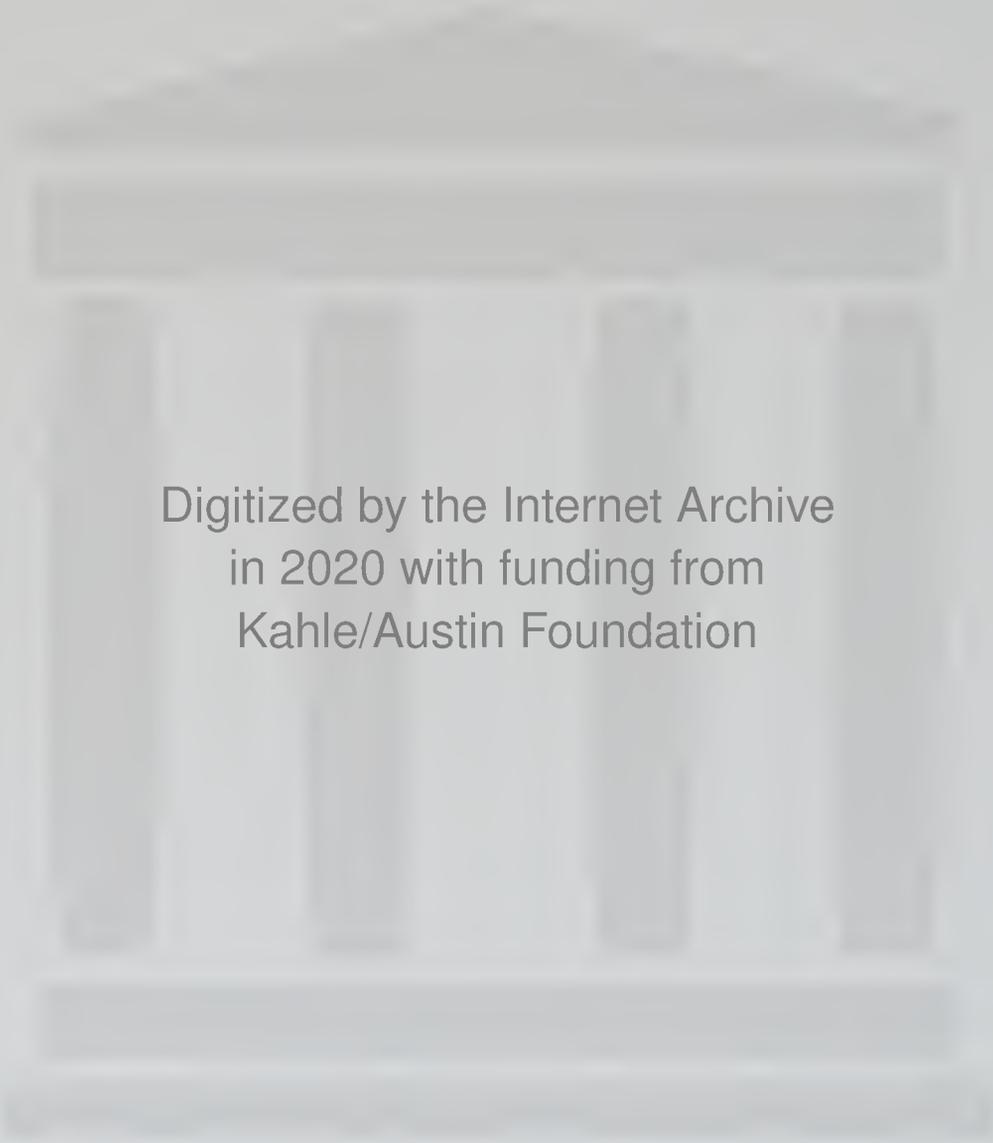
Ch. Elschenbroich, A. Salzer

Organometallics

A Concise Introduction



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Ch. Elschenbroich, A. Salzer

Organometallics



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Christoph Elschenbroich
Albrecht Sälzer

Organometallics

A Concise Introduction



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Preface

The present volume is the translation of the Second Edition (1988) of our text “Organometallchemie – Eine kurze Einführung”; corrections and a few results of very recent origin were included but otherwise the body was left unchanged.

Can a 500 page treatise on a branch of chemistry still be called “concise”? On the other hand, a section of only 20 pages covering transition-metal olefin complexes certainly must be regarded as short. This contrast illustrates the dilemma encountered if one sets out to portray the whole of organometallic chemistry in a single volume of tolerable size. The book developed from an introductory course (one semester, about 30 lectures) on organometallic chemistry for students confronted with the field for the first time. The material covered is a mixture of indispensable basic facts and selected results of most recent vintage. Attempts to systematize organometallic chemistry by relating molecular structures to the number and nature of the valence electrons are presented as are applications of organometallics in organic synthesis and in industrial processes based on homogeneous catalysis.

An apparent omission is the absence of a chapter specifically dealing with organometallic reaction mechanisms. It is our contention, however, that mechanistic organometallic chemistry has not yet reached the stage which would warrant a short overview form which useful generalizations could be drawn by the beginner. Note, for example, that even reactions as fundamental as metal carbonyl substitution are currently under active investigation, the intermediacy of 17 or 19 valence electron species opening up new possible pathways. Interspersed within the text, however, the reader finds several comments and mechanistic proposals ranging from well established kinetic studies to catalysis loops which at times have more the character of mnemotechnic devices than of kinetic schemes based on experimental evidence. Detailed mechanistic considerations should be deferred to the second act of the study of organometallic chemistry and several textbooks, mainly concentrating on organotransition metal compounds, offer a wealth of material with which to pursue this goal.

We have structured the text in the traditional way – following the periodic table for main-group element organometallics and according to the nature of the ligand for transition-metal complexes – which we find most suitable for an introduction. Apart from the Chapters 16 and 17 (Metal-metal bonds, clusters, catalysis) somewhat more specialized material is presented in sections called “Excursions”. Rigorous scientific referencing would be inappropriate in a text of the present scope. At the end, a literature survey (300 odd entries) is given which leads the reader to important review articles and key papers, including several classics in the field. Furthermore, in the running text authors names are linked to the facts described whereby the form (Author, year) designates the year of the discovery, usually in a short communication, and the form (Author, year R) the appearance of the respective full paper or review. The complete citation can

then be easily retrieved via consultation of Chemical Abstracts. A desired side-effect is to familiarize the student with author's names and their fields of endeavor. The many coworkers, who actually did the work, may forgive us that only the name of the respective boss is given.

Among our own coworkers who helped to bring this English Edition to completion, the native speakers Pamela Alean (Great Britain, now a resident of Zürich, Switzerland) and James Hurley (USA; resident of Marburg, Germany) stand out. They went a long way to eliminate our worst excesses of "Gerglish". The bulk of the structural formulae was drawn by one of the authors (A.S.) thereby keeping things in the right perspective and making the book easy to use. Monika Scheld, Marburg, helped with the preparation of the indexes and by checking the cross references. We are grateful to the editor Dr. Michael Weller and the production manager Bernhard Riedl (both of VCH Publishers) for a pleasant form of cooperation and their toleration of several last-minute changes. Finally, the authors mutually acknowledge their unflagging support during the various stages of the enterprise.

Ch. Elschenbroich
Marburg
Germany

March
1989

A. Salzer
Zürich
Switzerland

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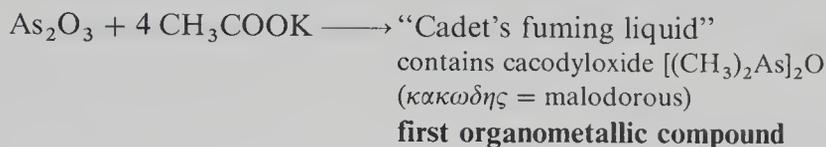
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Introduction

1 Historical Development and Current Trends in Organometallic Chemistry

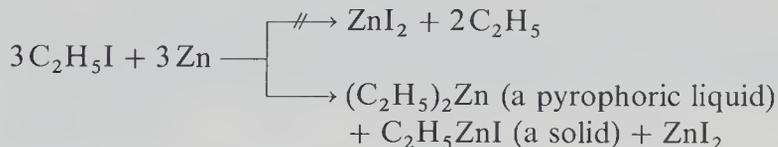
1760 The cradle of organometallic chemistry is a Paris military pharmacy. It is there that Cadet works on sympathetic inks based on cobalt salts. For their preparation, he uses cobalt minerals which contain arsenic.



1827 Zeise’s salt $\text{Na}[\text{PtCl}_3\text{C}_2\text{H}_4]$, **first olefin complex**

1840 R. W. Bunsen continues the study of cacodyl compounds which he names “alkarsines”. The weakness of the As–As bond in molecules of the type $\text{R}_2\text{As} - \text{AsR}_2$ led to a profusion of derivatives like $(\text{CH}_3)_2\text{AsCN}$ whose taste (!) is checked by Bunsen.

1849 E. Frankland, student of Bunsen’s at Marburg, attempts the preparation of an “ethyl radical” (cacodyl as well was taken to be a radical).



Frankland possesses admirable skill in the manipulation of air-sensitive compounds. As a protective atmosphere he uses hydrogen gas!

1852 Frankland prepares the important alkylmercury compounds:



additionally: $(\text{C}_2\text{H}_5)_4\text{Sn}$, $(\text{CH}_3)_3\text{B}$ (1860).

In the following years, **alkyl transfer reactions** using R_2Hg and R_2Zn serve in the synthesis of numerous main-group organometallics.

Frankland also introduced the concept of valency (“combining power”) and the term organometallic.

1852 K. J. König and M. E. Schweizer in Zürich first prepare $(\text{C}_2\text{H}_5)_4\text{Pb}$ from ethyl-iodide and Na/Pb alloy. In a similar manner, they also obtain $(\text{C}_2\text{H}_5)_3\text{Sb}$ and $(\text{C}_2\text{H}_5)_3\text{Bi}$.

1859 W. Hallwachs and A. Schafarik generate alkylaluminum iodides:



1863 C. Friedel and J. M. Crafts prepare **organochlorosilanes**:



1866 J. A. Wanklyn develops a method for the synthesis of halide-free magnesium alkyls:



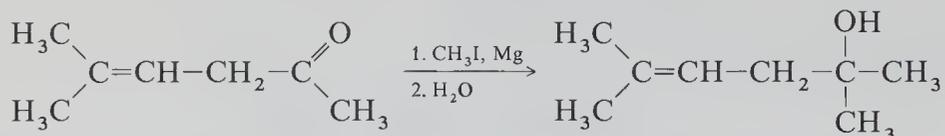
1868 M. P. Schützenberger obtains $[\text{Pt}(\text{CO})\text{Cl}_2]_2$, **first metal carbonyl complex**.

1871 D. I. Mendeleev uses organometallic compounds as test cases for his periodic table. Example:

Known:	predicted:	found:	
$\text{Si}(\text{C}_2\text{H}_5)_4$	Eka-Si(C_2H_5) ₄	$\text{Ge}(\text{C}_2\text{H}_5)_4$	(C. Winkler, 1887)
	$d = 0.96$	$d = 0.99$	
$\text{Sn}(\text{C}_2\text{H}_5)_4$	bp: 160°C	bp: 163.5°C	

1890 L. Mond: $\text{Ni}(\text{CO})_4$, **first binary metal carbonyl**, used in a commercial process for refining nickel. Mond is the founder of the English company ICI (Imperial Chemical Industries) as well as a renowned collector and patron of the arts.

1899 P. Barbier replaces Mg for Zn in reactions with alkyl iodides:



explored in more detail by Barbier's student V. Grignard (Nobel prize 1912 shared with P. Sabatier). Although less sensitive than ZnR_2 , RMgX is a more potent alkyl group transfer reagent.

1901 L. F. S. Kipping prepares $(\text{C}_6\text{H}_5)_2\text{SiO}$, suspects its high molecularity, and calls the material **diphenylsilicone**.

1909 W. J. Pope: formation of $(\text{CH}_3)_3\text{PtI}$, **first σ -organotransition-metal compound**.

1909 P. Ehrlich (inventor of chemotherapy, Nobel prize 1908) introduces Salvarsan for the treatment of syphilis.

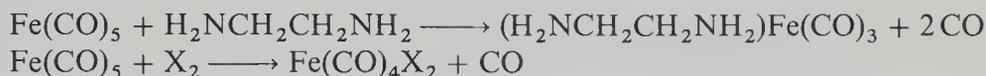
1917 W. Schlenk: Lithium alkyls via transalkylation.



1919 F. Hein from CrCl_3 and PhMgBr synthesizes polyphenylchromium compounds, now known to be sandwich complexes.

1922 T. Midgley and T. A. Boyd introduce $\text{Pb}(\text{C}_2\text{H}_5)_4$ as an antiknock additive in gasoline.

1928 W. Hieber inaugurates his systematic study of metal carbonyls:



1929 F. A. Paneth generates alkyl radicals through PbR_4 pyrolysis, radical identification by means of their ability to cause the transport of a metallic mirror. Paneth thus reaches a goal set by Frankland in 1849.

1930 K. Ziegler encourages more extensive use of organolithium compounds in synthesis by developing a simpler way of preparation.



1931 W. Hieber prepares $\text{Fe}(\text{CO})_4\text{H}_2$, **first transition-metal hydride complex**.

1938 O. Roelen discovers **hydroformylation** (the oxo process).

1939 W. Reppe starts work on the transition-metal catalyzed reactions of acetylenes.

1943 E. G. Rochow: $2\text{CH}_3\text{Cl} + \text{Si} \xrightarrow{\text{Cu-cat., } 300^\circ\text{C}} (\text{CH}_3)_2\text{SiCl}_2 + \dots$

This "direct synthesis" triggers large scale production and use of **silicones**. Preliminary work by R. Müller (Radebeul near Dresden) was interrupted by the Second World War.

1951 P. Pauson (GB) and S. A. Miller (USA) obtain ferrocene $(\text{C}_5\text{H}_5)_2\text{Fe}$, **first sandwich complex**.

1953 G. Wittig discovers the reaction bearing his name.

1955 E. O. Fischer: rational synthesis of bis(benzene)chromium $(\text{C}_6\text{H}_6)_2\text{Cr}$.

1955 K. Ziegler, G. Natta: **polyolefins** from ethylene and propylene, respectively, in a **low pressure process** employing mixed metal catalysts (transition-metal halide/ AlR_3).

1956 H. C. Brown: **hydroboration**.

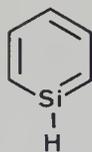
1959 J. Smidt, W. Hafner: preparation of $[(\text{C}_3\text{H}_5)\text{PdCl}]_2$, installation of the field of π -allyl transition-metal complexes.

- 1959 R. Criegee: stabilization of cyclobutadiene by complexation in $[(C_4Me_4)NiCl_2]_2$ verifying a prediction by H. C. Longuet-Higgins and L. Orgel (1956).
- 1960 M. F. Hawthorne: **carboranes**.
- 1961 L. Vaska: $(PPh_3)_2Ir(CO)Cl$ reversibly binds O_2 .
- 1963 Nobel prize to K. Ziegler and G. Natta.
- 1964 E. O. Fischer: $(CO)_5WC(OMe)Me$, first **carbene complex**.
- 1965 G. Wilkinson, R. S. Coffey: $(PPh_3)_3RhCl$ acts as a homogeneous catalyst in the hydrogenation of alkenes.
- 1968 A. Streitwieser: preparation of uranocene, $(C_8H_8)_2U$.
- 1969 P. L. Timms: synthesis of organotransition-metal complexes by means of metal-atom ligand-vapor cocondensation.
- 1970 G. Wilkinson: kinetically inert transition-metal alkyls through blockage of β -elimination.
- 1972 H. Werner: $[(C_5H_5)_3Ni_2]^+$, first **triple-decker sandwich complex**.
- 1973 E. O. Fischer: $I(CO)_4Cr(CR)$, first **carbyne complex**.
- 1973 Nobel prize to E. O. Fischer and G. Wilkinson.
- 1976 Nobel prize to W. N. Lipscomb: theoretical and experimental clarification of structure and bonding in boranes.
- 1979 Nobel prize to H. C. Brown and G. Wittig: applications of organoboranes and methylenephosphoranes, respectively, in organic synthesis.
- 1981 R. West: $(1,3,5-Me_3C_6H_2)_4Si_2$, first stable compound with a $\diagdown Si = Si \diagup$ **double bond**.
- 1981 Nobel prize to R. Hoffmann and K. Fukui: semiempirical MO-concepts in a unified discussion of structure and reactivity of inorganic, organic and organometallic molecules, **isobal analogies**.
- 1983 R. G. Bergman, W. A. G. Graham: intermolecular reactions of organotransition-metal compounds with alkanes (**C–H activation**).

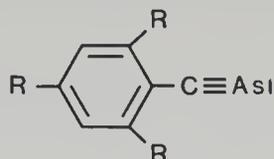
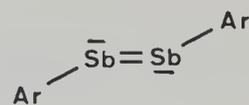
Current Trends

① Participation of higher main-group elements in $p_\pi-p_\pi$ multiple bonds

Examples:

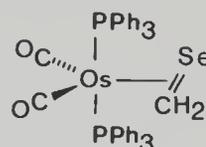
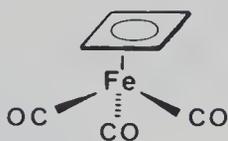


Silene, accessible in the gasphase and in matrix isolation

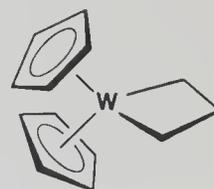
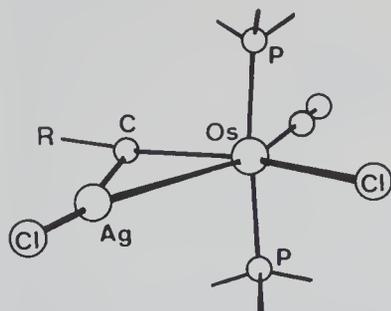
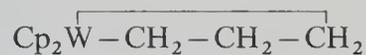
Arsaalkyne
R = *t*-BuDistibene
Ar = 1,3,5-*t*-Bu₃C₆H₂

② Stabilization of highly reactive species by metal coordination

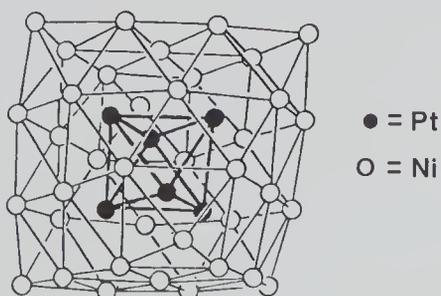
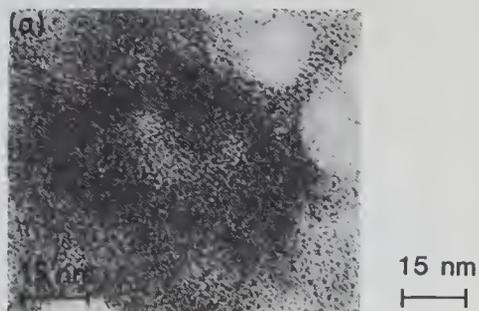
Examples: cyclobutadiene, aryne, carbyne, thiocarbonyl, selenoformaldehyde.



③ Metallacycles

Examples: $(\text{AgCl})(\text{CR})\text{Os}(\text{CO})(\text{PR}_3)_2\text{Cl}$ 

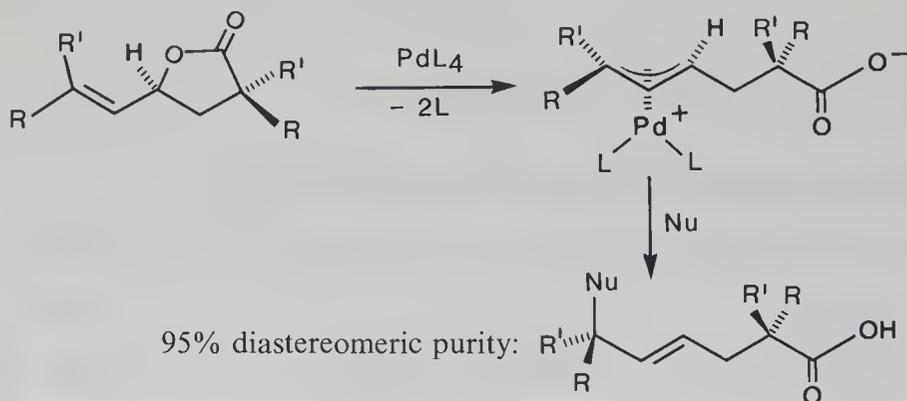
④ Study of organometallic clusters

Example: $[\text{Me}_3\text{NCH}_2\text{Ph}]_5[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}]$ Metal skeleton of the cluster anion
(X-ray diffraction)Electron micrograph
of the supported material

⑤ Catalysis via organometallic intermediates

Examples of *industrial processes*: technical improvements in the hydroformylation reaction (oxo process), developments in the areas of Fischer-Tropsch chemistry, alkene metathesis and C–H activation.

Example of an *organic synthesis*: PdL₄-catalyzed enantioselective allylic alkylation (transfer of chirality).



⑤ profits from fundamental work carried out on the topics ②–④.

Production figures of organometallic compounds:

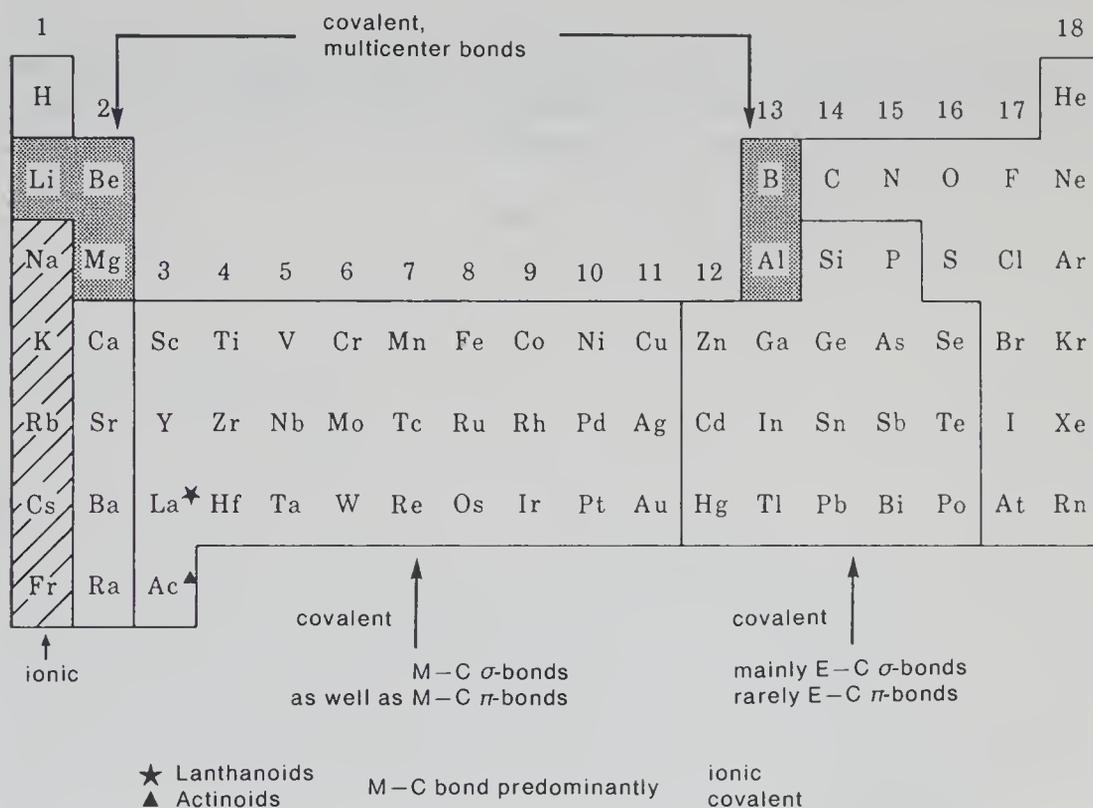
1. Silicones	700 000 t/a
2. Pb-alkyls	600 000 t/a (declining)
3. Organo-Al	50 000 t/a
4. Organo-Sn	35 000 t/a
5. Organo-Li	900 t/a

Even more impressive than the figures for main-group organometallics is the volume of organic intermediates and of polymers which are produced through the use of organo-transition-metal catalysis:

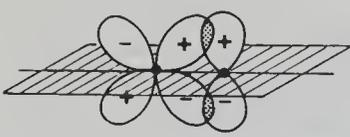
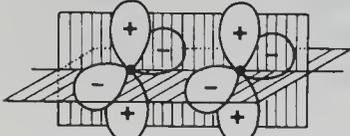
1. Polypropylene	7.7×10^6 t/a
2. "Oxo products"	5.0×10^6 t/a
3. Acetaldehyde	2.2×10^6 t/a
4. Acetic acid	1.0×10^6 t/a

2 Demarcation and Classification of Organometallic Compounds

Organometallic compounds (metal organyls, organometallics) are defined as materials which possess direct, more or less polar bonds $M^{\delta+} - C^{\delta-}$ between metal and carbon atoms. In many respects, the organic chemistry of the elements B, Si, P and As resembles the chemistry of the respective metallic homologues. Therefore, the term organoelement compounds is used occasionally in order to include for consideration the aforementioned non- and semi-metals. A convenient classification of organometallics is based on the bond type:



The designation σ -, π -, δ -bond is defined as follows:

Overlap	Number of nodal Planes including the Bond Axis	Bond Type	Example
	0	σ	$\text{B}-\text{CH}_3$
	1	π	$(\text{CO})_5\text{Cr}=\text{CR}_2$
	2	δ	$[\text{R}_4\text{Re}\equiv\text{ReR}_4]^{2-}$

In evaluations of bond polarity, the electronegativity difference between the neighboring atoms is usually employed. The electronegativity values in table 2-1 are based on Pauling's thermochemical method of determination:

Table 2-1: Electronegativity values according to Pauling

H																					
2.2																					
Li	Be																B	C	N	O	F
1.0	1.6																2.0	2.5	3.0	3.4	4.0
Na	Mg																Al	Si	P	S	Cl
0.9	1.3																1.6	1.9	2.2	2.6	3.1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br					
0.8	1.0	1.3	1.5	1.6	1.6	1.6	1.8	1.9	1.9	1.9	1.7	1.8	2.0	2.2	2.6	2.9					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I					
0.8	1.0	1.2	1.3	1.6	2.1	1.9	2.2	2.3	2.2	1.9	1.7	1.8	1.8	2.0	2.1	2.6					
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At					
0.8	0.9	1.1	1.3	1.5	2.3	1.9	2.2	2.2	2.3	2.5	2.0	1.6	1.9	2.0	2.0	2.2					
					Lanthanoids:		1.1-1.3														
					Actinoids:		1.1-1.3														

Source: L. Pauling, *The Nature of the Chemical Bond*, 3. Ed., Ithaca (1960); A. L. Allred, *J. Inorg. Nucl. Chem.* 17 (1961) 215.

In accordance with the similar electronegativities of carbon and hydrogen, the division ionic/covalent of organoelement compounds bears a strong resemblance to the classification of element hydrides.

Contrary to the element hydrides, however, the dependence of the electronegativity of carbon $EN(C)$ on the hybridization ratio has to be taken into account in organoelement compounds. Since s electrons are exposed to a stronger effective nuclear charge than p electrons of the same principal quantum number, $EN(C)$ increases with increasing s character in the hybrid: the value $EN(C_{sp^3}) = 2.5$ applies to sp^3 hybridized carbon, whereas for cases of higher s character the values $EN(C_{sp^2}) = 2.75$ and $EN(C_{sp}) = 3.29$ have been proposed (Bent, 1961). This gradation also reflects the increase in CH acidity according to $C_2H_6 < C_2H_4 \ll C_2H_2$ and suggests that the $M-C$ bond is considerably more polar in alkynylmetal complexes (p. 208) than in metal alkyls. Furthermore, it should not be overlooked that in compounds of the type L_nM-CR_3 , the electronegativity of the metal $EN(M)$ will be modified by the ligands L and the electronegativity of carbon $EN(C)$ by the groups R . A lucid discussion of the concept of electronegativity and its applications is found in J. E. Huheey, *Inorganic Chemistry – Principles of Structure and Reactivity*, New York: Harper and Row, 1982.

By way of generalization, it may be stated that the chemistry of main-group organometallics is governed by the group the metal belongs to, whereas for organotransition-metal compounds, the nature of the ligand dominates. Consequently, the material in chapters 4–11 is arranged in conformity with the periodic table, while that of chapters 12–15 is presented according to the types of ligand.

3 Energy, Polarity and Reactivity of the M–C Bond

In discussions of the properties of organometallics it is important to distinguish between **thermodynamic (stable, unstable)** and **kinetic (inert, labile)** factors.

M–C single bonds are encountered throughout the periodic table (examples: MgMe_2 , PMe_3 , MeBr , $[\text{LaMe}_6]^{3-}$, WMe_6). For organotransition-metal compounds special rules apply which are derived from the large number of valence orbitals and the higher tendency of transition-metal atoms to engage in multiple bonding (see chapter 16).

Typical M–C bond lengths d in pm and calculated covalent radii r for main-group elements, $r = d - r_{\text{carbon}} = d - 77$.

Group			Group			Group			Group		
2, 12			13			14			15		
<i>M</i>	<i>d</i>	<i>r</i>									
Be	179	102	B	156	79	C	154	77	N	147	70
Mg	219	142	Al	197	120	Si	188	111	P	187	110
Zn	196	119	Ga	198	121	Ge	195	118	As	196	119
Cd	211	134	In	223	146	Sn	217	140	Sb	212	135
Hg	210	133	Tl	225	148	Pb	224	147	Bi	226	149

Source: *Comprehensive Organometallic Chemistry (COMC) I* (1982) 10

3.1 Stability of Main-group Organometallics

Compared with the strengths of M–N, M–O and M–Hal bonds, **M–C bonds** must be deemed **weak**. This bond weakness is reflected in the uses that organometallics find in synthesis. Since standard entropies are seldom known for organometallic compounds, enthalpies of formation ΔH_f^0 are often used in place of free enthalpies of formation ΔG_f^0 , when evaluating thermodynamic stabilities. A decisive factor in the low ΔH_f^0 values of organometallics is the high bond energy of the constituent elements (M, C, H) in their respective standard states (see table 3-1).

A limitation in the use of mean bond enthalpies $\bar{E}(\text{M–C})$ when assessing the reactivity of organometallics is the fact that stepwise bond dissociation energies $D_{1,2,\dots,n}$ may deviate strongly from the mean value $\bar{E} = 1/n \sum_i^n D_i$. As an example dimethylmercury may be considered:

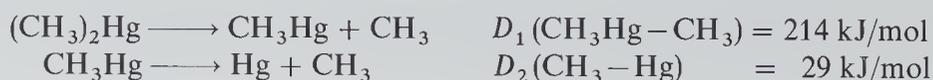
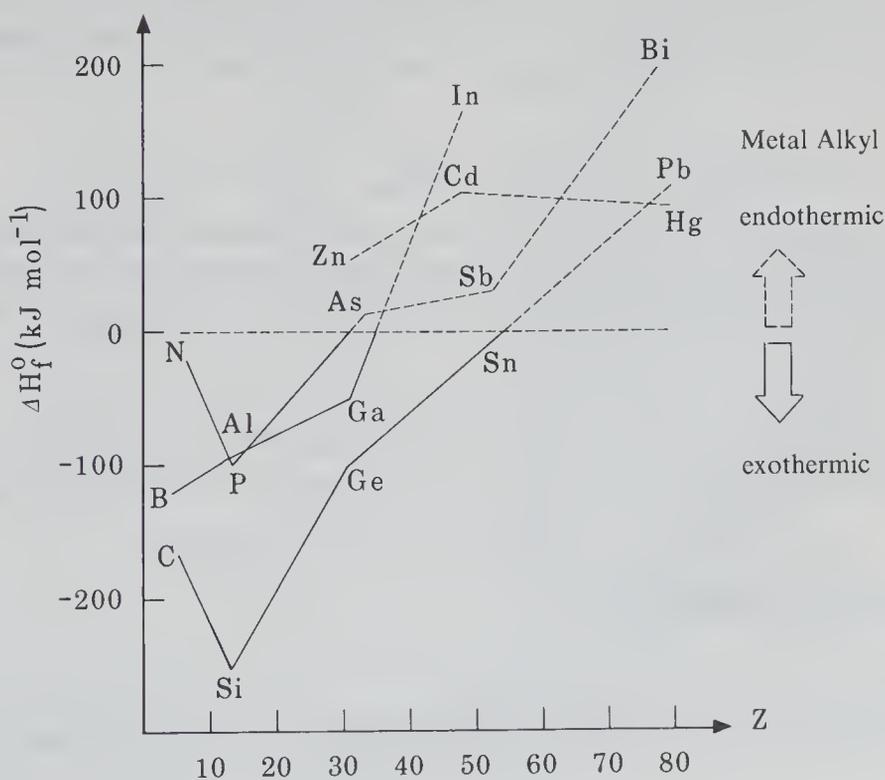


Table 3-1: Comparison of standard enthalpies ΔH_f^0 in kJ/mol and mean bond enthalpies $\bar{E}(M-C)$ in kJ/mol of methyl derivatives in the gas phase with values $\bar{E}(M-X)$, $X = Cl, O$

Group											
12 MMe ₂			13 MMe ₃			14 MMe ₄			15 MMe ₃		
M	ΔH_f^0	\bar{E}	M	ΔH_f^0	\bar{E}	M	ΔH_f^0	E	M	ΔH_f^0	\bar{E}
			B	-123	365	C	-167	358	N	-24	314
			Al	-81	274	Si	-245	311	P	-101	276
Zn	50	177	Ga	-42	247	Ge	-71	249	As	13	229
Cd	106	139	In	173	160	Sn	-19	217	Sb	32	214
Hg	94	121	Tl	—	—	Pb	136	152	Bi	194	141
c.f.			B-O		526	Si-O		452	As-O		301
			B-Cl		456	Si-Cl		381	Bi-Cl		274
			Al-O		500	Si-F		565			
			Al-Cl		420	Sn-Cl		323			

Data for M-C: *Comprehensive Organometallic Chemistry, 1* (1982) 5

Data for M-X: J. E. Huheey, *Inorganic Chemistry*, 3. Ed., A-32



Generalizations:

- **M–C bond energies cover a wide range**

Compound	(CH ₃) ₃ B	(CH ₃) ₃ As	(CH ₃) ₃ Bi
$\bar{E}(\text{M}-\text{C})$ kJ/mol	365	229	141
bond	relatively strong	medium	weak

- The **mean bond energy** $\bar{E}(\text{M}-\text{C})$ within a main-group decreases with increasing atomic number. This trend also applies to the bonds of M to other elements of the second row. A rationale for this effect is the increasing disparity in the radial extension and concomitant unfavorable overlap of the atomic orbitals contributing to the M–C bond.
- **Ionic bonds** are encountered if M is particularly electropositive and/or the carbanion is especially stable.

Examples:



- **Multicenter bonding** (“electron deficient bond”) arises if the valence shell of M is less than half filled and the cation M^{n+} is strongly polarizing (possesses a large charge/radius ratio).

Examples:



3.2 Lability of Main-group Organometallics

Predictions of the thermal behavior of organometallics which are based on the respective standard enthalpies of formation meet with limited success because usually, rather than decomposition into the elements, other, more complicated decomposition pathways are observed.

Examples:



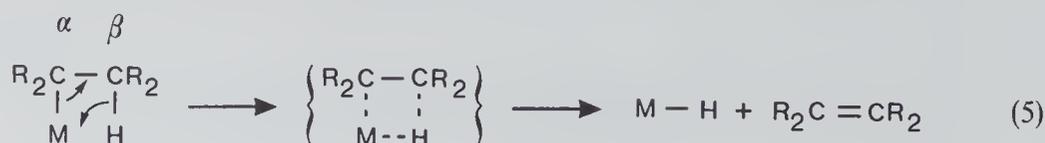
Factors which contribute to the driving force of this reaction include the enthalpy of formation $\Delta H_f^\circ(\text{C}_2\text{H}_6)$ of the product as well as an entropy term $\Delta S > 0$. Besides reaction (1), additional reaction paths have been established for the thermolysis of tetramethyllead:



The appearance of ethylene in the product mixture suggests that **homolytic cleavage**



is accompanied by **β -elimination**



The concerted nature of decomposition pathway (5) entails a lowering of the activation energy. However, this path is limited to molecules with hydrogen atoms in β -position. It is plausible, therefore, that the temperature of decomposition is higher for $\text{Pb}(\text{CH}_3)_4$ than for $\text{Pb}(\text{C}_2\text{H}_5)_4$ (p. 139).

A further condition for β -elimination to occur is the availability of an empty valence orbital on M to interact with the electron pair of the $\text{C}_\beta\text{—H}$ bond. It is for this reason that the β -elimination mechanism plays a more important role for the organometallics of groups 1, 2 and 13 (valence configurations s^1 , s^2 and $s^2 p^1$) as compared to for those of groups 14, 15 and 16 ($s^2 p^2$, $s^2 p^3$ and $s^2 p^4$). If a binary organometallic species has an empty coordination site at its disposal, β -elimination can be blocked and thermal stability increased through formation of a Lewis base adduct [Example: $(\text{bipy})\text{Be}(\text{C}_2\text{H}_5)_2$, $\text{bipy} = 2,2'$ -bipyridyl]. β -Elimination assumes a position of prime importance in the chemistry of organotransition-metal compounds (chapter 13).

As with organic compounds, all organometallic materials are thermodynamically unstable with respect to oxidation to MO_n , H_2O and CO_2 . Nevertheless, large differences in the ease of handling of organometallics are encountered which may be traced back to differences in **kinetic inertness**. Example:

	Heat of combustion	Thermodynamics	Property	Kinetics
$\text{Zn}(\text{C}_2\text{H}_5)_2$	−1920 kJ/mol	unstable	pyrophoric	labile
$\text{Sn}(\text{CH}_3)_4$	−3590 kJ/mol	unstable	airstable	inert

Particularly labile against O_2 and H_2O are organometallic molecules which possess free electron pairs, low lying empty orbitals and/or high polarity of the M—C bonds. Compare:

	In air:	In water:	Relevant factors:
Me_3In	pyrophoric	hydrolysed	electron gap at In, high bond polarity.
Me_4Sn	inert	inert	Sn shielded well, low bond polarity.
Me_3Sb	pyrophoric	inert	free electron pair on Sb.
Me_3B	pyrophoric	inert	electron gap at B is closed by means of hyperconjugation, low bond polarity.
Me_3Al	pyrophoric	hydrolysed	electron gap at Al in the monomer, nucleophilic attack via $\text{Al}(3d)$ in the dimer, high bond polarity.
SiH_4	pyrophoric	hydrolysed	Si shielded ineffectively, attack of O_2 and of nucleophiles via $\text{Si}(3d)$.
SiCl_4	inert	hydrolysed	Si relatively electron-poor, high polarity of Si—Cl bonds, nucleophilic attack via $\text{Si}(3d)$.
SiMe_4	inert	inert	Si shielded effectively, low polarity of Si—C bonds.

This brief survey is only intended to furnish a few qualitative arguments which have to be weighed with respect to their specific applications.

MAIN-GROUP ORGANOMETALLICS

4 Methods of Preparation in Perspective

Procedures for the formation of bonds between main-group metals and carbon may roughly be divided into the following reaction types:

oxidative addition [1], exchange [2]–[7], insertion [8]–[10] and elimination [11]–[12].

Metal + Organic Halide

Direct Synthesis [1]

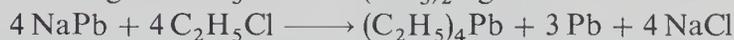


Examples :



The high enthalpy of formation of the salt MX_n generally renders this reaction exothermic. This is, however, not true for elements of high atomic number ($M = \text{Tl, Pb, Bi, Hg}$) which form weak $M-C$ bonds. Here $\Delta H_f^0(R_nM) > 0$ is not compensated for by $\Delta H_f^0(MX_n) < 0$ and an additional contribution to the driving force must be provided. One possibility is the use of an alloy which, in addition to the metal to be alkylated, contains a strongly electropositive element.

Mixed Metal Synthesis



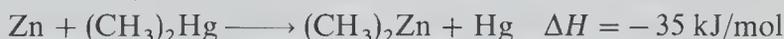
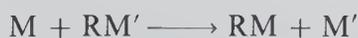
[$\Delta H_f^0(\text{NaX})$ boosts the driving force]

By their very nature direct syntheses are **oxidative additions** of RX to M^0 whereby $RM^{II}X$ is produced. The generation of new $M-C$ bonds by means of the addition of RX to a low-valent metal compound is closely related to direct synthesis. Example:



Metal + Organometallic

Transmetallation [2]



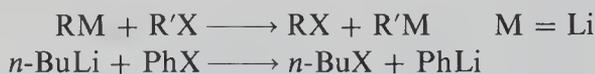
This general method may be applied to $M = \text{Li}-\text{Cs}$, $\text{Be}-\text{Ba}$, Al , Ga , Sn , Pb , Bi , Se , Te , Zn , Cd . RM' should be of weakly exothermic or, preferentially, of endothermic nature [e.g. $(\text{CH}_3)_2\text{Hg}$, $\Delta H = +94 \text{ kJ/mol}$]. The decisive factor in its feasibility really is the difference in the free enthalpies of formation $\Delta(\Delta G_f^0) RM, RM'$.

Organometallic + Organometallic**Metal Exchange** [3]

Precipitation of Ph_4Sn shifts this equilibrium to the right and good yields of vinyl lithium are obtained. Vinyl lithium is accessible by other methods only with difficulty.

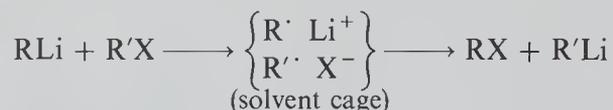
Organometallic + Metal Halide**Metathesis** [4]

The equilibrium lies on the side of the products if M is more electropositive than M'. For RM = alkali metal organyl, this procedure has wide applicability since the formation of MX makes a large contribution to the driving force.

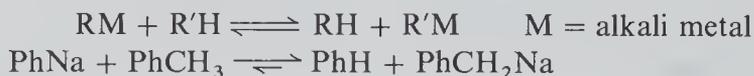
Organometallic + Aryl Halide**Metal Halogen Exchange** [5]

The equilibrium is shifted to the right if R' is superior to R in stabilizing a negative charge. Therefore, this reaction is practicable for aryl halides only ($\text{X} = \text{I}, \text{Br}$, rarely Cl , never F). Competing reactions are alkylation (Wurtz coupling) and the metallation of $\text{R}'\text{X}$. Metal halogen exchange is, however, a comparatively fast reaction and is favored at low temperatures (**kinetic control**).

Current mechanistic ideas include the intermediate formation of radicals (Reutov, 1976 R). Accordingly, metal halogen exchange is initiated by a single electron transfer (SET) step:



F in $\text{C}_6\text{H}_5\text{F}$ is not exchanged for Li. Instead, the sequence: orthometallation, LiF elimination to yield an aryne and addition of $\text{C}_6\text{H}_5\text{Li}$ to the $-\text{C}\equiv\text{C}-$ triple bond affords the coupling product $\text{R}-\text{R}'$.

Organometallic + C-H Acid**Metallation** [6]

Metallations (**replacement of H by M**) are acid/base equilibria $\text{R}^- + \text{R}'\text{H} \rightleftharpoons \text{RH} + \text{R}'^-$ which, with increasing acidity of $\text{R}'\text{H}$, are shifted to the right side. The practical success of a metallation is intimately linked to the **kinetic CH-acidity** (p. 28).

Substrates with an exceptionally high CH-acidity (acetylenes, cyclopentadienes) may also be metallated by alkali metals in a redox reaction:



Mercuric Salt + C–H Acid**Mercuration** [7]

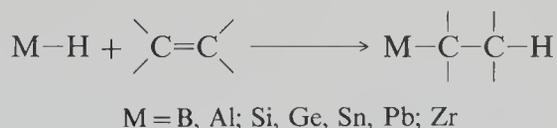
By their very nature, mercurations are also metallations. In the case of **nonaromatic substrates**, they are confined to molecules of high CH-acidity (alkynes, carbonyl-, nitro-, halogeno-, cyano compounds etc.).



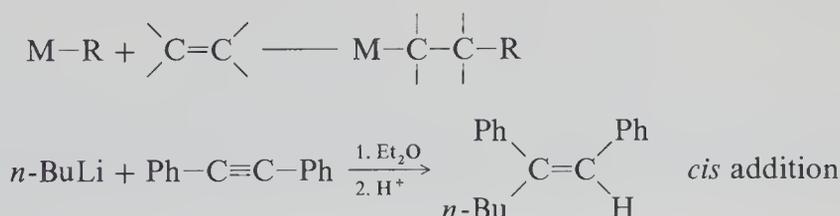
If $\text{Hg}(\text{CH}_3\text{COO})_2$ is used as a mercurating agent, the second step usually requires forcing conditions. A reaction of very wide scope is the **mercuration of aromatic compounds**:



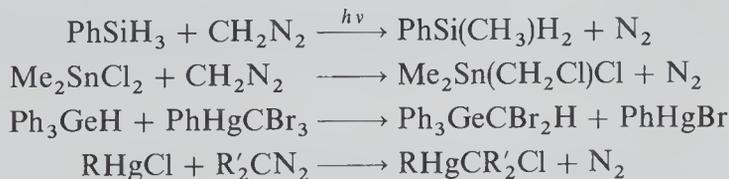
From a mechanistic point of view, this reaction is an electrophilic aromatic substitution.

Metal Hydride + Alkene (Alkyne)**Hydrometallation** [8]

Propensity to addition: Si–H < Ge–H < Sn–H < Pb–H

Organometallic + Alkene (Alkyne)**Carbometallation** [9]

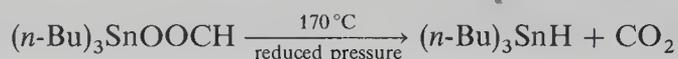
In contrast to M–H, insertions into M–C bonds only proceed if M is very electropositive (M = alkali metal, Al).

Organometallic + Carbene**Carbene Insertion** [10]

Note that insertions of carbenes into M–C bonds are avoided, the insertion into an M–H or an M–X bond being strongly favored.

Pyrolysis of Carboxylates**Decarboxylation** [11]

The group R should contain electron withdrawing substituents (R = C₆F₅, CF₃, CCl₃ etc.). Decarboxylation of organometallic formiates leads to hydrides:

**Metal Halide (Hydroxide) + Aryldiazonium Salt**

[12]

In synthetic organometallic chemistry, this is a method of limited importance.



5 Alkali Organometallics

5.1 Organolithium Compounds

PREPARATION: With methods 1, 2, 3, 5, 6, 9

Methods **1** (starting from Li metal) and **6** are of prime importance (*n*-BuLi is commercially available).

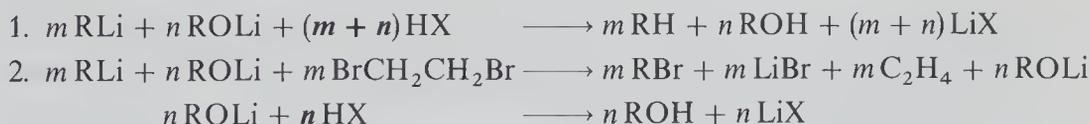


Perlithiated hydrocarbons are formed in the cocondensation of Li vapor with chlorohydrocarbons (Example: CLi_4 from CCl_4 and Li). The air sensitivity of organoalkali compounds requires them to be manipulated under the **protective atmosphere** of an inert gas (N_2 , Ar). Whereas, for reasons of solubility, Grignard reagents must be prepared in ethers, the preparation of organolithium compounds may be carried out more economically in inert hydrocarbons such as hexane.

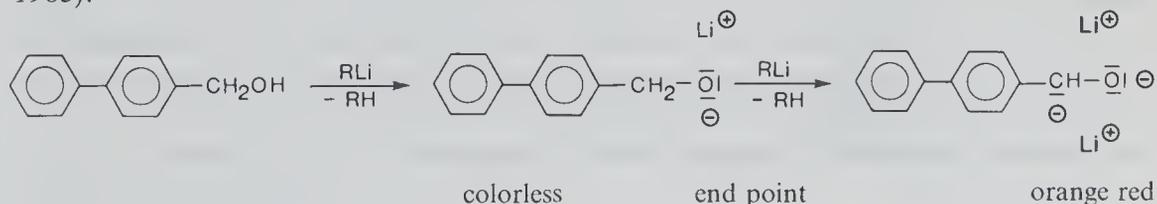
For the **assay of RLi** solutions, volumetric methods are available. A simple acid/base titration following hydrolysis



is inapplicable since alkoxides, stemming from the reaction of RLi with O_2 or from ether cleavage, would suggest too high an RLi content. Therefore, a double titration method has been developed (Gilman, 1964). The RLi concentration amounts to the difference $(m + n) - n$:



More recently, methods of determination which include self-indicating reagents like 4-(hydroxymethyl)biphenyl have been employed. They permit direct titrations (Juaristi, 1983):

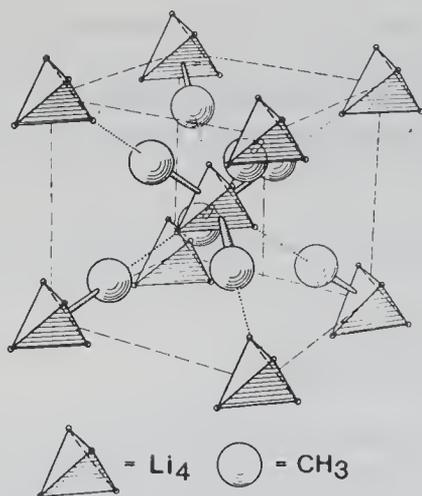


Solutions of concentrations $[RLi] > 0.1 \text{ M}$ can be conveniently checked by means of $^1\text{H-NMR}$ spectroscopy using an internal concentration standard ($-1.0 > \delta \text{RCH}_2\text{Li} > -1.3 \text{ ppm}$).

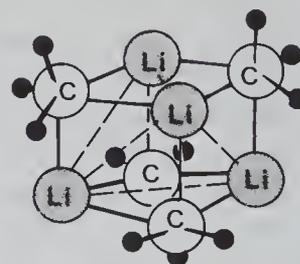
STRUCTURE AND BONDING

A conspicuous feature of organolithium compounds is their tendency to form **oligomeric units** in solution as well as in the solid state. A classic example is the structure of solid **methyl lithium** which is best described as cubic body-centered packing of $(\text{LiCH}_3)_4$ units, the latter consisting of Li_4 -tetrahedra with methyl groups capping the triangular faces (E. Weiss, 1964).

(a) Unit cell of $(\text{LiCH}_3)_4$ (s)



(b) Schematic drawing of the unit $(\text{LiCH}_3)_4$



$d(\text{Li}-\text{C}) = 231 \text{ pm}$	$(\text{LiCH}_3)_4$
$d(\text{Li} \cdots \text{C}) = 236 \text{ pm}$	$(\text{LiCH}_3)_4$
$d(\text{Li}-\text{Li}) = 268 \text{ pm}$	$(\text{LiCH}_3)_4$
compare: $d(\text{Li}-\text{Li}) = 267 \text{ pm}$	$\text{Li}_2(\text{g})$
$d(\text{Li}-\text{Li}) = 304 \text{ pm}$	$\text{Li}(\text{m})$

The building blocks of the lattice are distorted cubes, with alternate occupation of the corners by C and Li atoms (b). This type of **heterocubane** arrangement is encountered frequently for species of constitution $(\text{AB})_4$.

A closer inspection of the $\text{Li}-\text{C}$ distances reveals that the methyl groups of one $(\text{LiCH}_3)_4$ unit interact with the Li atoms of a neighboring Li_4 -tetrahedron. These intermolecular forces are responsible for the low volatility and the insolubility of LiCH_3 in non-solvating media.

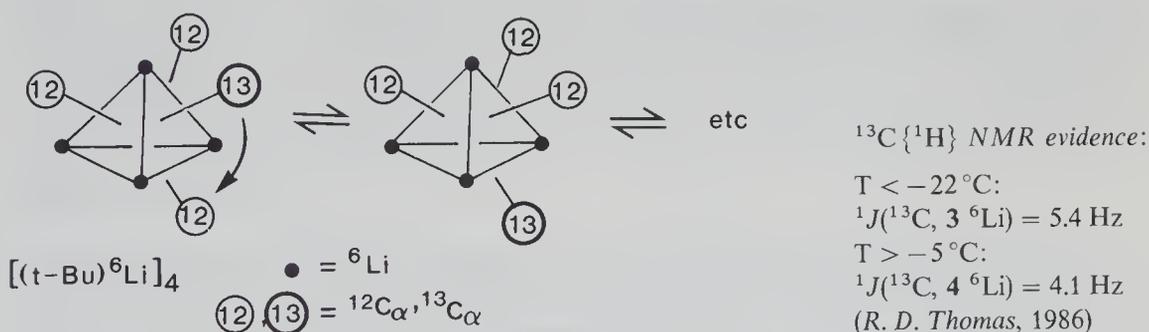
The structure of *t*-butyllithium is very similar to that of methyl lithium, the intermolecular forces are however, weaker. As opposed to MeLi , *t*-BuLi is soluble in hydrocarbons and sublimates at $70^\circ\text{C}/1 \text{ mbar}$.

The **degree of association** of organolithium compounds is strongly dependent on the nature of the solvent:

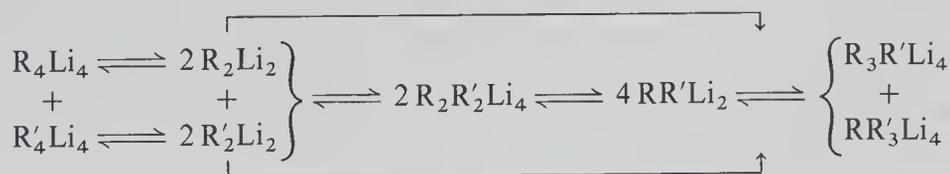
LiR	Solvent	Aggregation
LiCH ₃	hydrocarbon THF, Et ₂ O Me ₂ NCH ₂ CH ₂ NMe ₂ (TMEDA)	hexamer (Li ₆ octahedron) tetramer (Li ₄ tetrahedron) monomer
Li- <i>n</i> -C ₄ H ₉	cyclohexane Et ₂ O	hexamer tetramer
Li- <i>t</i> -C ₄ H ₉	hydrocarbon	tetramer
LiC ₆ H ₅	THF, Et ₂ O	dimer
LiCH ₂ C ₆ H ₅ (benzyl)	THF, Et ₂ O	monomer
LiC ₃ H ₅ (allyl)	Et ₂ O THF	infinite column (p. 23) monomer

The presence of oligomers (LiR)_n in solution is substantiated by osmometric measurements, by Li-NMR spectroscopy and by ESR experiments (p. 35). The mass-spectrometric observation of the fragment ion [Li₄(*t*-Bu)₃]⁺ shows that the association is maintained in the gas phase.

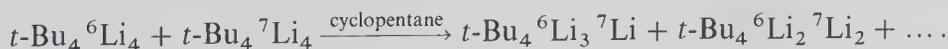
Thorough NMR studies by T. L. Brown (1970, R) and by G. Fraenkel (1984, R) have established that, much like Grignard reagents (p. 43), solutions of organolithium compounds represent complicated equilibrium mixtures. The dynamic processes in these solutions comprise **intramolecular bond-fluctuation**:



as well as **intermolecular exchange**:



It has been demonstrated by means of mass spectrometry that these scrambling reactions proceed via cleavage of the Li₄ units rather than by ligand transfer, whereby the integrity of the Li₄ units would be maintained (T. L. Brown, 1970):

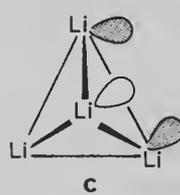
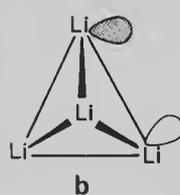
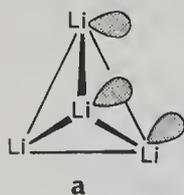
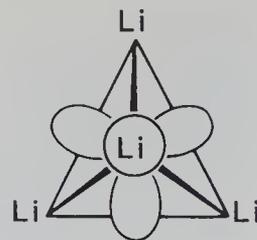


The kinetic parameters of these processes are strongly influenced by the nature of the medium and the group R.

The tendency of organolithium compounds to associate in the solid state as well as in solution is due to the fact that in a single molecule LiR , the number of valence electrons is too low to use all the available Li valence orbitals for two-electron two-center ($2e2c$) bonding. In the aggregates $(\text{LiR})_n$ this "electron deficiency" is compensated for by the formation of multicenter bonds. This is illustrated for the tetrahedral species $(\text{LiCH}_3)_4$:

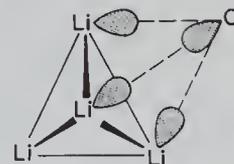
Li_4 skeleton with 4 Li (sp^3) hybrid orbitals per Li atom. Directional properties of the Li valence orbitals:

1 \times **axial**, identical with one of the threefold axes of the tetrahedron,
3 \times **tangential**, pointing towards the normals of the triangular faces.

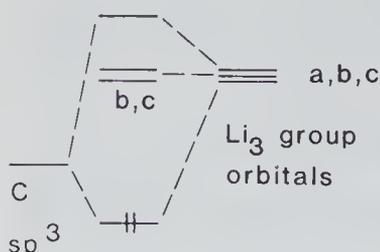


Group orbitals formed from three tangential Li (sp^3) hybrid orbitals originating at the corners of the Li_3 triangle.

Four-center bonding molecular orbital from the interaction of Li_3 group orbital **a** with a C (sp^3) hybrid orbital. This 4c-MO is Li–C as well as Li–Li bonding.

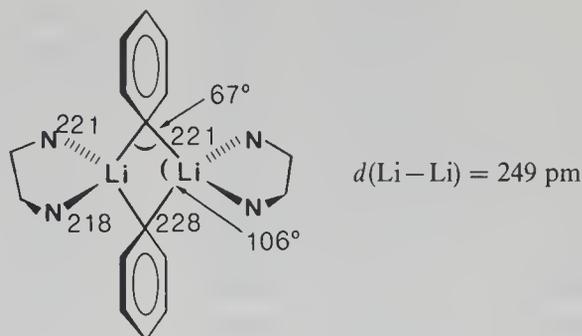


The electronegativity difference between lithium and carbon should manifest itself in the $2e4c$ bonding pair of electrons being located closer to the carbon than to the lithium atoms. The **bond polarity** $\text{Li}^{\delta+} - \text{C}^{\delta-}$ can be demonstrated experimentally, e.g. by means of NMR spectroscopy. LiCH_3 molecules in matrix isolation were reported to possess a dipole moment of about 6 Debye (Andrews, 1967), a value of 9.5 Debye being expected for the case of full charge separation (ionic limit). The degree of covalent and ionic character of the Li–C bond is still an open question; sizeable covalent contributions being favored by some authors (Lipscomb, 1980; Ahlrichs, 1986) and essentially ionic character by others (Streitwieser, 1976; v. Ragué Schleyer, 1988 R).

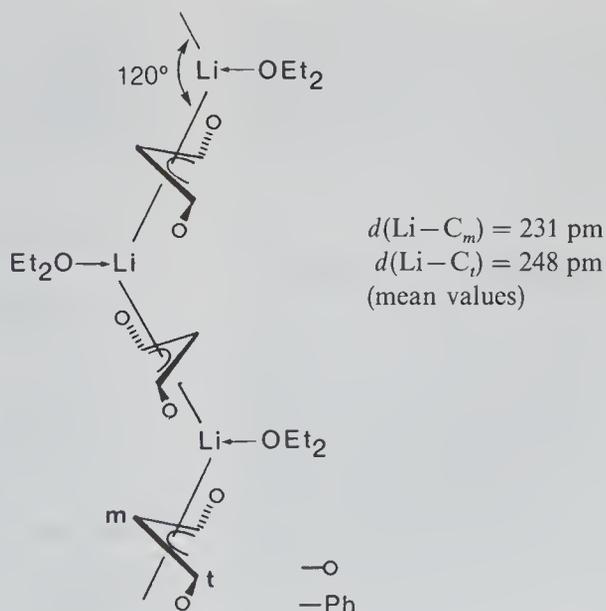


MO diagram for one of the four $2e4c$ bonds in R_4Li_4

The axial $\text{Li}(sp^3)$ hybrid orbitals, which are unoccupied in an isolated molecule of $(\text{LiCH}_3)_4$, are used in the crystal for interaction with methyl groups of neighboring $(\text{LiCH}_3)_4$ units and in solution for the coordination of σ -donors (Lewis bases, solvent molecules). An example is the tetrameric etherate of **phenyllithium**, $(\mu^3\text{-C}_6\text{H}_5\text{Li} \cdot \text{OEt}_2)_4$. In the presence of the chelating ligand N,N,N',N' -tetramethylethylenediamine (TMEDA, $\overline{\text{N}}-\overline{\text{N}}$), however, phenyllithium crystallizes in a dimeric structure which is reminiscent of triphenylaluminum (Al_2Ph_6 , p. 79) (E. Weiss, 1978):



A totally different type of association is encountered for organolithium compounds in which the carbanion represents a delocalized π -system. Instead of reducing the electron deficiency by means of clustering to Li_n ($n = 2, 4, 6$), interactions of partially solvated Li^+ ions with the π -electron system of the carbanion arise. In the case of **1,3-(diphenyl)allyllithium**, a columnar structure with bridging $\mu(\eta^3:\eta^3)$ allyl units is realized which resembles $(\text{C}_5\text{H}_5)\text{In}$ (p. 89) or a polydecker sandwich complex (p. 383). In contrast to the latter, however, ionic bonding appears to prevail in the η^3 -allyl lithium compound (Boche, Massa, 1986):



Excursion

⁶Li- and ⁷Li NMR of Organolithium Compounds

In organometallic research, NMR spectroscopy of the less common nuclei is often required. Experimental problems during the detection of metal resonances may be caused by a low natural abundance of the respective isotope and/or by the magnetic properties of the nucleus under investigation. Small magnetic moments lead to low Larmor frequencies and, because of an unfavorable Boltzmann-distribution, to low sensitivity. A division of the magnetic isotopes into two classes is based on the magnitude of the nuclear spin quantum number I .

a) Nuclei with the Spin Quantum Number $I = 1/2$

For small molecules, $I = 1/2$ nuclei usually yield sharp resonance lines with half widths $W_{1/2}$ (linewidth at half height) between 1 and 10 Hz. If, however, the magnetic interactions with the environment are weak, very long longitudinal and transverse relaxation times T_1 and T_2 may result [example: T_1 (¹⁰⁹Ag) up to 10³ s]. This severely complicates the detection of these resonances.

b) Nuclei with Spin Quantum Numbers $I \geq 1$

These nuclei possess electric quadrupole moments (deviations of the distribution of nuclear charge from spherical symmetry) which can cause extremely short nuclear relaxation times and concomitant large half widths $W_{1/2}$ (up to several ten thousand Hz).

$$W_{1/2} \sim \frac{(2I + 3) Q^2 q_{zz}^2 \tau_c}{I^2 (2I - 1)}$$

Q = quadrupole moment, q_{zz} = electric field gradient, τ_c = correlation time of molecular re-orientation (characteristic of the extent of tumbling motion).

I and Q are properties of a given nucleus. Thus, the NMR linewidth $W_{1/2}$ of this nucleus is governed by the chemical environment through the square of the electric field gradient q_{zz}^2 and through the correlation time τ_c . Relatively narrow lines are obtained for molecules of low molecular weight (τ_c is small) if the quadrupolar nuclei are embedded in ligand fields of cubic (tetrahedral, octahedral) symmetry. In these cases, an important relaxation path is blocked due to the absence of an electric field gradient. The correlation time τ_c may be controlled to a certain extent by the viscosity of the medium (choice of solvent and temperature). A rough measure of the chance of observing the magnetic resonance of a nucleus X is given by its receptivity. The **relative receptivity**, related to that of the proton ($D_x^p = 1.000$), is defined as follows:

$$D_x^p = \frac{\gamma_x^3 N_x I_x (I_x + 1)}{\gamma_p^3 N_p I_p (I_p + 1)}$$

$$\gamma = \frac{\text{magnetic moment}}{\text{angular momentum}} = \frac{\mu_x}{I \cdot h/2\pi} \frac{\text{rad}}{\text{s}}$$

I = nuclear spin

N = natural abundance (%)

γ = magnetogyric ratio

In table 5-1 the properties of "unconventional" nuclei are contrasted with the routine cases ¹H, ¹¹B, ¹³C, ¹⁹F and ³¹P:

Table 5-1: Magnetic properties of "unconventional" nuclei in contrast with "routine" cases ^1H , ^{11}B , ^{13}C , ^{19}F and ^{31}P

Nucleus	N in %	I	Q in 10^{-28} m^2 (barn)	NMR frequency in MHz at 2.35 T	Standard	Relative Receptivity D_x^p
^1H	99.9	1/2	—	100	Me_4Si	1.000
^6Li	7.4	1	$-8.0 \cdot 10^{-4}$	14.7	Li^+ (aq)	$6.31 \cdot 10^{-4}$
^7Li	92.6	3/2	$-4.5 \cdot 10^{-2}$	38.9	Li^+ (aq)	0.27
^{11}B	80.4	3/2	$3.55 \cdot 10^{-2}$	32.1	$\text{BF}_3 \cdot \text{OEt}_2$	0.13
^{13}C	1.1	1/2	—	25.1	Me_4Si	$1.76 \cdot 10^{-4}$
^{19}F	100	1/2	—	94.1	CCl_3F	0.83
^{23}Na	100	3/2	0.12	26.5	Na^+ (aq)	$9.25 \cdot 10^{-2}$
^{25}Mg	10.1	5/2	0.22	6.1	Mg^{2+} (aq)	$2.71 \cdot 10^{-4}$
^{27}Al	100	3/2	0.15	26.1	$\text{Al}(\text{acac})_3$	0.21
^{29}Si	4.7	1/2	—	19.9	Me_4Si	$3.7 \cdot 10^{-4}$
^{31}P	100	1/2	—	40.5	H_3PO_4	$6.63 \cdot 10^{-2}$
^{51}V	99.8	7/2	0.3	26.3	VOCl_3	0.38
^{57}Fe	2.19	1/2	—	3.2	$\text{Fe}(\text{CO})_5$	$7.39 \cdot 10^{-7}$
^{59}Co	100	7/2	0.4	23.6	$[\text{Co}(\text{CN})_6]^{3-}$	0.28
^{71}Ga	39.6	3/2	0.11	30.5	Ga^{3+} (aq)	$5.62 \cdot 10^{-2}$
^{77}Se	7.6	1/2	—	19.1	Me_2Se	$5.26 \cdot 10^{-4}$
^{103}Rh	100	1/2	—	3.2	$\text{Rh}(\text{acac})_3$	$3.12 \cdot 10^{-5}$
^{119}Sn	8.6	1/2	—	37.3	Me_4Sn	$4.44 \cdot 10^{-3}$
^{125}Te	7.0	1/2	—	31.5	Me_2Te	$2.2 \cdot 10^{-3}$
^{183}W	14.4	1/2	—	4.2	WF_6	$1.04 \cdot 10^{-5}$
^{195}Pt	33.8	1/2	—	21.4	$[\text{Pt}(\text{CN})_6]^{2-}$	$3.36 \cdot 10^{-3}$

Source: R. K. Harris, B. E. Mann, *NMR and the Periodic Table*, Academic Press, New York, 1978.

The extensive use of organolithium compounds in organic synthesis justifies a brief discussion of Li NMR spectroscopic characteristics. The choice between the two isotopes ^6Li ($I = 1$) and ^7Li ($I = 3/2$) must take the nature of the specific problem into account.

^7Li displays higher receptivity; due to the larger quadrupole moment, the linewidths are large, however. ^6Li presents reduced linewidths, albeit at the cost of lower receptivity (Wehrli, 1978). Therefore, ^7Li NMR offers **higher sensitivity** and ^6Li NMR **superior resolution** of coupling patterns (^6Li carries the smallest of all known nuclear quadrupole moments).

Among the alkali metal organometallics, organolithium compounds are not only the most widely used in the laboratory, they also boast the greatest variety of structures and bonding situations. The study of lithium organometallics in solution has greatly benefited from the application of Li NMR. The NMR spectra of the organometallics of the heavier alkali metals Na—Cs reflect the nature of the $\text{M}(\text{solv})^+$ complex, since ionic bonding dominates and the organic counterion contributes to the shielding of M^+ only insignificantly. Li NMR spectra show a larger diversity because the bonding modes range from mainly covalent, in the

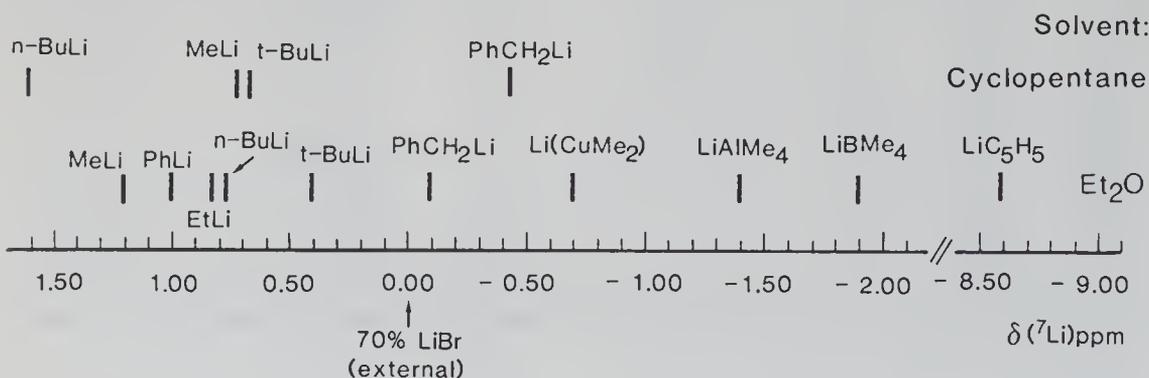
case of lithium alkyls, to ion pairing as encountered for lithium tetraorganometallates and for compounds in which the organic group is effectively stabilized by resonance (triphenylmethyl, cyclopentadienyl). As would be expected, solvent effects play an important role in Li NMR, in that the solvating power affects the polarity of the Li–C bond and governs the degree of association (p. 21). The NMR shifts $\delta(^7\text{Li})$ cover a small range of only 10 ppm, which shrinks to about 2 ppm if only those organolithium compounds are considered in which the bonding is thought to be essentially covalent. This sets a limit to the value of Li NMR in routine analysis.

- The method of choice for investigations of structural dynamics in organolithium chemistry is the application of ^6Li NMR to ^{13}C -enriched materials.

Examples:

Structure of Ion Pairs $\text{Li}^+\text{C}_m\text{H}_n^-$

If the group C_mH_n^- of an organolithium compound is furnished with significant resonance stabilization, ionic bonding will dominate and the role of the solvent will be to favor one of two alternative structures known as **contact ion pair** and **solvent separated ion pair**. Since the en-



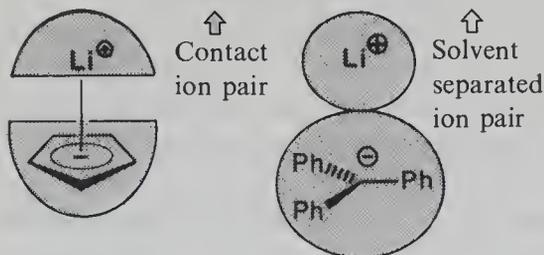
However, the following generalizations may be made:

- ^7Li NMR signals for the more covalent organolithium compounds appear at low magnetic field, those for species with a large ionic contribution to the bond are shifted to higher field.
- Solvent shifts are pronounced, although it is difficult to predict their direction.
- The observation of scalar couplings $^1J(^{13}\text{C}, ^6\text{Li})$ or $^1J(^{13}\text{C}, ^7\text{Li})$ may be taken as evidence for a covalent contribution to the Li–C bond. Surprisingly, couplings $J(^6\text{Li}, ^7\text{Li})$ have not as yet been discovered.

environment of the Li^+ cation strongly differs in these situations, characteristic ^7Li NMR shifts result. Thus, in addition to the diagnosis of the prevailing bond type, ^7Li NMR furnishes information on the disposition of the cation Li^+ relative to the organic anion. This will be illustrated for cyclopentadienyllithium and for triphenylmethylithium (Cox, 1974). In the case of $\text{Li}^+\text{C}_5\text{H}_5^-$, the strong high-field shift of the ^7Li NMR signal points to a structure in which the Li^+ cation resides above the plane of the cyclic carbanion, that is in the shielding region of the aromatic ring current.

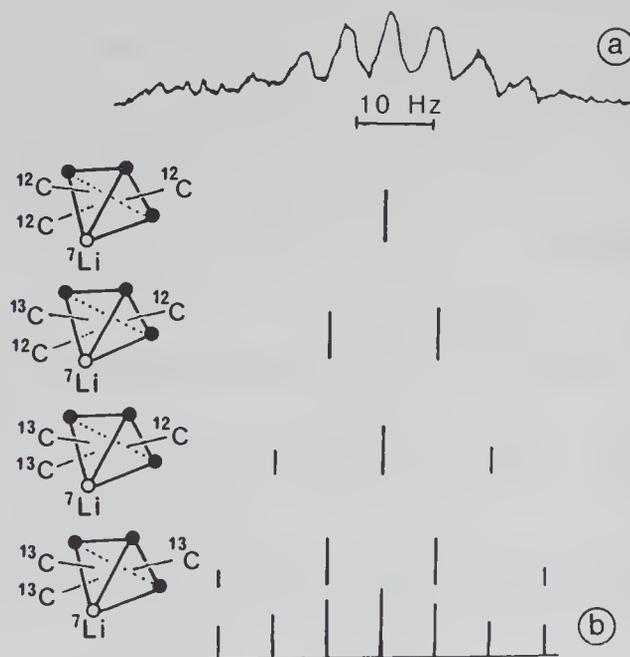
$\delta(^7\text{Li})$ (External standard: 1.0 M LiCl in H_2O)

Organo-Li compound	Solvent			
	Et ₂ O	THF	DME	HMPA
$\text{Li}^+\text{C}(\text{C}_6\text{H}_5)_3^-$		-1.11	-2.41	-0.88
$\text{Li}^+\text{C}_5\text{H}_5^-$	-8.60	-8.37	-8.67	-0.88



Whereas in the weakly solvating media tetrahydrofuran (THF) and dimethoxyethane (DME), $\text{Li}^+\text{C}(\text{C}_6\text{H}_5)_3^-$ and $\text{Li}^+\text{C}_5\text{H}_5^-$ form different types of ion pairs, in the strongly solvating medium hexamethylphosphoric trisamide (HMPA) both compounds exist as solvent-separated ion pairs, as inferred from the identical chemical shifts $\delta(^7\text{Li})$.

The Tetrameric Structure of *t*-Butyllithium in Solution



The reconstruction (b) of the experimental spectrum (a) [^7Li NMR of *t*-BuLi (0.1 M) in cyclohexane, RT, 57% ^{13}C -enriched at the α -positions] is a superposition of isotomeric species in which the observed nucleus ^7Li is coupled to 0, 1, 2 and 3 neighboring ^{13}C nuclei, $^1J(^{13}\text{C}, ^7\text{Li}) = 11$ Hz. The agreement between (a) and (b) demonstrates that the association of (*t*-BuLi)₄ units, which structural analysis revealed for the solid state, is maintained in solution. This also applies to methyl lithium in the solid state and in THF at -70°C (McKeever, 1969).

REACTIONS OF ORGANOLITHIUM COMPOUNDS

In their chemical behavior, organolithium compounds resemble Grignard reagents; they are, however, more reactive.

a) Metallation and Subsequent Reactions

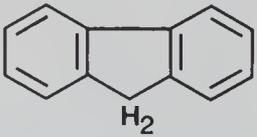
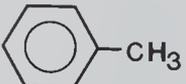
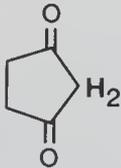
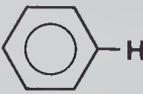


A prominent feature of this important method of introducing lithium is the discrepancy between equilibrium position and acceptable rate of reaction. If organometallic compounds $R-M$ are regarded as salts of the corresponding CH-acids $R-H$, with increasing CH-acidity of $R'-H$ the metallation equilibrium is shifted to the right. Table 5-2 compares the CH-acidity of organic CH-acids to inorganic acids.

Consequently, the stronger CH-acid, benzene, should be amenable to high yield metallation by *n*-butyllithium, a salt of the weaker CH-acid, butane:

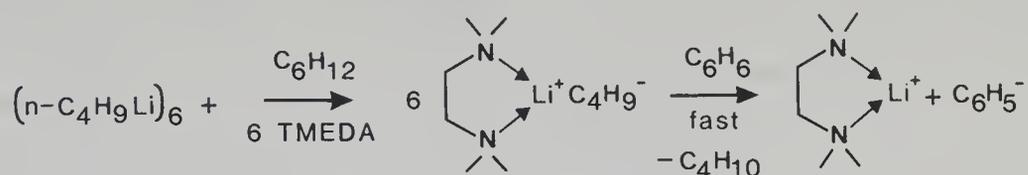


Table 5-2: CH acid exponents for organic CH-acids in nonaqueous media* and values of inorganic acids for comparison:

Compound	pK _a	Compound	pK _a
(CN) ₃ C-H	-5		21
H ₂ SO ₄	-2	HC≡C-H	24
(NO ₂) ₃ C-H	0	Ph ₃ C-H	30
HClO ₃	0		~35
	4.5		~37
CH ₃ COOH	4.7	C ₃ H ₇ CH ₂ -H	~44
HCN	9.4	(alkanes)	
O ₂ N-CH ₃	10		
	15		
H ₂ O	15.7		

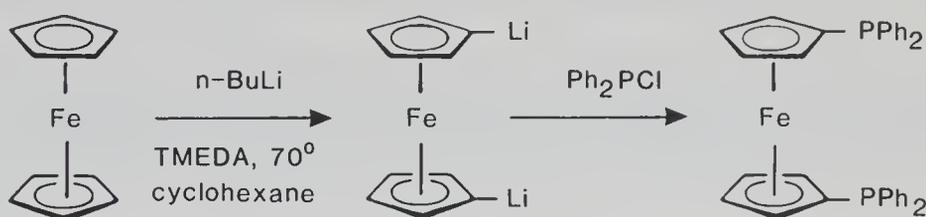
* The pK_a values are linked to the conventional scale in aqueous media by means of a conversion factor.

This reaction is unmeasurably slow. Rapid Li/H exchange occurs, however, upon addition of a strong σ -donor like tetramethylethylenediamine (TMEDA) or *t*-butoxide (*t*-BuO⁻):



TMEDA effects both the cleavage of *n*-BuLi oligomers and, through complexation of the Li⁺ cation, a polarization of the Li–C bond. In this way, the carbanionic character and therefore the reactivity of the butyl group is increased. The fact that monomerization is essential for the metallation reaction to proceed smoothly is indicated by the observation that the rates of metallation by PhCH₂Li (monomeric in THF) exceed those of CH₃Li (tetrameric in THF) by a factor of 10⁴, although CH₃⁻ is the stronger base as compared with PhCH₂⁻.

Example:

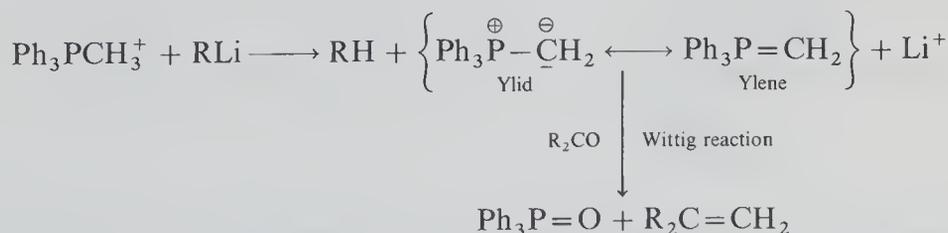


Metallations of geminal dichlorides are followed by LiCl elimination, resulting in **chloro-carbene** formation:



Often, there is no experimental evidence for the intermediacy of free carbenes in these reaction sequences. The α -haloalkyllithium compounds are then more generally referred to as **carbenoids**.

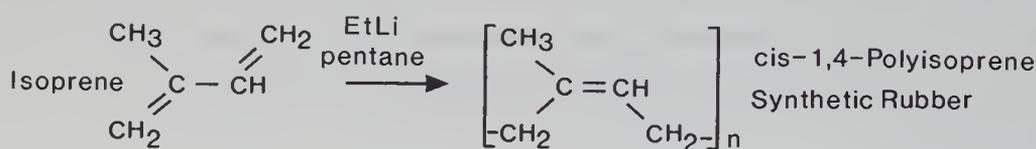
b) Deprotonation of Organophosphonium Ions



This reaction is employed in the synthesis of terminal olefins.

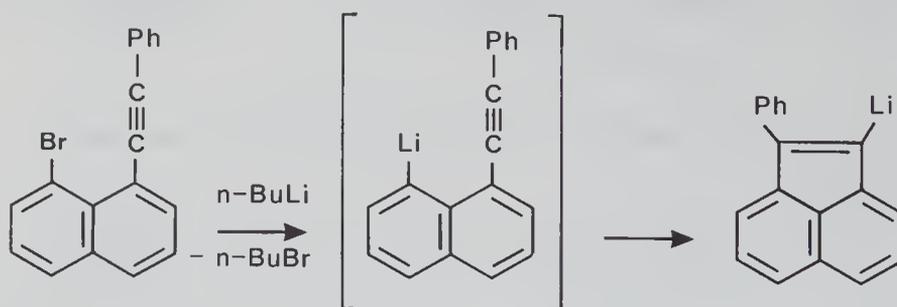
c) Addition to Multiple Bonds (Carbolithiation)

In their tendency to add to **C–C multiple bonds**, organolithium compounds lie between Grignard reagents and organoboron- or organoaluminum compounds, respectively: $\text{RMgX} < \text{RLi} < \text{R}_3\text{B}, (\text{R}_3\text{Al})_2$. Under mild conditions, organolithium compounds only add to conjugated dienes and to styrene derivatives. As in the case of metallation, the presence of strong σ -donors like TMEDA exerts an activating effect on RLi additions (example: *n*-BuLi/TMEDA initiates the polymerization of ethylene). The alkyllithium-initiated polymerization of isoprene produces a synthetic rubber which mimics the natural product in many respects (Hsieh, 1957). This discovery led to the first large scale application of organolithium compounds.

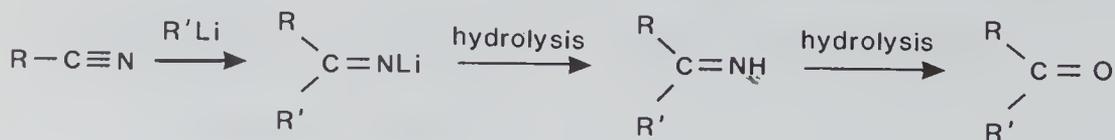


If Et_2O or THF is used as a solvent, the undesired *trans*-1,4-, -3,4-, and -1,2 additions are favored.

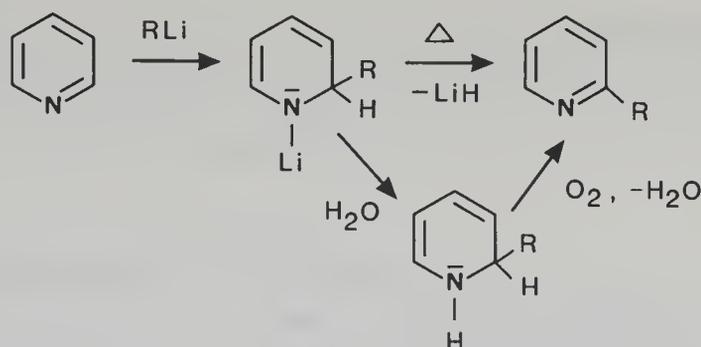
Carbolithiations of C–C multiple bonds may also proceed intramolecularly:



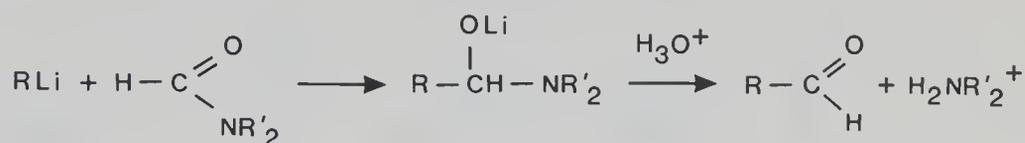
Among the additions of RLi to **C–N multiple bonds**, the reaction with nitriles deserves mention since it constitutes a versatile method for the preparation of ketones,



as well as the reaction with pyridine in which, similar to the Chichibabin reaction, 2-substituted pyridine derivatives are obtained:



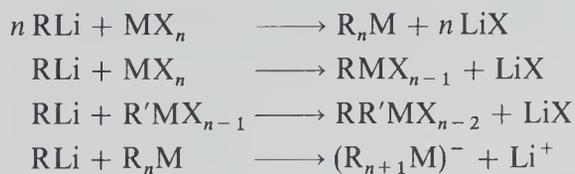
Additions of organolithium compounds to **C–O multiple bonds** closely resemble the reactions of Grignard reagents, however the tendency for side reactions to occur is lower with RLi. As an example, the addition of RLi to *N,N*-dimethylformamide, which affords aldehydes, may be cited:



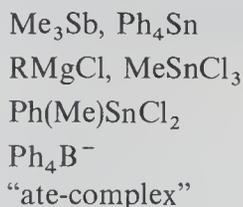
Whereas reactions of organolithium compounds with free carbon monoxide are non-specific and have found little use, additions of RLi to CO, bound to transition metals, are of great importance from a principal as well as from a practical point of view. Note that this reaction led to the discovery of transition-metal carbene complexes (p. 210).

d) Reactions with Main-Group- and Transition-Metal Halides

Conversions of the type $\text{RLi} + \text{MX} \rightarrow \text{MR} + \text{LiX}$ have already been introduced as a synthetic procedure [4] for **main-group organometallics** (p. 16); due to their wide applicability, these may well be the most frequently conducted reactions in organometallic chemistry. For the halides of high valent elements, the reaction proceeds in several steps which do not always lend themselves to efficient control, necessitating separations of product mixtures. In some cases, addition of an excess of RLi leads to the formation of “ate-complexes”.

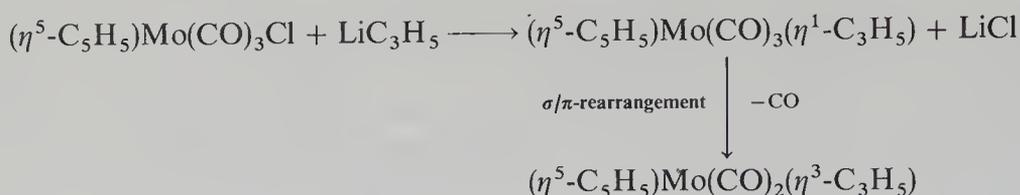


Examples:

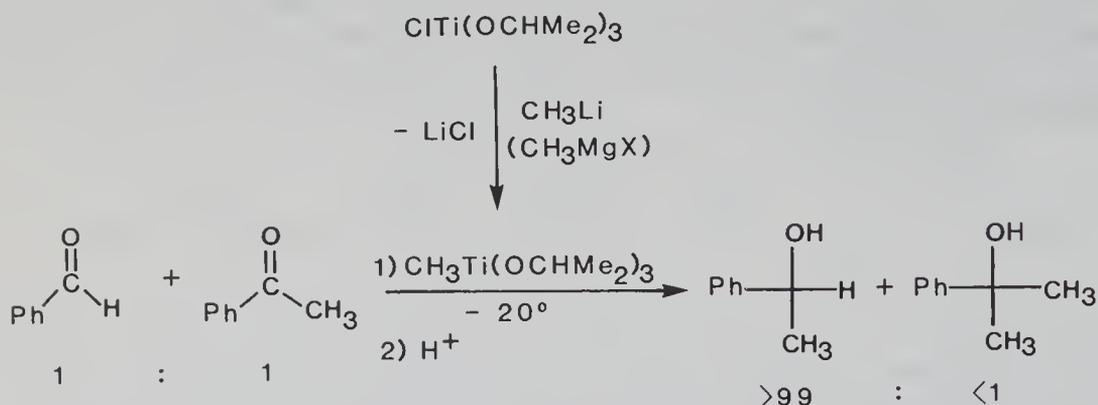


In the case of **transition metals** which, compared to main-group elements, display a larger variety of bonding types to organic groups, coupling reactions are often followed by

ligand displacement (p. 245, 281):



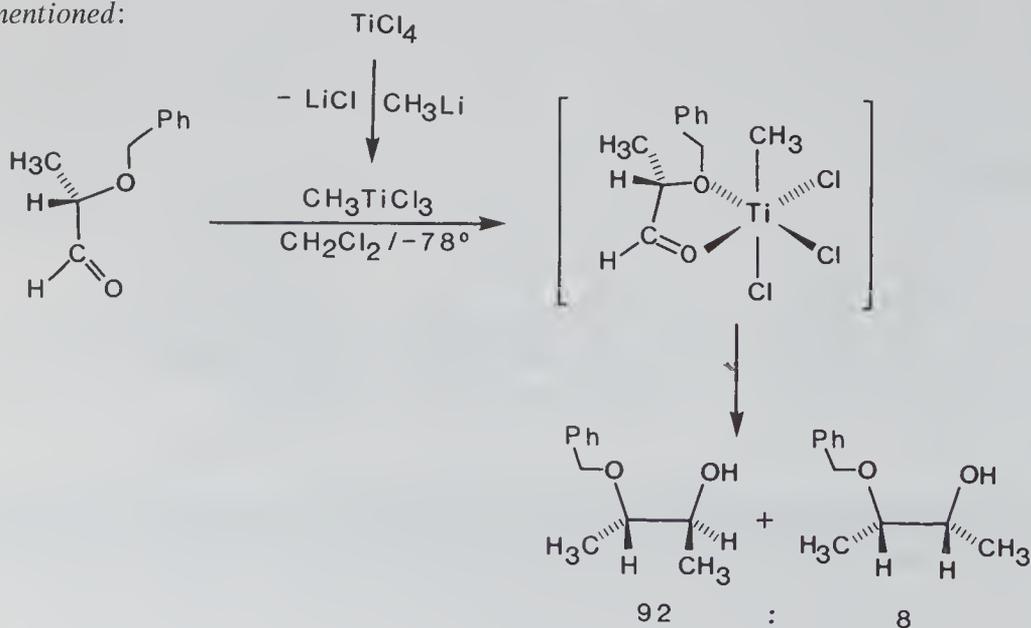
The intermediate alkylation of titanium is the basis of a procedure which achieves high **chemo- and stereoselectivity of carbanion addition** to carbonyl groups (Reetz, Seebach, 1980). In contrast to RLi or RMgX, the organotitanium reagent $\text{RTi}(\text{O-iso-Pr})_3$ attacks aldehyde functions in a highly chemoselective way:



In comparison, the analogous reaction of CH_3Li produces a 50 : 50 mixture of the secondary and tertiary alcohols. Under the mild reaction conditions, other functional groups like CN, NO_2 and Br remain unaffected.

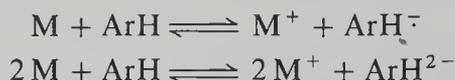
It is assumed that the Ti–C bond is significantly less polar than the Li–C and $\text{XMg}-\text{C}$ bonds, resulting in a lower rate of reaction and higher selectivity for the former. An additional aspect is the higher steric demand of the $\text{Ti}(\text{O-iso-Pr})_3$ group, which leads to particularly effective discrimination between different transition states.

As an example for stereoselectivity, the reaction of CH_3TiCl_3 with α -alkoxyaldehydes will be mentioned:

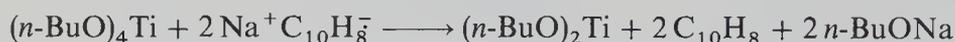


ADDITION COMPOUNDS OF THE ALKALI METALS

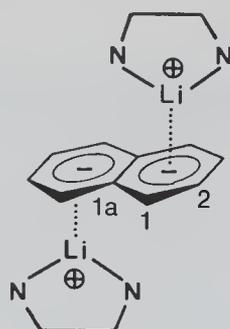
Besides alkali metal organyls, the generation of which involves the cleavage of a bond in the organic educt, there is a second class of compounds which are formed by an electron transfer from the alkali metal to the organic partner, with no bonds being split:



In this way **radical anions** ArH^- and dianions ArH^{2-} are obtained, the latter being diamagnetic in the majority of cases. They are of theoretical as well as of practical significance. Sodium naphthalenide $\text{Na}^+\text{C}_{10}\text{H}_8^-$ forms moss-green solutions in ethers like DME or THF and serves as a **self-indicating reducing agent** in the synthesis of metal complexes in low oxidation states. An attractive feature here is the availability of a very strong reducing agent which operates in homogeneous phase [$E_{1/2}(\text{C}_{10}\text{H}_8^{0/-1}) = -2.5$ V versus saturated calomel electrode]. Example:

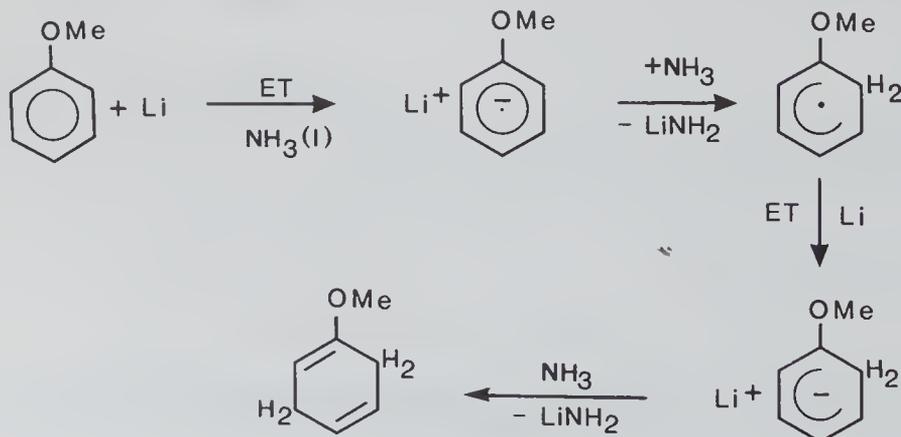


Alkali metal-arene addition compounds have also been obtained in crystalline form. The compound $[\text{Li}(\text{TMEDA})]_2\text{C}_{10}\text{H}_8$ may be regarded as an arene complex of a main-group element – no decision as to the prevailing bond type being implied by this designation!



$d(\text{Li}-\text{C}_{1a}) = 266$ pm
 $d(\text{Li}-\text{C}_1) = 233$ pm
 $d(\text{Li}-\text{C}_2) = 226$ pm
 (Stucky, 1972)

In the presence of proton donors the addition compounds undergo follow-up reactions. The **Birch reduction** consists of a sequence of electron transfer (ET)- and protonation steps which are used in synthesis. Example:



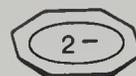
Electron transfer to cyclic conjugated systems often has **structural consequences**:



nonplanar
 $4n$ π -electrons
 antiaromatic

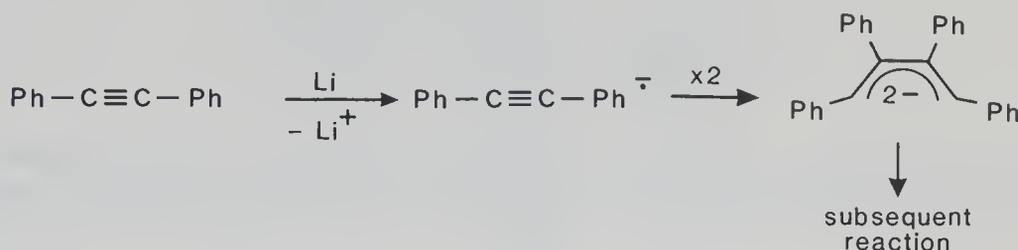


planar
 $(4n + 1)$ π -electrons



planar
 $(4n + 2)$ π -electrons
 aromatic

Whereas the radical anions of cyclic conjugated systems usually remain monomeric, radical anions of acyclic substrates tend to dimerize or to initiate polymerization. In the case of diphenylacetylene this tendency is exploited in a versatile **synthesis of five-membered heterocycles** containing B, Si, Sn, As, and Sb as heteroatoms (see p. 63, 110, 162).



Excursion

ESR Spectroscopy of Organoalkali Metal Compounds

a) Radical Anions of Aromatic π -Systems

In alkali-metal addition compounds M^+ArH^- , an unpaired electron resides in the lowest unoccupied molecular orbital (LUMO) of the neutral molecule ArH . Correspondingly, in radical cations ArH^+ , the highest occupied molecular orbital (HOMO) contains an unpaired electron. The ESR spectra of ArH^+ and of ArH^- furnish **information about the composition of the frontier orbitals HOMO and LUMO** from $\text{C}(p_\pi)$ atomic orbitals of the molecular frame. In view of the fact that regioselectivity of chemical reactions can be a result of frontier or-

bit control (Fukui), knowledge of the shape of these molecular orbitals is of practical significance.

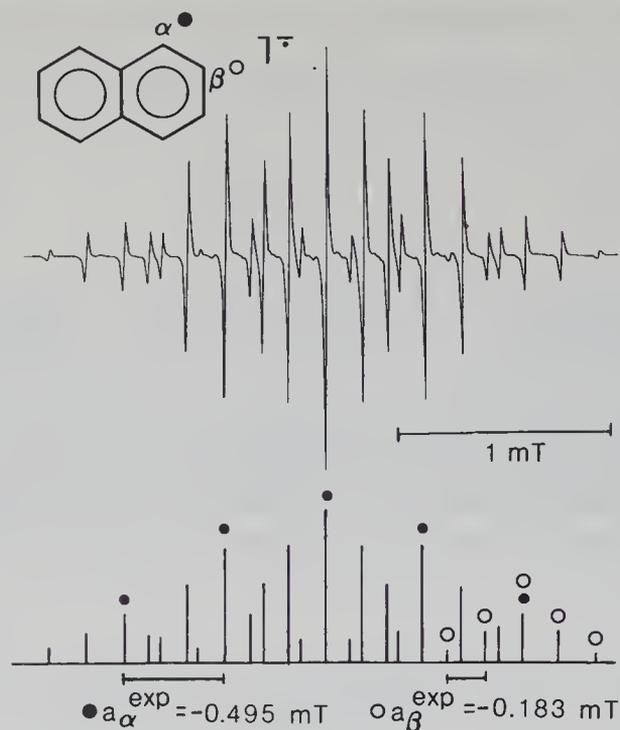
The form of the singly occupied MO ψ_K may be derived from an analysis of the ESR spectrum (**McConnell relation**):

$$a(^1\text{H}_\mu) = Q \cdot c_{K\mu}^2$$

$c_{K\mu}$ = coefficient of the π -AO at the atom C_μ in the singly occupied MO ψ_K

$a(^1\text{H})$ = isotropic hyperfine coupling constant (fluid solution)

$$Q = -2.3 \text{ mT}$$



In the naphthalene radical anion $C_{10}H_8^-$ the LUMO ψ_6 is singly occupied. Since the probability of finding the unpaired electron varies for the α - and for the β -position, differing electron-proton hyperfine coupling constants $a(^1H_\alpha)$ and $a(^1H_\beta)$ are encountered (Intensities not to scale).

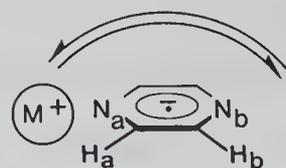
The parameter Q describes the efficiency of π - σ spin polarization. This is the mechanism, which in π -radicals is responsible for the occurrence of spin density at the proton and thus for the observation of isotropic hyperfine coupling.

The McConnell relation (and its refined version) has been applied to a large number of π -radicals and has confirmed quantum chemical calculations of molecular electronic structure.

It frequently happens that, in addition to hyperfine coupling to magnetic nuclei of the radical anion, splitting caused by the counterion (e.g. Na^+ , nuclear spin $I = 3/2$) is detected. In these cases, ESR spectroscopy yields unambiguous information about the structure of the ion pair M^+ArH^- .

Like NMR, ESR spectroscopy lends itself to the study of dynamic processes. The ion

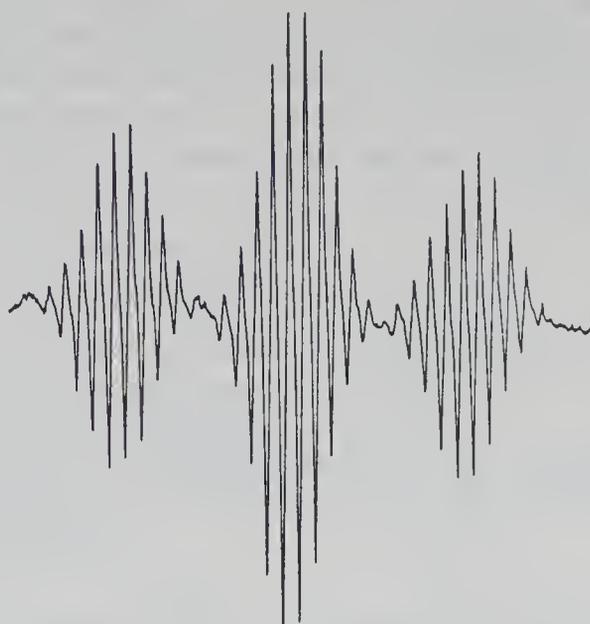
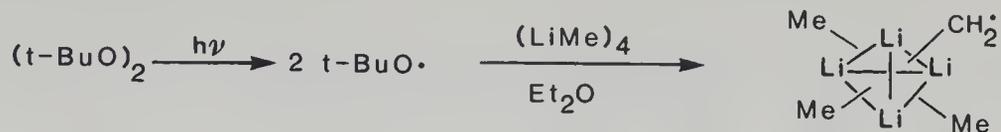
pair M^+ pyrazine $^-$ in THF may serve as an example (Atherton, 1966):



Li^+ is firmly coordinated to one of the two N atoms. This follows from the hyperfine pattern which is governed by unequal coupling constants $a(^1H_a) \neq a(^1H_b)$ and $a(^{14}N_a) \neq a(^{14}N_b)$.

Na^+ , however, undergoes an exchange between the two N sites (activation energy 30 kJ/mol) which at $-65^\circ C$ is slow and at $+23^\circ C$ is fast on the ESR time scale (10^{-6} – 10^{-8} s). In the fast exchange case a hyperfine structure with the coupling constants $a(4^1H) = 0.27$ mT, $a(2^{14}N) = 0.714$ mT and $a(^{23}Na) = 0.055$ mT is observed.

b) Preservation of the Tetrameric Structure of $(\text{LiCH}_3)_4$ in Solution



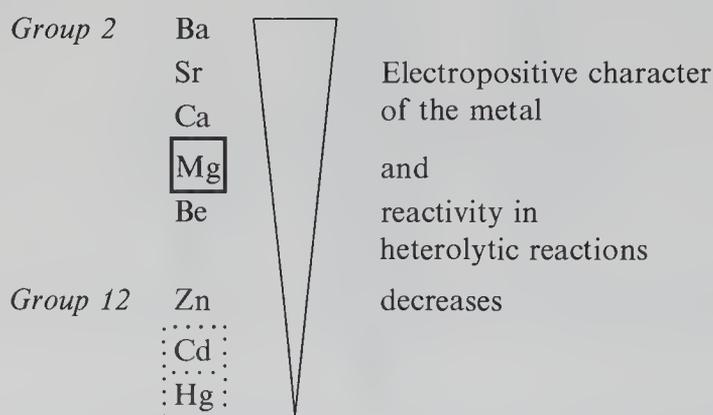
$$\begin{aligned} a(2 \text{ } ^1\text{H}) &= 1.83 \text{ mT} \\ a(3 \text{ } ^7\text{Li}) &= 0.17 \text{ mT} \end{aligned}$$

Photolytically generated radicals $\text{t-BuO}\cdot$ abstract an H atom from the $(\text{LiCH}_3)_4$ unit. The identity of the species $(\text{CH}_3)_3\text{Li}_4\text{CH}_2\cdot$ is revealed by the ESR spectrum which consists of a triplet ($2 \text{ } ^1\text{H}$, $I = 1/2$) of decets ($3 \text{ } ^7\text{Li}$, $I = 3/2$) (Kochi, 1973).

In addition to structural information, the observation of hyperfine coupling in fluid solution also provides hints as to the degree of covalency of the $\text{Li}-\text{C}$ bond.

6 Organometallics of Groups 2 and 12

Among the organometallic compounds of groups 2 (Be, Mg, Ca, Sr, Ba) and 12 (Zn, Cd, Hg), organomagnesium compounds are of prime importance because of their application in organic synthesis. To a lesser extent, organocadmium- and organomercury reagents have also found preparative use. The reactivity of these compounds increases with an increasing difference in electronegativity between metal and carbon:



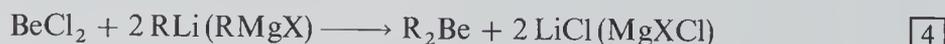
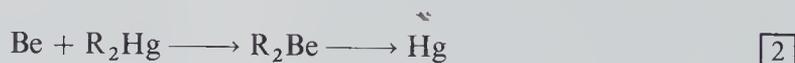
Organomagnesium compounds combine in a unique way high reactivity and ease of access. The high reactivity of R_2Hg in transmetallations may be traced to ready homolytic cleavage of the Hg–C bond (p. 51).

6.1 Organometallics of the Alkaline Earths (Group 2)

6.1.1 Organoberyllium Compounds

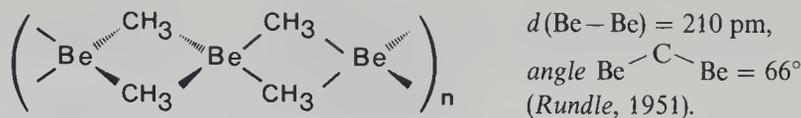
This group comprises highly toxic as well as air- and moisture-sensitive materials which display a number of structural peculiarities.

PREPARATION AND STRUCTURES

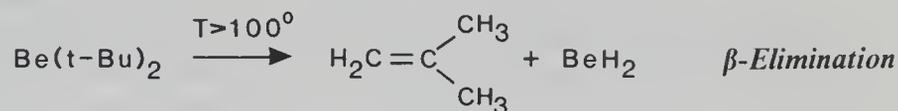


As a Lewis acid, BeR_2 forms stable etherates $(Et_2O)_2BeR_2$; they are obtained free of solvent only with difficulty.

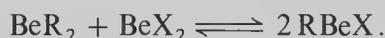
Like BeCl_2 , the compound $\text{Be}(\text{CH}_3)_2$ is a polymeric solid (structural type SiS_2). The bonding situation in the chain resembles that in the aluminum alkyls (2e 3c bonds, compare $\text{Al}_2(\text{CH}_3)_6$ p. 78, "diagonal relationship" Be – Al).



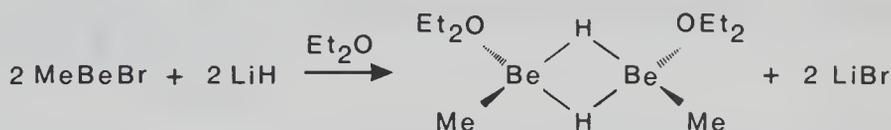
In the gas phase, BeR_2 is monomeric and linear and therefore is to be described by $\text{Be}(sp)$ hybridization. For steric reasons, $\text{Be}(t\text{-Bu})_2$ is monomeric even in the solid state. The thermolysis of $\text{Be}(t\text{-Bu})_2$ yields pure, unsolvated beryllium hydride:



$\text{Be}(\text{CH}_3)_2$, which is void of $\beta\text{-H}$ atoms, only decomposes at $T > 200^\circ\text{C}$. Similar to magnesium, organoberyllium compounds equilibrate with beryllium halides:



Organoberyllium hydrides, which can be prepared from RBeX and metal hydrides, according to their $^1\text{H-NMR}$ spectra feature hydride bridges and terminal methyl groups in *cis*- and *trans* configuration.

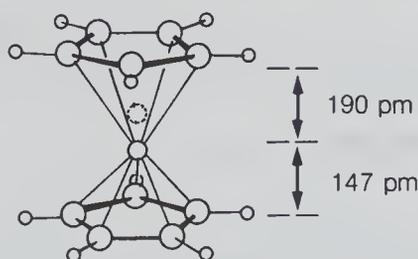


Thus, the formation of a **hydride bridge** is favored over an **alkyl bridge**, and isomerizations via intermediate cleavage of hydride bridges are slow on the NMR time scale.

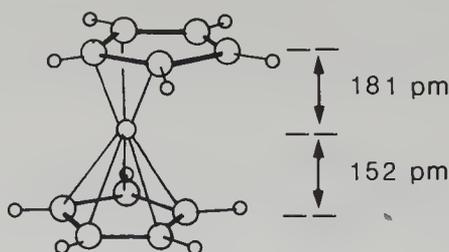
Beryllocene, accessible according to (E. O. Fischer, 1959)



still poses structural problems since investigations in different states of aggregation lead to different molecular geometries:



Structure of $(\text{C}_5\text{H}_5)_2\text{Be}$ in the gas phase (electron diffraction): symmetry C_{5v} . The energy minima of the Be atomic positions lie on the fivefold axis. In both positions, the Be atom has different distances to the two ring centers.



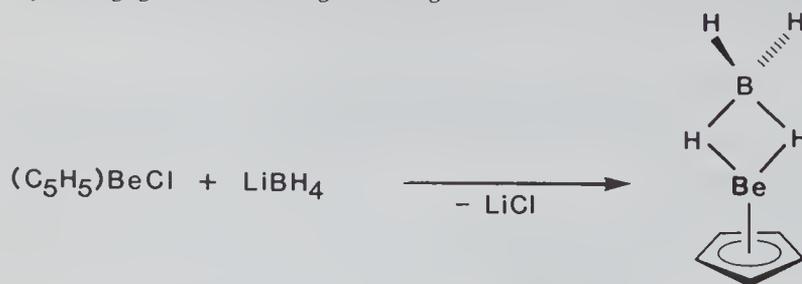
Structure of $(C_5H_5)_2Be$ in the crystal (X-ray diffraction, $-120^\circ C$): symmetry C_s , η^3 -, η^5 -structure, "slipped sandwich". A re-interpretation of the electron diffraction data led to the conclusion that this structure may also pertain to beryllocene in the gas phase (Haaland, 1979).

On the one hand, $(C_5H_5)_2Be$ possesses a dipole moment ($\mu = 2.24$ Debye in cyclohexane). On the other hand, judging from the 1H -NMR spectrum, beryllocene displays two equivalent C_5H_5 rings. Evidently, an exchange of the Be atom between two positions on the fivefold axis takes place, which is fast on the 1H -NMR time scale (**fluxional structure**). The bonding in beryllocene is essentially ionic. The structural peculiarities may arise from the fact that the optimal bond distance between Be^{2+} and $C_5H_5^-$ is smaller than half the van der Waals distance between two $C_5H_5^-$ ions.

From beryllocene and dimethylberyllium a half-sandwich compound is obtained which, in the spirit of Wade's rules (p. 68), may be referred to as a nido cluster:



The compound $(C_5H_5)BeCl$ belongs to the same category, $d(Be-Cl) = 187$ pm, $d(Be-C_5H_5_{center}) = 145$ pm. The structure of cyclopentadienylberyllium boranate demonstrates that Be and B share the propensity to engage in $2e\ 3c$ bridge bonding:



6.1.2 Organomagnesium Compounds

PREPARATION



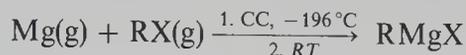
1

The addition of I_2 activates the Mg surface; MgI_2 thus formed, binds the last traces of water in the reaction mixture. In a more economical technical variation, hydrocarbon/

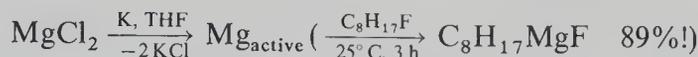
ether mixtures are used as solvents:



Unsolvated **Grignard reagents** can be prepared by means of cocondensation (CC) of magnesium vapor with the vapor of the alkyl halide on a cooled surface (Klabunde, 1974):



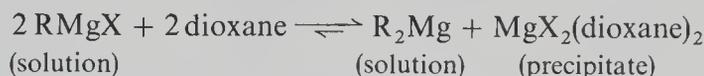
An extremely reactive form of magnesium is obtained according to Rieke (1977), if anhydrous MgCl_2 is reduced with potassium:



The preparation of binary organomagnesium compounds is accomplished by transmetalation



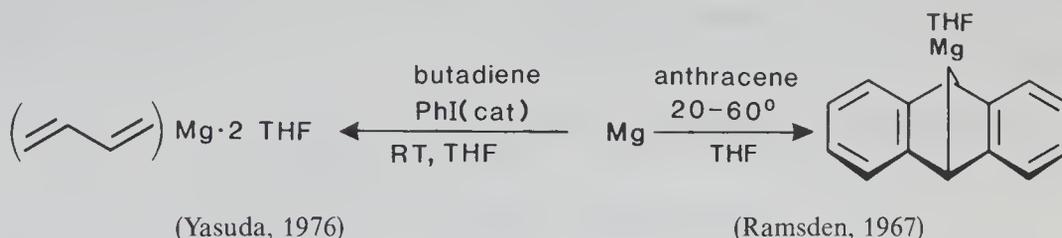
as well as by solvent-induced shifts in the equilibrium position:



The latter procedure may lead to **magnesacycles**:

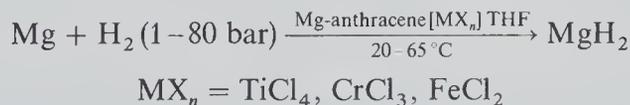


Besides organic halides, a number of compounds with conjugated C=C double bonds react with magnesium:



Mg-butadiene, [(2-butene-1,4-diyl)magnesium] a white, polymeric, sparingly soluble material of unknown structure acts as a source for butadiene dianions $\text{C}_4\text{H}_6^{2-}$. It is the reagent of choice for the introduction of butadiene as a ligand in transition-metal complexes (p. 255).

Mg-anthracene, orange-yellow crystals, reacts with anhydrous transition-metal halides to form catalysts which serve in the hydrogenation of magnesium under mild conditions (Bogdanović, 1980):

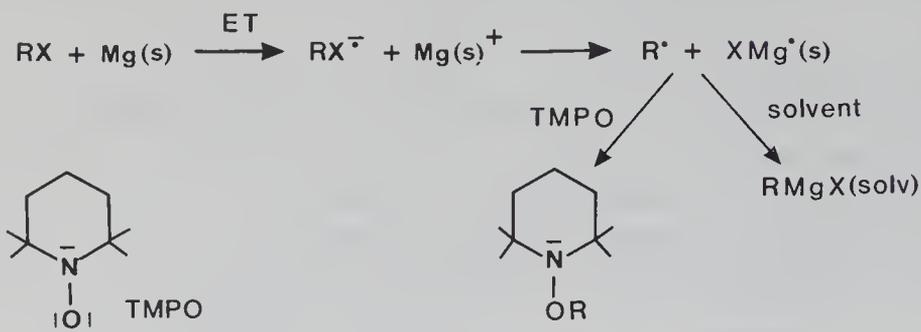


MgH_2 adds to 1-alkenes (**hydromagnesation**) and, upon cleavage above 300°C , affords pyrophoric Mg free from solvent and halide for synthetic use. Furthermore, MgH_2 is a high-temperature storage medium for molecular hydrogen.

MECHANISM OF FORMATION AND CONSTITUTION OF ORGANOMAGNESIUM COMPOUNDS

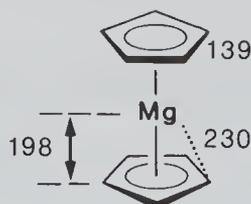
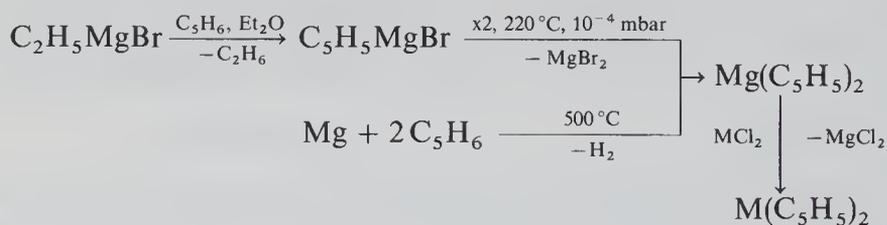
Notwithstanding the extensive use of Grignard reagents in organic synthesis, details concerning their modes of formation, aggregation in solution, and mechanisms of consecutive reactions are still topics of current research (Ashby and others).

Recent results suggest that the formation of "RMgX" is initiated by an electron transfer step (*ET*). A hint as to the intermediacy of radicals $R\cdot$ is furnished by the reaction with the trapping agent 2,2,6,6-tetramethylpiperidine nitroxyl, TMPO (Whitesides, 1980):



The possibility that *ET*-reactions are involved, and the experience, that the latter are catalyzed by transition-metal ions dictates the use of ultrapure magnesium in mechanistic studies and invalidates many previous investigations in this field.

$Mg(C_2H_5)_2$, like $Be(C_2H_5)_2$, possesses a **polymeric chain structure** with $Mg^{\leftarrow}Et-Mg(2e3c)$ bridge bonds. From ethers, Grignard reagents crystallize as solvates, e.g. $RMgX(Et_2O)_2$. The readily accessible **magnesocene**, $Mg(C_5H_5)_2$ (Fischer, Wilkinson, 1954), is a useful reagent for the introduction of C_5H_5 groups:



$Mg(C_5H_5)_2$ forms white, pyrophoric crystals which start to sublime at $50^\circ C/10^{-3}$ mbar, dissolve in non-polar as well as in polar aprotic media and undergo vigorous hydrolysis. The structural parameters apply to the crystalline state (*X-ray diffraction, E. Weiss, 1975*). In the gas phase, the bond distances are slightly elongated and the eclipsed conformation is favored (*electron diffraction, Haaland, 1975*).

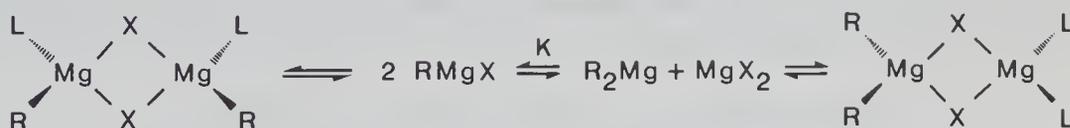
The driving force of cyclopentadienylations of transition-metal halides by means of $\text{Mg}(\text{C}_5\text{H}_5)_2$ is largely provided by the formation of MgX_2 . The bonding situation in magnesocene, especially the question of the dominance of covalent or ionic bonding, is still a matter of debate. The structural similarities to ferrocene and the absence of a dipole moment do not constitute unequivocal evidence for covalent bonding since in the case of purely ionic bonding, an axially symmetric sandwich structure would also be the (electrostatically) favored configuration. Furthermore, the realization of a molecular crystal lattice does not necessarily imply covalent bonding within the $\text{Mg}(\text{C}_5\text{H}_5)_2$ units because, due to the disparate sizes of Mg^{2+} and C_5H_5^- , an arrangement in which the lattice points are occupied by triple-ions $\text{Mg}^{2+}(\text{C}_5\text{H}_5^-)_2$ is more favorable than a genuine ionic lattice. Observations which ascribe a high degree of polarity to the bonding in $\text{Mg}(\text{C}_5\text{H}_5)_2$ are the electric conductivity of solutions in NH_3 or in THF, brisk hydrolysis to $\text{Mg}(\text{OH})_2$ and C_5H_6 and the similarity of the ^{13}C -NMR shifts to those of alkali metal cyclopentadienyls:

Dominant bond type:	Ionic			Covalent
	$\text{Li}(\text{C}_5\text{H}_5)$	$\text{Na}(\text{C}_5\text{H}_5)$	$\text{Mg}(\text{C}_5\text{H}_5)_2$	$\text{Fe}(\text{C}_5\text{H}_5)_2$
^{13}C -NMR δ/ppm	103.6	103.4	108.0	68.2

^{25}Mg -NMR evidence which implies extensive charge neutralization between magnesium and cyclopentadienyl has added new momentum to the discussion of bonding in magnesocene (Benn, 1986 R).

GRIGNARD REAGENTS IN SOLUTION

A concise description of the situation prevailing in solution is given by the **Schlenk equilibrium** (1929):



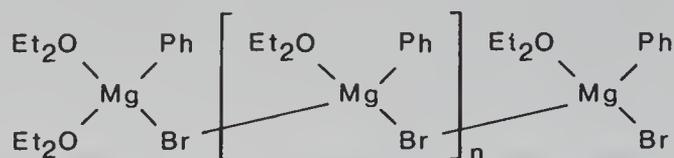
L = solvent molecule with donor properties, usually ether

$K = 0.2$ for EtMgBr (equilibrium constant)

An equimolar solution of MgX_2 and R_2Mg in ether behaves identically to a conventional Grignard reagent RMgX . Radioactive ^{28}Mg (β^- emission, $\tau_{1/2} = 21.2$ h), added to the solution as $^{28}\text{MgBr}_2$, is rapidly scrambled among the species MgX_2 , RMgX and R_2Mg . The dynamic character of the Schlenk equilibrium also manifests itself in the ^1H -NMR spectrum of CH_3MgBr in solution. At room temperature, only one signal is observed for the methyl protons, attesting to rapid exchange of CH_3 between CH_3MgBr and $(\text{CH}_3)_2\text{Mg}$. Separate signals appear at $T < -100^\circ\text{C}$ (slow exchange). The most direct approach in the study of the Schlenk equilibrium is provided by ^{25}Mg -NMR spectroscopy through which the various species involved can be characterized separately (Benn, 1986 R).

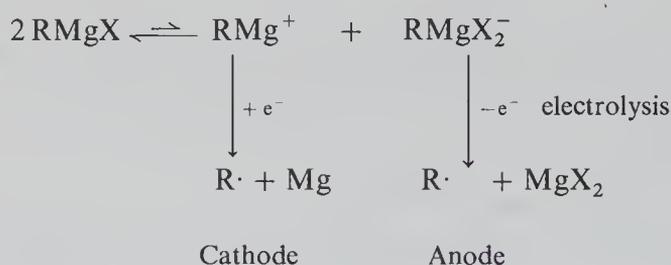
Example (THF, 37°C): Et_2Mg $\delta = 99.2$, EtMgBr $\delta = 56.2$, MgBr_2 $\delta = 13.9$ ppm. At 67°C , coalescence to a single signal, $\delta = 54$ ppm, occurs. These data reflect the kinetics of exchange as well as the temperature dependence of the Schlenk equilibrium.

The detailed study of the influence of solvent, concentration and the nature of R has revealed that the reality must be more complicated than the description given by the Schlenk equilibrium. In THF, RMgX exists as the monomeric species $\text{RMgX}(\text{THF})_2$ over a wide range of concentrations. In Et_2O , however, RMgX is monomeric only in dilute solution ($< 0.1\text{M}$) whereas at higher concentrations oligomers (chains and rings) are formed:



In general, **halide bridges are preferred over alkyl (2e3c) bridges**. In the case of $t\text{-BuMgX}$, only monomeric and dimeric units are encountered.

Solutions of RMgX in Et_2O show electrical conductivity, although the extent of dissociation is small:



During electrolysis, radicals $\text{R}\cdot$ are generated at both electrodes. If these radicals are relatively long lived, dimerization can occur:

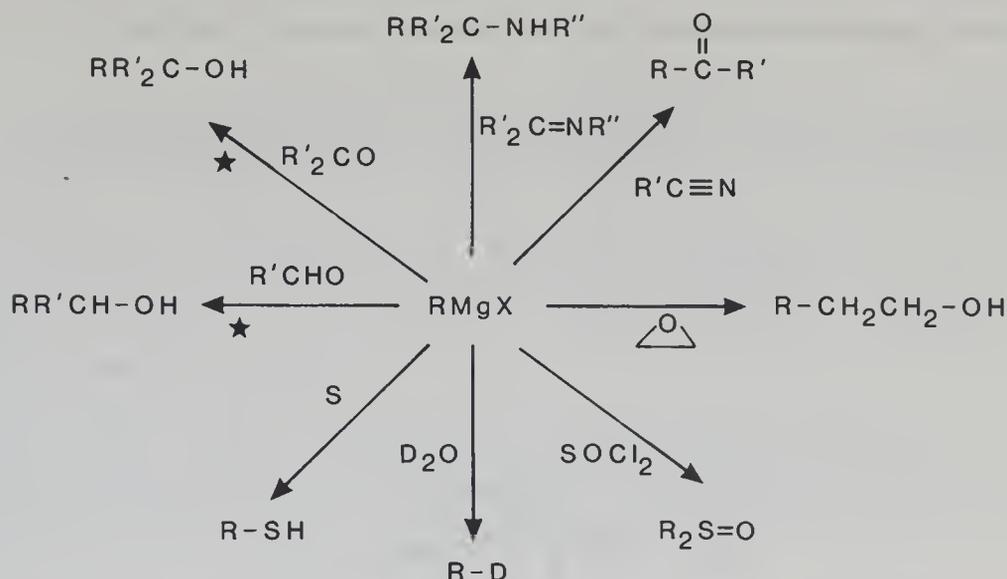


Alternatively, the radicals can react with the electrode material as in a commercial process for the production of tetraethyllead (p. 139):



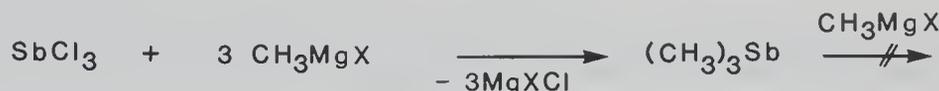
REACTIONS OF ORGANOMAGNESIUM COMPOUNDS

From the breadth of applications of Grignard reagents in organic synthesis, only a small selection will be presented here (products after hydrolysis):



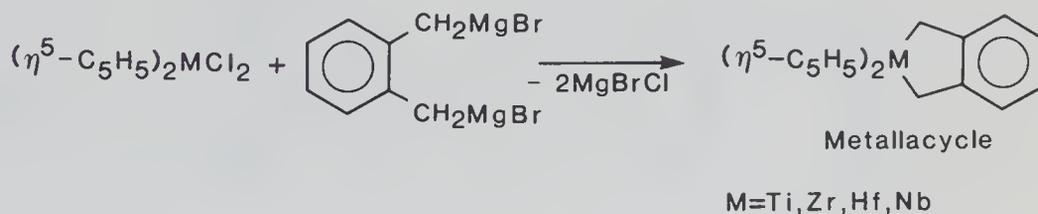
* The intermediate conversion of RMgX into $\text{RTi}(\text{OCHMe}_2)_3$ renders the addition to carbonyl functions highly chemo- and stereoselective (p. 32).

Like organolithium compounds, Grignard reagents serve as alkylating and arylating agents for main-group and transition-metal halides:

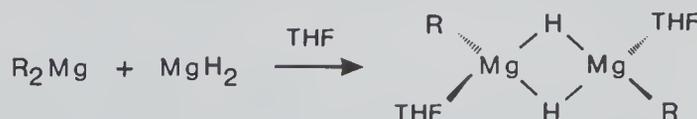


RMgX is less reactive than RLi , however. In contrast to the latter, no "ate complexes" like $[(\text{C}_6\text{H}_5)_6\text{Sb}]^-$ are obtained from reactions with Grignard reagents.

The following example illustrates the synthesis of a metallacycle:



Organomagnesium hydrides RMgH are prepared according to:

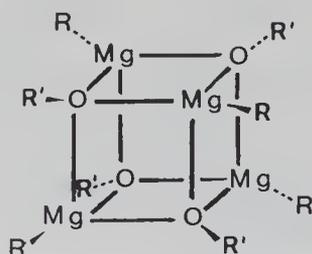
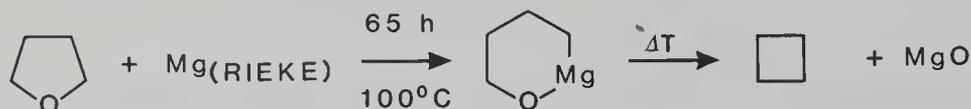


Note the preference for (2e 3c)hydride- over (2e 3c)alkyl bridging.

Organomagnesium alkoxides RMgOR are products of partial alcoholysis:

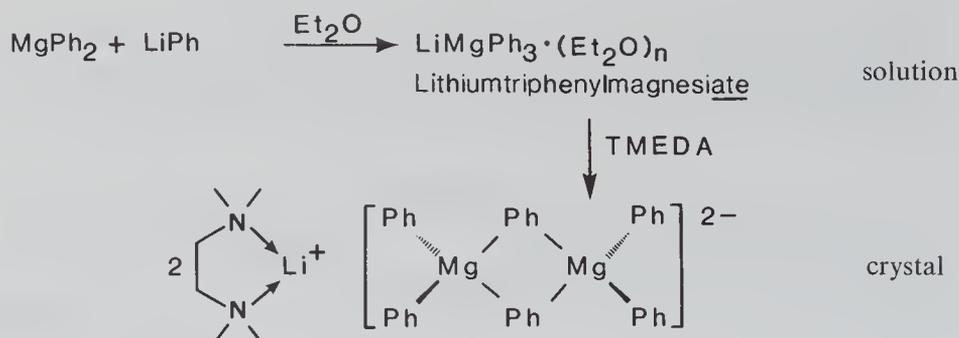


or of the reaction of Rieke magnesium (p. 41) with ethers (Bickelhaupt, 1977):



The structure of the aggregates $(\text{RMgOR}')_n$ is governed by the ability of alkoxide ions to function as triply bridging ligands. The tetramer $(\text{RMgOR}')_4$ is an example of a heterocubane $(\text{AB})_4$.

Magnesium-“ate-complexes” $\text{M}_x\text{Mg}_y\text{R}_z$ ($\text{M} = \text{group 1, 2 or 13 metal}$) were first described by Wittig (1951):



$[\text{Mg}_2\text{Ph}_6]^{2-}$ is isoelectronic and isostructural to $[\text{Al}_2\text{Ph}_6]$ (p. 79). The less electropositive metal usually appears in the “ate-complex”-anion. In the case of two metals of comparable electropositive character, an essentially covalent structure with $(2e\ 3c)$ alkyl bridges is realized:



6.1.3 Organocalcium-, Strontium- and Barium Compounds

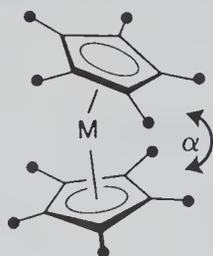
The preparation of the heavier alkaline earth organometallics is difficult, requiring meticulous control of the reaction conditions. Since the products do not offer any advantages over Grignard reagents, their chemistry has not been studied extensively. Organobarium compounds have found limited application as initiators for polymerizations. Like the organyls of the heavier alkali metals, the Grignard homologues RMX ($M = \text{Ca}, \text{Sr}, \text{Ba}$) are best described by ionic bonding; they also attack ethers at the α -position. This property, as well as the lack of solubility in nonpolar solvents complicates the study of RMX in homogeneous solution.

The preparation of the di(cyclopentadienyl) compounds of Ca, Sr and Ba should not be dismissed as an exercise in "bean counting", since a number of thought-provoking structural features has emerged from their study. $\text{Ca}(\text{C}_5\text{H}_5)_2$ in the crystal forms polymeric chains (Stucky, 1974). Structural information concerning the isolated molecules is available only for the permethylated derivatives $\text{M}(\text{C}_5\text{Me}_5)_2$.

Special features of the ligand pentamethylcyclopentadienyl C_5Me_5^- (Cp^), compared to C_5H_5^- (Cp):*

- stronger π -donor, weaker π -acceptor properties (p. 319)
- increased covalent character of the cyclopentadienyl-metal bond
- increased thermal stability of the metal complexes
- kinetic stabilization effected by steric shielding of the central metal
- attenuation of intermolecular interactions, decreased tendency towards polymeric structures, increased vapor pressure and solubility.

The latter aspect allowed the structural analyses of $\text{M}(\text{C}_5\text{Me}_5)_2(\text{g})$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) by means of electron diffraction (Blom, 1987):



M	α	
	$\text{M}(\text{C}_5\text{Me}_5)_2$	MI_2
Mg	180	180
Ca	154	148
Sr	149	144
Ba	148	138

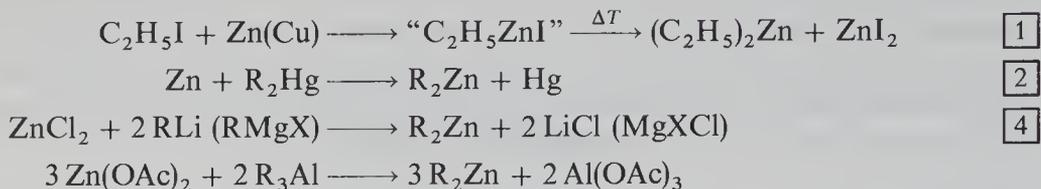
It came as a surprise to find that the di(cyclopentadienyl)metal complexes of the heavier alkaline earths possess bent sandwich structures. A comparable bending is, however, also encountered within the corresponding metal halides in the gas phase (Kasparov, 1979) – the reasons for the lowering of symmetry in these two classes of compounds should be related. Whereas in the case of the compounds $\text{M}(\text{C}_5\text{H}_5)_2$, $M = \text{Ge}, \text{Sn}, \text{Pb}$, the existence of a lone pair of electrons at the central metal atom may enter into explanations of the bent structure (p. 134), its absence in complexes with $M = \text{Ca}, \text{Sr}, \text{Ba}$ calls for a more subtle interpretation. Ironically, both covalent (Coulson, Hayes, 1973) and ionic bonding models (Guido, 1976) have been used in this context.

6.2 Organometallics of Zn, Cd, Hg (Group 12)

The elements of group 12 possess completely filled *d* shells of low energy, void of donor or acceptor properties. Therefore, a discussion of the organometallic chemistry of Zn, Cd, and Hg in connection with that of the group 2 elements is warranted.

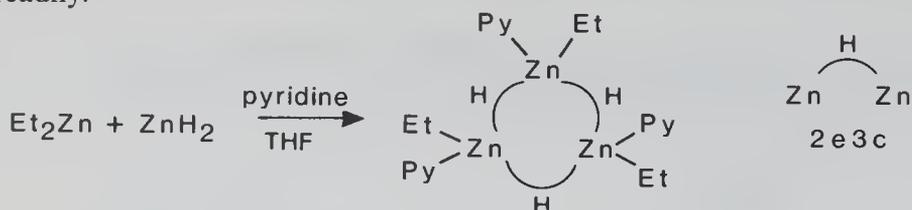
6.2.1 Organozinc Compounds

PREPARATION

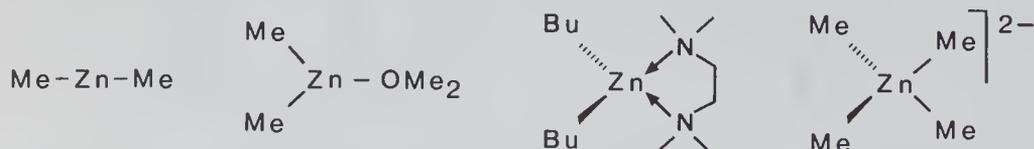


STRUCTURE AND PROPERTIES

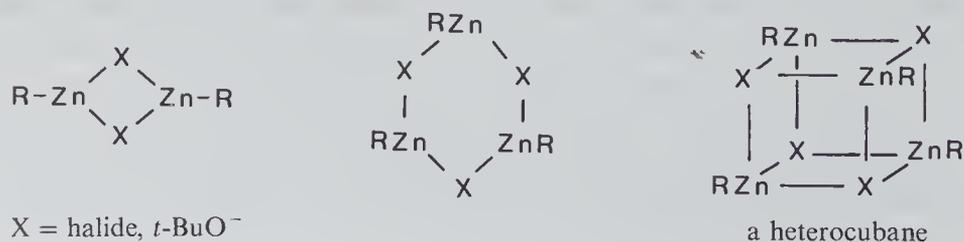
In contrast to BeR_2 and MgR_2 , binary organozinc compounds ZnR_2 ($\text{R} = \text{alkyl or aryl}$) are monomeric. The molecules are linear and have low melting- and boiling points [e.g. $\text{Zn}(\text{C}_2\text{H}_5)_2$: mp -28°C , bp 118°C , pyrophoric]. Whereas self-association via $\text{Zn}-\text{R}-\text{Zn}$ ($2e3c$) bridges is apparently disfavored, $\text{Zn}-\text{H}-\text{Zn}$ ($2e3c$) bridges are formed readily:

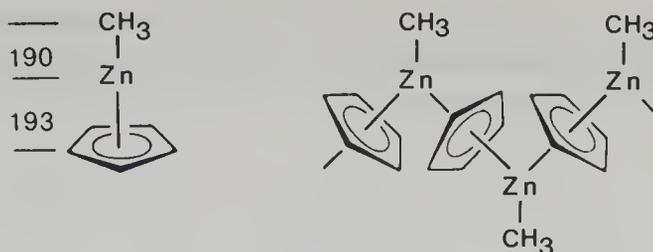


σ -Donor ligands also coordinate to binary organozinc molecules:

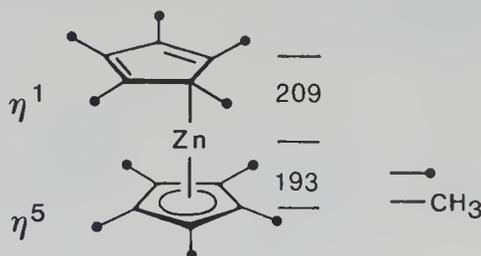


They effect the association of molecules of the type RZnX :





(Cyclopentadienyl) (methyl)zinc, which is monomeric in the gas phase, forms chains with bridging Cp ligands in the crystal.

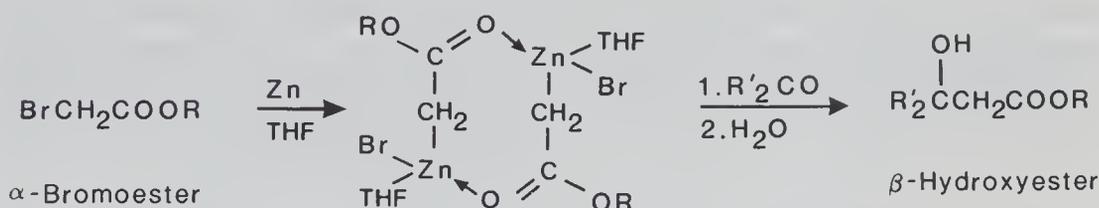


The structure of bis(pentamethylcyclopentadienyl)zinc in the gas phase features η^1 -, η^5 -coordination. In this way, as in the case of CpZnMe, an 18 valence-electron shell is created for the Zn atom. Cp₂Zn in solution gives rise to one ¹H-NMR signal only, which indicates a rapid haptotropic change between η^1 - and η^5 -coordination (Haaland, 1985).

Cp₂Zn, like CpZnMe, is polymeric in the solid state. In their chemical behavior, organozinc compounds resemble organomagnesium- and organolithium compounds, their reactivity in addition reactions being reduced, however. In organometallic synthesis, ZnR₂ replaces LiR and RMgX if relatively mild, non-basic conditions are called for:

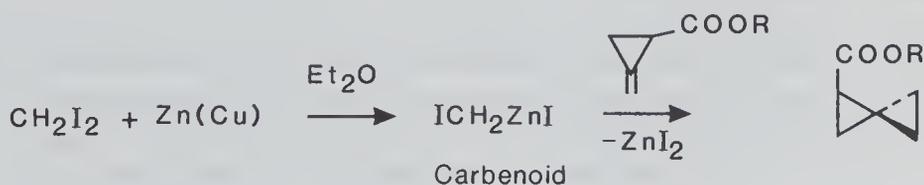


The well known **Reformatsky reaction** proceeds via an organozinc intermediate:

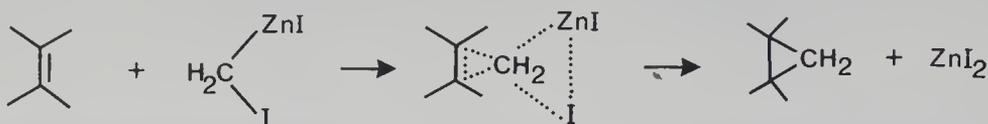


The dimeric structure of the Reformatsky reagent is maintained in solution (van der Kerk, 1984).

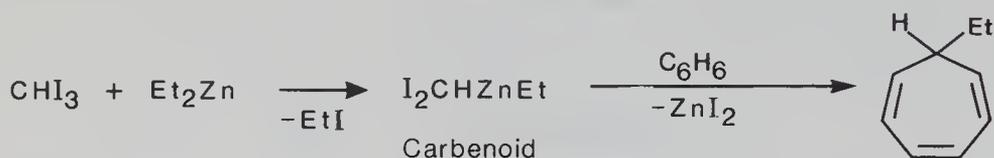
Organozinc carbenoids play an important role in organic synthesis. An example is the **Simmons-Smith reaction** (1973 R), by which cyclopropanations are effected:



Free carbenes are not formed during the course of this process; instead, attack by the carbenoid is thought to occur whereby the extent of side reactions is reduced. The addition probably follows a concerted path:



Organozinc carbenoids also lend themselves to ring expansions of arenes to yield cycloheptatriene derivatives (Hashimoto, 1973):

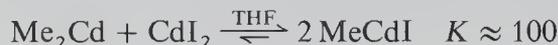


6.2.2 Organocadmium Compounds

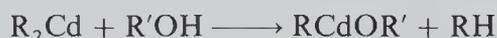
The method of choice for the preparation of binary organocadmium compounds is metathesis



Organocadmium halides equilibrate with their binary counterparts:



Organocadmium alkoxides are obtained by partial alcoholysis:



With regard to structure and reactivity, organocadmium compounds resemble their zinc congeners. The Lewis acidity of R_2Cd is lower than that of R_2Zn , however (tetraorganocadmicates CdR_4^{2-} are unstable). The diminished reactivity of organocadmium compounds is exploited in a **synthesis of ketones from acid chlorides**:



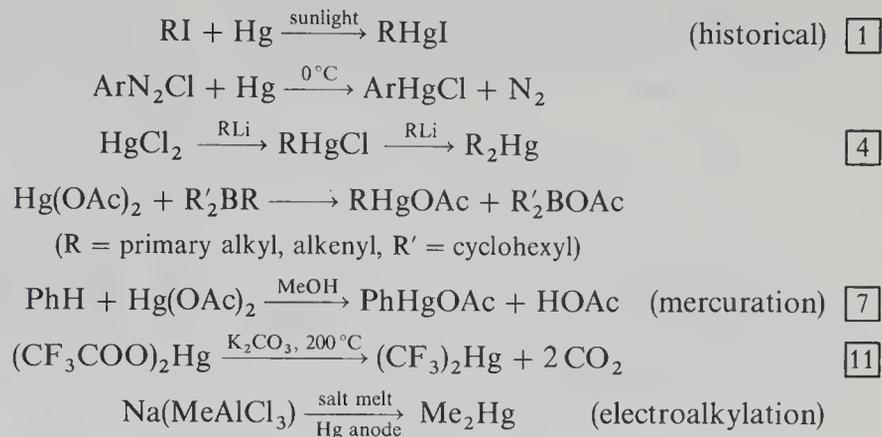
This procedure is practicable in the presence of the functionalities >C=O , $-\text{COOR}$, and $-\text{C}\equiv\text{N}$ to which organocadmium reagents, as opposed to Grignard reagents, do not add.

6.2.3 Organomercury Compounds

Historically, the extensive search for pharmacologically active compounds has transformed organomercury chemistry into a very broad field. The same is true for organoarsenic chemistry. In addition, the inert character of the $\text{Hg}-\text{C}$ bond towards attack by air and water facilitated studies during the infancy of organometallic chemistry.

Traditionally, organomercury alkoxides PhHgOR' have found application as **fungicides, bactericides and antiseptics**, but their use is currently on the decline. Today, a few organomercury compounds are still utilized in organic synthesis.

PREPARATION



STRUCTURE AND PROPERTIES

In accordance with the similar electronegativities of mercury and carbon, the $\text{Hg}-\text{C}$ bond is essentially covalent. The organometallic chemistry of mercury is almost exclusively that of the oxidation state Hg^{II} . Species of the kind $\text{R}-\text{Hg}^{\text{I}}-\text{Hg}^{\text{I}}-\text{R}$ have occasionally been proposed, but never unequivocally identified. Thermochemically, the instability of organomercury (I) compounds is reflected in the strongly differing dissociation energies for the first and the second methyl group in $(\text{CH}_3)_2\text{Hg}$, $D(\text{MeHg}-\text{Me}) = 214 \text{ kJ/mol}$, $D(\text{Hg}-\text{Me}) = 29 \text{ kJ/mol}$. Therefore:



R_2Hg species readily undergo homolytic cleavage if energy is supplied thermally or photochemically. This reaction represents a convenient **source of radicals** and can be applied to homolytic aromatic substitution:

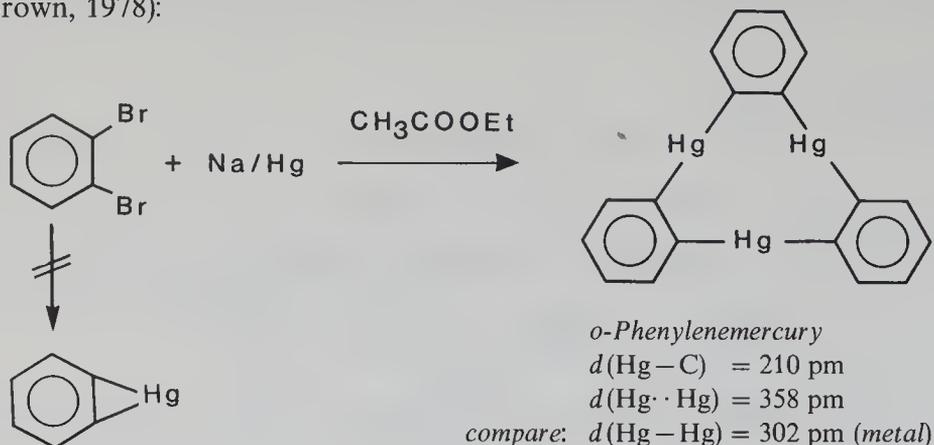


The utility of organomercury compounds as transmetallating agents (p. 15) is based on this inherent weakness of the $\text{Hg}-\text{C}$ bond. Conversely, organomercury compounds are practically inert against air and moisture. This may be traced to the weak acceptor character of molecules R_2Hg and RHgX . The formation of adducts with concomitant increase of the coordination number is observed for R_2Hg only if R bears an exceptionally high electron affinity. Example: $(\text{CF}_3)_2\text{Hg}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)$.

If donor ligands are proffered to organomercury halides, a redistribution often occurs wherein the organometallic component maintains its coordination number 2:



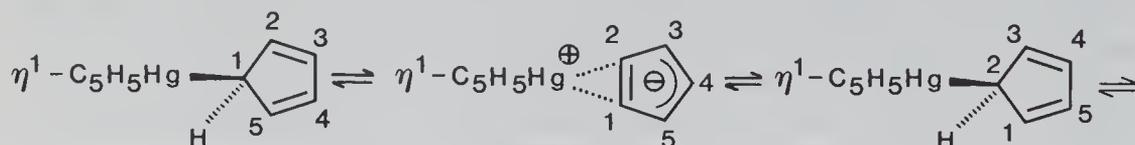
The molecules of RHgX and R_2Hg are **linear** (sp or $d_{z^2}s$ hybridization of Hg). Attempts to force bent $\text{C}-\text{Hg}-\text{C}$ moieties by means of “tricks” are evaded by oligomerization (D. S. Brown, 1978):



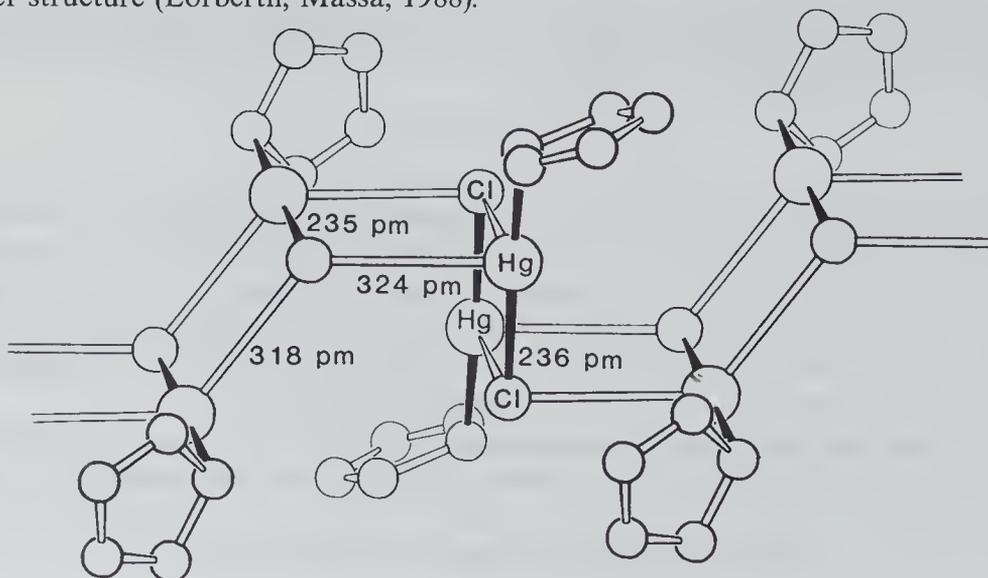
Di(cyclopentadienyl)mercury (C_5H_5)₂Hg, can be prepared in aqueous media



Although $(\text{C}_5\text{H}_5)_2\text{Hg}$ forms a Diels-Alder adduct with maleic anhydride and displays a $\text{Hg}^{\sigma}\text{C}$ stretching vibration in the IR spectrum, only one signal is observed in the $^1\text{H-NMR}$ spectrum. These findings are in accord with **structural fluxionality** for $(\eta^1-\text{C}_5\text{H}_5)_2\text{Hg}$, such that a sequence of **haptotropic shifts** renders all the ring protons equivalent on the $^1\text{H-NMR}$ time scale (Wilkinson, 1956):



The pentamethylcyclopentadienyl ligand Cp^* replaces only one chloride ion at HgCl_2 leading to Cp^*HgCl , a compound which in the solid state displays an interesting folded ladder structure (Lorberth, Massa, 1988):



The most important reactions with synthetic appeal, involving organomercury compounds as intermediates, are mercuration, solvomercuration/demercuration and carbene transfer.

- **Mercurations** are metallation reactions (H/M exchange) in which mercury(II)-acetate is used. They are applicable to arenes and to nonaromatic compounds of sufficient CH acidity (alkynes, nitro compounds, 1,3-diketones etc.):



Mechanistically, this is an electrophilic substitution (S_E). Mercurations are catalyzed by strong, non-coordinating acids which generate the attacking electrophile HgOAc^+ :



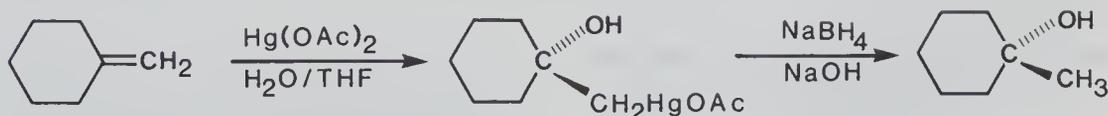
- **Solvomercuration/demercuration** constitutes an addition of HgX^+ and Y^- to an alkene with subsequent cleavage of the Hg–C bond:



(HY = solvent or component of the medium)

(Y = OH, OR, OAc, O₂R, NR₂ etc.)

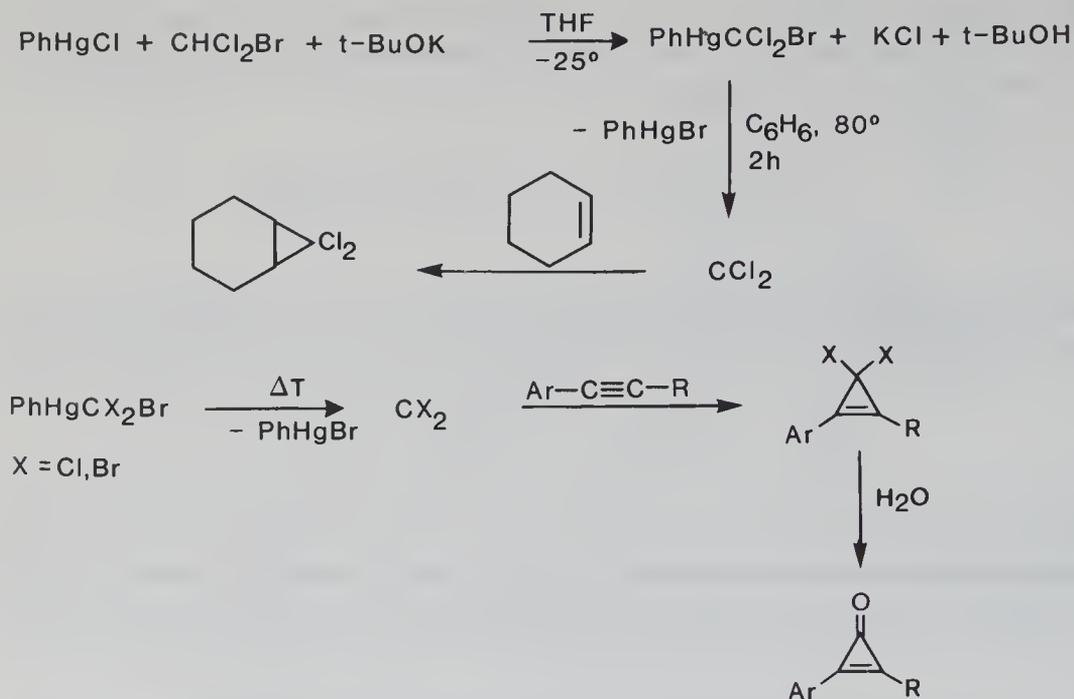
Example:



This procedure has been widely applied; it operates under particularly mild conditions, tolerates many functional groups and is rarely accompanied by rearrangements. The first step, called **oxymercuration** in this case, follows Markovnikov direction, and thus complements hydroborations (p. 60 f), which proceed in an anti-Markovnikov fashion. The utility of the mercuration products stems from the possibility of replacing mercury by hydrogen, halogen or other functional groups.

● **Carbene Transfer from Phenyl(α -halomethyl)mercury (Seyferth-Reagent)**

Compounds of the type PhHgCX_3 readily extrude dihalocarbenes CX_2 which can be used in consecutive reactions. From precursors $\text{PhHgCX}_2\text{X}'$ elimination occurs in such a way that PhHgX' retains the heavier halide. Examples:



These **cyclopropanations** proceed under rather mild conditions and, most notably, in the absence of basic reagents; the intermediate $\text{PhHgCX}_2\text{X}'$ has to be isolated, however. Functional groups like $-\text{COOH}$, $-\text{OH}$, and $-\text{NR}_2$ create problems, since they react with $\text{PhHgCX}_2\text{X}'$. In contrast to the Simmons-Smith reaction, the mechanism of the Seyferth dihalocyclopropanation is thought to involve free carbene intermediates.

Excursion

Organomercury compounds in vivo

As a result of the Minimata catastrophe in Japan (1953–1960) and of accidental mass poisonings by cereal seed in Iraq (1970/71), the reputation of the element mercury has been considerably maligned. In the first case, mercury from industrial waste waters found its way into marine organisms and sediments. In the second case, wheat, which had been treated with

the seed disinfectant ethylmercury *p*-toluenesulfonic anilide, was consumed. The threat posed by mercury in vivo is closely affiliated with organomercury chemistry:

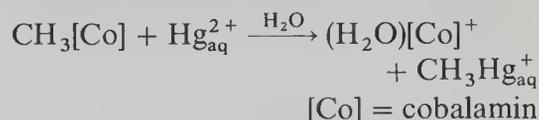
- Biological methylation converts inorganic Hg^{II} -compounds into the extremely toxic ion CH_3Hg^+ (Jernelöv,

1969). Daily oral intake of 0.3 mg of CH_3HgX by man leads to symptoms of poisoning. The generation of RHgX through oxidative alkylation of Hg^0 in the environment has not yet been established.

- Several compounds of the type CH_3HgX are water soluble. Thus, they are rapidly distributed in aqueous ecosystems and accumulate in certain organisms (particularly fish). Example: Water (Lake Powell, Arizona, 0.01 ppb) \rightarrow food chain \rightarrow trout (84 ppb), carp (250 ppb).

ple in chloralkali electrolysis, amounts to $> 90\%$.

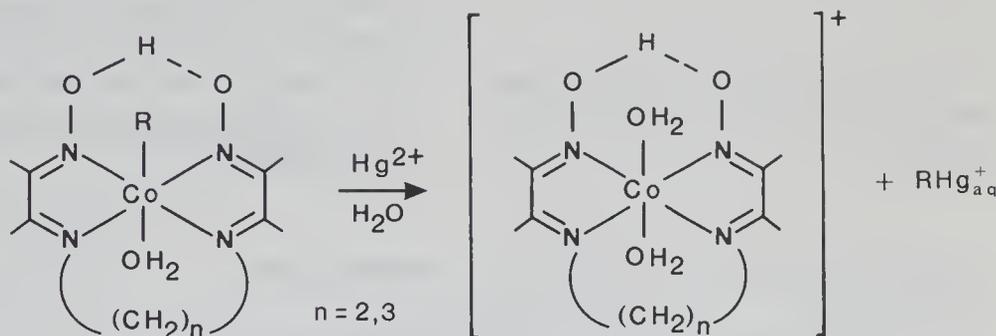
The **biological methylation** of Hg^{2+} ions to yield CH_3Hg^+ , and to a limited extent also $(\text{CH}_3)_2\text{Hg}$, is effected by microorganisms, which utilize methylcobalam in $\text{CH}_3[\text{Co}]$, a derivative of vitamin B_{12} coenzyme. $\text{CH}_3[\text{Co}]$ is the only natural product which is able to transfer the methyl group as a carbanion, as required in the reaction with Hg^{2+} (p.203):



In this context, two model reactions are of interest:



(Halpern, 1964)



With regard to the **origin** of mercury in natural waters, anthropogenic sources of modern times (retrieval of Hg from ores, fossil fuels, chloralkali electrolysis) are globally comparable to the natural sources (weathering, vulcanism). Because of the higher local concentrations, the former are more of an ecological threat, however. Admittedly though, the last decade has witnessed a remarkable reduction of Hg emission which, for exam-

Other metals which are subject to biological methylation include tin, lead and arsenic. Alkylated metal ions are usually more poisonous than the purely inorganic forms, maximal toxicity being reached for the permethylated monocations MeHg^+ , Me_3Sn^+ and Me_2As^+ .

The **distribution** of the CH_3Hg^+ cation between aqueous systems and living organisms is controlled by its coordination chemistry. Since organometallic Hg^{II} occurs almost exclusively with the coordination number 2, the following equilibria only have to be considered:

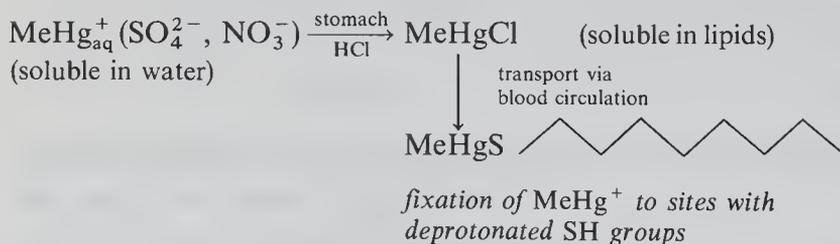


Formation constants: $\text{MeHgF} \ll \text{MeHgCl} < \text{MeHgBr} < \text{MeHgI} \ll \text{MeHgSMe}$

The ion MeHg^+ therefore should be classified as a **soft Lewis acid**. The preference of MeHg^+ for soft Lewis bases governs the solubility behavior of compounds MeHgX :

X	MeHgX
Hal^- , CN^- , SCN^- , SR^- (soft bases)	covalent bond MeHg-X , soluble in organic media
NO_3^- , SO_4^{2-} (hard bases)	ionic bond $\text{MeHg}^+ \text{X}^-$ soluble in water as $\text{MeHg}_{\text{aq}}^+$

The uptake of MeHg^+ by living organisms is thought to proceed in the following way:



In addition to the blocking of thiol groups of enzymes by MeHg^+ , bonding of the methylmercury cation to the pyrimidine bases uracil and thymine has also been suggested. The discovery that MeHg^+ causes chromosomal aberrations, i.e. is mutagenic, is thus explained. MeHgSR complexes are **thermodynamically stable**, but **kinetically labile**. This lability makes the ion MeHg^+ immediately available upon changes of the medium. It also forms the basis for chemotherapy which consists of the conversion of MeHg^+ into a chelate complex, which then is excreted. For this purpose, penicillamine (2-amino-3-methyl-3-thiobutyric acid) as well as synthetic ion-exchange resins carrying thiol groups, are being tested.

7 Organometallics of the Boron Group (Group 13)

Among the elements B, Al, Ga, In and Tl the organometallic chemistry of boron and aluminum clearly predominates. Organoboron chemistry is closely related to the chemistry of organoboranes; therefore boranes will also be touched upon in this chapter. Boranes and organoboranes are intriguing from a structural (borane clusters), bond theoretical (multicenter bonding) as well as from a practical point of view (hydroboration, carbaboration). At one time, boranes and carbaboranes were of interest as potential rocket propellants since their specific combustion value exceeds that of hydrocarbons by about 40%. However, complete combustion to form B_2O_3 and H_2O was never achieved in practice. Instead of B_2O_3 , suboxides like BO are always formed to a certain extent, negating their advantage over hydrocarbons. Certain organoboron compounds have entered nuclear medicine as neutron absorbers. The practical value of aluminum organyls is grounded in their use in a number of technical processes and, in the laboratory, as economical sources of carbanions.

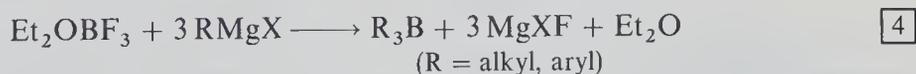
7.1 Organoboron Compounds

7.1.1 Organoboranes

PREPARATION

Organic derivatives of BH_3 are accessible in a multitude of ways. Direct syntheses are of no importance since pure elemental boron is both expensive and rather unreactive.

Binary organoboranes:

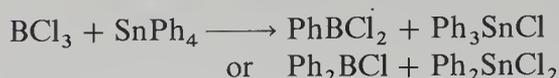


In the presence of an excess of $RMgX$, tetraorganoborates BR_4^- are formed:

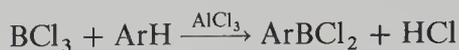


Contrary to lithium- and magnesium organyls, organoaluminum compounds do not effect quaternation at boron.

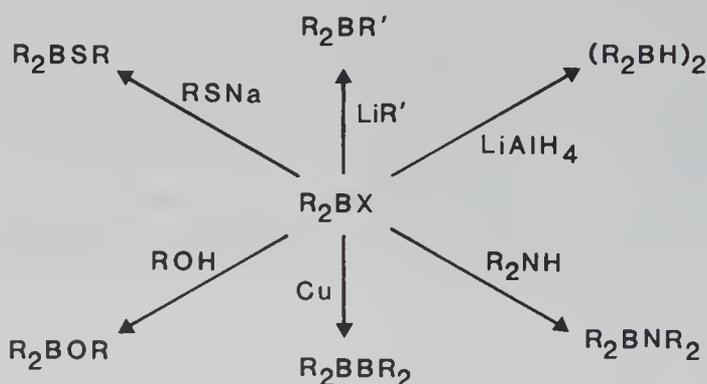


Organoboron halides:

4



Organoboron hydrides $(\text{R}_2\text{BH})_2$ and $(\text{RBH}_2)_2$ may be prepared from the respective organoboron halides $\text{R}_n\text{BX}_{3-n}$ by means of substitution of H for X, using LiH or LiAlH_4 . Organoboron halides also serve as intermediates in the synthesis of numerous other derivatives:



Tetraorganoborates BR_4^- are obtained from tetrahaloborates:



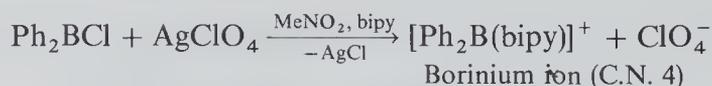
NaBPh_4 is sold in Germany under the name Kalignost® (“recognizing potassium”). The ion BPh_4^- forms precipitates with K^+ , Rb^+ , Cs^+ , Tl^+ , Cp_2Co^+ etc. and as the ammonium salt, can be used in small scale preparations of BPh_3 :



The radical anion Ph_3B^- , which is isoelectronic with $\text{Ph}_3\text{C}^\cdot$, is in equilibrium with its dimer (J. L. Mills, 1976):

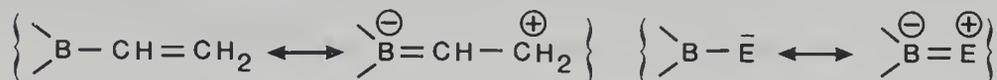


Organoborinium ions R_2B^+ only exist as Lewis base adducts (Nöth, 1985 R):

**PROPERTIES**

Because of the low polarity of the B–C bond, binary boranes R_3B are stable in water; they are easily oxidized, however. The more volatile boron trisalkyls are pyrophoric.

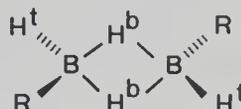
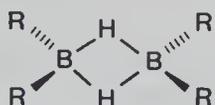
Contrary to BH_3 , BR_3 is monomeric. This may be traced to hyperconjugation with the alkyl substituents whereby the electron deficiency at boron is alleviated. Electron rich groups like vinyl or phenyl provide the B–C bond with partial double bond character. Substituents E with lone pairs of electrons act similarly:



The strength of the boron-heteroatom π -bonds in R_2BE increases in the order $\text{Cl} < \text{S} < \text{O} < \text{F} < \text{N}$. This is derived from the following observations:

E:	<u>Cl</u>	<u>SMe</u>	<u>OMe</u>	<u>F</u>	<u>NR₂</u>
Formation of an adduct $\text{R}_2\text{BE} \cdot \text{NR}_3$:	observed			not observed	

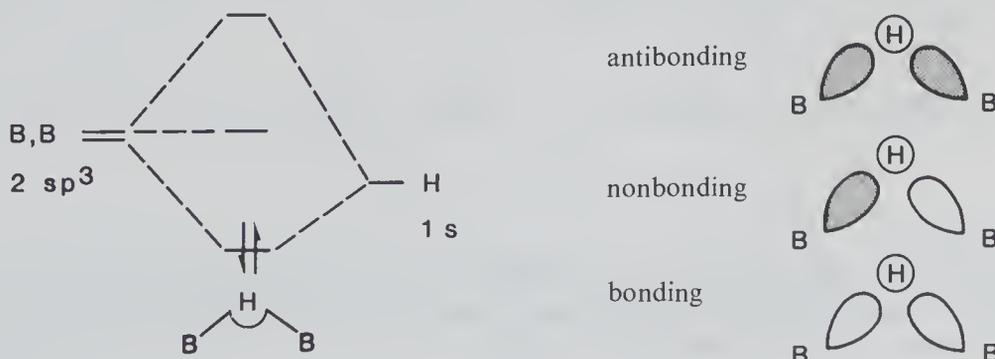
Organoboron hydrides R_2BH and RBH_2 form dimers which always display **hydride bridges** rather than alkyl bridges:



The structural elucidation of these derivatives of diborane by IR spectroscopy is based on the strongly differing B–H stretching frequencies for bridging (H^b) and terminal (H^t) positions:

	Stretching frequency	Intensity
$\nu(\text{B}-\text{H}^b-\text{B})$ symm.	1500–1600 cm^{-1}	strong
$\nu(\text{B}-\text{H}^b-\text{B})$ asymm.	1850	medium
$\nu(\text{B}-\text{H}^t)$	2500–2600	

The lower stretching frequency of hydride bridges is a consequence of the diminished bond order (0.5) which can be deduced from the interaction diagram of a $\text{B}-\text{H}-\text{B}$ ($2e3c$) bond.

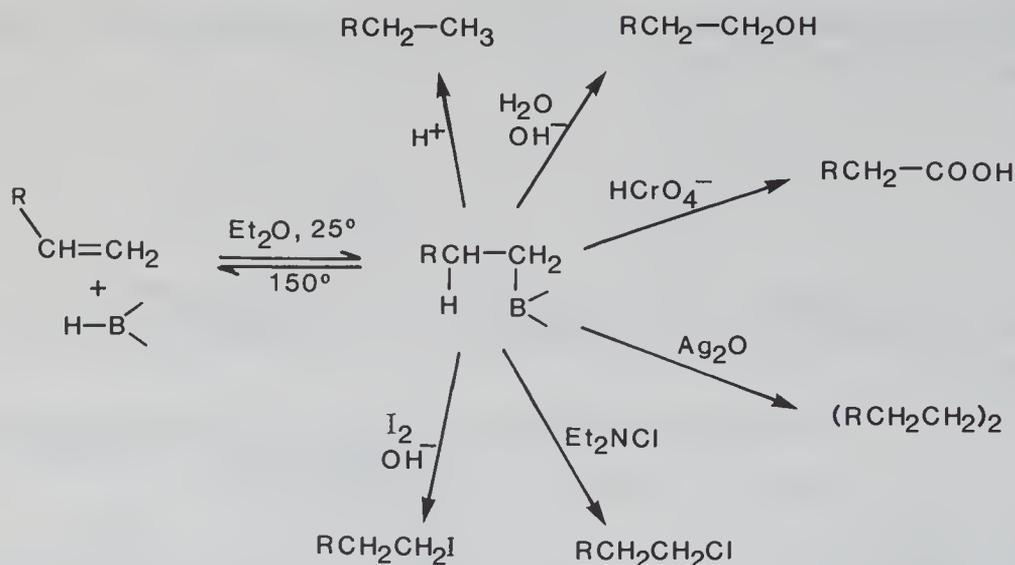


REACTIONS

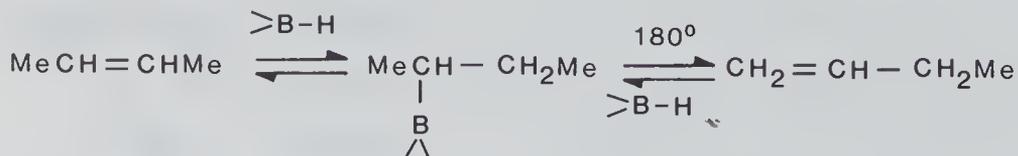
Controlled oxidation of organoboron compounds R_3B affords the **alkoxyboranes** R_2BOR (borinic esters), $RB(OR)_2$ (boronic esters) and $B(OR)_3$ (organoborates) which are also accessible through alcoholysis of the respective organoboron halides R_nBX_{3-n} . If an amine oxide is used as a source of oxygen, the liberated amine may be titrated; this is a method for the **determination of the number of B–C bonds** initially present:



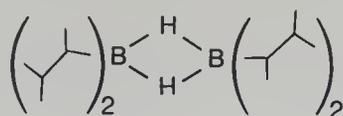
One of the most versatile methods in organic synthesis is **hydroboration** (H. C. Brown, 1956f.). Herein, rather than the resulting organoboranes themselves, the products of their subsequent reactions are important:



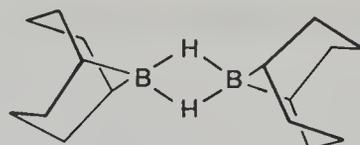
Hydroboration is **regioselective** (*anti*-Markovnikov direction), electropositive boron being attached to the carbon atom bearing the larger number of hydrogen atoms, and **stereoselective** (*cis* addition). Hydroboration is **reversible** which can be exploited for counter-thermodynamic isomerizations of olefins:



With organoboranes bearing bulky substituents, the selectivities achieved are particularly high. Thus, bis-(1,2-dimethylpropyl)borane (“disiamylborane”) adds to 1-pentene, leaving 2-pentene unaffected (selectivity > 99%).



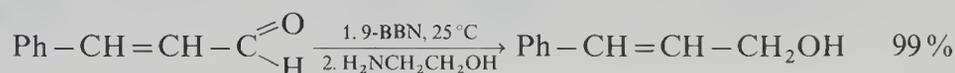
disiamylborane



9-BBN

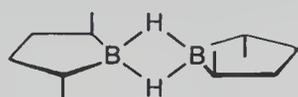
Bis-(9-borabicyclo[3.3.1]nonane) ("9-BBN"), which can be prepared from diborane and 1,5-cyclohexadiene, has the additional advantage of being easy to handle (solid, stable up to 200 °C, precautions required are comparable to those recommended for LiAlH₄).

9-BBN excels in the **regioselective reduction** of functional groups as in the conversion of α , β -unsaturated aldehydes and ketones to the corresponding allyl alcohols:

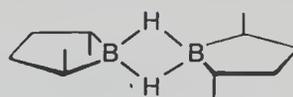


Enantioselective syntheses of chiral alcohols from prochiral alkenes can be effected by means of chiral boranes (H. C. Brown, 1961).

Exceptionally high enantiomeric excesses (*ee*) are obtained in hydroborations with the reagent *trans*-2,5-dimethylborolane (Masamune, 1985):

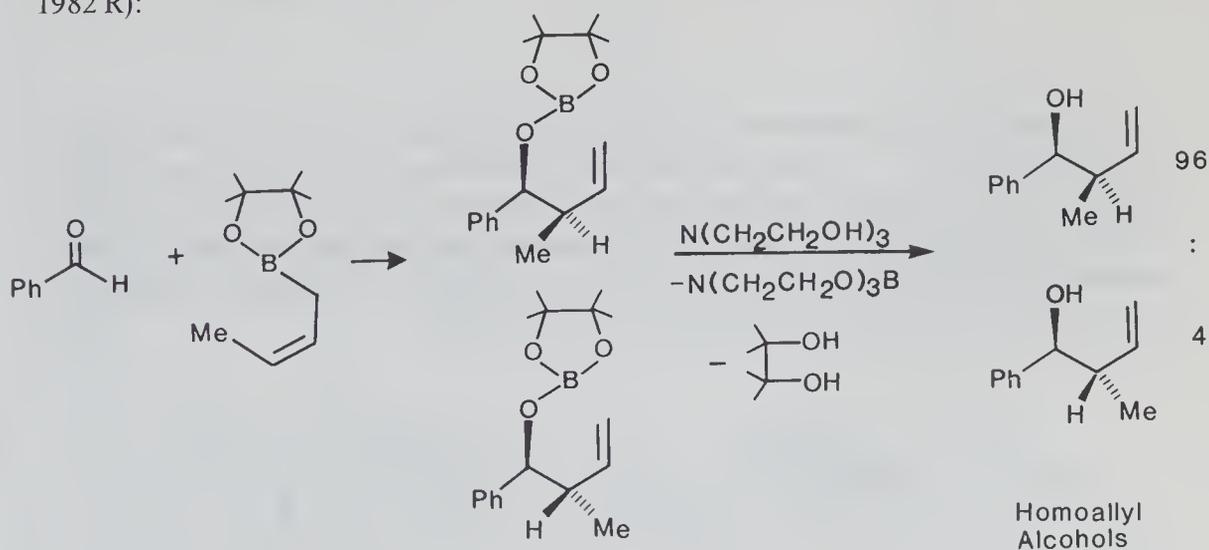


R,R



S,S

Early observations that allylboronic esters readily add across aldehyde functions (Gaudemar, 1966) have added impetus to the use of **carbaborations** in **organic synthesis**. They effect **diastereogenic C – C coupling** of high enantioselectivity. Example (R. W. Hoffmann, 1982 R):

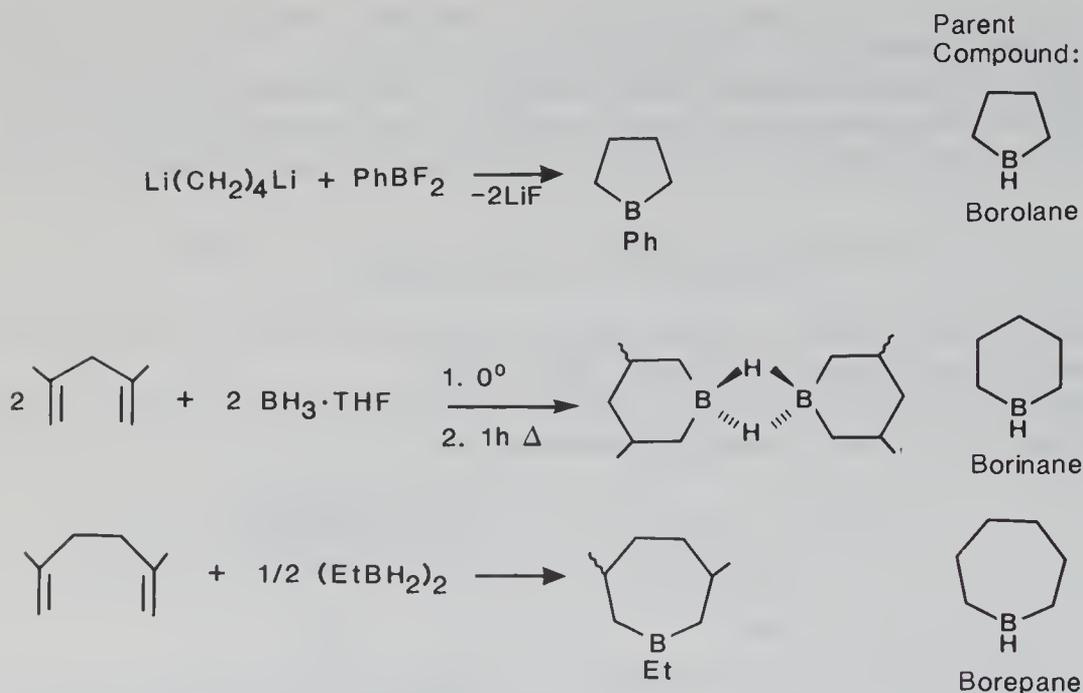


Note that it is the carbon atom in γ -position to boron which engages in C – C bond formation.

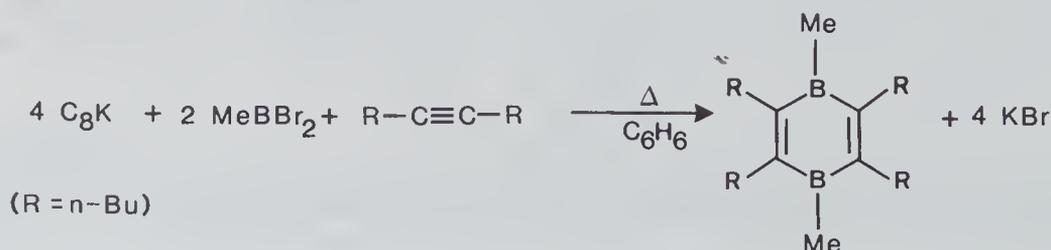
7.1.2 Boron Heterocycles

Boron is found in a large number of saturated and unsaturated heterocycles in such segments as C–B–C, C–B–N, N–B–N, O–B–O, C–B–O, C–B–S etc. Here, only a few examples will be given in which organometallic aspects dominate.

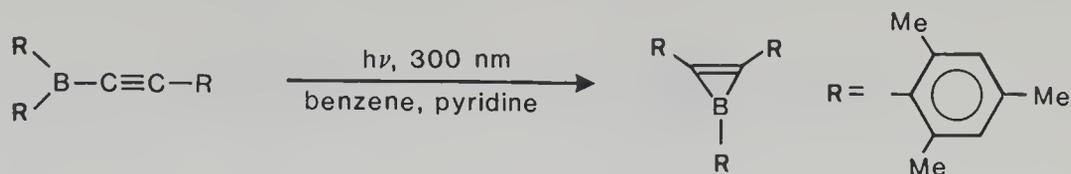
Boracycloalkanes (boracyclanes) are products of metathesis reactions or of cyclohydroborations:



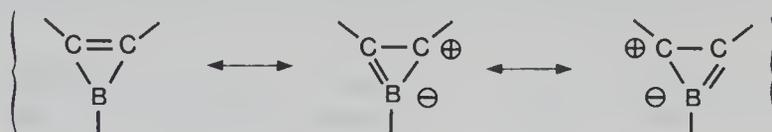
Boracycloalkenes and **boraarenes** are of interest in the context of π -electron delocalization across B(sp^2) centers. Therefore, the synthesis of **borirene** (boracyclopropene C_2BH_3), which is isoelectronic with the smallest Hückel system C_3H_3^+ , has been the subject of considerable synthetic effort. Attempts to prepare borirenes via addition of organoborane diyls (RB:) to alkynes often led to 1,4-dibora-2,5-cyclohexadienyl derivatives which formally are borirene dimers (van der Kerk, 1983):



Monomeric borirenes can be obtained photochemically if protection by sterically demanding substituents R is provided (Eisch, 1987):



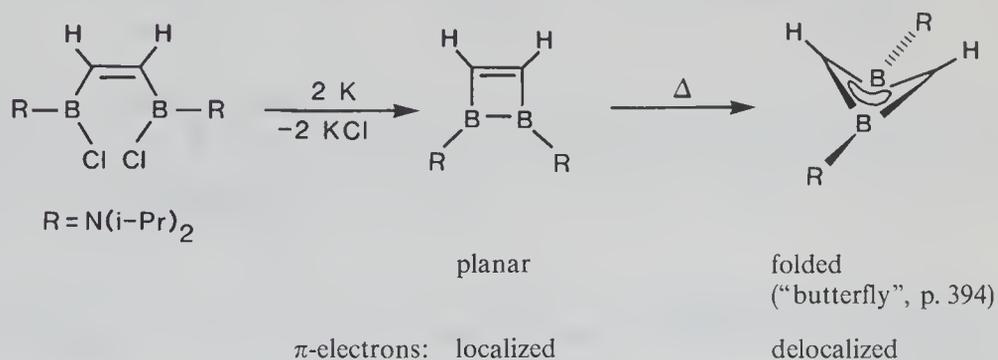
Structural and spectroscopic data point to extensive π -electron delocalization:



The isoelectronic series can be extended:

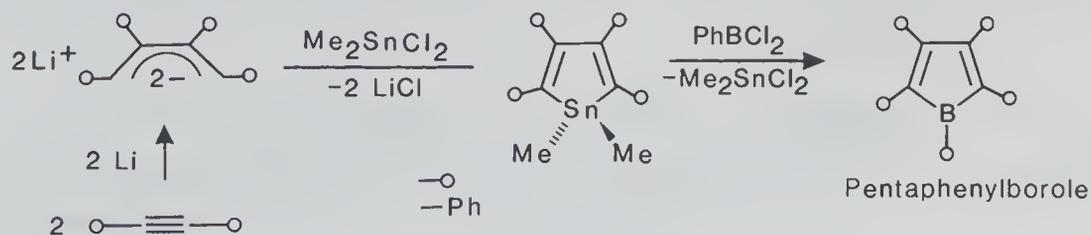


An intriguing aspect of the **dihydrodiborettes** (diboracyclobutenes) is the structural disparity of the two isomers (Siebert, 1985 R):



The higher thermodynamic stability as well as the folded structure of the 1,3-isomer had been predicted from theoretical considerations (v. R. Schleyer, 1981).

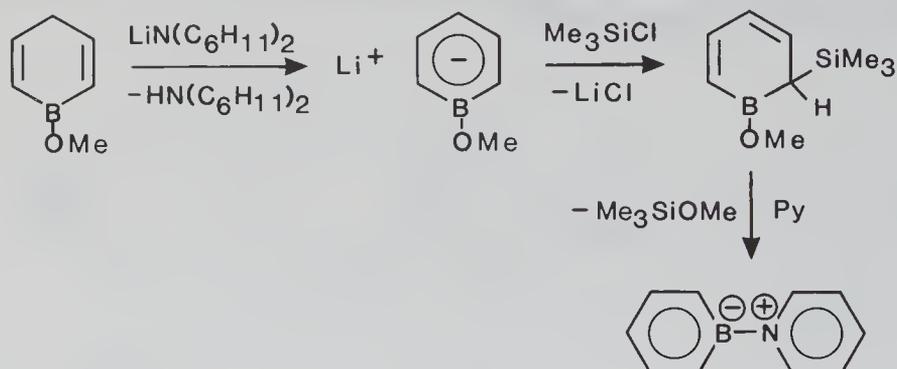
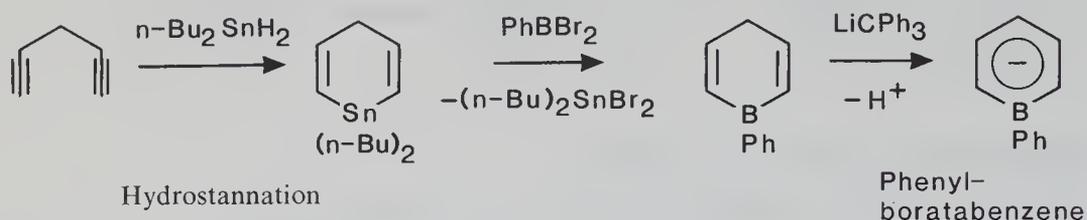
The antiaromatic **borole** $\text{C}_4\text{H}_4\text{BH}$ (4π -electrons) is labile even in perarylated form (Eisch, 1969):



Cocondensation of BF vapor with alkynes leads to 1,4-diboracyclohexa-2,5-dienes (Timms, 1968):



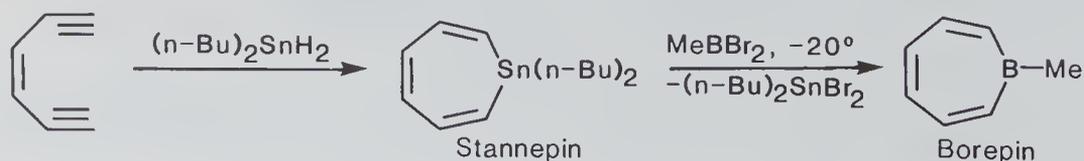
Borabenzene (Borin) $\text{C}_5\text{H}_5\text{B}$ as yet has only been obtained as Lewis base adduct or as an aromatic, anionic η^6 -ligand (p. 380) in transition-metal complexes (Ashe, 1971):



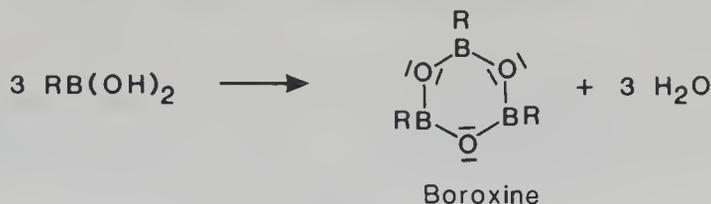
The prefix "*bora*" designates the replacement of a CH fragment by B, "*borata*" that of CH by BH^- .

The pyridine adduct of borabenzene (G. Maier, 1985) is isoelectronic with biphenyl. As gauged from spectroscopic data ($^1\text{H-NMR}$ in particular), boratabenzene $\text{C}_5\text{H}_5\text{BR}^-$ displays cyclic π -conjugation. Due to the difference in electron affinity, replacement of carbon by boron, however, acts as a perturbation.

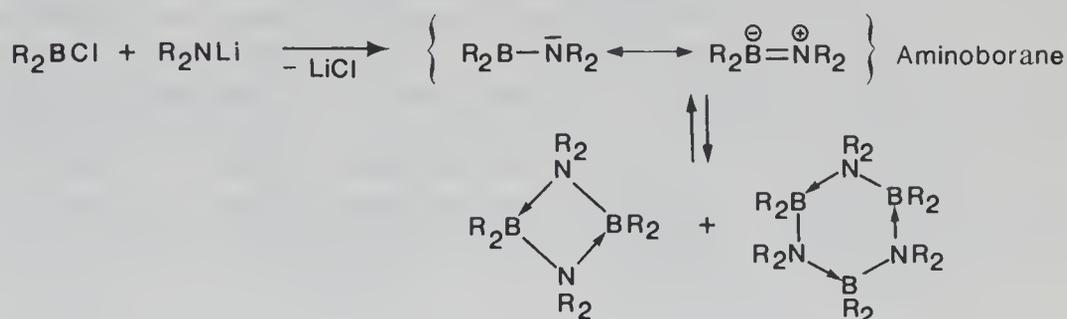
The tropylium ion C_7H_7^+ has found its isoelectronic counterpart in derivatives of **borepin** C_6BH_7 , the least substituted, known to date, being the Me-B derivative (Sakurai, 1987):



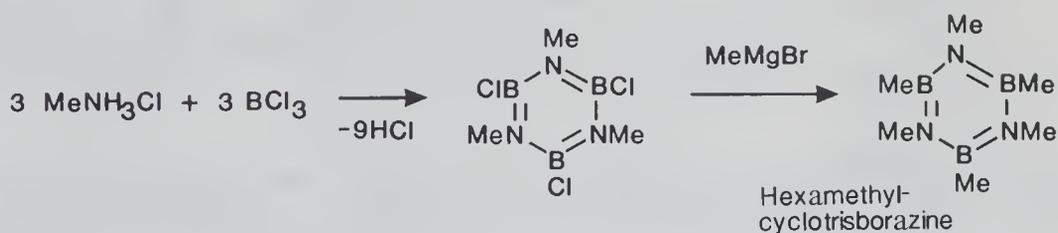
Boron heterocycles which only contain heteroatoms include the boroxines (condensation products of boronic acids), the cycloaminoboranes, and the borazines.



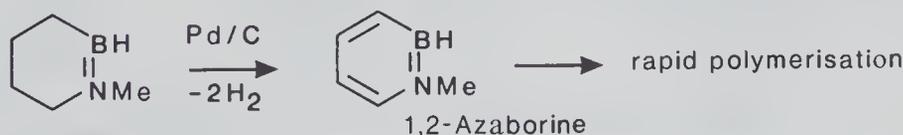
Boroxines are planar; yet, compared to the borazines, the free electron pairs in the former remain localized to a large extent. **Aminoboranes** as monomers are also planar. They equilibrate with puckered cyclic dimers and trimers, the position of these equilibria being governed by the size of the substituents R. In the monomeric as well as in the oligomeric forms, boron gains an octet configuration:



The isoelectronic nature of the units >C=C< and >B=N< suggests replacements of the former by the latter. In the case of benzene this leads into the class of **borazines** ($\text{B}_3\text{N}_3\text{H}_6$, cyclotrisborazine), also termed “borazoles” or “inorganic benzenes” since, in many regards, they mimic the properties of arenes:



If >C=C< units are only partially replaced by >B=N< , the analogy to benzene is lost, however:



Since the electronegativities of B and N are very different, 1,2-azaborine acts like a strongly polarized butadiene.

7.1.3 Polyhedral Boranes, Carboranes and Heterocarboranes

“Boranes: Rule breakers become pattern makers” K. Wade (1974)

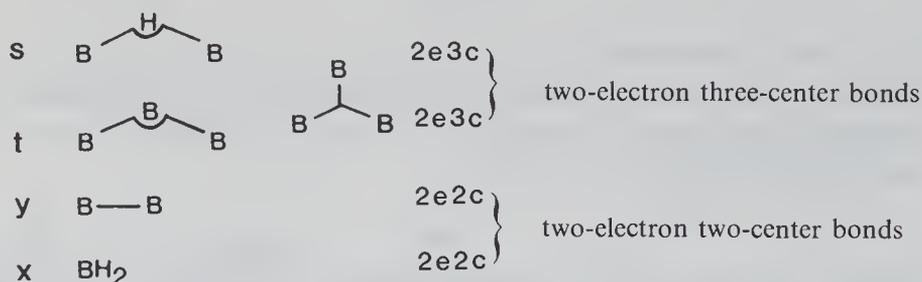
In the context of this section, a cursory treatment of the binary boranes is indispensable. Preparative results, in part dating back to A. Stock (1876–1946) revealed that, as for hydrocarbons, borane chemistry may also be organized in terms of homologous series:

B_nH_{n+6}	e.g. B_4H_{10} , B_9H_{15}
B_nH_{n+4}	B_2H_6 , B_5H_9
B_nH_{n+2} [only as $(B_nH_n)^{2-}$, $n = 5-12$]	$B_5H_5^{2-}$, $B_6H_6^{2-}$

As the structures of these boranes were unraveled, the desire grew to understand the bonding situation. In both of these areas, W.N. Lipscomb has earned merits.

Lipscomb devised a system to organize **borane topology** and he described the electronic structure even of the more complicated boranes in terms of the **valence bond (VB) model**. In boranes, the number of valence electron pairs is always less than the number of interatomic connecting lines which depict the molecular framework. Therefore, a certain number of $2e\ 3c$ bonds must be included. On p. 67, for a few boranes, molecular structures (left) are juxtaposed with the respective valence bond formulae (right). Whereas in the structural representations the number of connecting lines does **not** correspond to the number of electron pairs available for bonding, in the valence formula this is the case.

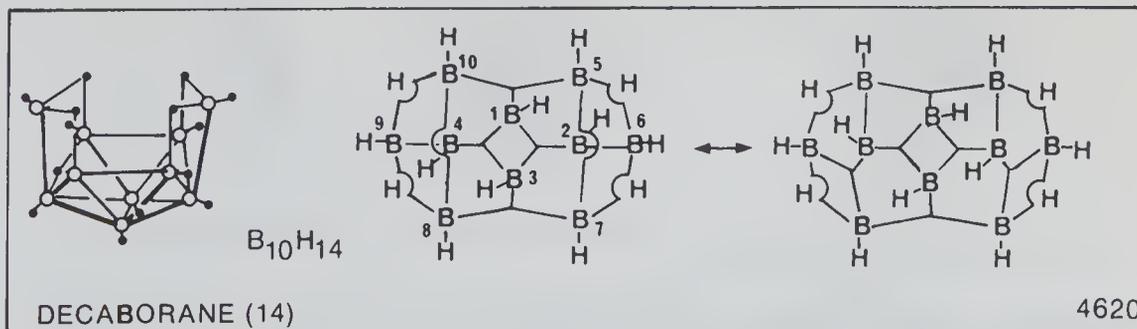
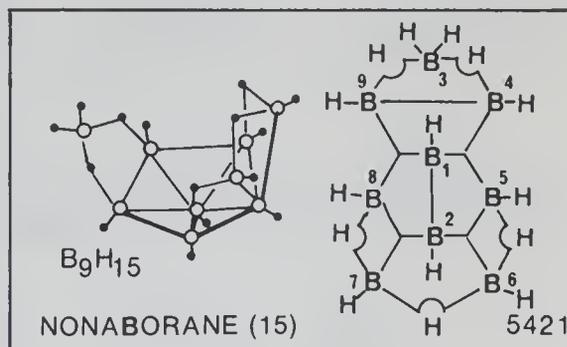
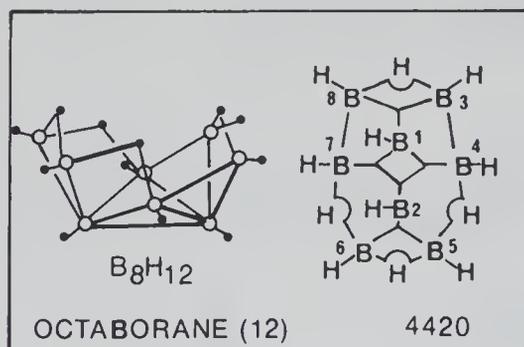
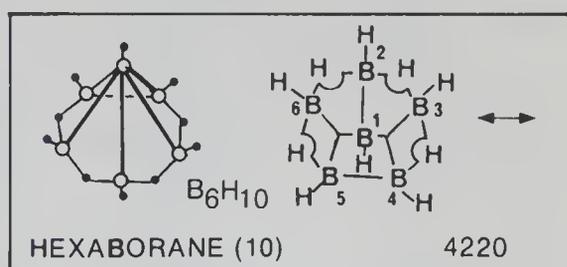
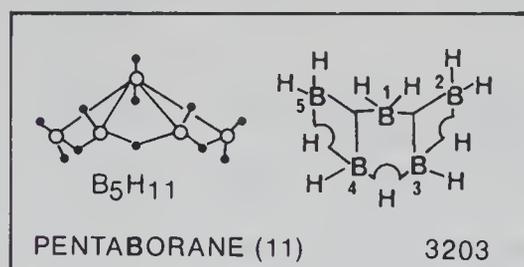
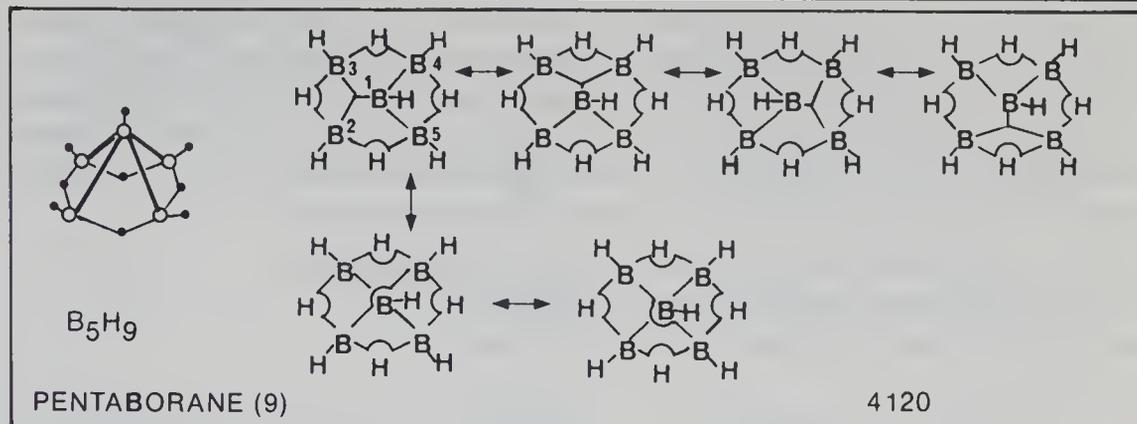
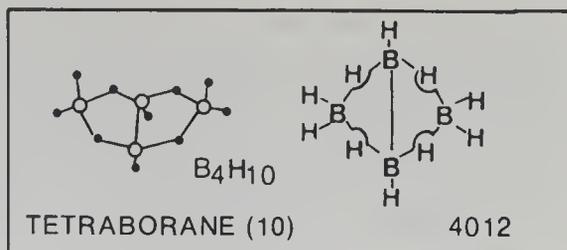
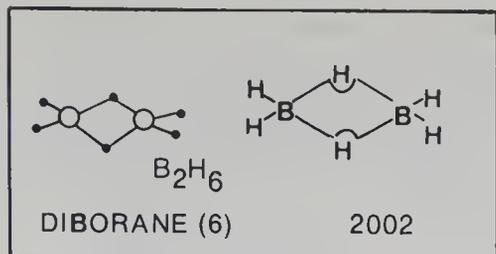
The symbols have the following meaning*:



According to the numbers s , t , y , x which tally the different bonding fragments present, a particular borane is assigned its specific **styx code**. Example: $styx(B_5H_9) = 4120$. For a borane of known composition, usually one styx code only exists, which is compatible with the total number of valence electrons and the number of B- and H atoms. In this way, structural predictions become possible, which then have to be confirmed by spectroscopic techniques or by diffraction methods.

* In the literature as well as at various places in this text, $2e\ 3c$ bonds are also represented by two lines. Examples:





Frequently, it is impossible to do justice to the symmetry of a borane molecule by writing a single valence-electron formula employing the symbols discussed on p. 66. In these cases, several canonical forms must be given which together represent a resonance hybrid. Example: B_5H_9 , symmetry C_{4v} . For decaborane(14), 24 canonical forms have to be considered. For the highly symmetrical borane anions $B_nH_n^{2-}$, valence bond representations become unwieldy because of the large number of canonical forms.

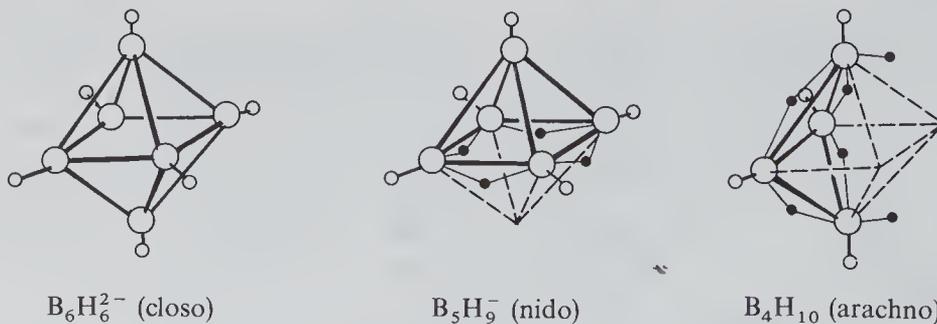
Contemporary descriptions of polyhedral boranes are based on **MO methods** introduced in the now classical work of Hoffmann and Lipscomb (1962) which constitutes an early example of the application of the Extended-Hückel method. Thus, given a certain **number n of skeletal atoms** (B, C or heteroatom), the number of electrons available for skeletal bonding fixes a certain structure. The following system has become known as **Wade's rules**; it is particularly successful in discussing the heteroboranes.

- Each of the n units $:B-H$ furnishes 2 skeletal bonding electrons
- Each additional $\cdot H$ furnishes 1 skeletal bonding electron
- Ionic charges must be included in the electron count

Borane	Skeletal bonding electron pairs	Structural type	Structure	Example
$B_nH_{n+2}^*$	$n + 1$	closo (closed)	Polyhedron with n vertices 0 vertices unoccupied	$B_{12}H_{12}^{2-}$
B_nH_{n+4}	$n + 2$	nido (nest)	Polyhedron with $n + 1$ vertices 1 vertex unoccupied	B_5H_9
B_nH_{n+6}	$n + 3$	arachno (cobweb)	Polyhedron with $n + 2$ vertices 2 vertices unoccupied	B_4H_{10}

* For binary boranes, the closo structure is only realized in the anions $B_nH_n^{2-}$

Therefore, the structures of the boranes $B_6H_6^{2-}$, B_5H_9 , and B_4H_{10} are derived from an octahedron with 0, 1 or 2 vertices, respectively, remaining unoccupied:



Increasing hydrogen content in the boranes leads to successively more “open” structures since the required number of BBB ($2e3c$) bonds decreases.

Idealized Structures of closo-, nido- and arachno-Boranes

Only the $(BH)_n$ skeleton is shown. BH_2 groups and $B-H-B$ bridges occur at the open face of the respective incomplete polyhedron. In the heteroboranes, one or more BH-units are replaced by other building blocks.

STRUCTURAL TYPE		closo	nido	arachno
SKELETAL BONDING ELECTRON PAIRS		$n + 1$	$n + 2$	$n + 3$
TRIANGULAR FACES	VERTICES			
6	$n = 5$			
8	6			
10	7			
12	8			
14	9			
16	10			
18	11			
20	12			

(adapted from R. W. Rudolph, 1972)

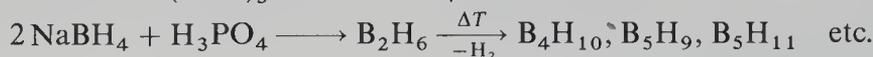
Horizontal:

Changes in skeletal structure with increasing hydrogen content (generally: with increasing number of skeletal bonding electrons).

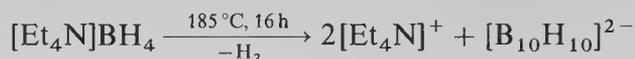
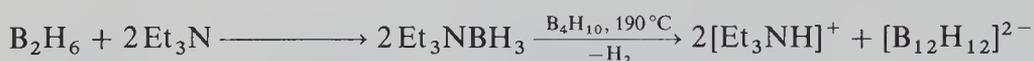
Diagonal:

Relation between open structures and the parent closed polyhedron.

PREPARATION

Nido- and arachno-boranes:**Borane pyrolysis**

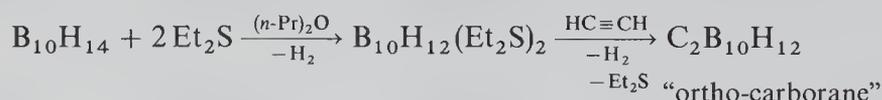
In addition, several special methods for the synthesis of the more exotic boranes have been devised. They rely on the meticulous control of temperature and pressure.

Closo-borane anions:**Tetrahydroborate pyrolysis**

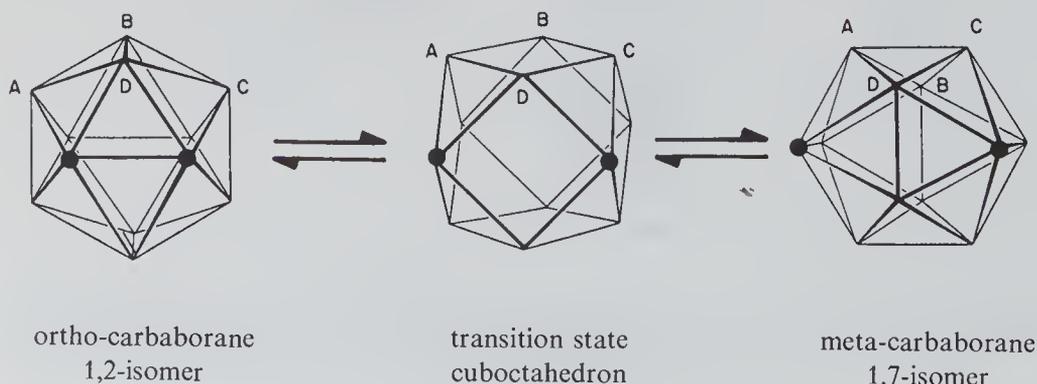
HETEROBORANES, CARBABORANES

Heteroboranes contain skeletal atoms different from boron (C, Sn, Pb, Al, transition metals etc.). The **carbaboranes**, pioneered by Hawthorne and Grimes, may be formally derived from boranes by isoelectronic replacement of BH^- by CH . Therefore, the neutral carbaborane $\text{B}_4\text{C}_2\text{H}_6$, like the dianion $\text{B}_6\text{H}_6^{2-}$, possesses a closo structure.

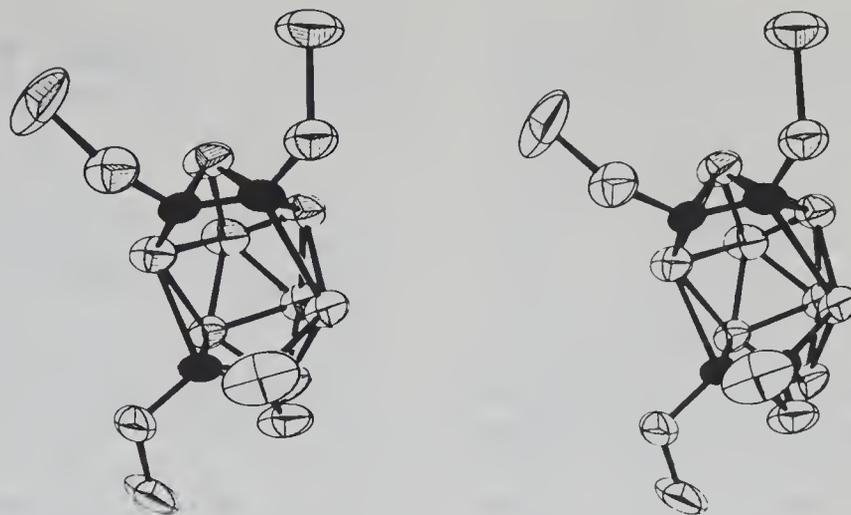
One of the most extensively studied carbaboranes is dicarba-closo-dodecaborane(12), $\text{C}_2\text{B}_{10}\text{H}_{12}$. Like the isoelectronic anion $\text{B}_{12}\text{H}_{12}^{2-}$ it forms an icosahedron.



The two carbon atoms are initially introduced in vicinal position (ortho-carbaborane). Under thermal conditions, isomerization to meta-carbaborane ($T = 600^\circ\text{C}$) and to para-carbaborane ($T \approx 700^\circ\text{C}$) occurs. This migration of carbon atoms on the surface of the icosahedron is thought to involve transition states of cuboctahedral symmetry:



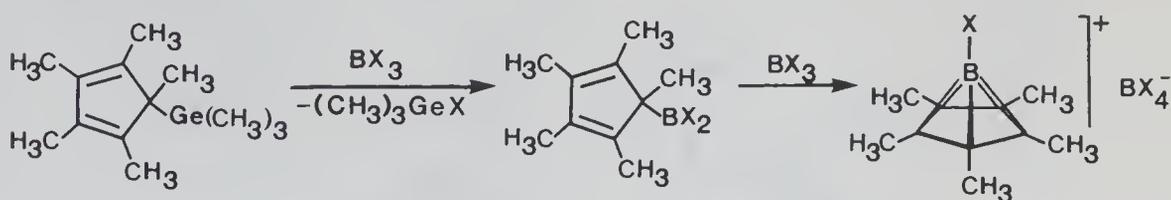
Carbaboranes of the nido- and arachno type have also been prepared. 1,2,3,4-Tetraethyl-1,2,3,4-tetracarbadodecaborane(12), which according to Wade's rules has a nido structure, may serve as an example. This carbaborane, like $B_{12}H_{12}^{4-}$, possesses $n + 2$ skeletal electron pairs.



Stereoview of the structure of $Et_4C_4B_8H_8$ (Grimes, 1984)

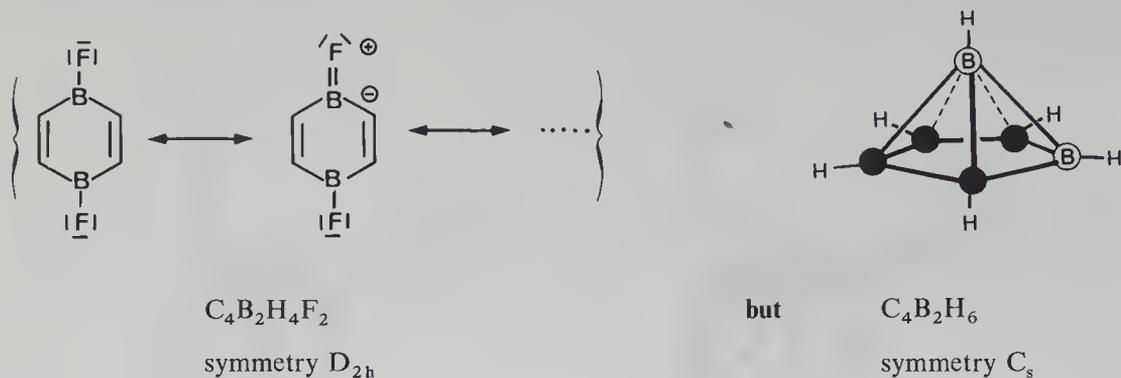
Guide to three-dimensional viewing: Place two fingers between the eyes and the plane of the paper so that the left eye sees only the left-side image, similarly, the right eye should only see the right-side image. The eyes, thus fixed along parallel axes, are then relaxed and adjusted to an "infinity setting". In a short time (and with a little practice!), the three-dimensional image of the molecule should appear, which remains even after removing the guide fingers. A prerequisite is, that the distance between the two stereo pictures approximates the separation between the eyes.

Nido-carbaboranes of the type $[C_5BH_6]^+$ bear resemblance to half-sandwich complexes (p. 309); a highly substituted derivative of this cation has been prepared by Jutzi (1977):

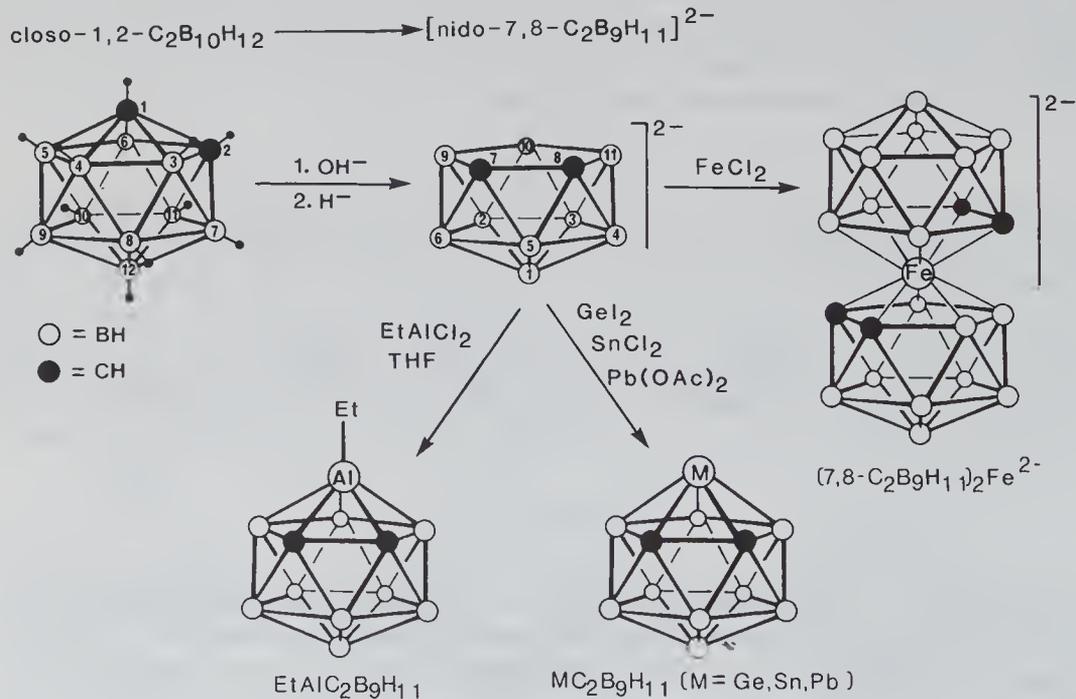


The nido structure of this carbaborane may be traced back to the isoelectronic nature of $C_5BH_6^+$ and $B_6H_6^{4-}$ ($n + 2$ skeletal electron pairs). The carbaborane anion $C_5BH_6^-$ ($n + 3$ skeletal electron pairs), in accordance with Wade's rules, features an arachno structure (compare the planar configuration of boratabenzene $C_5H_5BR^-$, p. 64). A limitation to Wade's structural scheme is imposed by substituents like halogens or amino groups, which can satisfy the electronic demand of boron by means of π back-bonding (p. 64). Thus, 1,4-difluoro-1,4-diboracyclohexadiene $C_4H_4B_2F_2$ has a planar rather than a nido

structure, the latter being predicted by Wade's rules for the parent carbaborane $C_4B_2H_6$ ($n + 2$ skeletal electron pairs):



The structures of the boron subhalides $(BX)_n$, $n = 4-10$, also do not comply with Wade's rules. Example: B_4Cl_4 is tetrahedral; this closo structure would, however, be predicted for the dianion $B_4H_4^{2-}$. Nido- and arachno-carbaboranes are building blocks in the synthesis of **heterocarbaboranes** which, in addition to B and C, contain other elements in their skeleton. The anion $[(7,8-C_2B_9H_{11})_2Fe]^{2-}$ is but one of numerous cases in which the five-membered ring of a partially disintegrated icosahedral carbaborane plays the role of the cyclopentadienyl ligand present in metallocenes.



The participation of Al, Ge, Sn, Pb and Fe in icosahedral frameworks is unique in the structural chemistry of these elements.

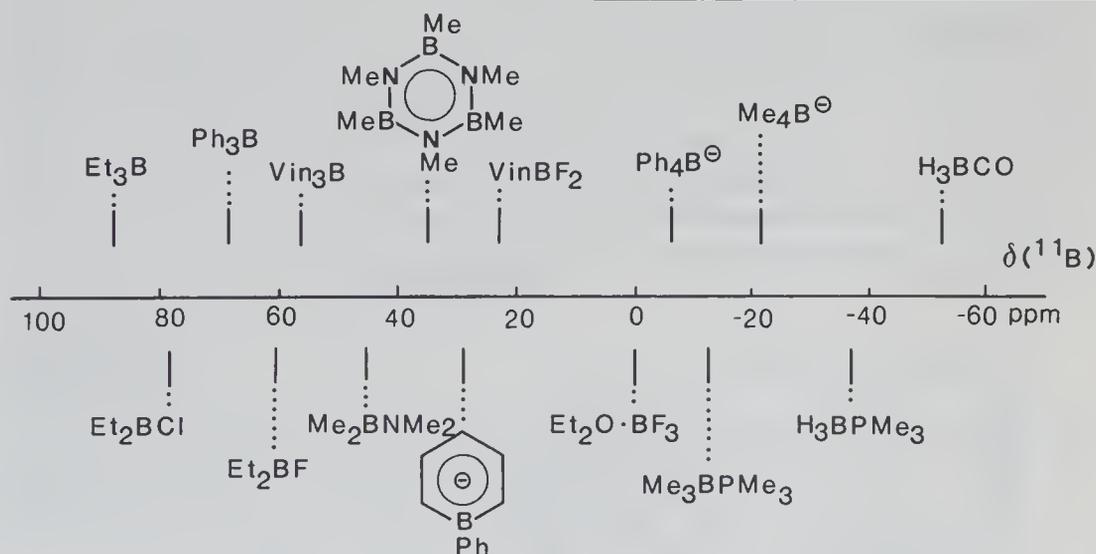
Excursion

^{11}B -NMR of Organoboron Compounds

Of the two boron isotopes, ^{10}B (20%, $I = 3$) and ^{11}B (80%, $I = 3/2$), the latter possesses superior NMR properties (cf. p. 24). Therefore, ^{11}B -NMR is performed almost exclusively.

The chemical shifts $\delta(^{11}\text{B})$ cover a range of about 250 ppm; they are ruled by the charge, the coordination number, and the substituents at boron. For triorganoboranes, the chemical shifts $\delta(^{11}\text{B})$ correlate with $\delta(^{13}\text{C})$ values of isoelectronic carbenium ions.

Chemical Shifts $\delta(^{11}\text{B})$ of Selected Organoboranes (external standard $\text{Et}_2\text{O} \cdot \text{BF}_3$):



venes the electronegativities of F and Cl, has been related to stronger π -bonding $\text{>B}^\ominus = \text{F}^\oplus$ as compared with $\text{>B}^\ominus = \text{Cl}^\oplus$, a consequence of the shorter length of the B–F σ -bond. An even stronger π -donor capacity is exhibited by the substituent NR_2 .

The ability of α, β -unsaturated organic groups to engage in π -conjugation with three-coordinate boron can be assessed from an inspection of $\delta(^{11}\text{B})$ - and $\delta(^{13}\text{C})$ values of **vinyl boranes** (Odom, 1975).

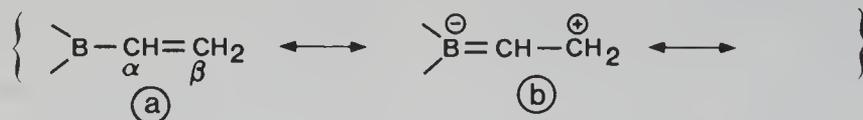
In this context, $\delta(^{13}\text{C}_\beta)$ rather than $\delta(^{13}\text{C}_\alpha)$ data are examined, since the shielding of the nuclei C_α , which are directly bonded to boron, is governed by mesomeric (π) and inductive (σ) effects.

Substituent effects on $\delta(^{11}\text{B})$ values are influenced by σ - as well as by π -bonding contributions. Thus, the nucleus ^{11}B is shielded more effectively in Et_2BF than in Et_2BCl . This gradation, which contra-

Furthermore, due to their vicinity to ^{11}B , a nucleus with a quadrupole moment, C_α nuclei often give rise to NMR signals which are broadened beyond detection (p. 295 f).

^{11}B - and ^{13}C -NMR Data

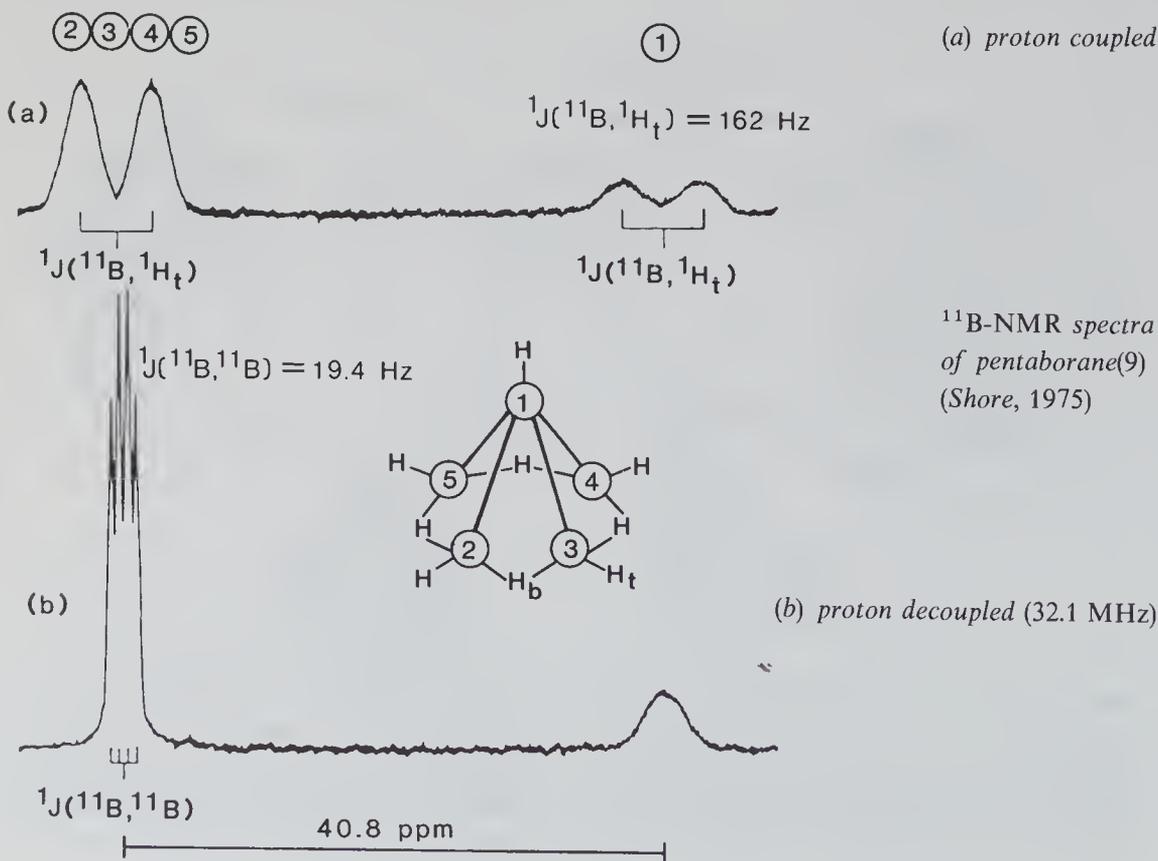
$\text{B}(\text{CH}_2\text{CH}_3)_3$		$\text{B}(\text{CH}=\text{CH}_2)_3$		$\text{CH}_2=\text{CH}_2$	
$\delta^{11}\text{B}$	86.8	$\delta^{11}\text{B}$	56.4		
$\delta^{13}\text{C}$ (CH_2)	19.8	$\delta^{13}\text{C}$ (CH) α	141.7		
$\delta^{13}\text{C}$ (CH_3)	8.5	$\delta^{13}\text{C}$ (CH_2) β	138.0	$\delta^{13}\text{C}$ (CH_2)	122.8



The contribution of canonical structure (b) in $\text{B}(\text{CH}=\text{CH}_2)_3$ manifests itself in the shielding of ^{11}B [compared to $\text{B}(\text{C}_2\text{H}_5)_3$] and in the deshielding of $^{13}\text{C}(\text{CH}_2)$ [compared to $\text{CH}_2=\text{CH}_2$]. Therefore, boron in α -alkenylboranes acts as a π -acceptor.

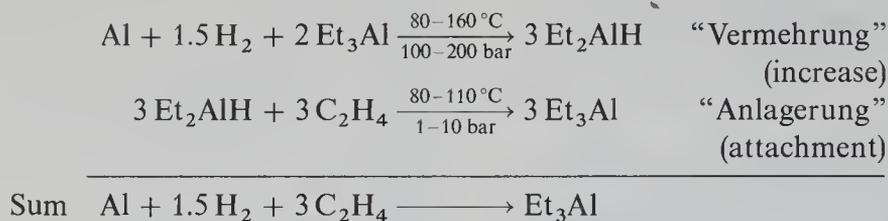
As expected, considerably stronger shielding is experienced by ^{11}B in Lewis base adducts [solvent effects on $\delta(^{11}\text{B})$] and in tetraorganoborate anions. A strik-

ing effect is the very strong shielding of ^{11}B in borane carbonyl H_3BCO . Note, however, that in borane carbonyl, as opposed to transition-metal carbonyls, CO can only function as a σ -donor. Another factor which may contribute to ^{11}B shielding in borane carbonyl is the diamagnetic susceptibility of the $\text{C}\equiv\text{O}$ triple bond [compare $\delta(^{11}\text{B})$ for H_3BPMe_3 and for H_3BCO].



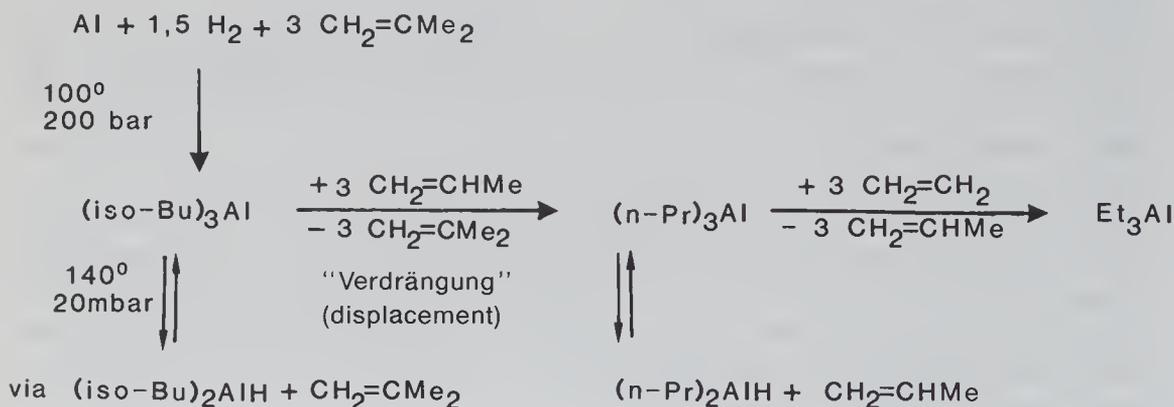
Aluminum is activated by grinding with Et_3Al in order to remove surface oxides. This process, patented by **Chemische Werke Hüls**, is only used to produce trimethyl- and triethylaluminum.

In the **Ziegler direct process** two observations (in the presence of aluminum alkyls, Al reacts with H_2 ; >Al-H adds to alkenes) are exploited:



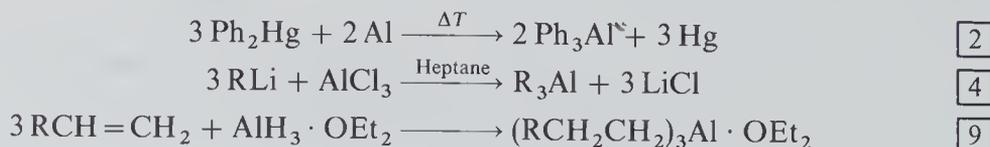
The reactivity of Al is enhanced by alloying it with 0.01–2% of Ti. If aluminum and the alkene are used in a molar ratio of 1:2, dialkylaluminum hydride is obtained.

Since hydroalumination is reversible and the affinity of >Al-H for alkenes increases in the order $\text{CH}_2=\text{CR}_2 < \text{CH}_2=\text{CHR} < \text{CH}_2=\text{CH}_2$, several other aluminum organyls can be prepared starting from *tris(iso-butyl)aluminum*:



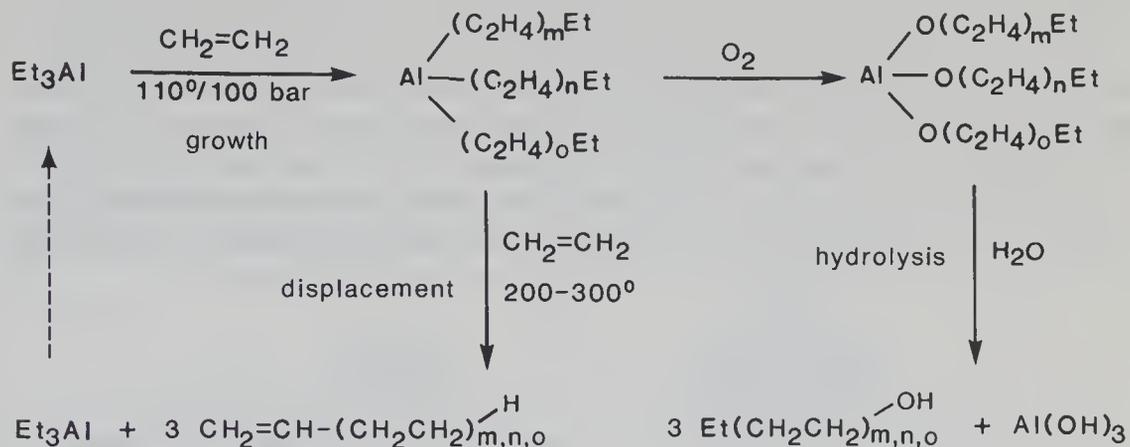
The less volatile, more heavily substituted alkene is condensed from the gas stream and the equilibrium shifted in favor of the desired, thermodynamically more stable aluminum alkyl. This is the method of choice for the generation of higher aluminum trisalkyls like *tris(n-octyl)aluminum* from *tris(iso-butyl)aluminum*.

Due to the commercial availability of numerous aluminum alkyls, the task of preparing them in the laboratory will seldom arise. Nevertheless, a few approaches will be mentioned:



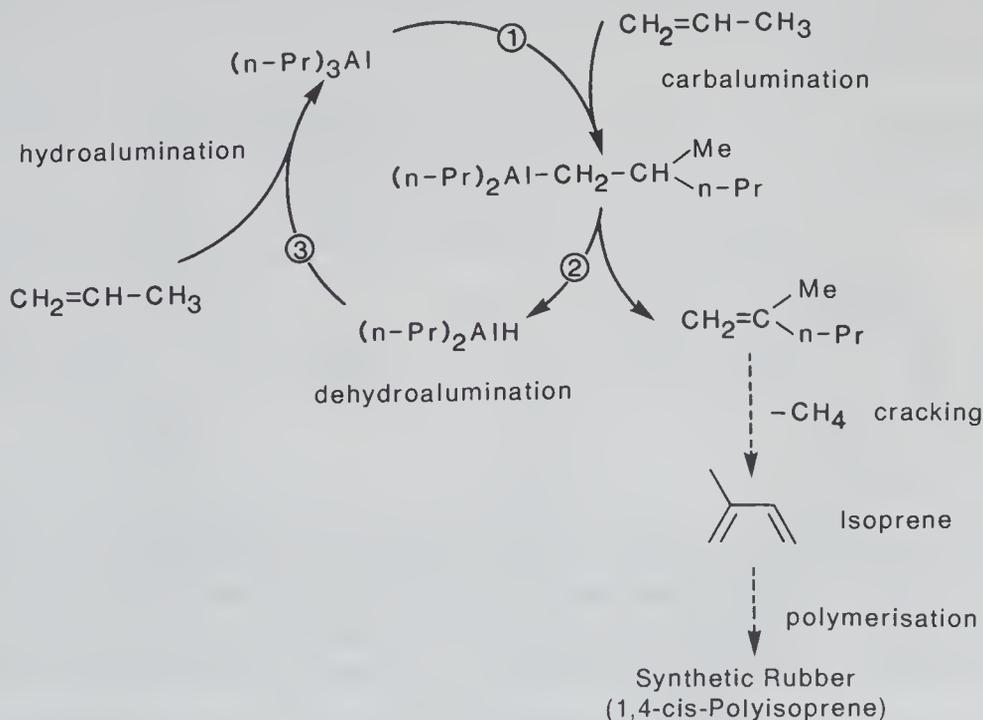
TECHNICAL APPLICATIONS OF TRIS(ALKYL)ALUMINUM COMPOUNDS

a) The multiple insertion of ethylene into the Al–C bond, discovered by K. Ziegler, has become known as the **Aufbaureaktion (growth reaction)**. It is used to produce 1-alkenes and unbranched primary alcohols.



The sequence of insertions can proceed up to chain lengths of about C_{200} . A limiting factor is the competition between the growth and displacement reactions. Among the products of this process, unbranched even 1-alkanols of chain lengths C_{12} – C_{16} (“**detergent alcohols**”) are of prime importance, since their sulfates are produced in bulk quantities to serve as biodegradable surfactants ROSO_3H .

b) If, instead of ethylene, propene or another 1-alkene is used, only a single insertion into the Al–C bond takes place. An example is the **catalytic dimerization of propene** which forms the basis of an important technical process for the production of isoprene:



c) **Olefin polymerization** employing mixed catalysts like $\text{Et}_3\text{Al}/\text{TiCl}_4$ in heptane (**Ziegler-Natta low-pressure process**) will be discussed in section 17.6.

PROPERTIES

The binary aluminum alkyls R_3Al are colorless, mobile liquids which violently react with air and water: Aluminum alkyls with short chain lengths are pyrophoric, with water they react explosively and their manipulation calls for utmost care and the **protective atmosphere of an inert gas** (N_2 or Ar). With the exception of alkanes and aromatic hydrocarbons, all solvents are rapidly attacked by aluminum alkyls. Thermal cleavage to form R_2AlH and alkene for aluminum alkyls with β -branched alkyl groups becomes appreciable at 80°C , for *tris*(*n*-alkyl)aluminum at about 120°C . The reactivity of organoaluminum halides $\text{R}_n\text{AlX}_{3-n}$ and -alkoxides $\text{R}_n\text{Al}(\text{OR}')_{3-n}$ is considerably lessened.

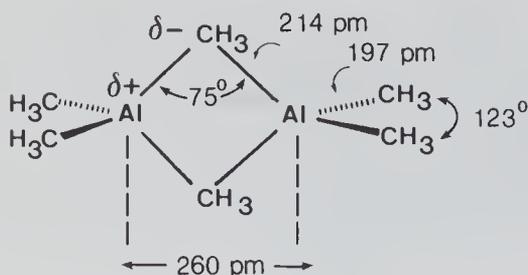
STRUCTURE AND BONDING OF BINARY ALUMINUM ORGANYLs

Aluminum organyls have a pronounced tendency towards the formation of **dimeric units** Al_2R_6 . This association is opposed by bulky ligands R:

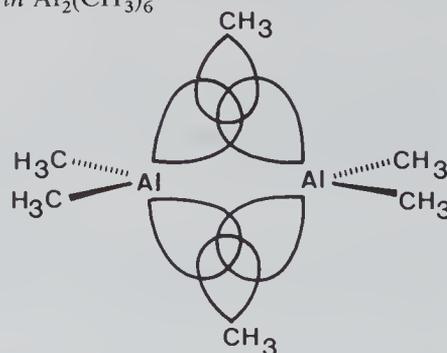
	Solid state	Solution (in hydrocarbons)	Gas phase
AlMe_3	dimeric	dimeric	dimeric \rightleftharpoons monomeric
AlEt_3 , $\text{Al}(n\text{-Pr})_3$	dimeric	dimeric	monomeric
$\text{Al}(iso\text{-Bu})_3$	dimeric	monomeric	monomeric
AlPh_3	dimeric	dimeric \rightleftharpoons monomeric	monomeric

Among the organometallics MR_3 of group 13, dimerization is only observed for the aluminum organyls.

Structural data
for $\text{Al}_2(\text{CH}_3)_6$



$\text{Al}-\overset{\text{C}}{\text{Al}}$ ($2e\ 3c$) bonds
in $\text{Al}_2(\text{CH}_3)_6$

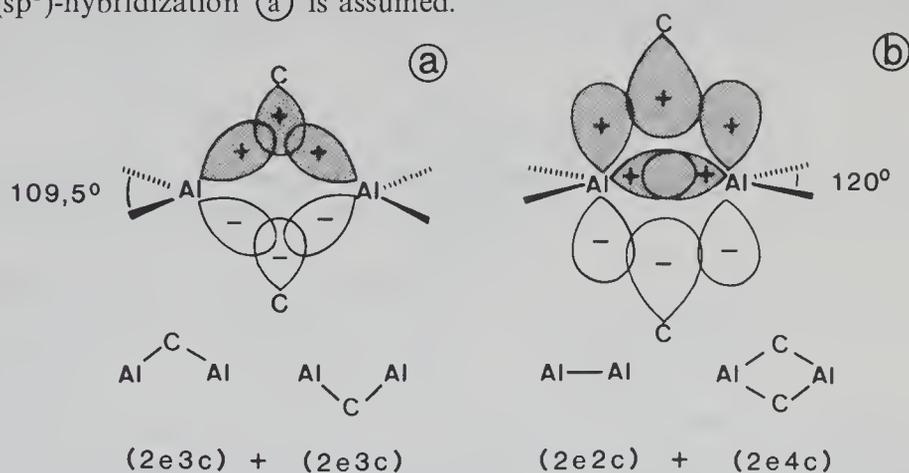


In a simplified discussion of the structural parameters of **aluminum alkyls**, sp^3 -hybridization at carbon as well as at aluminum is assumed. Whereas the four terminal bonds $\text{Al}-\text{C}_t$ display "normal" length, the larger bond distance $d(\text{Al}-\text{C}_b)$ in the bridging region signals a reduced bond order. As in the case of boranes (p.66), the bridge $\text{Al}-\overset{\text{C}}{\text{Al}}$ may be described as a two-electron three-center ($2e\ 3c$) bond, formed by

the interaction of one $C(sp^3)$ orbital with two $Al(sp^3)$ orbitals. Since the fragments $2(CH_3)_2Al\cdot$ and $2CH_3\cdot$ furnish a total of 4 electrons for bonding, 2 electrons per $Al-C-Al$ bridge are available.

The bond angles and the $Al-Al$ distance prompt a more refined interpretation, however. In particular, the distance $d(Al-Al)=260\text{pm}$ in Al_2Me_6 is significantly shorter than the corresponding distance in dimeric aluminum halides which possess $Al-X-Al$ bridges, consisting of two $(2e2c)$ bonds [example: Al_2Cl_6 , $d(Al-Al)=340\text{pm}$]. The short distance $d(Al-Al)$ in Al_2Me_6 is indicative of a direct $Al-Al$ interaction, for this length only marginally surpasses the sum of the covalent radii of two Al atoms ($2 \times 126\text{pm}$).

In an extreme representation, which presupposes an $Al-Al$ σ -bond, $Al(sp^2)$ (b) rather than $Al(sp^3)$ -hybridization (a) is assumed.

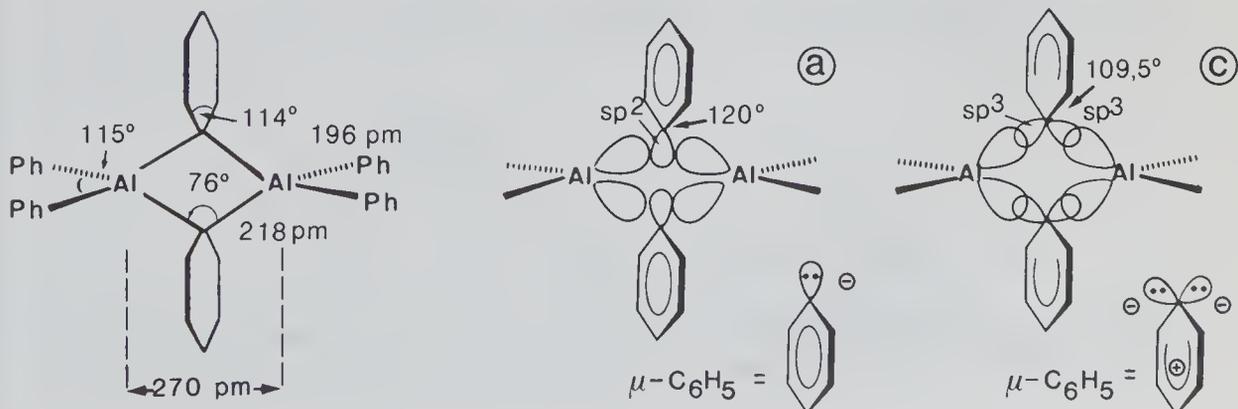


Description (b) concurs with the considerable opening of the angle C_iAlC_i beyond $109,5^\circ$. The smaller bond angle AlC_bAl reflects a compromise between maximal orbital overlap and tolerable $Al^{\delta+}/Al^{\delta+}$ repulsion. The actual situation probably resides between the alternatives (a) and (b).

The structure of **triphenylaluminum** Al_2Ph_6 , which is dimeric in the solid state, also points to a bonding situation which lies between two limiting cases. Two pertinent aspects, the small angle $C-C_b-C$ at the bridging carbon atom and the disposition of the plane of the phenyl ring, perpendicular to the $Al-Al$ axis, must be mentioned.

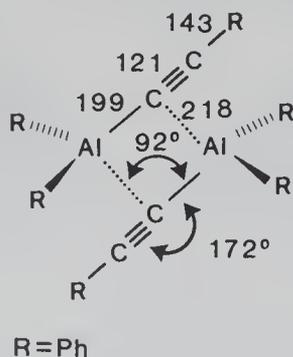
Structural data for $Al_2(C_6H_5)_6$

Alternative hybridizations at the bridging C atom



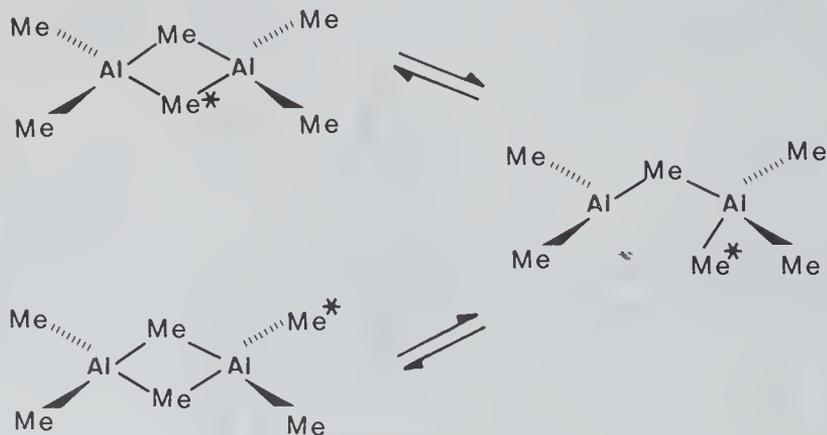
In model (a) the phenyl carbanion contributes a $C_b(sp^2)$ orbital and one electron pair to the $(2e\ 3c)$ bond in the bridge $Al-C_b-Al$. Aromatic conjugation would remain unaffected in this mode. In description (c), the ion $C_6H_5^-$ acts as a $4e$ ligand, supplying two $C_b(sp^3)$ orbitals to the bridge bond $Al-C_b-Al$. In this variant, the bridge would be formed by two $(2e\ 2c)$ bonds, and the electron deficiency in the bridging region abated at the expense of aromatic conjugation in the ligand. The angle CC_bC of 114° again implies a bonding situation between the two borderline cases.

Aluminum organyls offer yet another bridging mode: **alkynyl groups** form particularly strong bridges which are maintained even in the gas phase (Haaland, 1978). They are characterized by disparate bonding relations of the bridging atom C_α to the Al atoms.

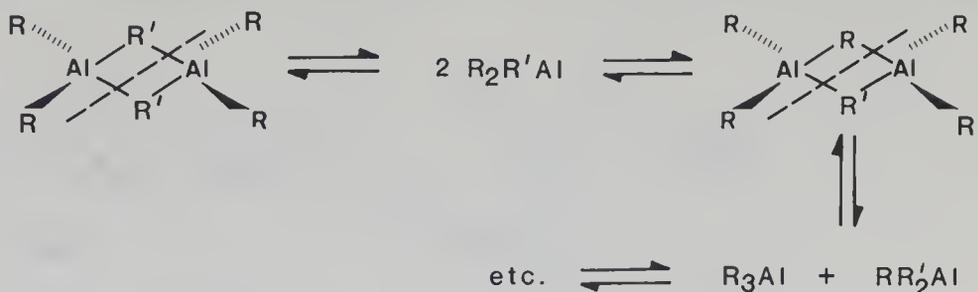


Structure of $[Ph_2Al-C\equiv CPh]_2$ in the crystal (Stucky, 1974): C_α forms a σ bond to one and a π -donor bond to the other Al atom. This mode is reminiscent of σ/π bridges, which occur for transition-metal carbonyls (p. 225). The alkynyl ligand may be regarded as a donor of three electrons ($1\ \sigma$ -e, $2\ \pi$ -e) which renders alkynyl bridges less electron deficient than alkyl bridges, thereby accounting for their robust nature.

The association of certain aluminum organyls **in solution** is confirmed by spectroscopic methods, especially by 1H - and ^{13}C -NMR. Thus, trimethylaluminum at $-50^\circ C$ shows two 1H -NMR signals of relative intensities 1:2 [$\delta(CH_3, \text{bridging})$ 0.50 ppm; $\delta(CH_3, \text{terminal})$ -0.65 ppm] which coalesce at $-25^\circ C$ and appear as one sharp line [$\delta(CH_3)$ -0.30 ppm] at $+20^\circ C$. This result is sufficiently accounted for by intramolecular exchange:



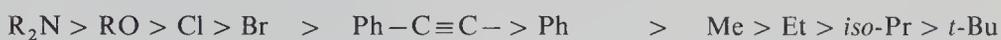
Additionally, intermolecular exchange also takes place. Therefore, pure compounds Al-RR'R'' , which bear different alkyl groups at aluminum, cannot be isolated:



Values for the enthalpy change ΔH , affiliated with the monomer/dimer equilibrium, are accessible by $^1\text{H-NMR}$:



Furthermore, NMR studies of species with a mixed ligand sphere allow an evaluation of the **relative ability of substituents to form bridges**:



Two ($2e\ 2c$) bonds,
trend follows the
Lewis basicity

unsaturated bridges,
 σ - and π -interactions

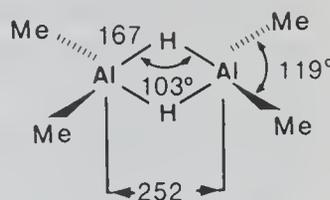
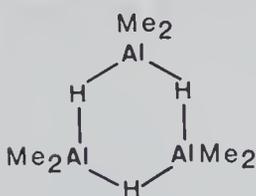
one ($2e\ 3c$) bond,
steric demand
is decisive

Bridges of exceptional strength are formed by the hydride ion in compounds $(\text{R}_2\text{AlH})_n$:

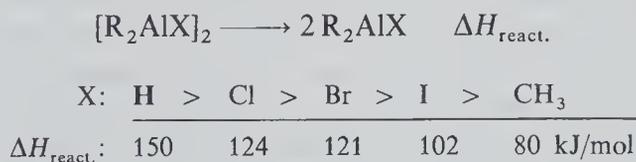
solution
 $n = 3$

neat, liquid
 $n > 3$

neat, gas phase
 $n = 2$

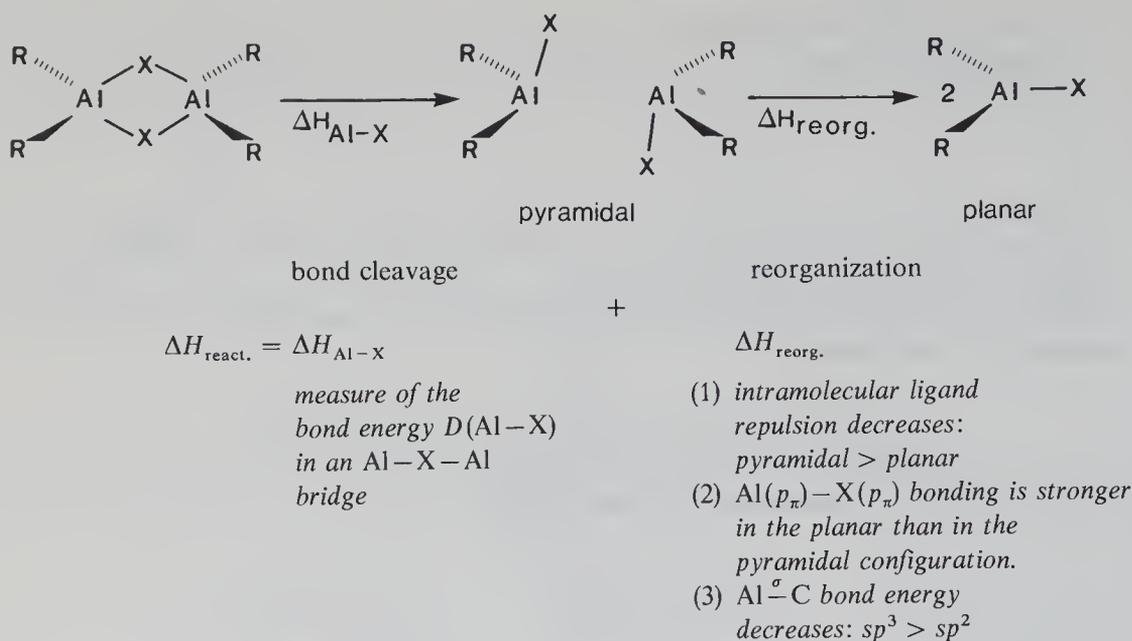


In this context, a brief **discussion of the energetics** is instructive. The enthalpy changes $\Delta H_{\text{react.}}$, pertaining to the cleavage of $[\text{R}_2\text{AlX}]_2$ into monomeric units, decrease in the following order:



This is, however, **not** the sequence of decreasing bond energy $D(\text{Al}-\text{X})$ in the bridges $\text{Al}-\text{X}-\text{Al}$ because the listed values for $\Delta H_{\text{react.}}$ relate to a process which, apart from bond

cleavage, includes additional changes. First of all, it must be borne in mind that in the dimer, the aluminum atom is in a tetrahedral environment whereas in the monomer it finds itself in a trigonal planar coordination.



After correction for $\Delta H_{\text{reorg.}}$, the enthalpy changes accompanying Al-X cleavage in Al-X-Al bridges now vary as:

$$\Delta H_{\text{Al-X}}: \text{Cl} > \text{Br} > \text{I} > \text{H} > \text{Me}$$

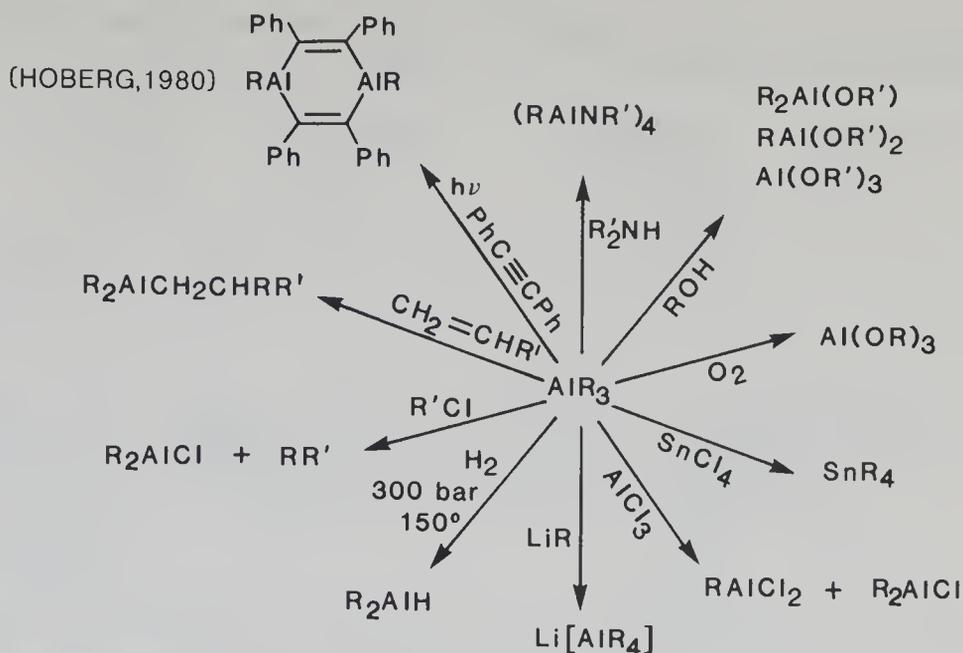
The inescapable conclusion is that hydride bridges appear to be so strong, because the enthalpy of reorganization $\Delta H_{\text{reorg.}}$ is small for R_2AlH . This must be related to the minor role, relief of interligand repulsion plays for the small hydride ligand on going from pyramidal to trigonal planar geometry, and to the absence of a stabilizing π -bonding contribution in the trigonal planar form.

REACTIONS OF ALUMINUM ORGANYLs

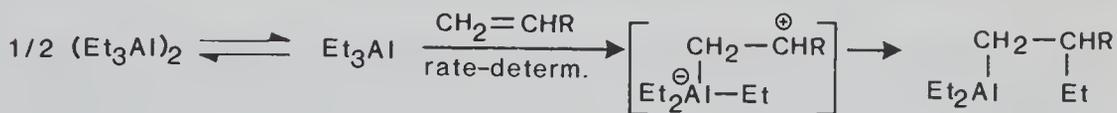
The exceptional reactivity of organoaluminum compounds AlR_3 has led to a multitude of synthetic applications which can only be treated in a cursory fashion here. The reactivity of RAlX_2 is very much reduced as compared to that of AlR_3 . Hence, in many cases only one of the three Al-C bonds can be utilized in synthesis.

Reactions of the higher hydrocarbons with aluminum alkyls must be performed with circumspection: the contact of AlR_3 with CHCl_3 or CCl_4 has led to explosions. For synthetic applications, it is of significance that in their chemoselectivity, lithium organyls, Grignard reagents and aluminium organyls complement each other.

Whereas LiR and RMgX typically add to polar multiple bonds like C=O and $-\text{C}\equiv\text{N}$, addition to >C=C< double bonds usually being confined to conjugated systems (p. 30, AlR_3 also adds to isolated multiple bonds >C=C< and $-\text{C}\equiv\text{C}-$ (carbalumination). As in the case of hydroboration, it is the products of subsequent reactions of the initial



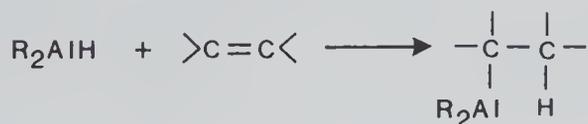
organoaluminum adducts which are of practical interest. The rate law for carbalumination is compatible with a monomer/dimer pre-equilibrium:



$$\text{Rate} = k[(\text{Et}_3\text{Al})_2]^{1/2} \cdot [\text{Alkene}]$$

Carbaluminations invariably proceed as *cis*-additions; alkynes react faster than alkenes and terminal alkenes more rapidly than internal alkenes. The R₂Al fragment usually attaches itself to the least substituted (= terminal) carbon atom of the alkene.

Closely related to carbalumination is **hydroalumination** (cf. "attachment" in the Ziegler direct process, p. 76):

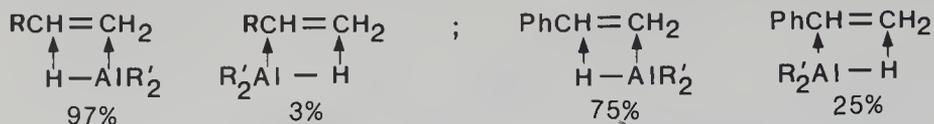


The readiness to undergo hydroalumination increases in the order:

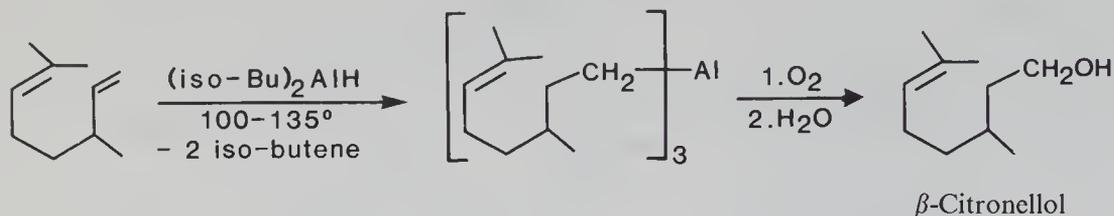


An inverse trend is observed for dehydroaluminations where alkenes are liberated (p. 76).

Hydroaluminations are highly stereoselective (*cis*); the degree of regioselectivity (*anti-Markovnikov*) varies, however:



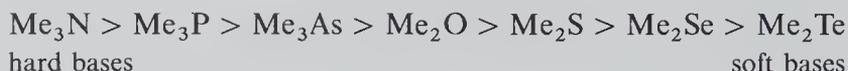
Example:



An advantage of hydroalumination over hydroboration is the ease of Al–C cleavage which does not require the use of peroxides. As a disadvantage, the lower chemoselectivity must be mentioned: besides C=C multiple bonds, functional groups are also attacked and, in the case of terminal alkynes, metallation at the CH-acidic position $\text{R}-\text{C}\equiv\text{C}-\text{H}$ occurs.

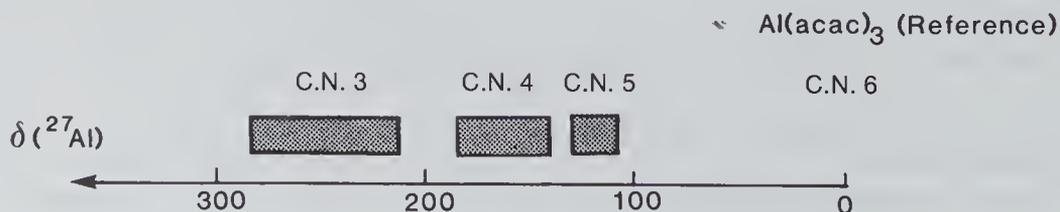
LEWIS-BASE ADDUCTS OF ALUMINUM ORGANYLs

Aluminum organyls are stronger Lewis acids than organoboron compounds. They number among the **hard acids** (in the Pearson sense) because Lewis basicity towards AlMe_3 decreases as follows:

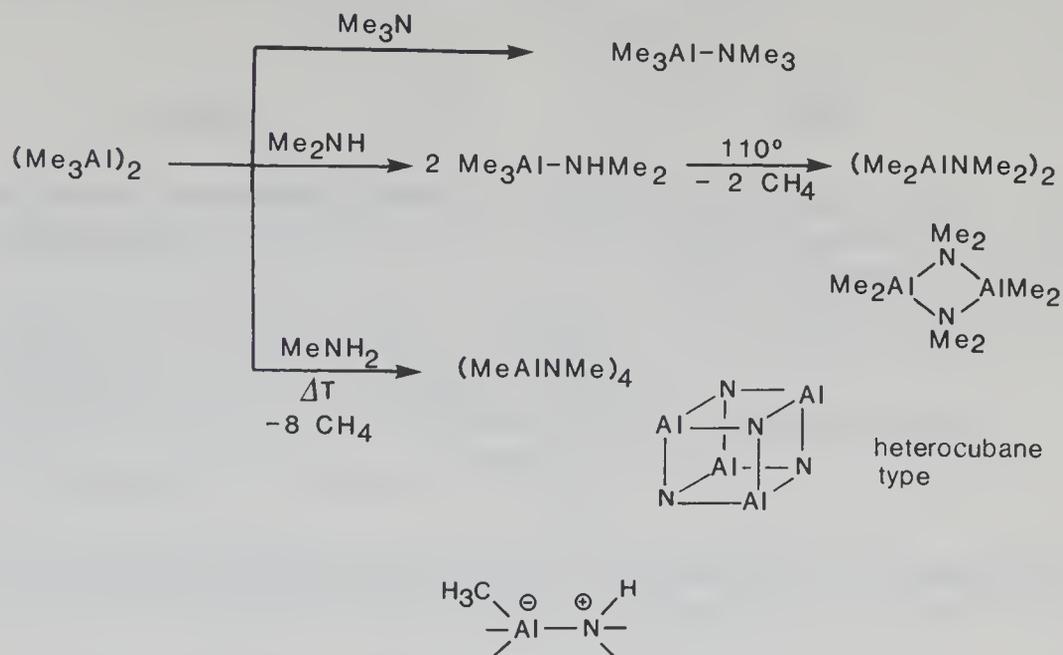


With Me_2S and Me_2Se , complicated equilibrium mixtures are formed since the strength of the bridge $\text{Al}-\text{CH}_3-\text{Al}$ is comparable to that of the Lewis-acid/base interaction $\text{Me}_3\text{Al} \cdot \text{EMe}_2$. The finding that in group 13 only the aluminum organyls form dimers is another expression of the high Lewis acidity of AlR_3 .

The determination of the coordination number (C.N.) at Al for adducts present in solution often poses difficulty – especially in cases where multidentate Lewis bases are involved. For compounds of the type $(\text{R}_n\text{AlX}_{3-n})_m$ ($m = 1, 2, 3$) and $[\text{R}_2\text{AlO}(\text{CH}_2)_2\text{Y}]_2$ ($\text{Y} = \text{OR}', \text{NR}'_2$) chemical shifts in the ^{27}Al -NMR spectra can provide insights (Benn, 1987 R):

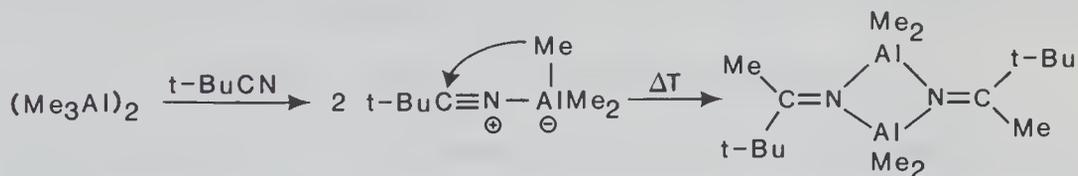


Reactions of R_3Al with **tertiary amines** usually terminate with adduct formation; in the cases of **secondary and primary amines**, consecutive reactions follow:

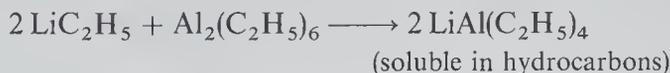


The Lewis-acid/base interaction results in an increase of carbanion character of the CH_3 group as well as an increase in NH acidity. The elimination of CH_4 in the reactions shown above is thereby facilitated.

Adducts of aluminum alkyls with unsaturated Lewis bases can rearrange via alkyl migration such that carbalumination of the multiple bond is effected. In this way, nitriles are transformed into dimeric bis(organo)aluminum ketimides:



Carbanions add to AlR_3 to form tetraorganoalates:

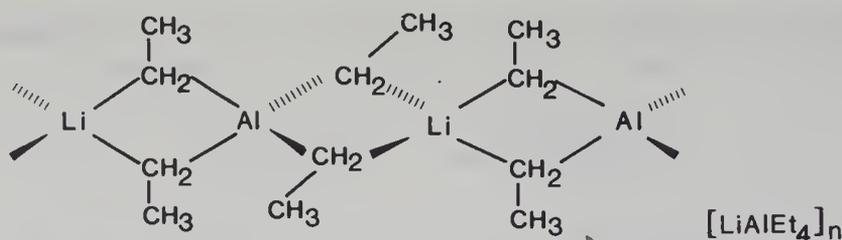


These “ate complexes” also arise from reductions with alkali metals:

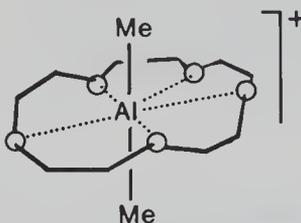


$LiAlEt_4$, like $BeMe_2$, has a polymeric structure which can be described as a chain of edge-sharing tetrahedra, in which alternating Li and Al atoms are connected by

$M-C-M$ ($2e3c$) bridges:



Similar to R_2B^+ (p. 58), the extremely Lewis acidic bis(organo)aluminum cation R_2Al^+ can only be isolated as its Lewis base adduct. As expected, aluminum adopts a higher coordination number than boron.



$\{\text{Me}_2\text{Al}[\text{15}]\text{crown-5}\}^+$: the linear cation Me_2Al^+ assumes a central position here. In the interior of the larger macrocycle [18]crown-6, Me_2Al^+ is located excentrically (Atwood, 1987).

7.3 Gallium-, Indium-, and Thallium Organyls

The organometallic compounds of gallium, indium, and thallium are far less important than those of boron and aluminum. Ga- and In-organyls serve as doping agents in the manufacture of semiconductors. Thus, via thermal decomposition of gaseous mixtures of trimethylgallium and arsane, layers of galliumarsenide can be deposited:



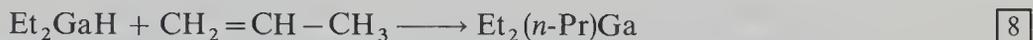
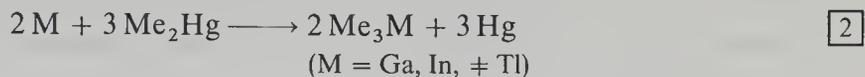
Despite their high toxicity, organothallium compounds have found use in organic synthesis.

The organometallic chemistry of gallium in many respects still resembles that of aluminum; it is confined almost exclusively to the oxidation state Ga^{III} . For indium, besides In^{III} , a few organyls of In^{I} have been reported [Example: $(\text{C}_5\text{H}_5)\text{In}$]. In the case of thallium, Tl^{III} as well as Tl^{I} is encountered in organometallic compounds.

7.3.1 σ -Organyls of Ga, In, Tl and their Lewis-Base Adducts

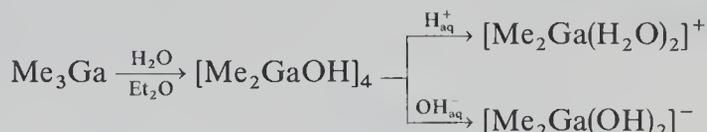
The organyls R_3M ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) have virtually no tendency to form dimers. Furthermore, as dissociation enthalpies for the adducts $\text{R}_3\text{M} \cdot \text{NMe}_3$ indicate, the Lewis acidities of species R_3M decrease for the heavier homologues of aluminum ($\text{B} < \text{Al} > \text{Ga} > \text{In} > \text{Tl}$).

The preparation of R_3Ga , R_3In and of the mixed ligand species R_nMX_{3-n} proceeds according to standard methods of organometallic chemistry:



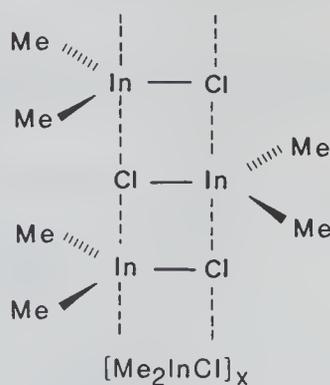
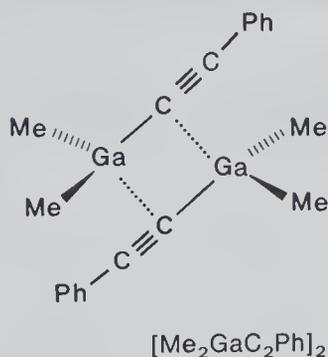
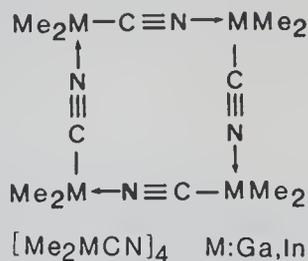
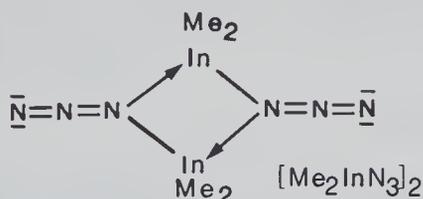
The binary organyls R_3Ga and R_3In are **monomeric** in solution and in the gas phase; they are highly air-sensitive. Alkyl-group scrambling among the mixed trisalkyls $RR'R''M$ only takes place at elevated temperatures.

The electron deficiency at Ga can be relieved by means of **complex formation**:



In view of the pyrophoric nature of the majority of binary organyls R_3Ga , the resistance of the Ga–C bonds towards hydrolysis and oxidation in the species $[R_2GaL_2]^{+,-}$ is remarkable.

Rather than by complex formation, an octet configuration at Ga and In can also be attained by **self-association**:



The dimeric nature of $Me_2GaC\equiv CPh$, which contrasts with most other compounds R_3Ga , is another example of the aforementioned strong inclination for bridge formation exhibited by alkynyl groups (p. 80) (Oliver, 1981).

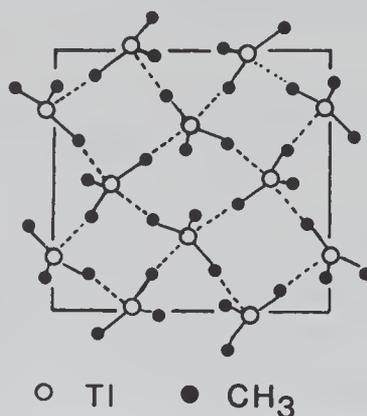
In the organometallic chemistry of thallium – as opposed to that of Ga and In – changes in oxidation state M^{III}/M^I play an important role. Thus, the yields of thallium trisalkyls in syntheses starting from inorganic Tl^{III} compounds and Li alkyls or Grignard reagents, are impaired by the oxidizing action of Tl^{III} . Conversely, *tris*(organo)thallium compounds may be formed via oxidative addition of RI to Tl^I compounds:



The air- and water-sensitive binary compounds R_3Tl are subject to ready, occasionally even explosive decomposition. Another indication of the weakness of the $Tl-C$ bond is the alkylation of mercury by means of R_3Tl :

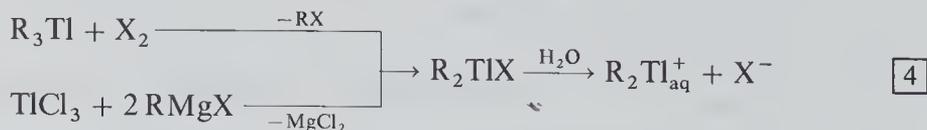


Trimethylthallium, which is monomeric in solution and in the gas phase, forms a three-dimensional network in the crystalline state, whereby each thallium atom possesses three short and two long bonds to neighboring carbon atoms, with mean values of 228 and 324 pm respectively (Sheldrick, 1970):



A projection of the structure of Me_3Tl in the crystal reveals that Tl has the coordination number 5, four CH_3 groups assuming bridging positions and the fifth CH_3 group being terminal. The large differences in the $Tl-C$ bond lengths within the $Tl-C-Tl$ bridges suggest that three center bonding ($2e3c$) is only weakly present.

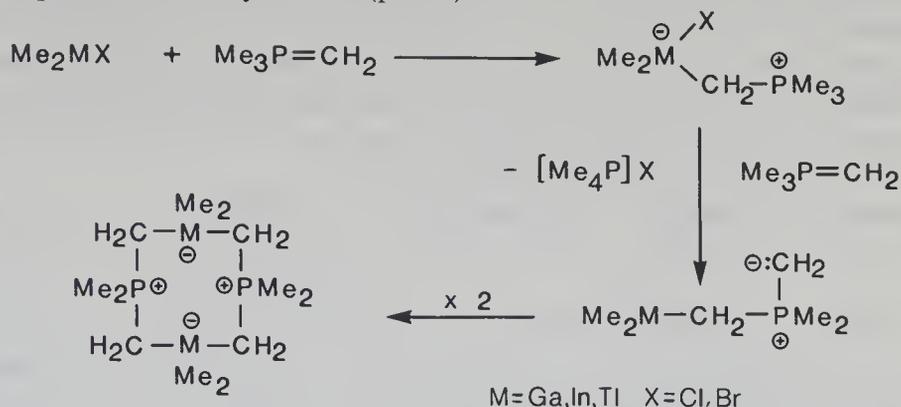
$Tl-C$ bond cleavage in R_3Tl by means of a dihalogen leads to bis(organo)thallium halides which in polar media form very stable cations:



Like the isoelectronic species R_2Hg and R_2Sn^{2+} , R_2Tl^+ is linear. R_2TlOH in aqueous solution acts as a strong base:

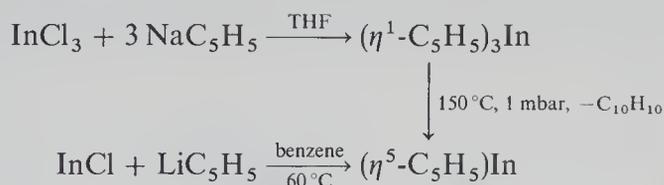


With methylenephosphoranes, organometal halides of Ga^{III} , In^{III} and Tl^{III} form oligomeric ylid complexes via transylidation (p. 180):

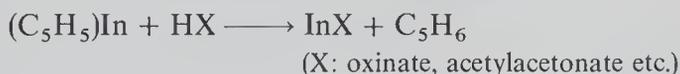


7.3.2 π -Complexes of Ga, In, and Tl

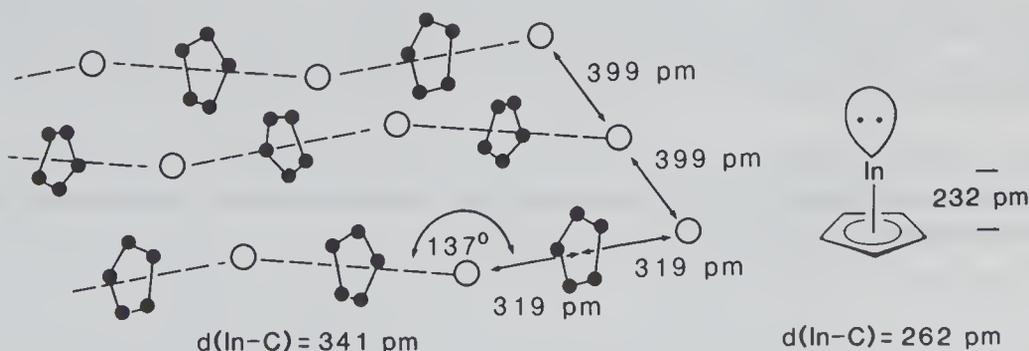
Cyclopentadienyl compounds of indium are known for the oxidation states In^{III} (σ -organyls) and In^{I} (π -complexes) (E. O. Fischer, 1957):



$(\text{C}_5\text{H}_5)_3\text{In}$ displays one $^1\text{H-NMR}$ signal only even at -90°C ; it is thought to be fluxional. $(\text{C}_5\text{H}_5)\text{In}$, a sublimable, water-stable but air-sensitive material, is the only easily accessible compound of In^{I} and serves as a starting material for the preparation of other In^{I} compounds:



An interesting aspect of the structure of $(\text{C}_5\text{H}_5)\text{In}$ is the strongly differing metal-ring distance in the crystal and in the gas phase. This points at higher covalency of the $\text{In}-\text{C}$ bond in the isolated molecule.



$(\text{C}_5\text{H}_5)\text{In}$ in the crystal:
polymer chains $[(\text{C}_5\text{H}_5)\text{In}]_x$
(Panattoni, 1963)

$(\text{C}_5\text{H}_5)\text{In}$ in the gas phase:
monomeric half-sandwich
complex (L. S. Bartell, 1964)

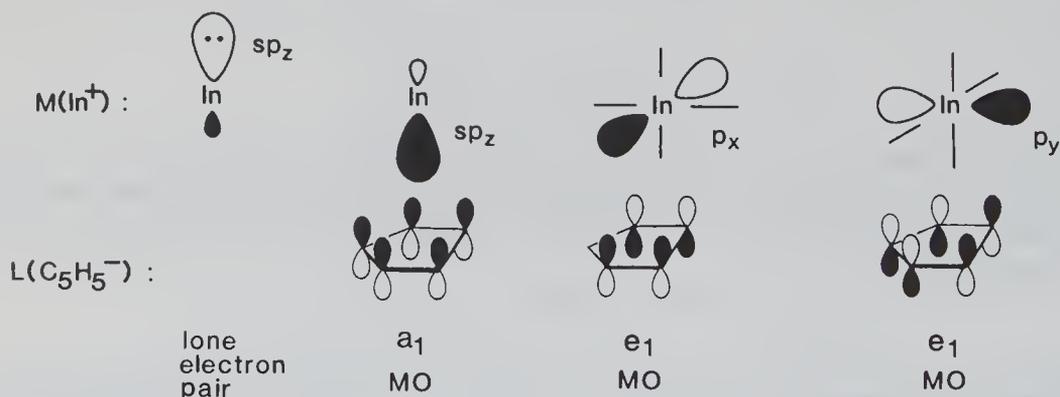
(C₅H₅)In possesses a dipole moment of 2.2 Debye, the indium atom and its lone pair forming the negative end of the molecule (Tuck, 1982). The structure of (C₅Me₅)In in the solid state differs fundamentally from that of parent (C₅H₅)In: whereas the latter forms zig-zag polymeric chains, the former is packed as octahedral (C₅Me₅)₆In₆ units which bear resemblance to the cluster (C₅H₅)₆Ni₆ (p. 409). The high volatility of (pentamethylcyclopentadienyl)indium indicates, however, that bonding between the (C₅Me₅)In monomers in the hexamer is weak (Beachley, 1986).

The best known organometallic compound of Tl^I, (C₅H₅)Tl, can even be prepared in an aqueous medium:



(C₅H₅)Tl is sublimable, sparingly soluble in organic solvents and can be handled in air; it is a convenient cyclopentadienyl-transfer agent for use with transition metal ions. The structure of (C₅H₅)Tl largely resembles that of (C₅H₅)In.

(C₅H₅)In may serve as a model for discussing the bonding situation in *main-group element cyclopentadienyls* (C₅H₅)M (Canadell, 1984). The rather small difference in the electronegativities of In and C leads one to expect that the metal-ligand bond in isolated molecules of (C₅H₅)In should be predominantly covalent. If the molecule is mentally constructed from the fragments :In⁺ (sp-hybrid) and C₅H₅⁻ (6π-e), the following metal-ligand interactions are conceivable:

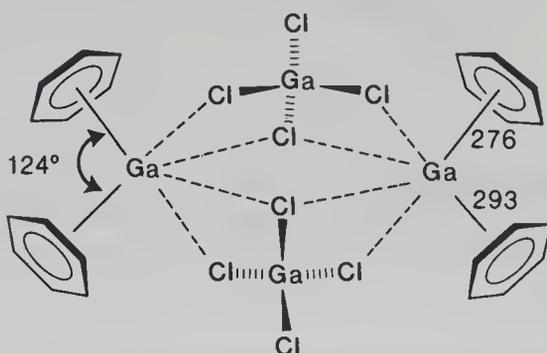


All three interactions generate a charge transfer L → M. The extent of this charge transfer and the ensuing covalent nature of the bond are governed by the energies of the basis orbitals which in individual cases have to be established by means of quantum chemical calculations. Similar considerations apply to the isolobal (p. 396) fragments R–Be⁺, R–Mg⁺, R–B²⁺, R–Al²⁺, as well as Ge²⁺, Sn²⁺ (p. 136) and Pb²⁺.

Besides variation of the metal component, varying the organic ligand is also conceivable. This leads to the question whether the ligand C₆H₆, which is iso-π-electronic with C₅H₅⁻, can form **main-group element arene π-complexes**:

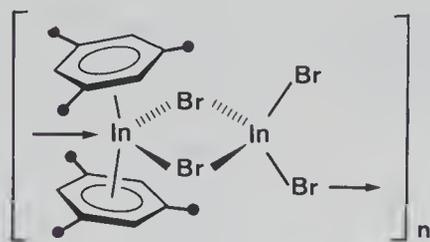


While the surprisingly high solubility of $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{Cl}_4]$ in benzene has been known for some time, implying some kind of Ga^{I} -arene interaction, the isolation and structural characterization of these adducts was achieved only recently (Schmidbauer, 1985 R). The compound $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ga}]\text{GaCl}_4 \cdot 3\text{C}_6\text{H}_6$ features tilted bis(arene)gallium^I cations, which are linked through GaCl_4^- -tetrahedra to form dimeric units.



Structure of $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ga}]\text{GaCl}_4 \cdot 3\text{C}_6\text{H}_6$ in the crystal. Three benzene molecules of the empirical formula are outside the coordination sphere of gallium. The distances $d(\text{Ga}-\text{Cl})$ differ, as do the distances $d(\text{Ga}-\text{C})$ (mean values 308 and 323 pm for the two $\text{Ga}-\text{C}_6\text{H}_6$ segments).

In a related mesitylene π -complex of In^{I} , bridging by InBr_4^- -tetrahedra leads to a polymeric structure:

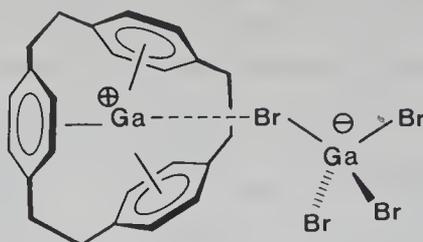


Unit from the chain structure of $\{[(\eta^6\text{-mesitylene})_2\text{In}]\text{InBr}_4\}_n$ in a schematic representation. The tilting angle amounts to 133° , the two arenes are almost equidistant from the central metal; $d(\text{In-ring center}) = 283$ and 289 pm.

A property common to these materials is the ease with which the arene ligands are cleaved off thermally. Herein, complex stability decreases in the order $\text{Ga}^{\text{I}} > \text{In}^{\text{I}} > \text{Tl}^{\text{I}}$; it increases with increasing degree of alkylation of the arene. Furthermore, the tendency to maintain the favorable coordination to halide ions is evident.

Contrary to (arene)transition-metal π -complexes [$(\text{C}_6\text{H}_6)_2\text{Cr}$ melts without decomposition at 284°C !], bonding in (arene)main-group π -complexes falls into the domain of **weak interactions**. Without delving into a detailed discussion here, only one plausible reason for these disparate properties will be mentioned: the stability of the transition metal-ligand bond is derived from the σ -donor/ π -acceptor synergism (p. 185); d -electrons for backbonding are, however, not available for main-group elements, since electrons in the subultimate d -shell are essentially core-electrons, being strongly bonded to the nucleus (p. 190).

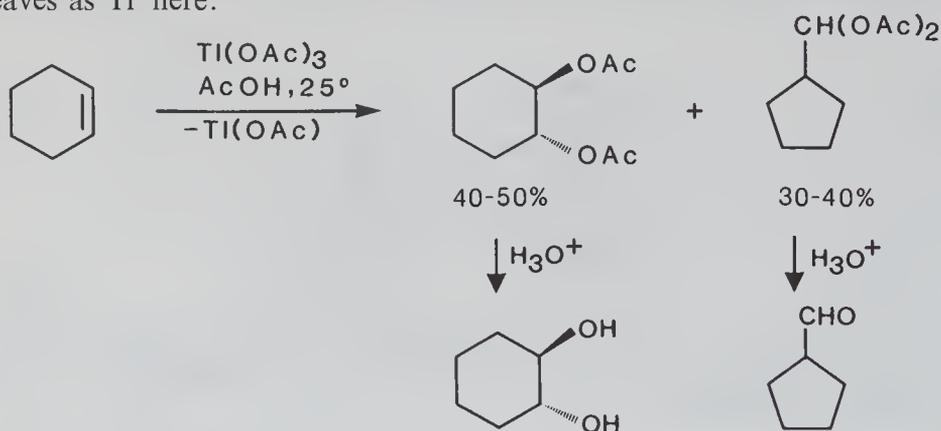
Hence, it is all the more remarkable that a mode of coordination of an arene to Ga^I has been discovered, which is without precedent in the area of transition metal π -complexes (Schmidbaur, 1987):



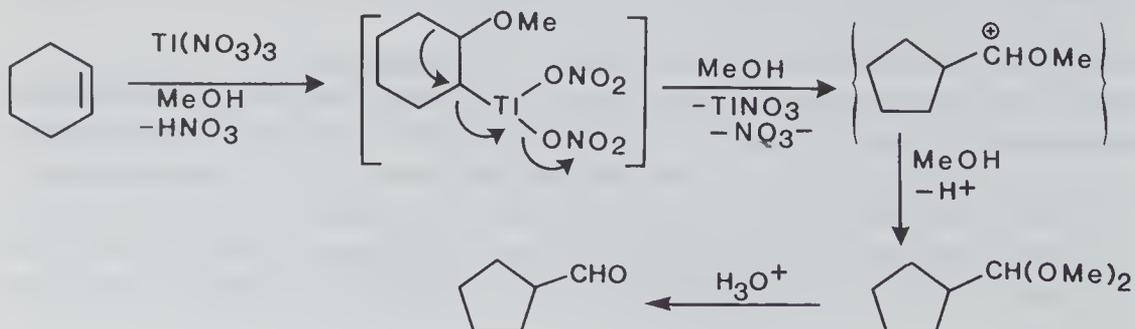
In the ion pair $\{(\eta^{18}\text{-[2.2.2]paracyclophane})\text{Ga}^{\text{I}}\} \text{GaBr}_4^-$ the central atom Ga^I exhibits nearly equal distances to the three ring centers; it is, however, displaced away from the ligand center along the three-fold axis by 43 pm in the direction of the counter ion GaBr₄⁻. Unquestionably, the chelate effect exerts a stabilizing function here.

7.3.3 Applications of Thallium Organyls in Organic Synthesis

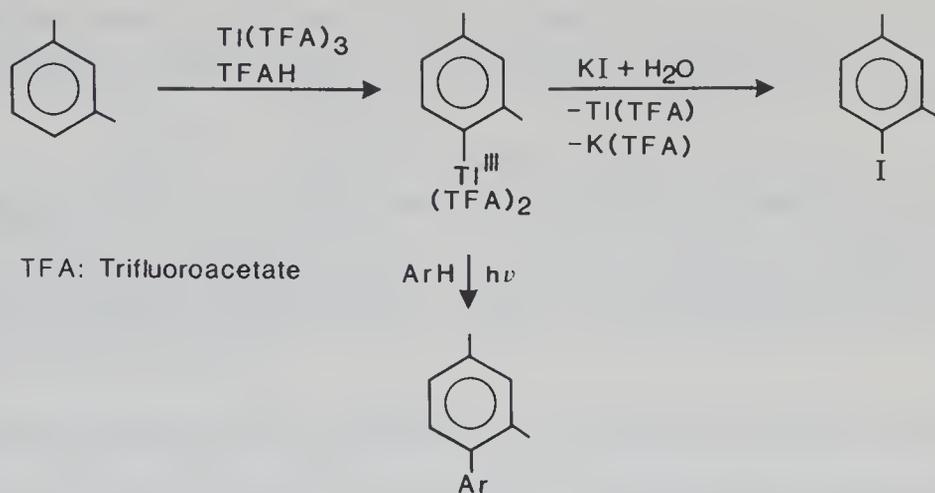
Thallium^{III} salts attack alkenes, whereby a solvent anion enters vicinally to the Tl–C bond formed (**oxythallation**). These organothallium intermediates decompose more rapidly than the primary products of the otherwise similar oxymercuration (cf. p. 53). The metal leaves as Tl^I here:



The product distribution in this olefin oxidation strongly depends on the nature of the medium and the counterions of Tl^{III}. Thus, oxythallation of cyclohexene with Tl(NO₃)₃ in MeOH almost exclusively yields the cyclopentanecarbaldehyde. Mechanistically, this ring contraction may proceed as follows:



A process of high regioselectivity is the **electrophilic aromatic thallation** by means of thallium trifluoroacetate, $\text{Tl}(\text{TFA})_3$, in trifluoroacetic acid, TFAH. In subsequent reactions, which are accompanied by a change in oxidation state $\text{Tl}^{\text{III}} \rightarrow \text{Tl}^{\text{I}}$, the new substituent enters at the position of the former $\text{Tl}-\text{C}$ bond. In this way, iodination of benzene can be effected under particularly mild conditions. Photolysis of the intermediary arylthallium trifluoroacetates in aromatic solvents lends itself to the preparation of unsymmetrical biphenyls:



8 Organoelement Compounds of the Carbon Group (Group 14)

Compounds in which carbon is bonded to one of its homologues – silicon, germanium, tin or lead – form that branch of organometallic chemistry which as yet has found the most extensive technical application (cf. p. 100, 137, 139):

- Silicones are materials with unique properties
- Organotin compounds are widely applied as stabilizers for plastics and as fungicides in crop protection.
- Lead alkyls, because of their use as antiknock agents, were for a long time the top organometallic commodity produced by industry. Recently, production figures are declining.

Accordingly, the literature abounds with reports dealing with their structures and reactions.

Two characteristics distinguishing the organoelement compounds of the carbon group from the organyls of the boron group are the **lower polarity of the E–C bond and, in compounds ER₄, the presence of an octet configuration.** Consequently, molecules ER₄ show no tendency to associate via (2e3c) alkyl- or aryl bridges. The reactivity towards nucleophiles is diminished and, as opposed to the corresponding compounds of the neighboring groups like AlMe₃ or PMe₃, the species ER₄ usually are water-stable and often even air-stable (examples: SiMe₄, SnPh₄, “soft organometallics”). It is instructive to examine a few group trends concerning the E–C bond:

E	Thermal stability	Bond energy <i>E</i> (E–C) in kJ/mol	Bond length <i>d</i> (E–C) in pm	Bond polarity E ^{δ+} –C ^{δ-}	Electronegativity <i>EN</i>
C		358	154		2.5
Si		311	188		1.9
Ge		249	195		2.0
Sn		217	217		1.8
Pb		152	224		1.9

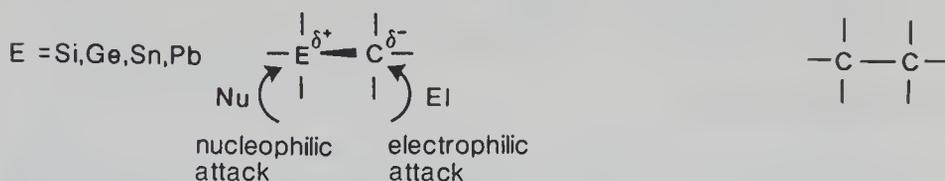
These trends shape the reactivities in **homolytic reactions**:



but



as well as in heterolytic reactions:

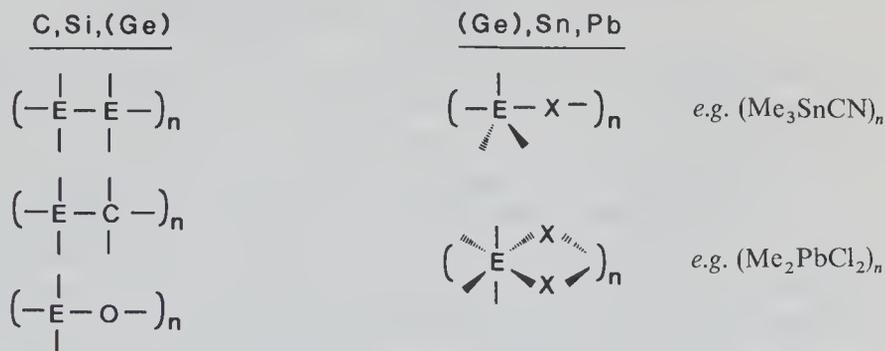


The availability of empty *nd* orbitals at E renders **associative mechanisms (A or I_A)** of substitution **possible**, coordination number 5 being adopted by the intermediate.

Example: hydrolysis of R₃SiCl.

d-orbitals of appropriate energy are unavailable. Associative mechanisms of nucleophilic substitution at saturated carbon are unfavorable.

Successive replacement of R by more electronegative groups X in R_nEX_{4-n} increases the affinity of E for attacking nucleophiles. Thus, SnMe₄ is inert towards hydrolysis and SnMe₆²⁻ is unknown, whereas SnCl₄ is readily hydrolysed and SnCl₆²⁻ can be prepared. Characteristic differences are also found among the **modes of catenation**:



E maintains its coordination number 4

E increases its coordination number to 5 or 6

8.1 Organosilicon Compounds

8.1.1 Silicon Organyls of Coordination Number 4

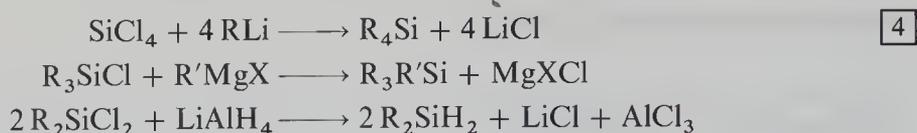
PREPARATION

Because of their great technical importance, many of the simple organosilanes can be obtained commercially so that their preparation in the laboratory is seldom necessary.

In the technical **direct process** (Rochow-Müller) for the production of methylchlorosilanes, Si/Cu alloys are used:



Special organosilanes are prepared by means of **metathesis reactions**:



or via **hydrosilation** (Speier process):



*Hydrosilations, which may also be initiated photochemically and which are catalyzed by radical forming reagents, transition-metal complexes, or Lewis bases, proceed in an **anti-Markovnikov direction**. Polyenes are hydrosilated in a **regio- and stereospecific** fashion. If chiral metal complexes are employed as catalysts, **enantioselective hydrosilation of prochiral alkenes** becomes possible.*

Arylsilanes are also accessible by means of the **Vollhardt cyclization** (p. 277) of silylalkynes.

PROPERTIES AND REACTIONS

Reactions involving Si–C Bond Cleavage

C–C and Si–C bonds are energetically very similar

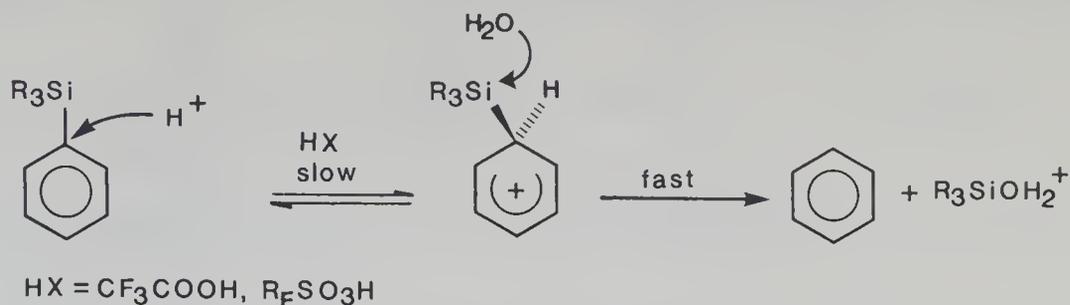
$$[D(\text{C}-\text{C}) = 334, D(\text{Si}-\text{C}) = 318 \text{ kJ/mol}].$$

For organosilanes, high thermal stability is therefore expected. Thus, **homolytic cleavage** of tetramethylsilane only sets in at temperatures exceeding 700 °C and tetraphenylsilane can be distilled in air at 430 °C without decomposition! Due to the low polarity of the Si–C bond, **heterolytic cleavage** also does not occur readily; this type of degradation requires harsh reaction conditions which have to be adapted well to the specific case. Since the organosilyl group formally leaves as R_3Si^+ , the propensity for Si–C cleavage in $\text{R}_3\text{SiR}'$ correlates with the CH-acidity of the parent hydrocarbon R'H (Example: Silylalkynes $\text{R}_3\text{Si}-\text{C}\equiv\text{CR}$ are easily desilylated).

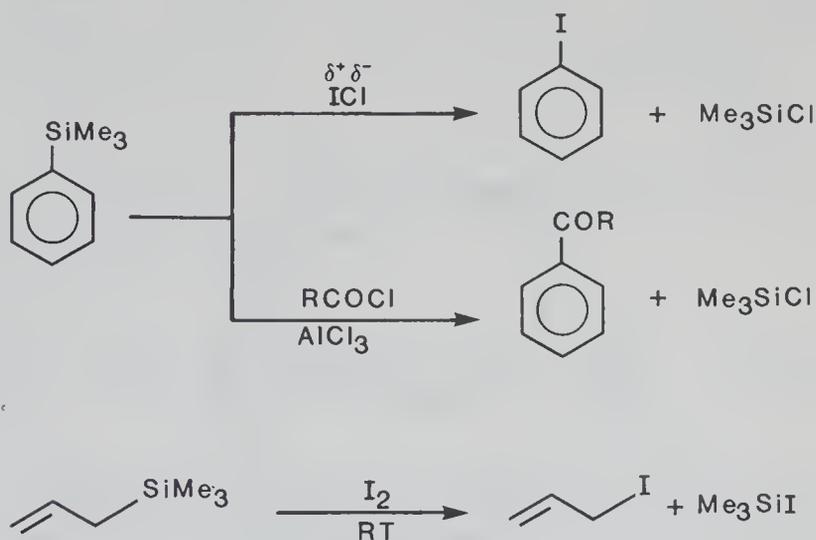
Heterolytic Si–C cleavage can in principle be initiated in four different ways which differ in the nature of the attacking agent (electrophile El or nucleophile Nu) and in the site of attack (Si or C). The establishment of a generally applicable order of reactivities is complicated by the fact that substituents at Si or C may exert a considerable influence. Bearing in mind these complications, the following gradation of the **readiness to undergo Si–C bond cleavage** summarizes the experimental evidence:

Type:	<i>I</i>	>	<i>II</i>	>	<i>III</i>	>	<i>IV</i>
	Si–C(aryl)		Si–C(aryl)		Si–C(alkyl)		Si–C(alkyl)
attacking species:	↑ El		↑ Nu		↑ El		↑ Nu

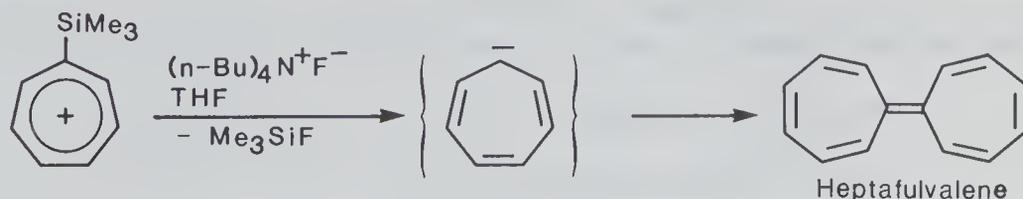
I. Si–C cleavage occurs most readily in **arylsilanes** and related compounds via **electrophilic attack at carbon**. Example:



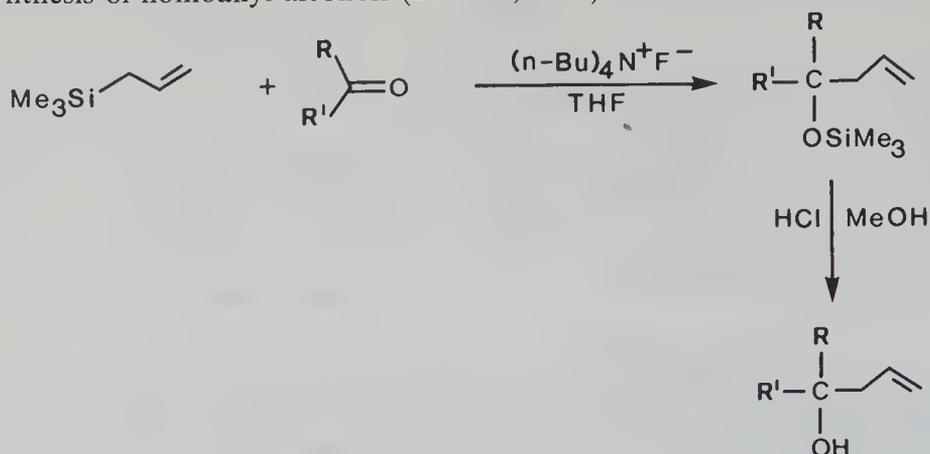
Mechanistically this **protodesilylation** resembles electrophilic aromatic substitution (Eaborn, 1975 R); it proceeds 10^4 times faster than proton exchange in the corresponding Si-free arene. Further examples for Si–C cleavages effected by electrophiles:



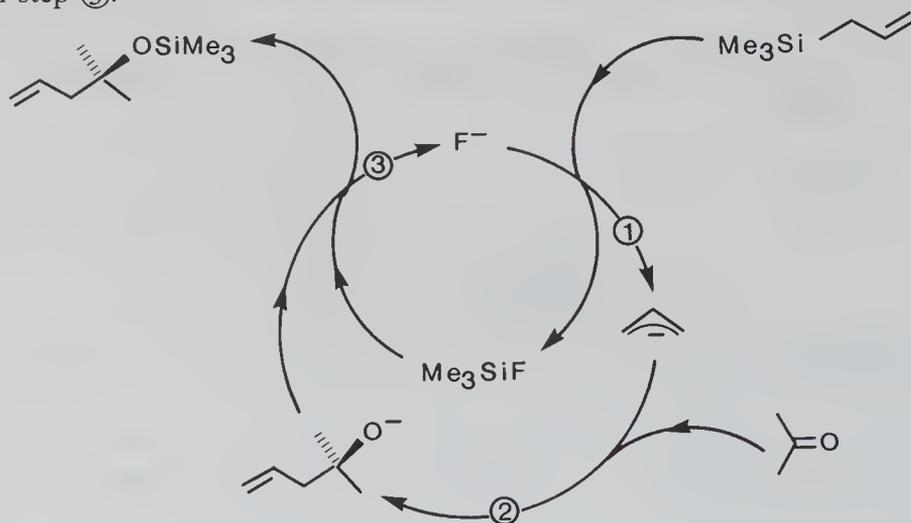
II. Si–C cleavage of arylsilanes, initiated by **nucleophilic attack at Si**, proceeds less readily. Yet, this variant has gained some practical importance since it constitutes a way of generating carbenes and carbanions which circumvents strongly basic or reducing conditions. The nucleophile of choice is the fluoride ion which possesses an exceptionally high affinity for Si [$E(\text{Si}-\text{F}) = 565 \text{ kJ/mol}$, strongest of all single bonds]. The fluoride ion is usually introduced as a component of the salt $(n\text{-Bu})_4\text{N}^+\text{F}^-$ (Ku wajima, 1976). Example (R. W. Hoffmann, 1978):



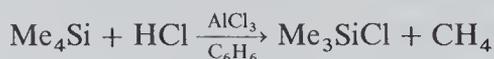
Besides this stoichiometric use, $(n\text{-Bu})_4\text{N}^+\text{F}^-$ may also be applied in catalytic quantities. In the following example, the intermediary generation of an allyl carbanion is employed in the synthesis of homoallyl alcohols (Sakurai, 1978):



The fact that only catalytic amounts of $(n\text{-Bu})_4\text{N}^+\text{F}^-$ suffice may be traced to the trans-silylation step ③:



III. Si–C cleavages in **alkylsilanes**, which are initiated by **electrophilic attack at carbon**, require the presence of strong Lewis acids as catalysts:



Slow cleavage is also effected by concentrated sulfuric acid, though:

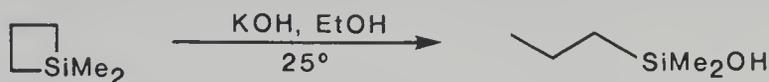


IV. Si–C cleavages in **alkylsilanes** by means of **nucleophilic attack at Si** are generally slow; they are only observed for very strong nucleophiles in polar, aprotic media:



HMPA = *hexamethylphosphoric trisamide*

The origin of the proton in the above reaction sequence is not always clear. These desilylations proceed much more rapidly if they are accompanied by a relief of ring strain:



or if good leaving groups are present (β -effect):



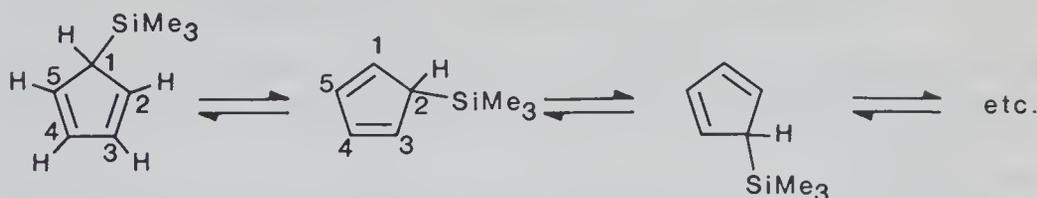
In this way, the plant growth substance Alsol® (PhCH_2O)₂MeSiCH₂CH₂Cl releases ethylene, which accelerates the ripening of bananas.

A sequence of Si–C bond cleavages and bond formations is also responsible for the dynamic behavior of trimethylsilylcyclopentadiene which manifests itself in the ¹H-NMR spectrum (H. P. Fritz, 1965):

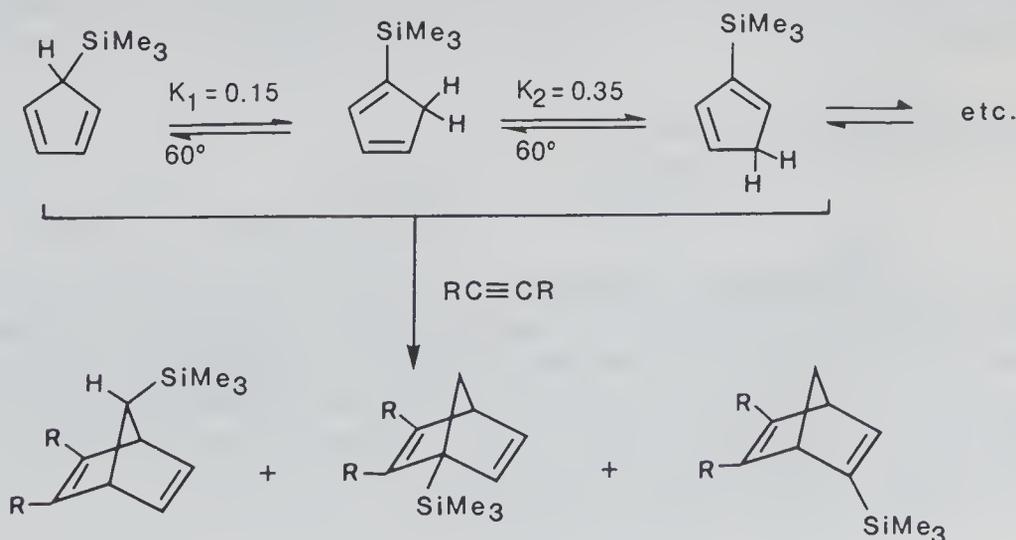
$$\text{Me}_3\text{SiCl} + \text{NaC}_5\text{H}_5 \longrightarrow \text{Me}_3\text{Si}(\eta^1\text{-C}_5\text{H}_5) + \text{NaCl}$$

δ (¹ H)	Si–CH ₃	H ₁	H _{2,5}	H _{3,4}	
–30 °C	0.2	3.31	6.44	6.55	ppm
+120 °C	0.2	5.75			ppm

These data are rationalized by a series of **metallotropic 1,2-shifts** ($k_{30^\circ} = 10^3 \text{ s}^{-1}$, $E_a = 55 \text{ kJ/mol}$), the molecule is **fluxional**:



In addition, considerably slower **prototropic 1,2-shifts** occur (relative rate 10^{-6}) which lead to an equilibrium mixture. The composition of this mixture can be determined by analyzing the Diels-Alder adducts (Ashe, 1970):



Reactions not involving Si–C Bond Cleavage

Due to the relatively inert character of the Si–C bond, R_3Si- and $R_2Si<$ units in many cases remain unaffected, playing a spectator role. Therefore, in the chemistry of organosilyl halides, -hydroxides, -alkoxides and -amides, organometallic aspects in the narrower sense recede. With the exception of the industrially important **organochlorosilane hydrolysis**, reactions of organosilyl derivatives containing silicon–heteroatom bonds will be assigned to the inorganic chemistry of the main-group elements, and will be treated here in a cursory way only. Another important aspect of organosilicon chemistry, the use of R_3Si as a **protecting group** in organic syntheses, will also be neglected here.

Organosilanols and Silicones

Organochlorosilanes R_nSiCl_{4-n} are subject to swift hydrolysis to form the corresponding silanols $R_nSi(OH)_{4-n}$ which, like silicic acid $Si(OH)_4$, readily undergo condensation reactions. In the simplest case, that of trimethylchlorosilane, hexamethyldisiloxane is obtained:



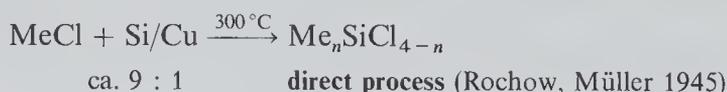
The driving force of this hydrolysis is largely governed by the high Si–O bond energy [cf.: $\bar{E}(\text{Si}-\text{Cl}) = 381 \text{ kJ/mol}$, $\bar{E}(\text{Si}-\text{O}) = 452 \text{ kJ/mol}$] and the solvation enthalpies of H^+ and Cl^- . The hydrolysis of bifunctional organosilanes Me_2SiCl_2 leads to higher condensation products:



The formation of polysiloxane chains and rings $(R_2SiO)_n$ (polysilicoketones), which contrasts with the monomeric nature of ketones R_2CO , reflects the weakness of the $\text{Si}=\text{O} (p_\pi-p_\pi)$ bond.

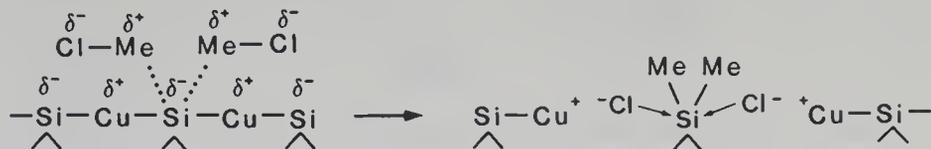
Silicone oils were first obtained by Ladenburg in 1872; pioneering work concerning silicones proper was carried out by Kipping, starting in 1901. However, large-scale production of silicones was only triggered by the demand for new materials with special properties, the elucidation of the principles of polymerization (Staudinger, Nobel prize in 1953) and by the development of a rational method to prepare the monomers (Rochow and Müller).

Industrial Production of the Monomers:



Rather than being a nuisance, the formation of a mixture of various methylchlorosilanes is highly desirable since, after distillative separation, these intermediates fulfill different functions. Apart from Cu (5–10%, added as Cu_2O), 0.1–1% of electropositive metals like Ca, Mg, Zn or Al are added to Si. In this way, the product distribution of the species $\text{Me}_n\text{SiCl}_{4-n}$ can be steered to a certain extent. Addition of small amounts (0.001–0.005%) of As, Sb or Bi as “promoters” increases the rate of reaction.

In a crude picture of the *mechanism of the Müller-Rochow direct process*, a negative polarization of silicon (towards copper silicide) is assumed. This would increase the ease of electrophilic attack at Si.

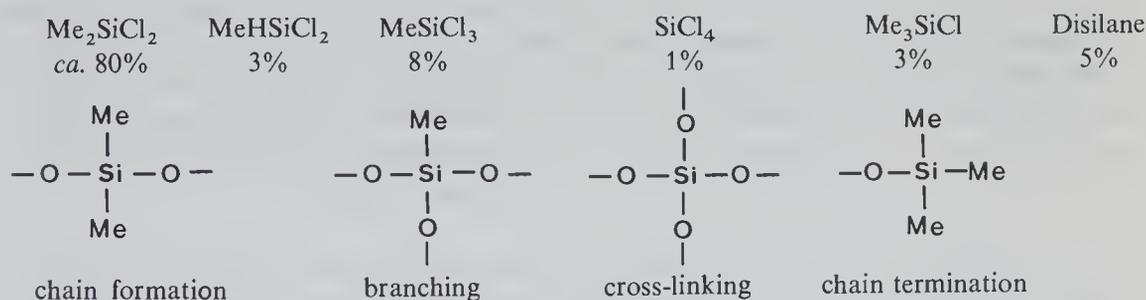


Recent studies have shown, that the reaction of CH_3Cl occurs at the phase $\eta\text{-Cu}_3\text{Si}$ (Falconer, 1985).

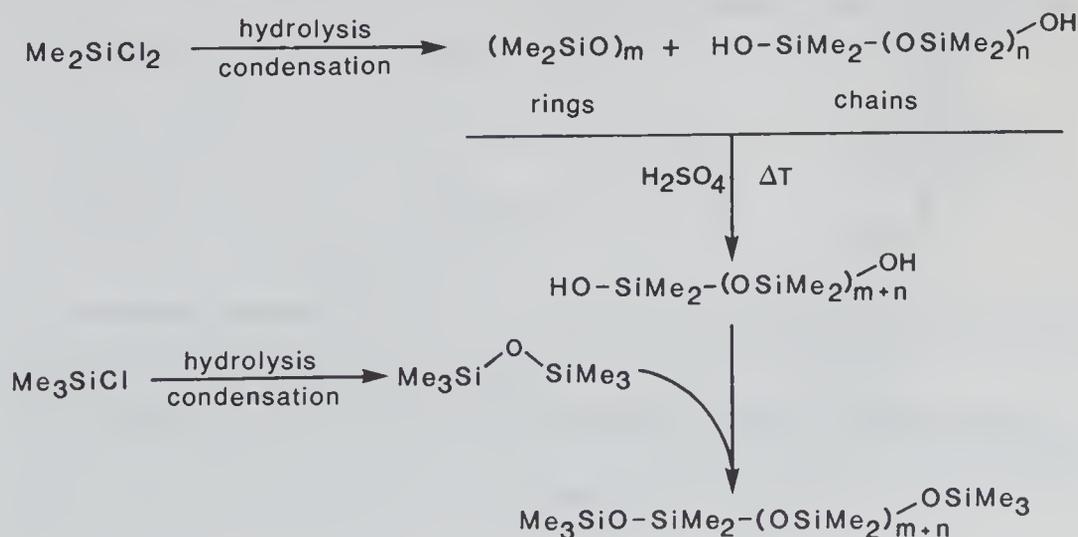
An alternative view starts from the premise that the Si surface is oxidized by CuCl which is formed from Cu and CH_3Cl . Finally, it has also been proposed that CH_3Cu is formed as an intermediate which decomposes at the surface into Cu and $\text{CH}_3\cdot$ radicals, the latter attacking silicon. The heterogeneous nature of the reaction and the large number of components which participate render the mechanistic study of the Müller-Rochow process exceedingly difficult.

The production of bulk silicones involves organochlorosilane hydrolysis and subsequent thermal treatment in the presence of catalytic amounts of H_2SO_4 , often after addition of certain cross-linking agents.

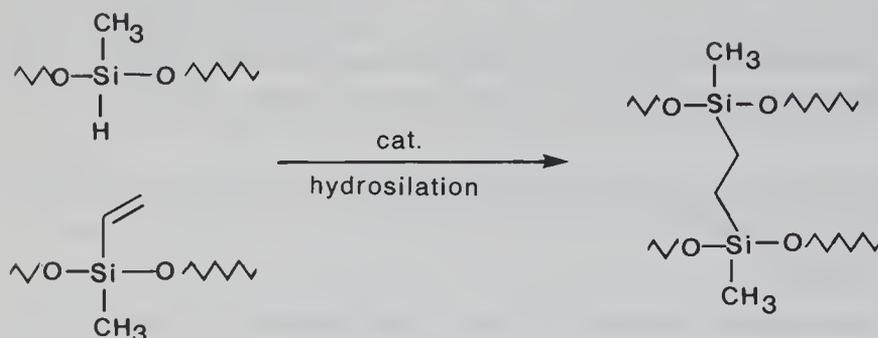
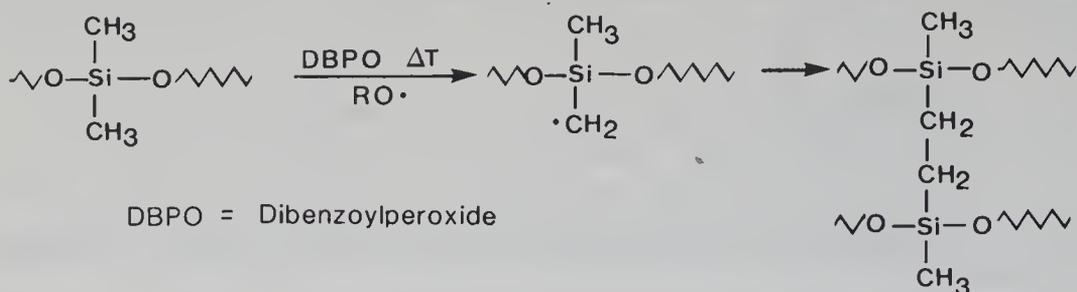
Composition of the crude organochlorosilane mixture from the direct process and applications of the individual components:



The thermal treatment under acidic conditions serves to generate specific chain lengths:

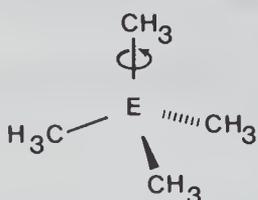


Final cross-linking is achieved in a number of ways:



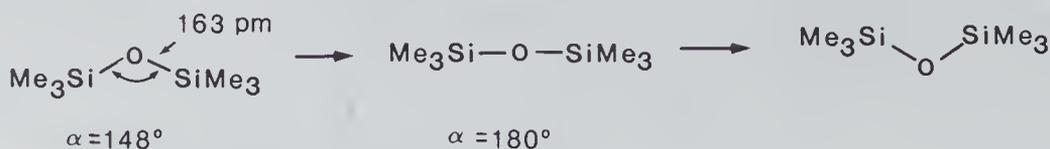
Depending on the structure of the siloxane skeleton, silicone oils, -elastomers or -resins are obtained. Thanks to their outstanding properties, silicones are almost ubiquitous in modern technology. Their advantages include high thermal stability and corrosion resistance, small temperature coefficients of viscosity, favorable dielectric properties, foam suppressing and water repelling action combined with their physiologically innocuous nature (applications in plastic surgery, use as flatulence drugs).

The extraordinary properties of silicone materials may be traced back to the idiosyncrasies of the **Si–O–Si (siloxane) bond**. The high **flexibility** of $(-\text{Me}_2\text{SiO}-)_n$ chains suggests **low barriers of conformational changes**. This can be demonstrated by an examination of the rotational barriers in $(\text{CH}_3)_4\text{E}$:



E:	C	Si	Ge	Sn	Pb
Rot.Bar.:	18	7	1.5	0	kJ/mol
d(E–C):	154	188	194	216	230 pm

Flexibility is also ensured by the low energy of the **Si–O–Si bending vibration**:



8.1.2 Silicon Organyls of Coordination Numbers 2 and 3 and their Subsequent Products

This topic encompasses the following species:

R_2Si	R_2SiSiR_2	R_3Si^-
Silylene (Silene)	Disilylene (Disilene)	Silyl anion (silanion)
		$R_3Si\cdot$ Silyl radical
		R_3Si^+ Silicinium ion

Follow-up products with a higher coordination number at silicon, which are closely related to these moieties, are the polysilylenes (= organopolysilanes), the carbosilanes, and the Lewis-base adducts of silicinium ions.

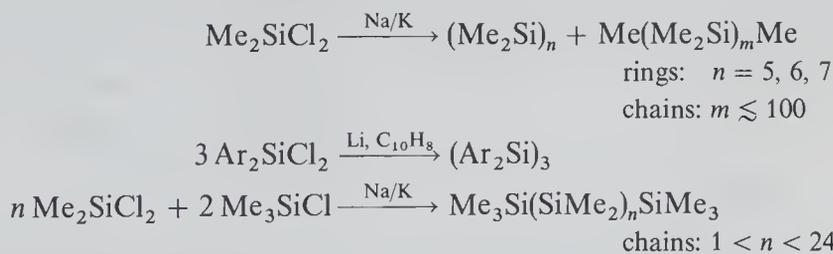
The species R_2E ($E = Si, Ge, Sn, Pb$) may be regarded as substituted homologues of methylene. They contain the elements of group 14 in the oxidation state E^{II} whose stability increases with increasing atomic number. The organic derivatives generally represent short-lived intermediates which can be investigated in monomeric form under special conditions only ($R = \text{alkyl, aryl}$):

R_2C	R_2Si	R_2Ge	R_2Sn	R_2Pb
Methylene	Silylene	Germylene	Stannylene	Plumbylene

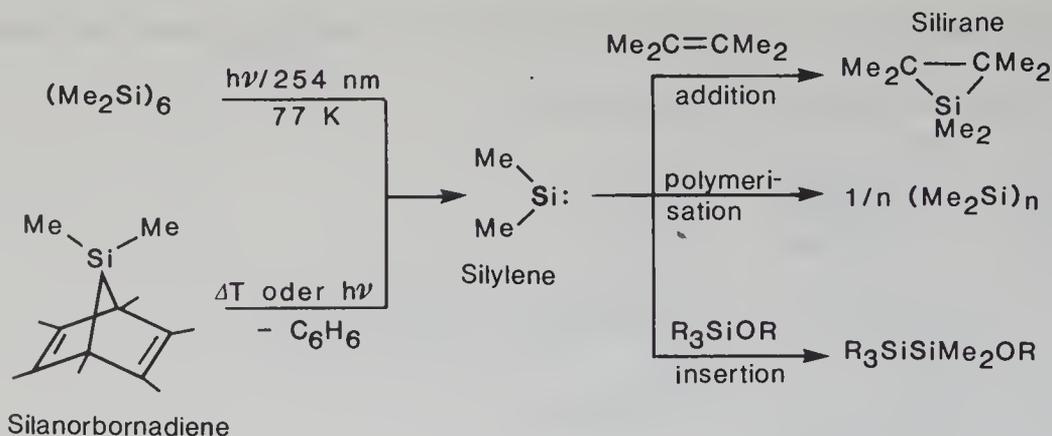
Their identification as intermediates usually involves an analysis of oligomerization- or trapping products or spectroscopic studies in matrix isolation.

Silylenes and Polysilylenes (Organopolysilanes)

Dehalogenation of organochlorosilanes affords **organopolysilanes** which are thought to be formed via silylene intermediates. The degree of polymerization and the ratio linear/cyclic depend on the respective reaction conditions. Examples:

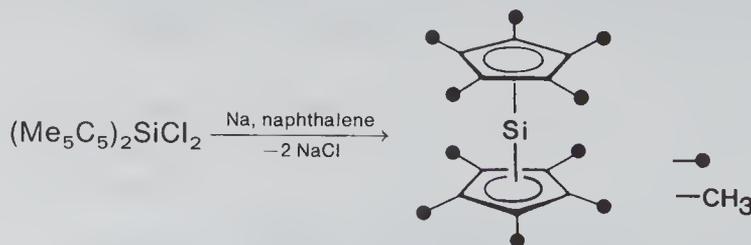


Larger groups R increase the solubility of the oligomers in organic solvents. From organocyclosilanes **silylenes** can be generated; their identity can be inferred from follow-up reactions (Kumada, 1973):



In the context of the reactivity of carbenes and their homologues, their **molecular and electronic structure** as well as the associated **spin states** are of interest. Experimentally a triplet ground state is found for Me_2C (2 unpaired electrons, $S = 1$). Me_2Si , Me_2Ge and Me_2Sn possess a singlet ground state (no unpaired electrons, $S = 0$). Whereas the bond angle in CH_2 is approximately 140° (ESR), in SiH_2 it amounts to only 92° (IR, Raman; UV). The disparate magnetic and structural features of CH_2 and SiH_2 may be rationalized by means of differing hybridization ratios. In the CH_2 molecule, two $\text{C}(2s, 2p)$ hybrid orbitals serve for $\text{C}-\text{H}$ bonding, because the angle HCH (140° , experiment) lies between 120° (expected for sp^2 hybrids) and 180° (sp hybrid). The remaining two $\text{C}(2s, 2p)$ hybrid orbitals would then accommodate two non-bonding electrons with parallel spin ($S = 1$). In SiH_2 , on the other hand, $\text{Si}(3p_x)$ and $\text{Si}(3p_y)$ orbitals are thought to be used for $\text{Si}-\text{H}$ bonding (90°); the two non-bonding electrons then occupy the $\text{Si}(3s)$ orbital ($S = 0$), $\text{Si}(3p_z)$ remaining empty. The difference is probably a consequence of the growing energetic separation between ns and np orbitals upon going to heavier elements within a group (limiting case: "inert s electron pair") which renders the participation of s electrons in chemical bonding increasingly unfavorable. In a more refined discussion, the electronic and steric properties of the groups R at ER_2 have to be taken into account explicitly.

A rather special silylene is the compound $(\text{C}_5\text{Me}_5)_2\text{Si}$, **decamethylsilicocene** (Jutzi, 1986):



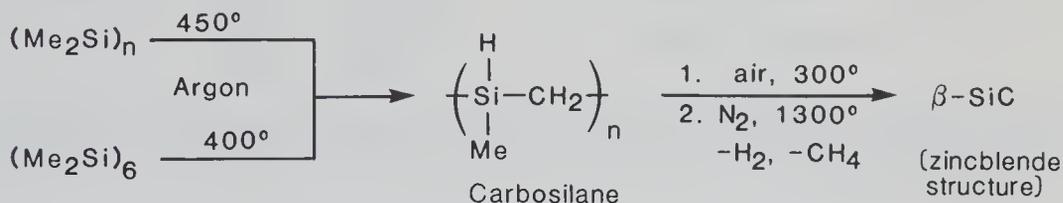
This diamagnetic, thermally stable but highly air-sensitive molecule has the structure of an axially symmetric metallocene.

The cyclic **organopolysilanes** $(\text{R}_2\text{Si})_n$ possess singly folded ($n = 4, 5$) or doubly folded ($n = 6$) structures. The **electronic properties** of organopolysilanes are unexpected:

- In the UV spectra of alkanes, absorption bands appear only for $\lambda < 160$ nm. Polysilanes, however, absorb at $\lambda \leq 350$ nm (Gilman, 1964).
- Contrary to cycloalkanes $(R_2C)_n$, cyclosilanes $(R_2Si)_n$ may be reduced to radical anions and oxidized to radical cations. The persistent species $(R_2Si)_n^-$ and $(R_2Si)_n^+$ can be studied by ESR spectroscopy (Bock, 1979 R).
- Upon doping with AsF_5 , organopolysilanes become semiconducting (West, 1983).

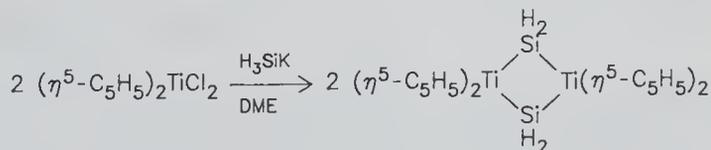
These peculiarities may be crudely explained as follows: Due to similar energy and spatial extension of $C(2s)$ and $C(2p)$ orbitals, the carbon atoms in alkanes approach ideal sp^3 hybridization and form localized ($2e\ 2c$) bonds along the carbon chain; the σ/σ^* splitting is large. For silicon, on the other hand, s orbital contraction leads to less perfect hybridization, the $Si(3s)$ contribution to bonding being reduced. Since Si in the polysilanes is tetravalent but reluctant to fully allocate its $3s$ electrons to bonding, a certain degree of electron deficiency arises which can be alleviated by multicenter bonding along the Si_n backbone. Thus, some one-dimensional metallic character can be assigned to the Si_n chain in poly-silanes, which would explain the aforementioned experimental facts (Schöller, 1987).

Organopolysilanes have recently been the focus of attention for certain technical applications; they have found use as precursors in the manufacture of **ceramic fibres** consisting of **β -silicon carbide**. In a first step, pre-ceramic polycarbosilanes (molecular weight ≈ 8000) are drawn from the melt and spun into fibres. Subsequently, in a two stage thermal process, they are converted into β -SiC, a material with extremely high tensile strength (Yajima, 1975):



Besides addition, polymerization, and insertion, bonding to a transition metal must be considered as one further carbene-analogous reaction of silylenes. However, whereas the field of transition-metal carbene complexes is highly developed (p. 210) and germylene-, stannylene-, and plumbylene complexes have also been obtained, no silylene-metal complex with the coordination number 3 at Si has yet been identified unequivocally.

A complex bearing two bridging silylene ligands is formed in an unexpected reaction (E. Weiss, 1973):

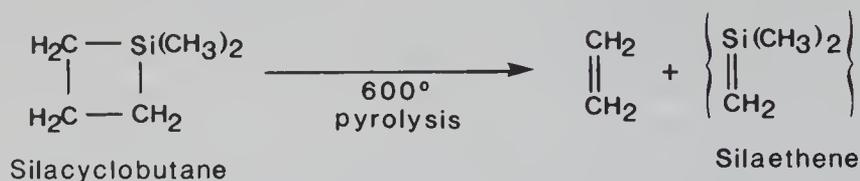


The μ -silylene ligand can be regarded as a doubly metallated silane, a molecule containing Si^{IV} . This may explain why μ - R_2Si complexes, as opposed to complexes containing terminal silylene ligands, are readily accessible.

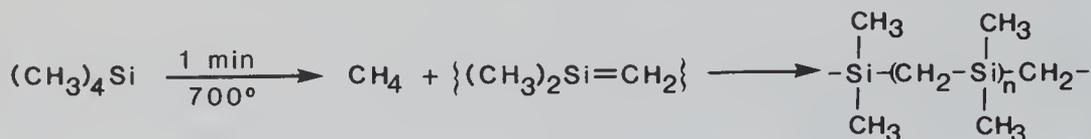
Molecules with Si = E ($p_\pi - p_\pi$) Bonds

Numerous exceptions to the **double bond rule** ("Elements of the third and higher rows avoid forming compounds containing $p_\pi - p_\pi$ multiple bonds") have provoked experiments to synthesize molecules containing >Si=C< and >Si=Si< segments.

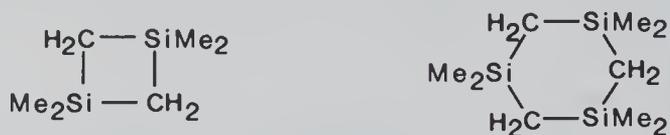
Si = C ($p_\pi - p_\pi$) bonds were originally proposed to exist in reactive intermediates. Thus, silaethene could be characterized spectroscopically at 10 K in an argon matrix (Guselnikov, 1966):



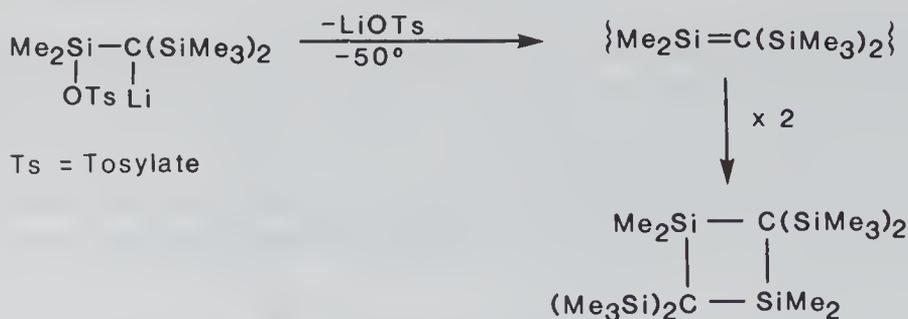
Pyrolysis of Me_4Si yields a multicomponent mixture of carbosilanes, whereby silaethenes are proposed as reaction intermediates (G. Fritz, 1987 R):



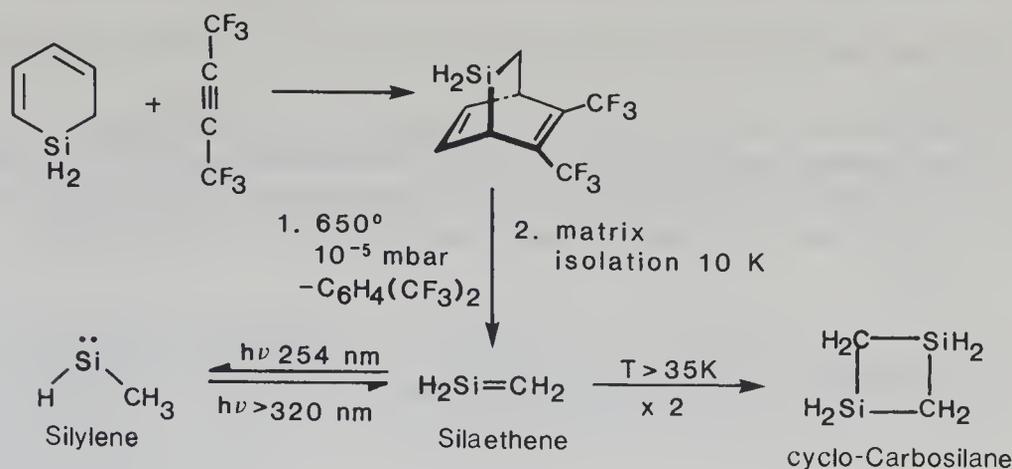
The fraction of cyclic carbosilanes amounts to about 15%.



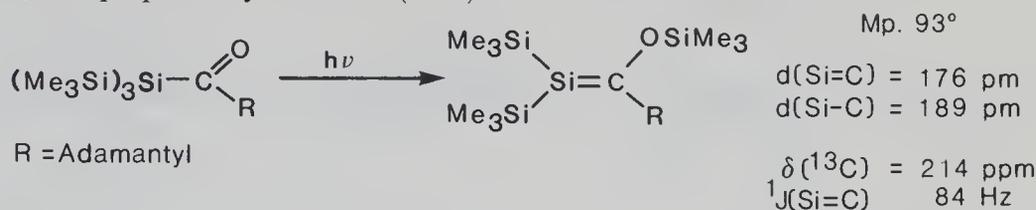
Silaethenes also arise from salt eliminations; they immediately dimerize to 1,3-disilacyclobutanes (Wiberg, 1977):



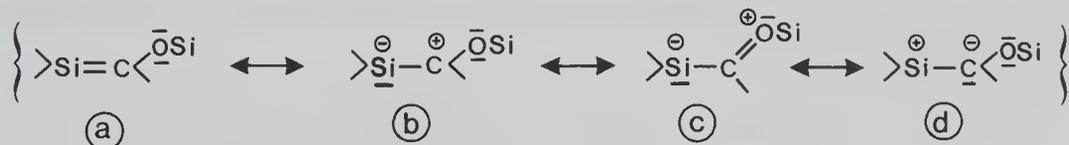
A monomeric silaethene, stabilized by metal coordination, has been claimed for the complex $(\text{C}_5\text{H}_5)(\text{CO})_2\text{HW}(\eta^2-\text{CH}_2=\text{SiMe}_2)$ (Wrighton, 1983) and characterized by X-ray diffraction in the compound $(\text{Me}_5\text{C}_5)(\text{Cy}_3\text{P})\text{HRu}(\eta^2-\text{CH}_2=\text{SiPh}_2)$ (Tilley, 1988). In a convenient method for the generation of sparingly substituted or unsubstituted silaethenes the retrodiene cleavage of a silabicyclo[2.2.2]octadiene is exploited (Barton, 1972; Maier, 1981):



The first molecule featuring an Si=C ($p_\pi - p_\pi$) bond, which is stable at ambient temperature, was prepared by A. Brook (1981):

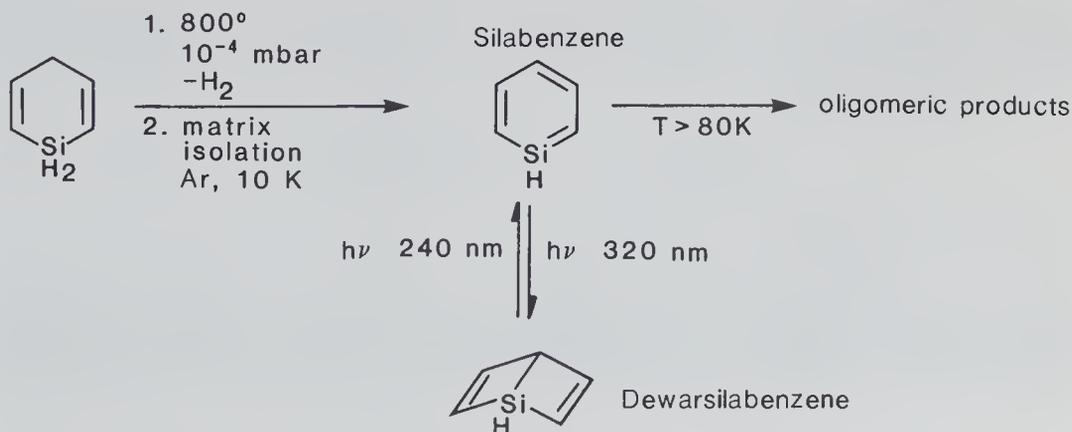


The dimerization or polymerization of this molecule to carbosilanes is prevented by bulky trimethylsilyl- and adamantyl groups.



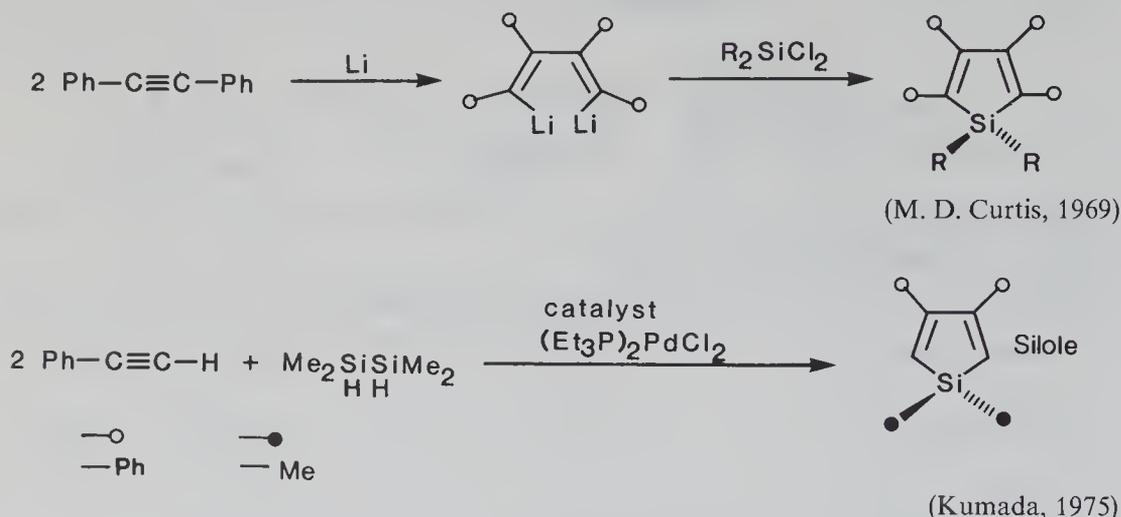
Apparently, the canonical structure (a) heavily contributes to the resonance hybrid since, according to $^1\text{H-NMR}$ evidence, rotation around the central Si-C bond axis is blocked. A certain contribution of the structures (b) and (c) is suggested by $^{13}\text{C-NMR}$ data (resemblance to chemical shifts observed for carbene complexes). The strong deshielding of the carbon nucleus argues against a participation of the silyl ylid canonical form (d).

Closely related to the silaethene problem is the inclusion of the Si atom into aromatic heterocycles. Silabenzene C_5SiH_6 has been generated by means of flash thermolysis and studied in the gas phase (Bock, 1980) and in matrix isolation (G. Maier, 1982):

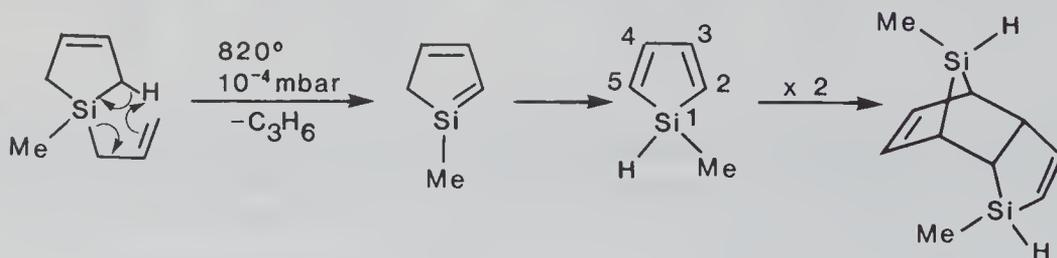


In the UV spectrum, silabenzene is identified as an arene which is weakly perturbed by a donor atom.

In analogy to the ready formation of the aromatic anion $C_5H_5^-$ from C_5H_6 , deprotonation of **silacyclopentadiene (silole)** C_4SiH_6 to yield its anion would appear to be straightforward. The realization of this idea till now has been frustrated by competing reactions. Whereas heavily substituted siloles are readily accessible and easily characterized,

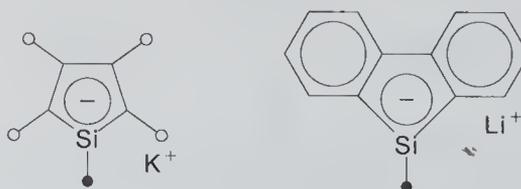


the less substituted siloles, which still possess Si-H bonds, tend to form Diels-Alder dimers (T. J. Barton, 1975):

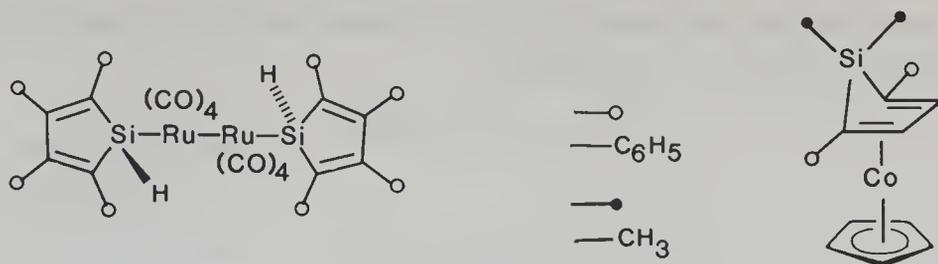


This type of dimerization is suppressed if the positions 3 and 4 bear alkyl substituents (Dubac, 1986).

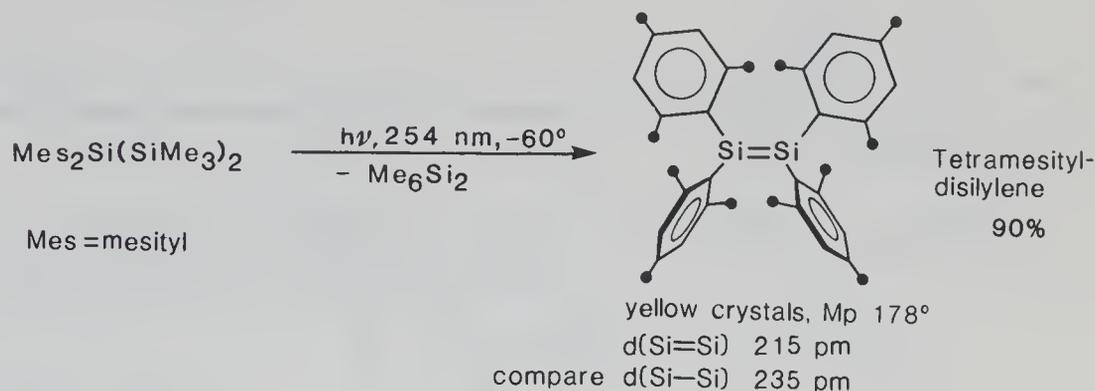
The preparation of a **silole anion** (silacyclopentadienyl) as yet has only been achieved in perphenylated (Boudjouk, 1984) or in benzanellated form (Gilman, 1958; Kumada, 1983):



Therefore, at the time of writing, silametalloenes are unknown. The few examples of silole complexes, which have been reported, contain the heterocycle as an η^1 - or an η^4 -ligand:

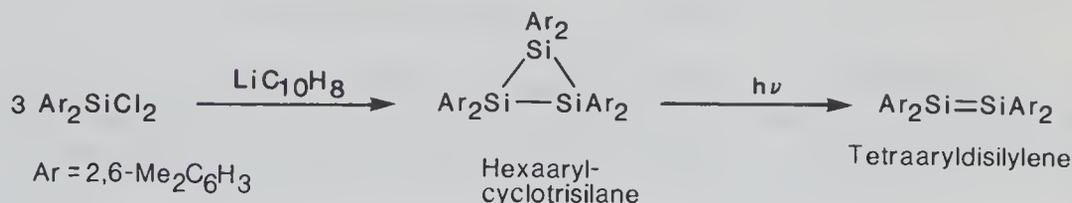


Si = Si ($p_\pi - p_\pi$)-bonds would be expected to be even less stable than Si = C double bonds because, due to the larger distance of the Si–Si σ -bond, $p_\pi - p_\pi$ overlap is unfavorable. Notwithstanding, a derivative of disilylene could be synthesized which is stable at room temperature (West, 1981):



Again it is the steric protection of the vulnerable Si = Si multiple bond by bulky groups which is responsible for the remarkable stability of this molecule. Precursors with sterically less demanding substituents only lead to organopolysilanes.

Disilylenes (and digermynes) were also prepared by Masamune (1982):

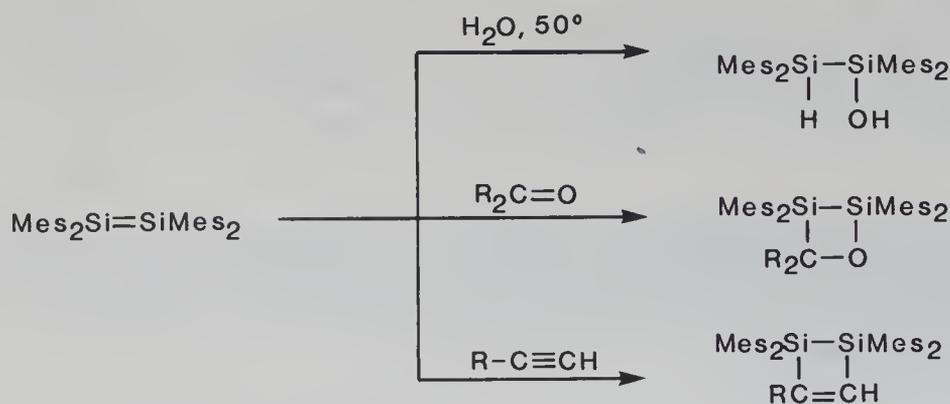


The decrease in bond distance in proceeding from Si–Si to Si = Si is comparable to the increment for the pair C–C and C = C; it is smaller in relative terms, however. As inferred from the NMR coupling constant $^1J(^{29}\text{Si}, ^{13}\text{C})$, the silicon atom in disilylenes is sp^2 hybridized. This judgement is based on the proportionality between the spin-spin coupling constant and the s -character of an intervening bond:

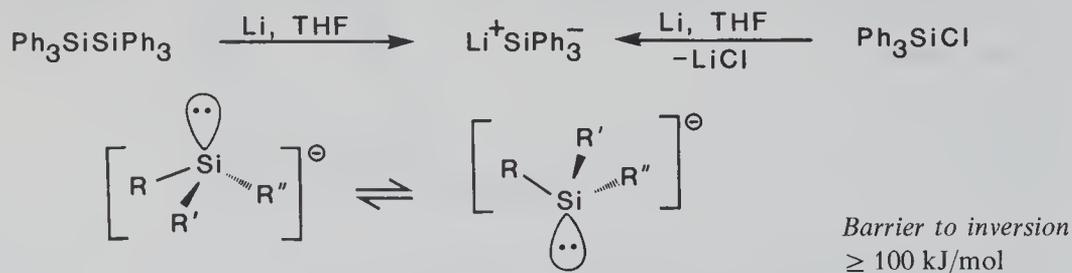
	Me ₄ Si	Mes ₂ Si = SiMes ₂	(Me ₃ Si) ₂ Si = C(OSiMe ₃)Ad
$^1J(^{29}\text{Si}, ^{13}\text{C})$ (Hz)	50.2	90.0	84.0
Hybridization at Si	sp^3	sp^2	sp^2

Mes = mesityl Ad = adamantyl

Despite steric shielding, the Si=Si double bond in $\text{Mes}_2\text{Si}=\text{SiMes}_2$ is considerably more reactive than a typical C=C double bond:



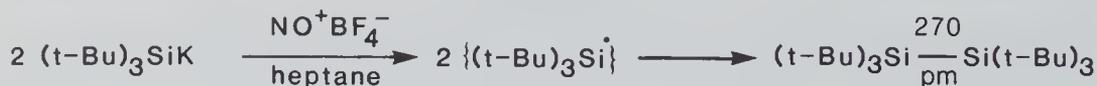
Silyl anions R_3Si^- are present in solutions of R_3SiLi in ionizing solvents. The structure of silyl anions is pyramidal. Temperature dependent $^1\text{H-NMR}$ studies demonstrate that the barrier to inversion is high:



Silyl anions R_3Si^- are isoelectronic with phosphanes R_3P and, like the latter, may serve as ligands in transition metal complexes:

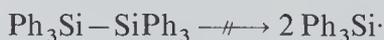


Mild oxidizing agents convert silyl anions into the respective disilanes. In the case of the anion $(t\text{-Bu})_3\text{Si}^-$, a disilane is thus formed which, compared to the standard value of $d(\text{Si}-\text{Si}) = 234 \text{ pm}$, boasts an extraordinarily long Si-Si bond (Wiberg, 1986):



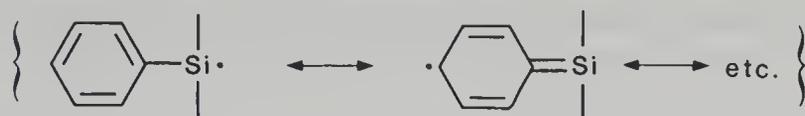
Incidentally, hexa(*t*-butyl)ethane is unknown.

Silyl radicals $\text{R}_3\text{Si}\cdot$ are also pyramidal; they are much more reactive than their carbon analogues $\text{R}_3\text{C}\cdot$. Thus, $\text{Ph}_3\text{Si}-\text{SiPh}_3$ shows no inclination to homolytic cleavage:



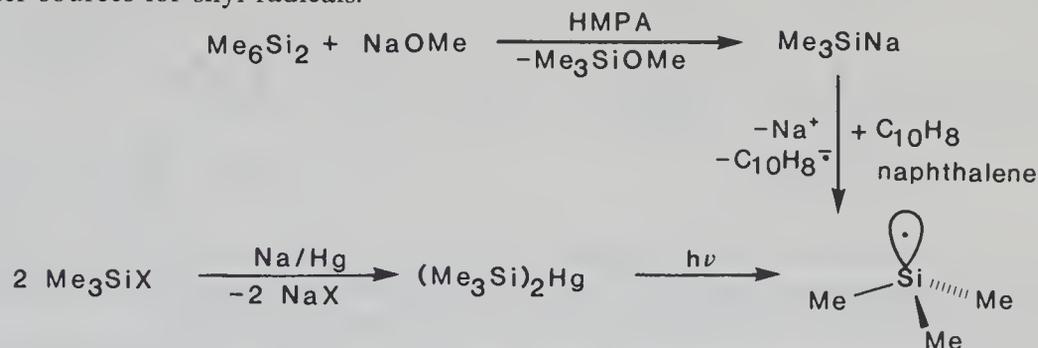
In fact, the bond energy $E(\text{Si}-\text{Si})$ is smaller than the value $E(\text{C}-\text{C})$ (p. 94) but the repulsion of the substituents, which would promote dissociation, is reduced because of the

large Si–Si bond lengths. Furthermore, resonance stabilization of silyl radicals according to

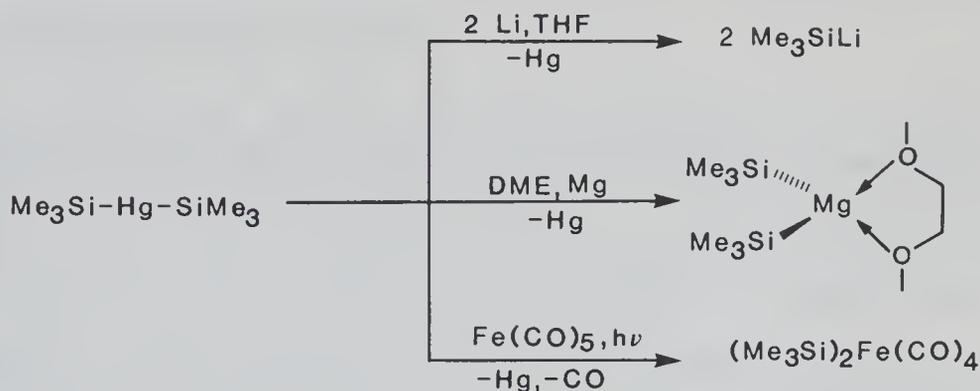


is insignificant due to unfavorable C=Si ($p_\pi-p_\pi$) overlap. Dissociation into radicals has, however, been observed for the sterically congested disilane $\text{Me}_3\text{Si}-\text{SiMe}_3$ (Neumann, 1984).

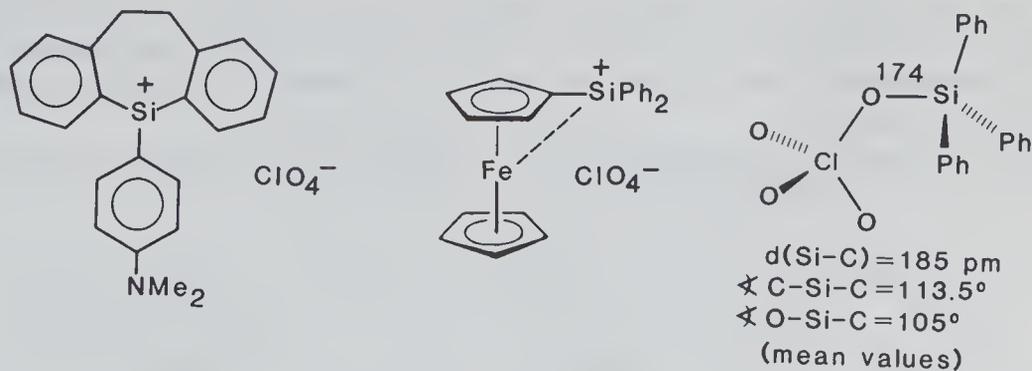
Other sources for silyl radicals:



Bis(trimethylsilyl)mercury (linear structure, mp: 101 °C), serves admirably in the synthesis of other compounds with **silicon-metal bonds**:



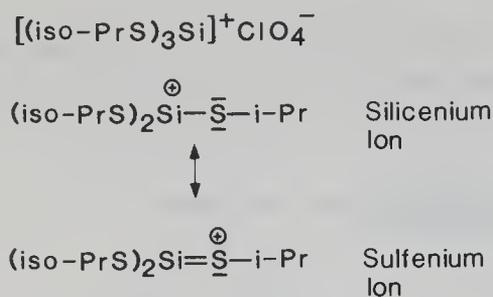
Silicenium ions R_3Si^+ as such are still controversial. In cases where their existence has been postulated, tight association with a counter ion could not be excluded, the limiting case being a silanol ester:



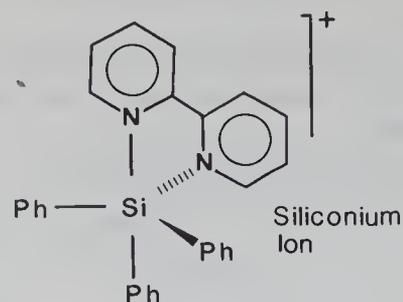
(J. Corey, 1975)

(Olah, Bau, 1987 R)

The species R_3Si^+ may in principle be stabilized by means of polarizable (soft) substituents or by the coordination of chelating ligands. In the latter case, because of the increase in coordination number from 3 to 5, the products are referred to as **siliconium ions**.



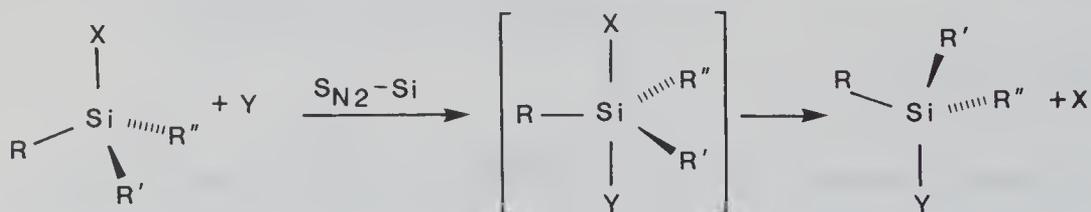
(Lambert, 1983)



(West, 1963)

As for the low tendency towards formation of R_3Si^+ ions, the strength of the Si–O or Si–halogen bond, respectively, as well as the insignificant resonance stabilization involving canonical structures with Si=C double bonds must be mentioned.

Therefore, **nucleophilic substitution at silicon** does not proceed dissociatively (D, S_N1) via intermediary silicenium ions. Instead, an associative mechanism (A, S_N2) must be assumed (Sommer, 1965 R):

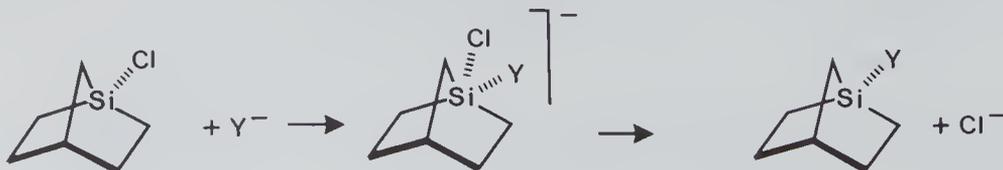


(X = good leaving group, i.e. the conjugate base of a strong acid)

This is supported by the dependence of the substitution rate on the nature of the attacking nucleophile Y, by the rate decrease in the presence of electron releasing groups R, and by the frequently observed inversion.

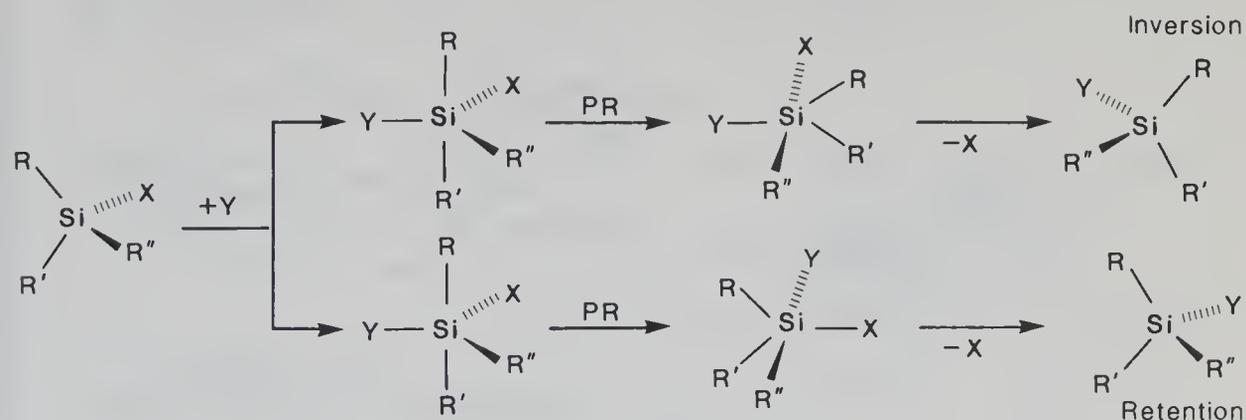
An uncritical transfer of diagnostic criteria used in studies of substitution at carbon to those dealing with silicon is inappropriate, because the ready increase of the coordination number at silicon and the rearrangement of the trigonal-bipyramidal intermediates via pseudorotation invalidate arguments, which rest on observations of inversion or retention of configuration.

Thus, swift substitution proceeds even at a bridgehead Si atom, although back-side nucleophilic attack is blocked (Sommer, 1973):



This front-side attack of the nucleophile is rendered possible by the vacant d orbitals of silicon which stabilize the coordination number 5; it is accompanied by retention of configuration.

Racemization, which is frequently observed during the course of nucleophilic substitution at silicon, may erroneously suggest a dissociative mechanism. Racemization must not, however, be taken as evidence for the intermediary formation of silicenium ions, since a five-coordinate intermediate by means of rearrangements (pseudorotation, PR) can also result in racemization:



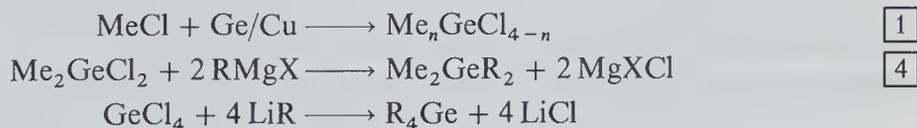
8.2 Organogermanium Compounds

Germanium, an element which is settled in the center of the periodic table, possesses typical properties of a semi-metal. For a long time tetraethylgermanium, prepared by Winkler in 1887, remained the only organogermanium compound. Since germanium organyls have as yet found little practical use, the accumulated results are mainly of academic interest. Among the elements Si, Ge, Sn and Pb, Ge most closely matches the electronegativities of H and C. Therefore the polarities of Ge–H and Ge–C bonds and the associated reactivities are strongly influenced by substituents.

8.2.1 Germanium Organyls of Coordination Number 4

PREPARATION

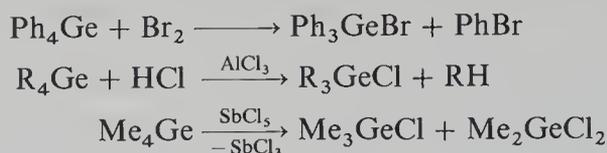
Direct syntheses, as for silicon, are also applicable to germanium. The resulting organogermanium halides may then be converted into other germanium organyls.



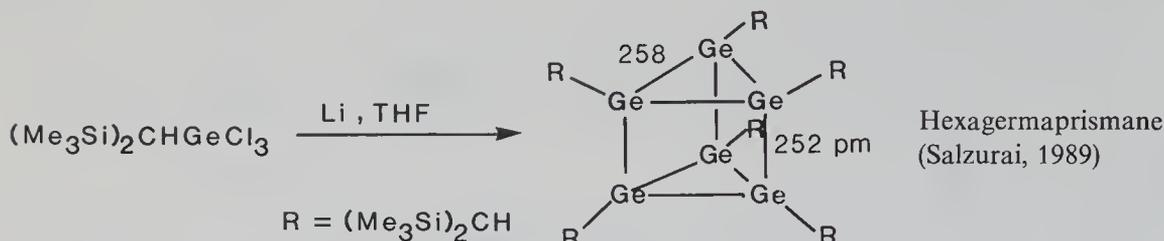
As compared to organosilicon chemistry, ligand scrambling for organogermanium compounds occurs more readily:



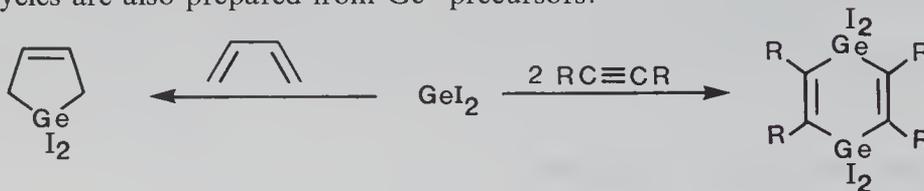
This also applies to Ge–C bond cleavage by means of X_2 or HX :



Furthermore, coupling reactions are of synthetic utility:

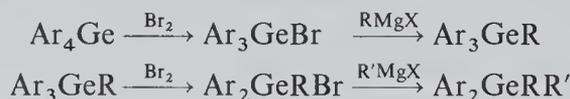


Germacycles are also prepared from Ge^{II} precursors:



PROPERTIES AND REACTIONS

Tetraorganogermanes R_4Ge are rather inert chemically; they are cleaved by strong oxidizing agents, often requiring the presence of Friedel-Crafts catalysts. This reaction is employed in the synthesis of ternary and quaternary organogermanes:

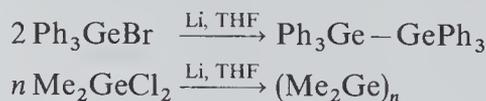


Note the selective cleavage of the Ge-aryl bond (c.f. p. 97). Like its silicon analog (p. 99) cyclopentadienyl(trimethyl)germane in solution is a **fluxional molecule**; it undergoes **metallotropic 1,2 shifts**:



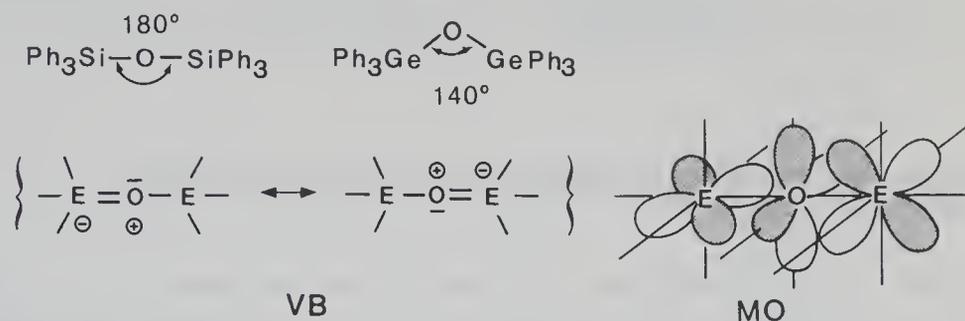
The migration of the Me_3Ge group along the C_5 periphery is faster than that of the Me_3Si group, since the C–Ge bond is weaker than the C–Si bond.

Organopolygermanes result from halogen abstractions using alkali metals or magnesium:



Among the cyclic organogermanes, those with $n = 4, 5$ and 6 are well characterized.

Organohalogermanes $R_n\text{GeX}_{4-n}$ like the corresponding silanes tend towards hydrolysis and condensation, albeit with attenuated vigor. The ease of hydrolysis of Ph_3GeX increases in the order $\text{X} = \text{F} < \text{Cl} < \text{Br} < \text{I}$. **Germanols** are stable in monomeric form if they carry bulky substituents: $(\text{iso-Pr})_3\text{GeOH}$ condenses to the **germoxane** $[(\text{iso-Pr})_3\text{Ge}]_2\text{O}$ only above 200°C . The diminished reactivity of $R_3\text{GeX}$, as compared to $R_3\text{SiX}$, reflects the reduced ability of germanium to utilize $\text{Ge}(4d)$ orbitals in order to stabilize coordination number 5 (cf. p. 115). This lessened inclination toward $\text{Ge}(4d)$ participation also manifests itself in a comparison of the bond angles EOE in siloxanes and germoxanes:



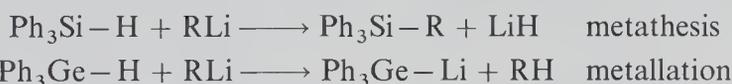
Organogermanes $R_n\text{GeH}_{4-n}$ are conveniently prepared by substitution of X^- by H^- :



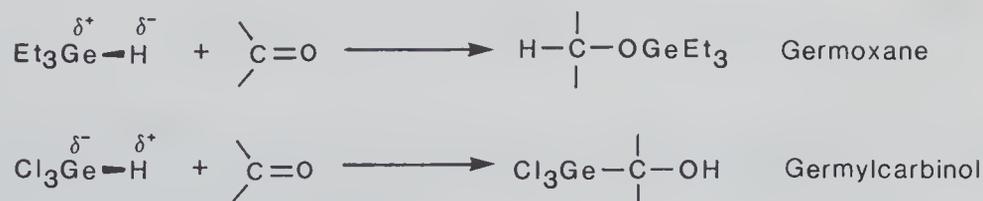
The similar electronegativities (Ge 2.0, H 2.1) result in a low polarity of the $\text{Ge}-\text{H}$ bond; consequently, their reactivity is low. Thus, organogermanes may even be prepared in aqueous media:



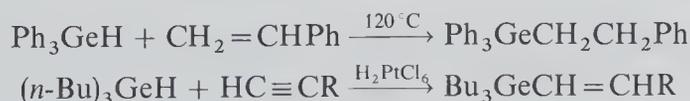
The reactivity pattern towards lithium organyls argues for hydridic character ($\text{H}^{\delta-}$) for Ph_3SiH and for protic character ($\text{H}^{\delta+}$) in the case of Ph_3GeH :



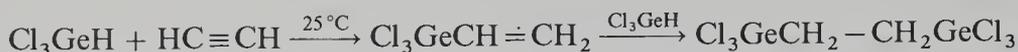
The polarity of the $\text{Ge}-\text{H}$ bond may, however, be reversed by the proper choice of substituents (Umpolung):



The most important reaction of the germanes $R_n\text{GeH}_{4-n}$ and $\text{X}_n\text{GeH}_{4-n}$ is **hydrogermation**; it is catalyzed by transition metal complexes or radical forming reagents and proceeds under milder conditions than hydrosilations:



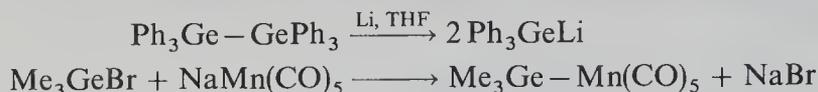
The halogermanes are particularly prone to addition:



Organogermanes are also suited for the preparation of molecules with **germanium-metal bonds**:

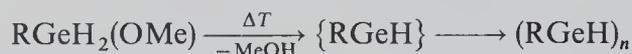


Further modes of formation of Ge-M bonds include

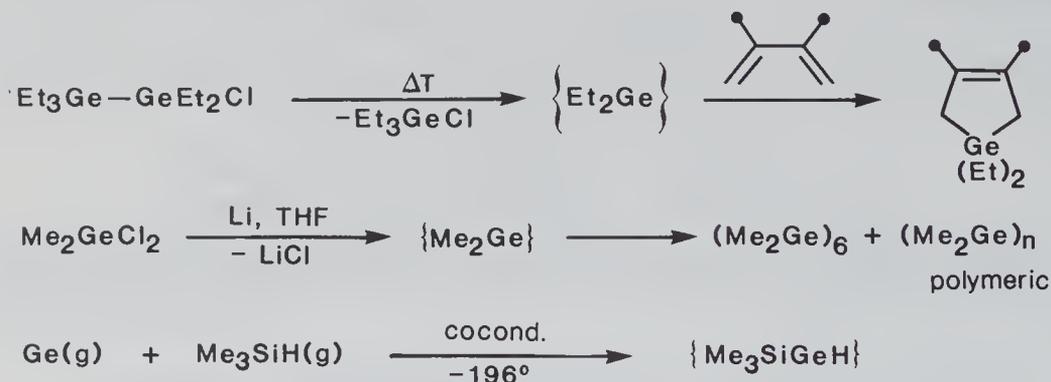


8.2.2 Germanium Organyls of Coordination Numbers 2 and 3 and their Subsequent Products

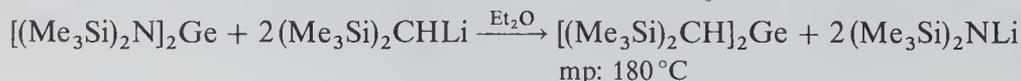
The chemistry of organogermanium compounds in low coordination states is largely analogous to that of silicon. The increasing preference for the oxidation state E^{II} , exhibited by the heavier elements in group 14, is expressed, i.a., in the formation of **germylenes** through α -elimination of alcohols from alkoxygermanes (Satgé, 1973 R):



Additional sources for germylenes are the following reactions:

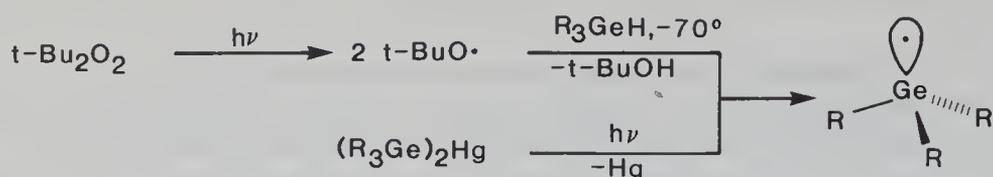


Whereas these simple, highly reactive germylenes can only be identified indirectly from the products of subsequent reactions like polymerization or adduct formation, germylenes with bulky substituents can be isolated in monomeric form at room temperature (Lappert, 1976):

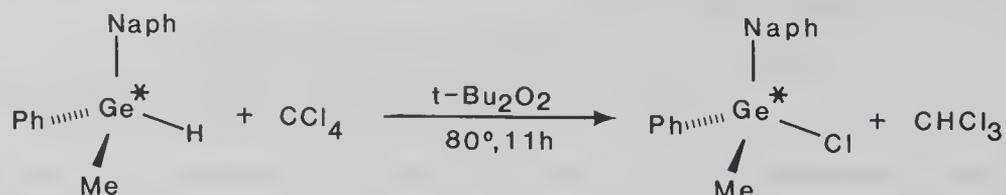


The simpler germylenes may also be stabilized as ligands in transition-metal complexes – albeit as thermolabile solvates only, displaying coordination number 4 at Ge (Marks,

Since, except for sterically crowded species, organodigermanes refrain from homolytic cleavage, **organogermyl radicals** R_3Ge^\bullet are generated as follows:

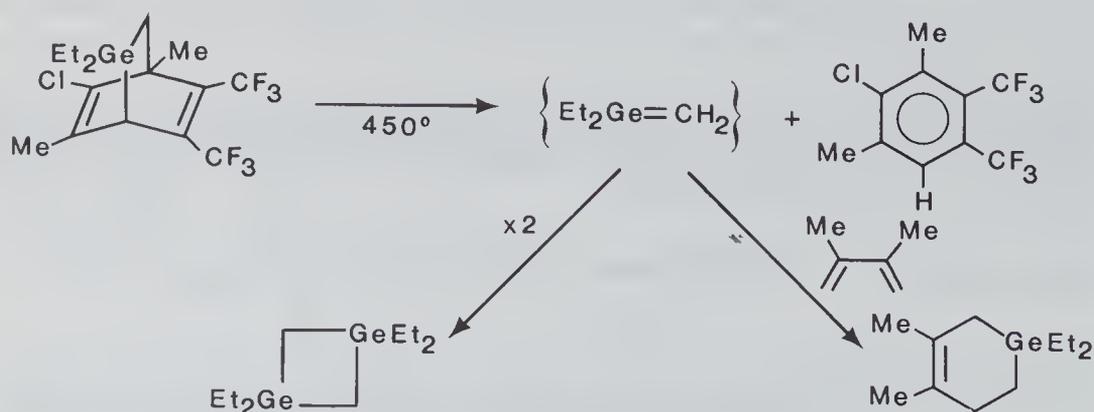


The Ge-centered radicals are identified by means of ESR spectroscopy, taking advantage of the hyperfine splitting by the nucleus ^{73}Ge (7.6%, $I = 9/2$). From the magnitude of the coupling constant $a(^{73}\text{Ge})$, a pyramidal structure of the radicals R_3Ge^\bullet can be inferred. This conclusion is based on the fact that isotropic hyperfine coupling constants are proportional to the s character of the singly occupied orbital. In this way, the ESR spectrum provides a hint as to the hybridization state of the radical center and therefore to its geometry. Independent evidence which supports nonplanarity of R_3Ge^\bullet radicals is the retention of configuration during the homolytic chlorination of chiral germanes (Gielen, 1978):

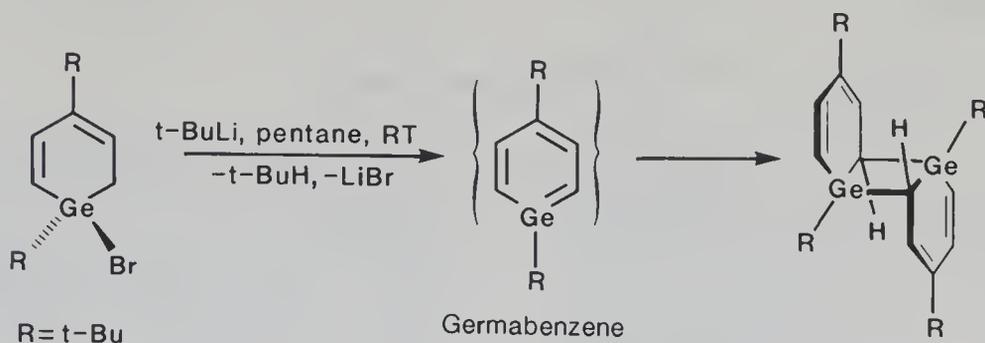


Experiments with chiral silanes point in the same direction.

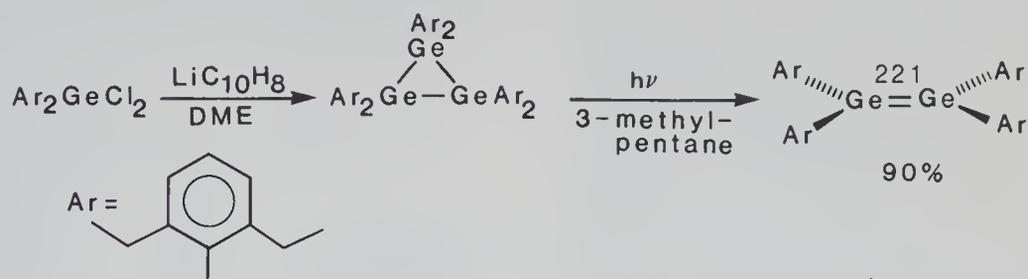
The kinds of experiments which are intended to lead to species with $\text{Ge}=\text{E}(p_\pi-p_\pi)$ bonds, resemble those performed for silicon (Barton, 1973):



The Ge=C double bond is extremely reactive, even if it is part of a 6 π -electron system (Märkl, 1980):



As in the case of silicon, double bonds >Ge=Ge< may be protected by steric shielding (Masamune, 1982):



8.3 Organotin Compounds

Due to a multitude of technical as well as synthetic applications, organotin compounds have become the subject of extensive industrial and academic research. A characteristic feature of organotin chemistry, compared to that of the lighter homologues Si and Ge, is the greater structural diversity. This may be traced back to the larger variety of accessible coordination numbers for tin. Thus, two aspects of organotin chemistry, namely the association of organotin halides $\text{R}_n\text{SnX}_{4-n}$ by means of Sn-X-Sn bridges and the ready formation of stannonium ions $[\text{R}_n\text{Sn}(\text{solv})]^{(4-n)+}$ in donor solvents originate from the ability of tin to increase its coordination number beyond 4. Another distinctive feature is the high reactivity of tin organyls in which C_α is part of an unsaturated system as in Sn-vinyl or Sn-phenyl segments.

Excursion

^{119}Sn -Mössbauer and ^{119}Sn -NMR Spectroscopy

Besides the standard methods of instrumental analysis and X-ray diffraction, these more specialized techniques are also well-suited to solve structural problems in organotin chemistry. Whereas ^{119}Sn -NMR is preferentially applied to species in solution, ^{119}Sn -Mössbauer spectroscopy, operating on solid samples, stands the test in cases where crystalline material for the application of diffraction methods is not available.

The Mössbauer effect rests on the recoil-free emission and resonance absorption of γ -rays. A Mössbauer spectrum furnishes the parameters **isomer shift** *IS* and **quad-rupole splitting** *QS*. In their ground- and excited nuclear spin states, atomic nuclei possess different radii and thus differing electrostatic interaction with the surrounding *s* electrons. Therefore, the energy difference between the ground- and the excited state is influenced by the *s* electron density at the nucleus. A comparison of nuclear spin excitation energies for nuclides like ^{119}Sn , which are subjected to different chemical environments, thus provides insight into the respective *s* electron densities. These excitation energies are usually listed as relative values with SnO_2 serving as a standard. They are then named isomer shifts *IS* and for experimental reasons, reported in mms^{-1} whereby a positive *IS* value implies an increased *s* electron density.

If the nuclear spin *I* of the respective nuclide in the ground and/or in the excited state exceeds 1/2, deviations of the electronic environment of the nucleus from cubic, octahedral or tetrahedral symmetry result in a splitting of the Mössbauer

signal. This is the quadrupole splitting *QS* which supplies additional structural information.

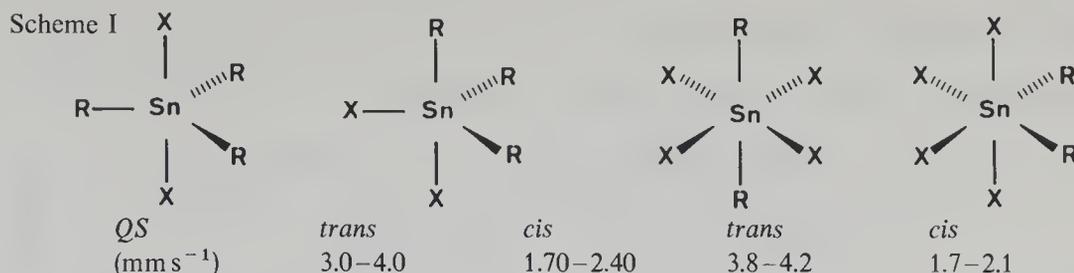
In the area of organometallics, nuclei suitable for Mössbauer spectroscopy besides ^{119}Sn include ^{57}Fe , ^{99}Ru , ^{121}Sb , ^{125}Te , ^{129}I , ^{193}Ir and ^{197}Au .

The **isomer shifts** *IS* in ^{119}Sn -Mössbauer spectra cover a range of $\pm 5 \text{ mms}^{-1}$ [typical values: $\text{Sn}^{\text{IV}} - 0.5$ to 1.8 , $\text{Sn}^{\text{II}} 2.5$ to 4.3 mm s^{-1}]. The following examples demonstrate how the isomer shift responds to changes in the environment of Sn:

	<i>IS</i> /mms ⁻¹	Variation of
$[\text{n-BuSnF}_5]^{2-}$	0.27	ligands
$[\text{n-BuSnCl}_5]^{2-}$	1.03	
$[\text{n-BuSnBr}_5]^{2-}$	1.38	
$\text{Ph}_4\text{Sn}^{\text{IV}}$	1.15	oxidation state
$\text{n-Bu}_4\text{Sn}^{\text{IV}}$	1.35	
$\text{Cp}_2\text{Sn}^{\text{II}}$	3.74	
<i>cis</i> - $\text{Me}_2\text{Sn}(\text{ox})_2$	0.88	geometry
<i>trans</i> - $\text{Me}_2\text{Sn}(\text{acac})_2$	1.18	

The **quadrupole splitting** *QS* reflects the stereochemistry at the Sn atom. Therefore, *QS* values may serve to distinguish between different isomeric forms, Scheme I (Bancroft, 1974).

Since these environments also occur in associated organotin compounds like $(\text{R}_3\text{SnX})_n$ and $(\text{R}_2\text{SnX}_2)_n$ the structure of these materials in the solid state is conveniently studied by means of ^{119}Sn -Mössbauer spectroscopy (cf. p.125, 133).



In the ^{119}Sn -NMR spectra of organotin^{IV} compounds, relative to the standard $(\text{CH}_3)_4\text{Sn}$, chemical shifts δ between +150 ppm (low field or high frequency, resp.) and -400 ppm (high field or low frequency, resp.) are observed. In Sn^{II} compounds, the tin nucleus is shielded much more extensively. The following compilation is intended to illustrate a few trends:

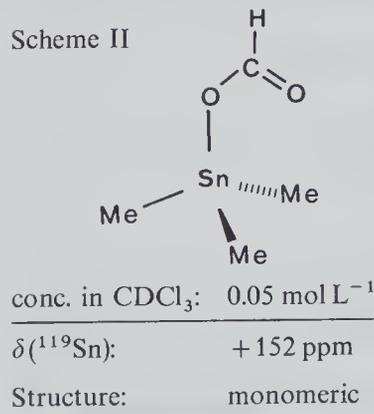
to C.N.5 or C.N.6 is attended by a high field shift which can be used as a diagnostic tool. As an example, consider the monomer/polymer equilibrium for trimethyltin formate (Scheme II).

On the other hand, for inert complexes like $\text{Me}_2\text{Sn}(\text{acac})_2$ (C.N.6) in which tin has a high coordination number in the molecular unit, the chemical shift is inde-

	$\delta(^{119}\text{Sn})/\text{ppm}$		$\delta(^{119}\text{Sn})/\text{ppm}$
$\text{Me}_3\text{SnCH}_2\text{Cl}$	+4	$(\eta^1\text{-C}_5\text{H}_5)_4\text{Sn}^{\text{IV}}$	-26
$\text{Me}_3\text{SnCHCl}_2$	+33	$(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}^{\text{II}}$	-2200
$\text{Me}_3\text{SnCCl}_3$	+85		
Me_4Sn	0	Me_3SnH	-104
Ph_2SnMe_2	-60	Me_2SnH_2	-224
Ph_4Sn	-137	MeSnH_3	-346
$(\text{H}_2\text{C}=\text{CH})_4\text{Sn}$	-157	$\text{Me}_3\text{SnCl}\cdot\text{py}$	+25
$\text{Me}_2\text{Sn}(\text{acac})_2$	-366	$[\text{Me}_3\text{Sn}(\text{bipy})]\text{BPh}_4$	-18

An important application of ^{119}Sn -NMR is the study of association processes in solution which are accompanied by an increase of the coordination number (C.N.) at Sn. The transition from C.N.4

pendent of concentration. Additionally, the coupling constants $^1J(^{119}\text{Sn}, ^{13}\text{C})$ and $^2J(^{119}\text{Sn}, ^1\text{H})$ also respond to changes in the coordination number of Sn, albeit in a less sensitive way.

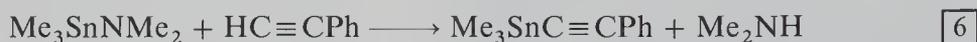


8.3.1 Tin Organyls of Coordination Numbers 4, 5 and 6

PREPARATION, STRUCTURE AND REACTIVITIES



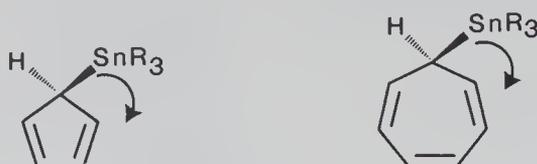
Compounds which are sufficiently CH-acidic are metallated by organotin amides:



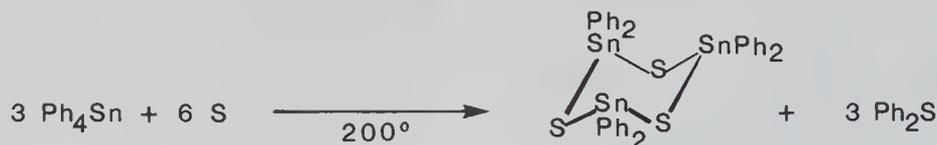
The **binary tin organyls** R_4Sn are inert towards attack by O_2 or H_2O ; usually they are also thermally stable. Me_4Sn decomposes above $400^\circ C$; organotin compounds with unsaturated residues are more labile, a fact which recommends them for synthetic applications:



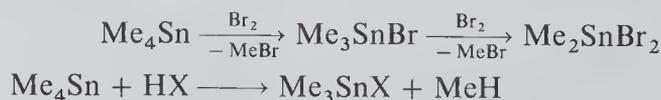
(Cyclopentadienyl)trisalkyltin (C_5H_5) SnR_3 , like the Si- and Ge analogues, is fluxional in solution. Such **metallotropic 1,2-shifts** of R_3Sn groups are also observed at the periphery of larger unsaturated rings:



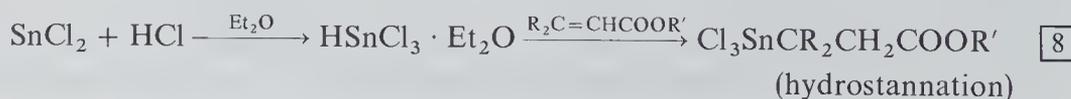
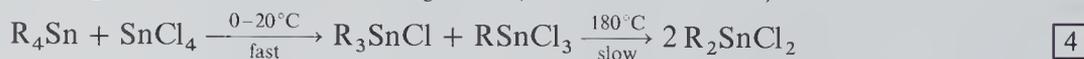
The thiophilic nature of tin expresses itself in the reaction of Ph_4Sn with sulfur whereby puckered six-membered rings (Ph_2SnS) $_3$ are formed:



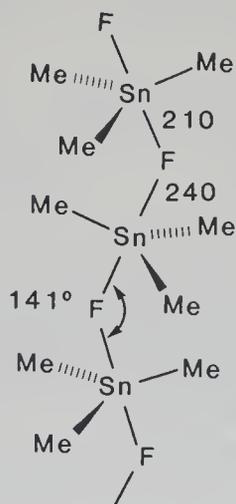
Sn-C bonds are also cleaved by dihalogens and by hydrogen halides. In this way, organotin halides are obtained:



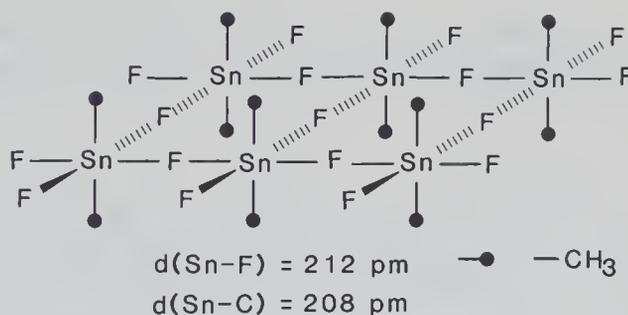
Further methods for the preparation of organotin halides are:



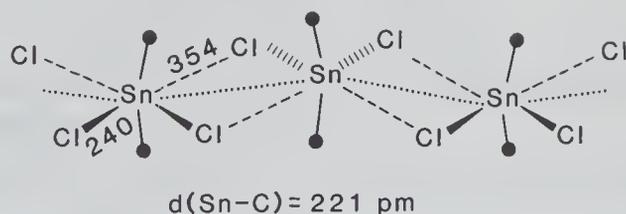
Organotin halides, -pseudohalides and -carboxylates tend to associate by means of σ -donor bridging:



Me_3SnF (decomp. 360°C before reaching the mp) forms chains of trigonal bipyramids, the apical fluoride ions being part of unsymmetrical Sn—F—Sn bridges (Trotter, 1964). Considerably weaker are the bridges Sn—Cl—Sn in solid Me_3SnCl (mp 37°C , bp 152°C) whose structure was studied by Mössbauer spectroscopy.

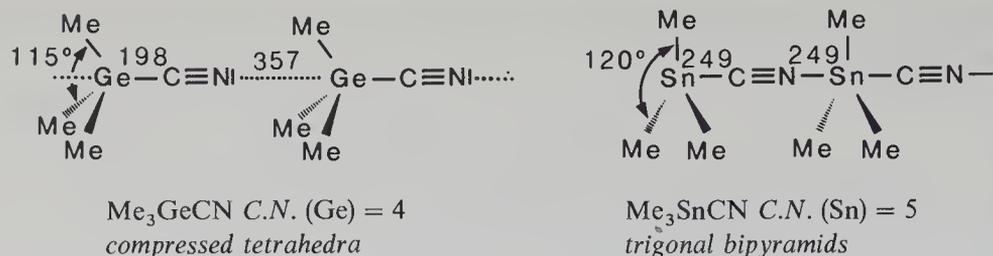


Me_2SnF_2 (decomp. 400°C), like SnF_2 , crystallizes in a lattice structure whereby two axial terminal methyl groups and four equatorial, bridging fluoride ions generate the coordination number 6 at Sn (Schlemper, 1966).



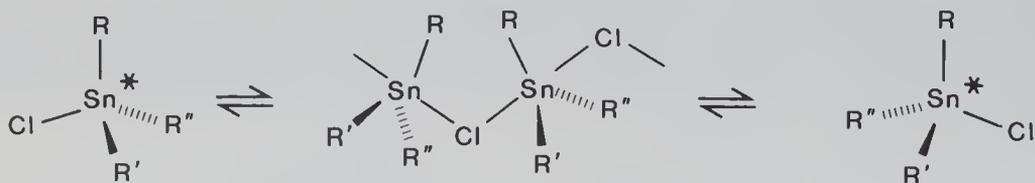
Me_2SnCl_2 (mp 106°C , bp 190°C), however, in the crystal forms zigzag chains of highly distorted edge sharing octahedra with weak chloride bridges (Davies, 1970).

A comparison of the structural data for $\text{Me}_3\text{GeCN}(s)$ and $\text{Me}_3\text{SnCN}(s)$ demonstrates the higher inclination of tin to expand its coordination sphere (Schlemper, 1966):

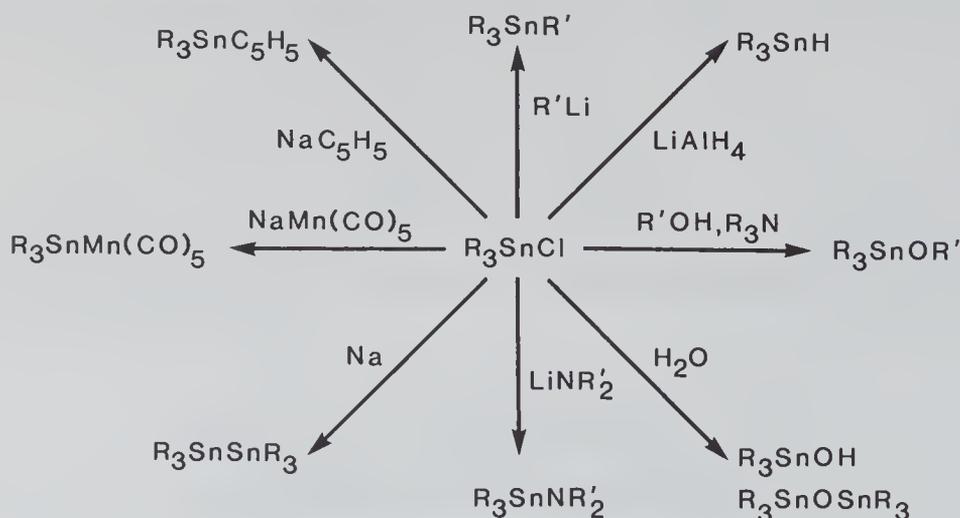


An even greater tendency for high coordination numbers is exhibited by lead, in that Ph_2PbCl_2 – in contrast to Me_2SnCl_2 – in the crystal adopts the coordination number 6 (chains of edge sharing octahedra, symmetrical bridges $\text{Pb}-\text{Cl}-\text{Pb}$). Thus, the tendency towards a high coordination number increases with the atomic number of the central atom and with ligand electronegativity.

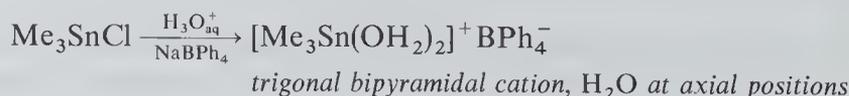
The high tendency to associate is responsible for the fact that chiral trisorganotin halides, as opposed to their C-, Si- and Ge counterparts, rapidly racemize in solution:



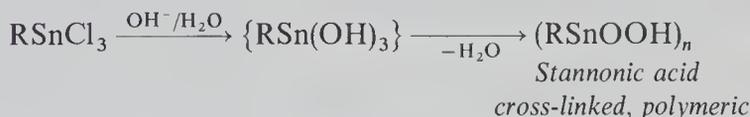
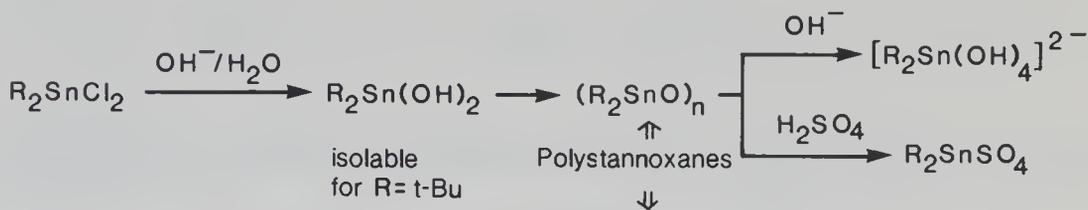
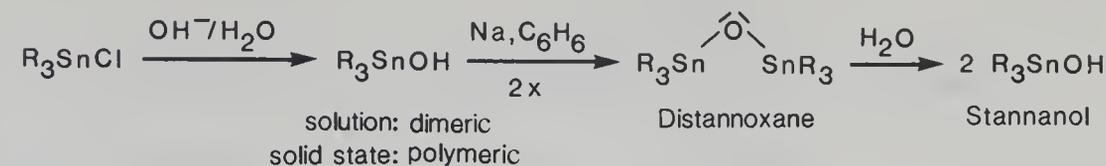
Follow-up reactions of organotin halides lead into several new classes of compounds:



Acid hydrolysis of the $\text{>Sn}-\text{Cl}$ bond under conservation* of the $\text{Sn}-\text{C}$ bonds initially yields hydrated **stannonium ions** $\text{R}_3\text{Sn}(\text{aq})^+$ which can be precipitated with large anions:

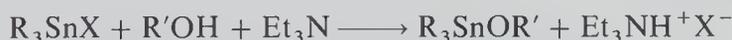


In alkaline aqueous media, organotin halides form the corresponding hydroxides; their propensity for condensation increases with decreasing degree of alkylation:



The amphoteric character of the stannoxanes is in marked contrast to the inert nature of siloxanes, which is reflected in the excellent material properties of the latter. The double chain structure of the polystannoxanes follows from ^{119}Sn -Mössbauer spectra.

Organotin alkoxides are prepared from the respective halides and alcohols using an auxiliary base:



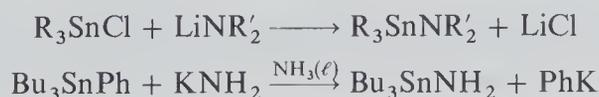
or via transalkoxylation:



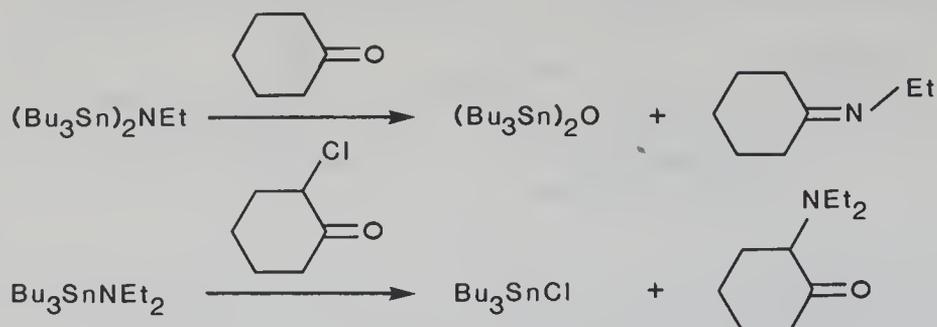
The synthesis of an organotin bis(acetylacetonate) with the coordination number 6 at tin proceeds in a related way:



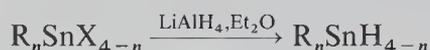
Organotin amides cannot be obtained by an ammonolysis of R_3SnCl ; they are prepared via nucleophilic substitution by amide:



Organotin amides have found application in organic synthesis:

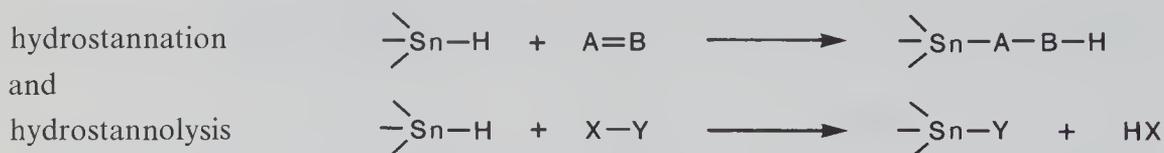


Organotin hydrides, in addition to the halides, are the most versatile reagents. They are easily obtained from the latter:

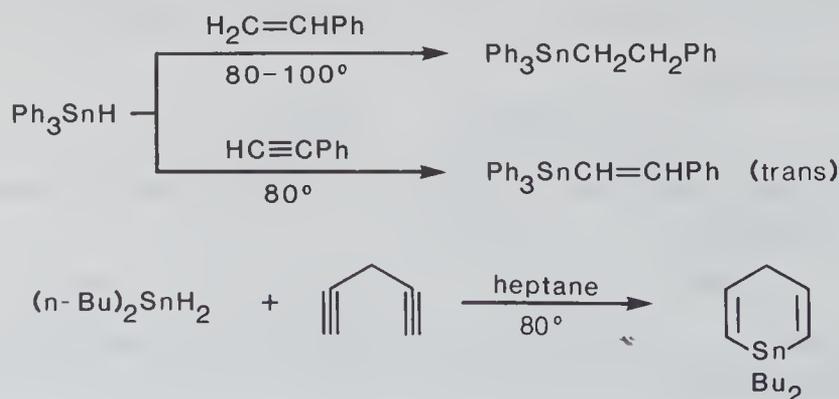


Organotin oxides or -alkoxides and NaBH_4 or sodium amalgam as reducing reagents are also suitable. The stability of the alkylstannanes $\text{R}_n\text{SnH}_{4-n}$ increases with increasing degree of alkylation: whereas SnH_4 slowly decomposes at room temperature, Me_3SnH is stable indefinitely in the absence of air.

The principal reactions of organostannanes are:

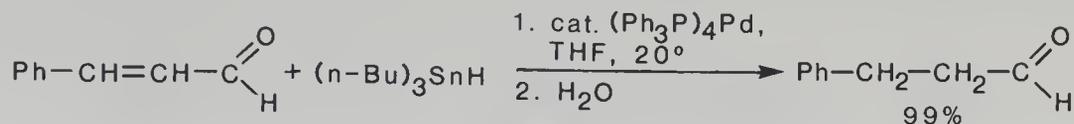


The **hydrostannation** reaction (van der Kerk, 1956) serves for the construction of new Sn-C bonds: it may proceed as 1,2- or as 1,4-addition:



Under these mild conditions and in the absence of catalysts (Lewis acids or radical forming reagents) polar double bonds like C=O and C=N are not attacked. Therefore,

hydrostannation is well-suited for **chemoselective hydrogenations** of activated C=C double bonds (Keinan, 1982):

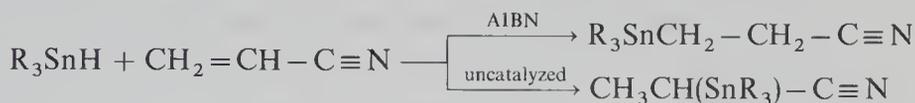


Note the complementary result obtained in the hydroboration of cinnamic aldehyde (p. 61).

In the presence of azoisobutyronitrile (AIBN), 1,4-addition to conjugated dienes occurs:



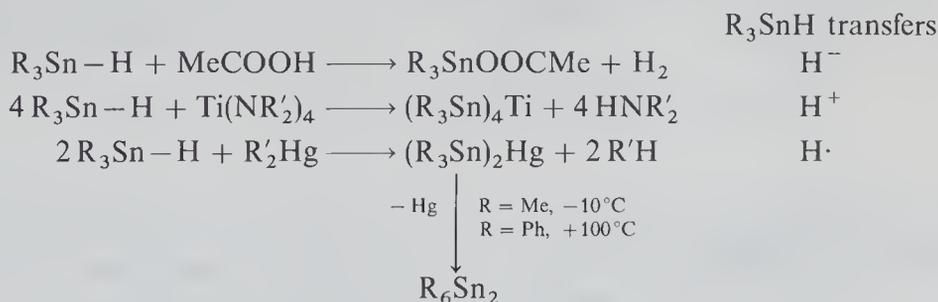
By appropriate choice of reaction conditions, regioselectivity may be achieved:



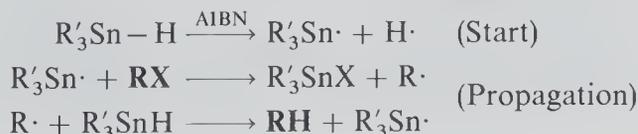
Compared to hydroboration and hydrosilation, hydrostannations are distinguished by their **mechanistic multiplicity** (Neumann, 1965). The relative weakness and low polarity of the Sn-H bond open up:

- **radical reaction pathways**, effected by AIBN and/or UV-irradiation and initiated by homolysis of the Sn-H bond and
- **hydride transfer processes** which proceed in media of high polarity in the presence of Lewis acid catalysts like ZnCl_2 or SiO_2 and which are favored for electrophilic substrates containing polarized multiple bonds.

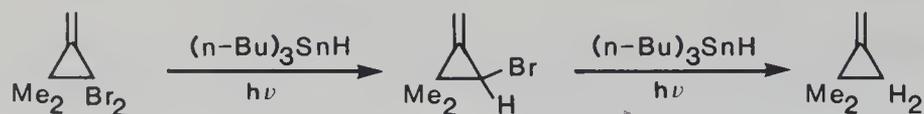
Hydrostannolysis as well may follow a homolytic or a heterolytic path. According to the aforementioned low polarity of Sn-H bonds, depending on the nature of the attacking agent organotin hydrides may act as a source of H^- , H^+ , or $\text{H}\cdot$:



The homolytic variant of hydrostannolysis constitutes one of the most convenient methods for the conversion $\text{R}-\text{X} \rightarrow \text{R}-\text{H}$; it proceeds as a chain reaction:

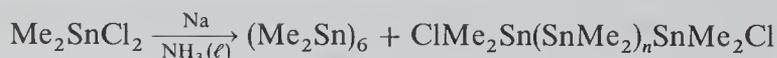
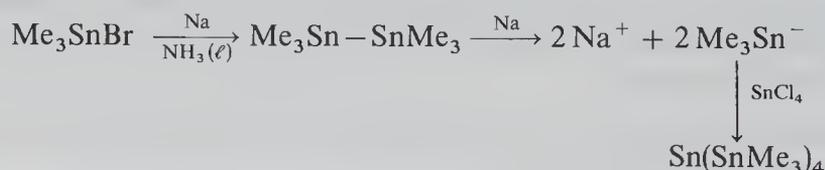


An example is the selective reduction of geminal dihalides in the presence of other sensitive groups:



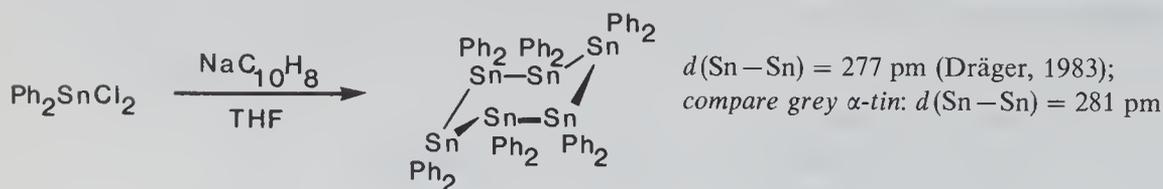
Organopolystannanes are of interest in studies concerned with the aptitude of main-group elements to form homonuclear chains. Although the tendency for catenation in group 14 decreases with increasing atomic number, in the case of tin several examples with linear, branched or cyclic structures are known.

In order to secure kinetic stability it is essential, however, to shield the vulnerable Sn–Sn bond [$E(\text{Sn}–\text{Sn}) = 151 \text{ kJ/mol}$, compare: $E(\text{Si}–\text{Si}) = 340 \text{ kJ/mol}$] by means of alkylation or arylation. In the case of the parent stannanes, no unambiguous evidence exists for congeners larger than Sn_2H_6 . The preparation of (organo)oligostannanes may be effected by **Wurtz coupling**:

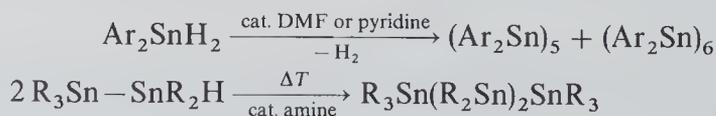


dodecamethyl-
cyclohexastannane

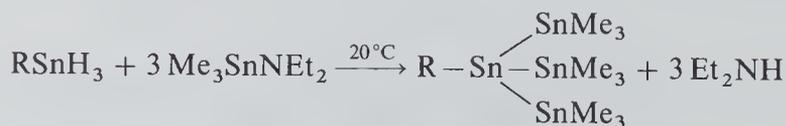
chain length varies depending on the
reaction conditions, $n \leq 12$



via **thermolysis of organotin hydrides**:

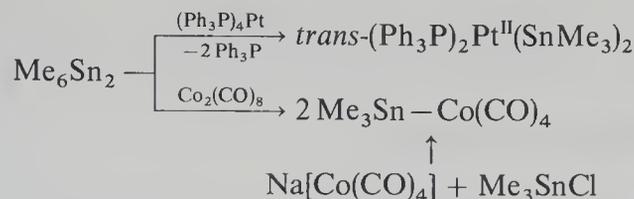


or by means of **hydrostannolysis**:



(Organo)oligostannanes are quite stable thermally (example: $\text{Ph}_3\text{Sn}-\text{SnPh}_3$, mp 237°) but considerably more air-sensitive than the peralkylated species R_4Sn . Hexamethyldistannane in air at room temperature slowly forms the stannoxane $(\text{Me}_3\text{Sn})_2\text{O}$; at its boiling point of 182°C , Me_6Sn_2 is pyrophoric.

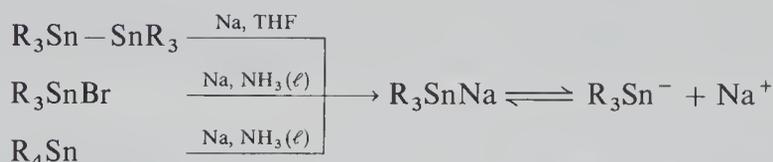
Hexaorganodistannanes have been used to generate transition metal-tin bonds:



These complexes illustrate the iso(valence)electronic nature of R_3Sn^- and R_3P .

8.3.2 Tin Organyls of Coordination Numbers 2 and 3

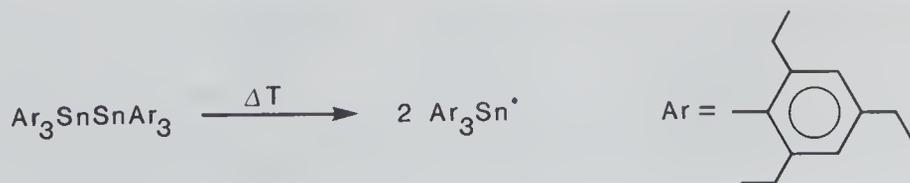
Organostannyl anions R_3Sn^- are accessible in a variety of ways:



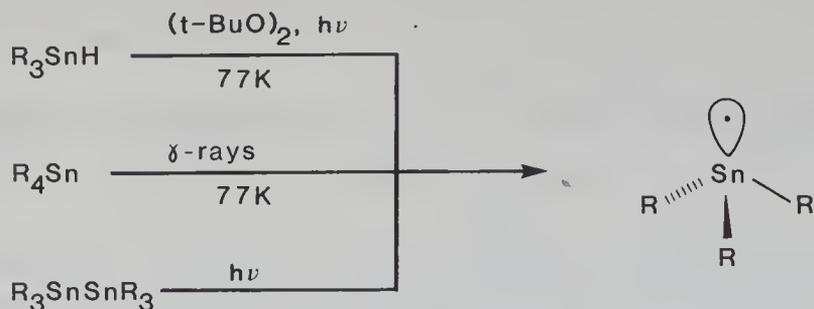
The position of the dissociation equilibrium depends on the nature of R and the solvating power of the medium. In the case of Ph_3SnNa and $\text{NH}_3(\ell)$, extensive dissociation is assumed; for Me_3SnLi in EtNH_2 , on the other hand, electrolytic conductivity is minute. Alkali-metal organostannites R_3SnM complement organodistannanes in the synthesis of transition metal-tin bonds:



Whereas – because of ion solvation – the assignment of coordination number 3 for organostannyl anions R_3Sn^- and -cations R_3Sn^+ (p. 126) is not warranted, it is without question that **organostannyl radicals** $\text{R}_3\text{Sn}\cdot$ do possess this coordination number. The spontaneous formation of $\text{R}_3\text{Sn}\cdot$ radicals through homolytic cleavage of distannanes only occurs if assisted by bulky substituents (cf. p. 113, 120):



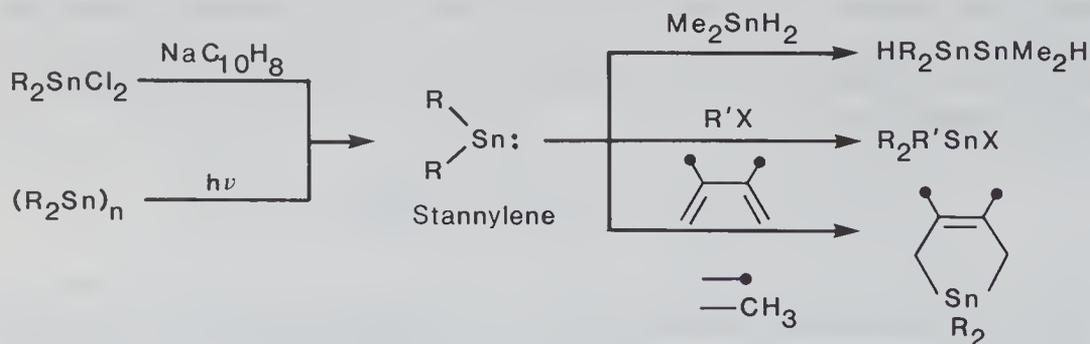
Additional sources for organostannyl radicals are:



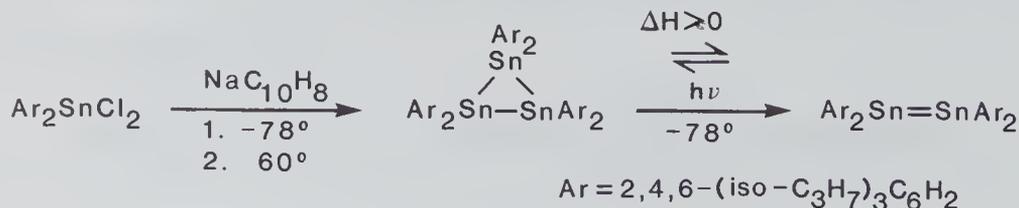
Stannyl radicals $R_3Sn\cdot$, formally Sn^{III} compounds, like $R_3Ge\cdot$ (but unlike $R_3C\cdot$) are pyramidal (Howard, 1972). This may be inferred from the large ESR hyperfine coupling constant $a(^{119}Sn)$ [example: $Ph_3Sn\cdot$, $a(^{119}Sn) = 155$ mT] according to which the singly occupied orbital possesses considerable Sn(5s) character. In the case of a planar structure and the single occupancy of an Sn(5p) orbital, a very small coupling constant would be expected which would have to be traced to spin polarization of doubly occupied Sn(s) orbitals or of Sn(sp^2) hybrid orbitals, respectively. A consequence of the pyramidal structure of $R_3Sn\cdot$ is the possibility that radical reactions of chiral organostannanes $RR'R''SnH$ proceed with retention of configuration. This has been demonstrated in a number of cases.

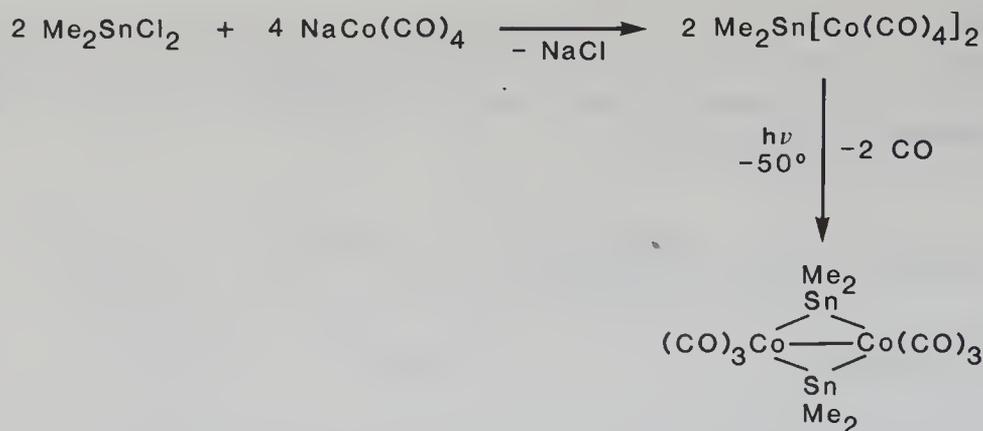
The life-time of organotin radicals $R_3Sn\cdot$ strongly depends on the bulkiness of the groups R: the range extends from diffusion-controlled dimerization in the case of $Me_3Sn\cdot$ to a half-life of about one year for $[(Me_3Si)_2CH]_3Sn\cdot$.

The stannylenes R_2Sn represent organotin molecules with the coordination number 2. With simple alkyl- or aryl substituents R these stannylenes – like the respective germynes, silylenes and carbenes – only occur as reactive intermediates which undergo typical follow-up reactions:

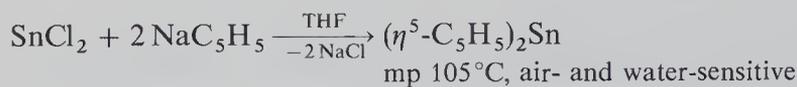


The bulky substituent 2,4,6-*tris(iso-propyl)phenyl* stabilizes a distannane which is in thermal equilibrium with the cyclotristannane (Masamune, 1985):

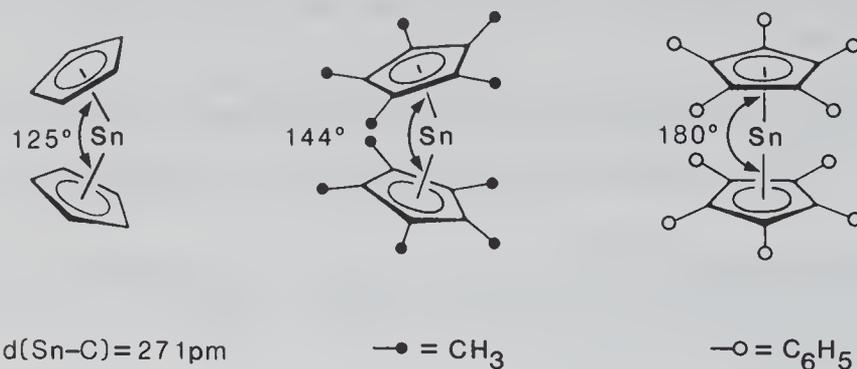




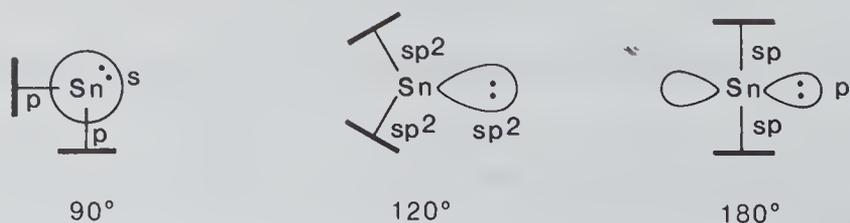
The longest known Sn^{II} organyl is bis(cyclopentadienyl)tin, **stannocene** (E. O. Fischer, 1956):



The parent stannocene $(\text{C}_5\text{H}_5)_2\text{Sn}$ has a tilted sandwich structure which approaches an axial structure with increasing steric demand from the peripheral substituents:

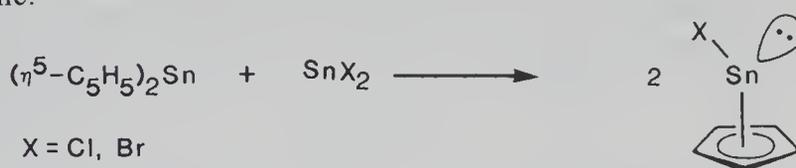


In a pedestrian discussion of these tilting angles, competition between the attempt to minimize ligand-ligand repulsion and the tendency to place nonbonding metal electrons in hybrid orbitals of high $\text{Sn}(5s)$ character is assumed. The following limiting cases of hybridization consider only the σ -interaction between atomic orbitals of tin and the a_{1g} molecular orbitals of the ligands C_5H_5 (cf. p.319):

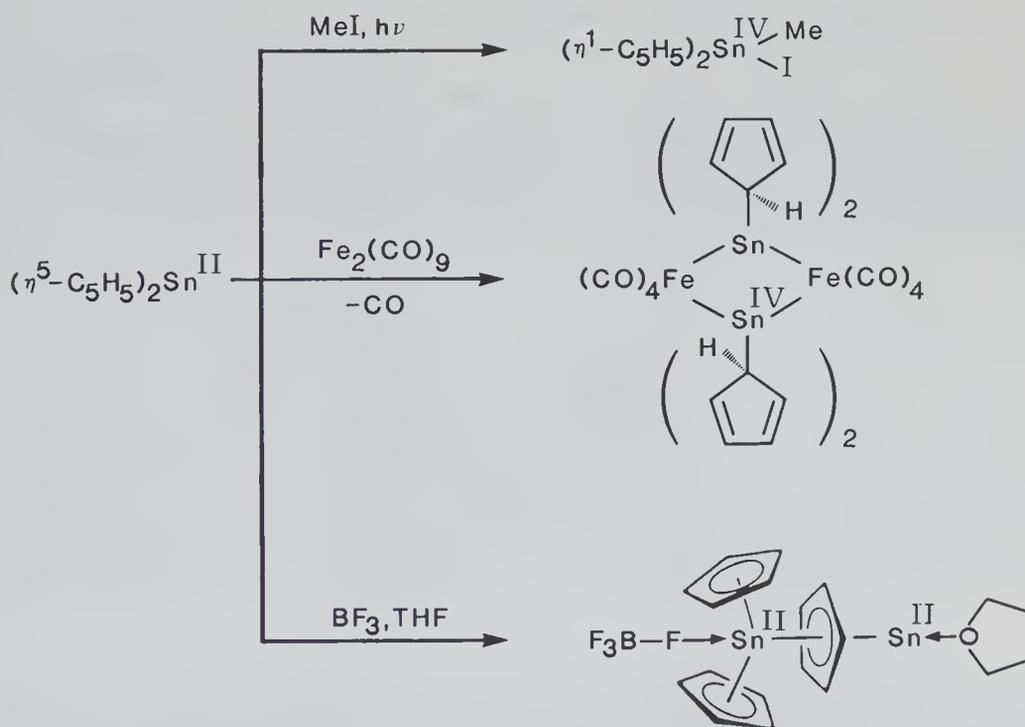


In this simple picture, stannocene is best described in terms of $\text{Sn}(sp^2)$ hybridization; the sp^2 hybrid orbital not required for metal-ring bonding is occupied by a nonbonding pair of electrons. Additional contributions to metal-ring bonding may stem from π interactions between filled MO's $e_1(\text{C}_5\text{H}_5)$ and empty AO's of Sn which possess the appropriate symmetry (cf. p.90). The high s electron density at the Sn nucleus, which follows from this bonding model, leads to strong magnetic shielding as shown by the appearance of ^{119}Sn -NMR signals at very high field (cf. p.123). The observation of a coupling $^3J(^{119}\text{Sn}, ^1\text{H})$ for $(\text{C}_5\text{Me}_5)_2\text{Sn}$ signifies an appreciable covalent contribution to the metal-ligand bond (Jutzi, 1988).

Ligand exchange between stannocene and tin dichloride leads to a half-sandwich complex (Noltes, 1975 R), whose bent structure can be interpreted along the lines given above for stannocene:

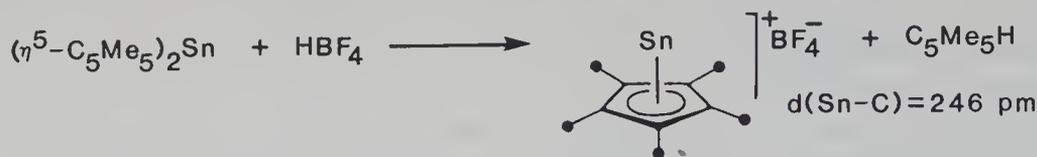


The numerous subsequent reactions of the stannocenes are shaped by the bonding alternatives $\eta^1\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{H}_5$, the change in oxidation state $\text{Sn}^{\text{II}} \rightarrow \text{Sn}^{\text{IV}}$ and the abstraction of a C_5H_5^- ligand upon attack by a Lewis acid:



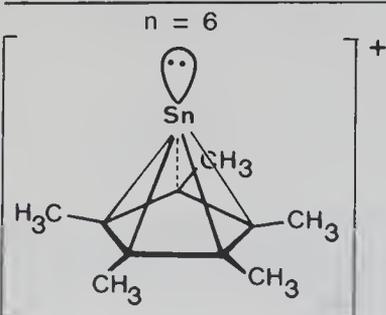
Contrary to an original assumption, the reaction of stannocene with BF_3 does not lead to the simple adduct $(\text{C}_5\text{H}_5)_2\text{Sn} \cdot \text{BF}_3$; instead, one cyclopentadienyl ligand is lost and and the binuclear complex with a bridging C_5H_5 unit is formed (Zuckerman, 1985). In

the case of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sn}$, ligand abstraction is effected by tetrafluoroboric acid; the resulting half-sandwich complex remains monomeric (Jutzi, 1979):

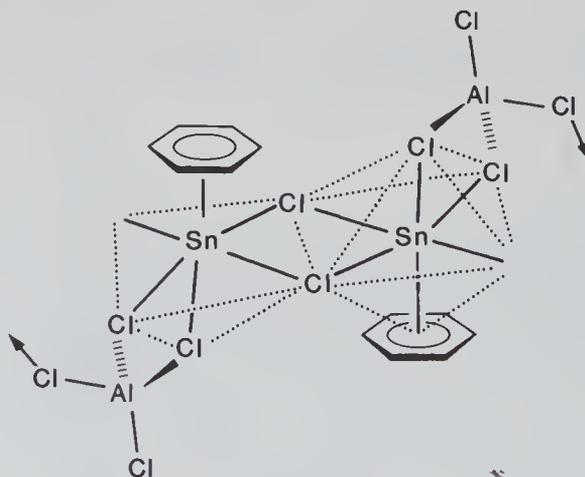


In the highly symmetric cation $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sn}]^+$ the six π electrons of the ligand and the two valence electrons of Sn^{II} create an octet configuration at tin.

However, the ion $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sn}]^+$ may also be regarded as a cluster, and its structure discussed in terms of Wade's rules (p. 68):

Number of vertices	Skeletal bonding electron pairs	Structural type	Geometry
$n = 6$	$8 \quad (n + 2)$	nido	pentagonal bipyramid
	$1 \times \text{Sn} \text{ (with lone pair)}^+$		one vertex unoccupied
	$5 \times \text{C}-\text{CH}_3$		

As in the case of Ga, In and Tl ($\text{C}_5\text{H}_5\text{M}$ versus $\text{C}_6\text{H}_6\text{M}^+$, p. 90), the question as to the existence of (arene)metal complexes must also be posed for the elements of group 14 ($\text{C}_5\text{H}_5\text{M}^+$ versus $\text{C}_6\text{H}_6\text{M}^{2+}$). In fact, from arenes, SnCl_2 , and AlCl_3 two types of complexes of composition $(\text{ArH})\text{Sn}(\text{AlCl}_4)_2 \cdot \text{ArH}$ and $(\text{ArH})\text{SnCl}(\text{AlCl}_4)$, respectively, were obtained (Amma, 1979 R). Whereas the former type structurally corresponds to the analogous lead compound (p. 146), the latter type as yet is limited to tin.



Section of the chain structure of $\text{C}_6\text{H}_6\text{SnCl}(\text{AlCl}_4)$ in the crystal. The backbone consists of a sequence of four-membered rings ($\text{Sn}_2\text{Cl}_2^{2+}$) and eight-membered rings (formed from one tin atom each of the neighboring $\text{Sn}_2\text{Cl}_2^{2+}$ units and two bridging AlCl_4^- ions). The loose coordination of a C_6H_6 molecule creates a distorted octahedral environment at tin. Note here again, that the energetically favorable coordination of Cl^- ions to Sn^{II} is largely preserved.

Technical Applications of Organotin Compounds

Tin organyls excel in the multitude of areas where they have found practical use. Since 1950 world production figures of organotin compounds have increased fifty-fold; 60% of the total output is used as stabilizers for polyvinylchloride, 30% as biocides and the rest in various special fields.

The toxicity of organotin compounds increases with the degree of alkylation and decreases with increasing chain length of the substituents. Maximal toxicity is therefore reached for materials which can release the ion Me_3Sn^+ , compounds of the type $(n\text{-Bu})_2\text{Sn}(\text{SCH}_2\text{COO-iso-C}_8\text{H}_{17})_2$ are virtually non-toxic. Plastics stabilizers R_2SnX_2 belong to the latter category. The mode of action of these stabilizers is thought to be the suppression of HCl release during the thermal processing of PVC at 180–200 °C by substituting chlorine atoms at the more reactive regions of the polymer by long chains. After processing, organotin additives also function as UV-stabilizers because of their capacity to terminate radical chain reactions. Another application is the generation of thin SnO_2 coatings on glass, accomplished by the treatment with Me_2SnCl_2 at 400–500 °C.

Compounds of the type R_3SnX serve as biocides in pest control, as fungicides, as antifouling agents in paint protection and, more generally, as disinfectants against gram-positive bacteria [examples: $\text{Ph}_3\text{SnOOCH}_3$, $(n\text{-Bu})_3\text{SnOOC}(\text{CH}_2)_{10}\text{CH}_3$, $(n\text{-Bu}_3\text{Sn})_2\text{O}$]. The final degradation to non-toxic $\text{SnO}_2 \cdot \text{aq}$ is an attractive aspect which has helped organotin compounds to find wide acceptance.

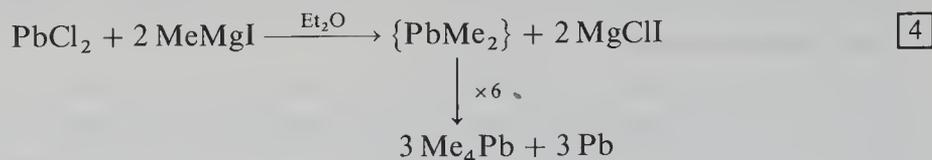
8.4 Organolead Compounds

The **technical use** of lead alkyls as gasoline additives, which still consumes about 20% of the annual world production of this metal, is a result of extensive industrial research and has led to the accumulation of a vast amount of factual material. Compared with the lighter homologues C, Si, Ge and Sn, the larger atomic radius of lead favors the realization of the higher coordination numbers 5–8. According to the metallic character of lead, in ionizing media, solvated organolead cations are encountered. The tendency towards the formation of homonuclear metal-metal bonds (catenation) in the case of lead has vanished almost completely [$E(\text{Pb} - \text{Pb}) \approx 100 \text{ kJ/mol}$]. In light of the fact that for purely inorganic compounds Pb^{II} is the favored oxidation state, the readiness of organolead compounds of intermediate oxidation state to disproportionate to Pb^0 and Pb^{IV} is remarkable. In terms of energetics, organolead chemistry is shaped by the **weakness and the polarizability of the Pb–C bond** [$E(\text{Pb} - \text{C}) = 152 \text{ kJ/mol}$] which paves the way for radical as well as for ionic reactions.

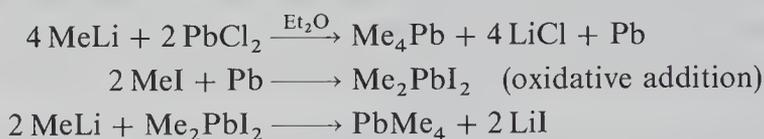
NMR spectroscopy as applied to organolead compounds profits from the existence of the isotope ^{207}Pb (23%, $I = 1/2$). The chemical shifts in ^{207}Pb -NMR spectra cover a range of 1300 ppm; the factors which lead to chemical shift differences resemble those for tin organyls. The coupling constants $^2J(^{207}\text{Pb}, ^1\text{H})$ can be retrieved either from ^{207}Pb -NMR or from ^1H -NMR spectra (^{207}Pb satellites). They lie between 62 Hz [Me_4Pb] and 155 Hz [$\text{Me}_2\text{Pb}(\text{acac})_2$], and provide insight into the $\text{Pb}(6s)$ character in the $\text{Pb}-\text{CH}_3$ bond.

8.4.1 Pb^{IV} Organyls

PREPARATION IN THE LABORATORY



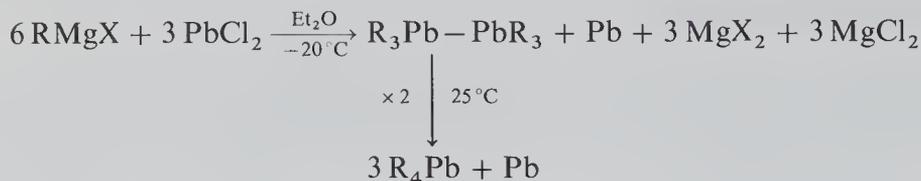
Complete consumption of the lead introduced into the reaction may be achieved by the addition of methyl iodide:



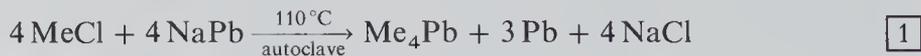
Mixed Pb^{IV} organyls are obtained as follows:



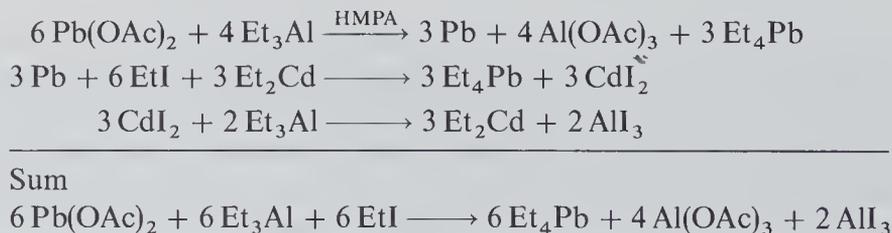
Hexaorganodiplumbanes are accessible from alkylations at low temperature:



INDUSTRIAL PROCESSES

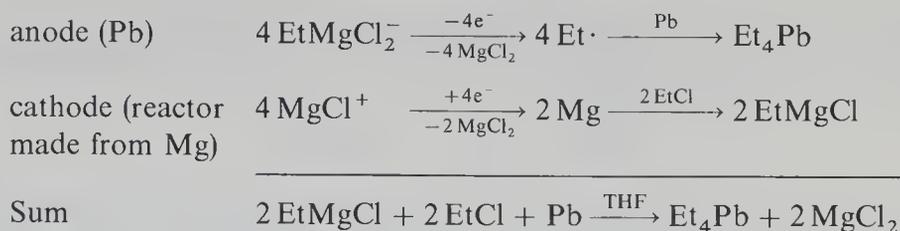


A disadvantage of this **direct synthesis** is the fact that lead is only partially consumed; elemental lead formed has to be recycled. This is circumvented in a process which uses aluminum alkyls in the presence of a catalytic amount of Et₂Cd:



The role of Et_2Cd is that of an alkyl-transfer agent to Pb; in this function, it is not consumed but regenerated continuously by means of the reaction between the CdI_2 formed and the actual alkylating agent Et_3Al .

The Nalco process (USA) operates electrochemically:

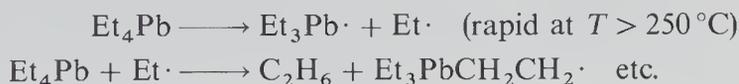


The commercial importance of these processes is declining; they are of interest, however, as examples of technical ingenuity.

PROPERTIES OF THE ORGANYLs R_4Pb

The simple organoplumbanes Me_4Pb (bp $110^\circ\text{C}/760$ mbar) and Et_4Pb (bp $78^\circ\text{C}/10$ mbar) are colorless, highly refractive, toxic liquids; Ph_4Pb (mp 223°C) is a white crystalline solid. Under ambient conditions, these compounds are neither attacked by air or water nor affected by light; at elevated temperatures, they are cleaved into Pb, alkanes, alkenes and H_2 . Thermal stability of R_4Pb decreases in the order $\text{R} = \text{Ph} > \text{Me} > \text{Et} > \textit{iso}\text{-Pr}$. The thermolysis of Me_4Pb to yield Pb and methyl radicals, and the transport of the lead mirror by means of the radicals present in the gas stream were the subject of a classical experiment (Paneth, 1929).

Tetraethyllead is (was) added to gasoline in a concentration of about 0.1% to serve as an antiknock compound. The action of Et_4Pb consists in the deactivation of hydroperoxides by PbO , as well as in the termination of radical chain reactions of the combustion process by the products of Et_4Pb homolysis:



Another additive, $\text{BrCH}_2\text{CH}_2\text{Br}$, converts PbO into volatile Pb compounds which then can exit the combustion chamber. In order to stem further contamination of the environment with toxic lead compounds, the use of methylcyclopentadienyl(tricarbonyl)manganese (p. 335) has been proposed as a substitute. Despite extensive research, the effectivity of tetraethyl lead, in use since 1922, has remained unsurpassed. In the long run, the total elimination of lead organyls as fuel additives (banned in the USA since 1986, still in use in some European and other countries) appears inevitable.

The chemistry of the substitution products of binary lead organyls $\text{R}_n\text{PbX}_{4-n}$ ($\text{X} = \text{Hal}, \text{OH}, \text{OR}, \text{NR}_2, \text{SR}, \text{H}$ etc.) differs only moderately from the respective organotin chemistry. Analogous reactions usually proceed under milder conditions for lead as compared to tin.

Organolead halides R_nPbX_{4-n} are accessible through Pb–C cleavage by means of dihalogen or, even better, by hydrogen halides or thionyl chloride:



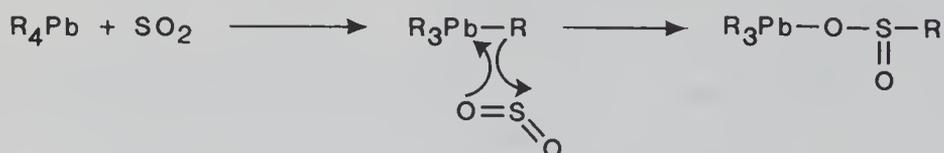
The reaction with HCl is 60 times faster for Ph_4Pb than for Ph_4Sn .

Compounds of the type $RPbX_3$ approach $PbCl_4$ in their instability. They can be prepared via oxidative addition of RI to PbI_2 :

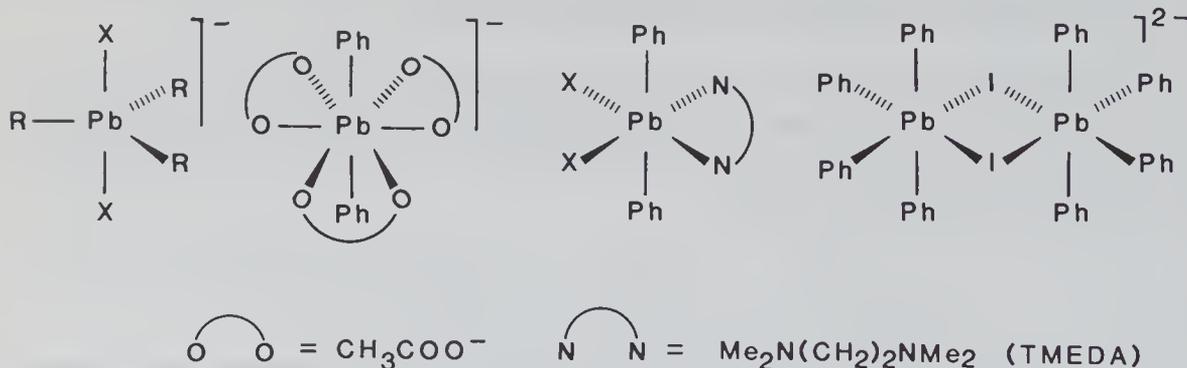


R_3PbX and R_2PbX_2 in solution exist as solvated monomers; in the solid, polymer chains with halide bridges, resembling organotin halides (p. 125f), are formed. The tendency to associate is more highly developed for the organolead compounds, however. Organolead carboxylates also form polymeric chain structures.

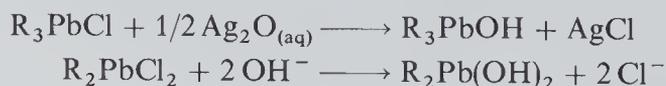
Organolead sulfinates arise through insertion of SO_2 into the Pb–C bond:



The readiness to increase the coordination number above four is expressed in the existence of numerous complex ions like the following:



Organolead hydroxides $R_nPb(OH)_{4-n}$ are formed in the hydrolysis of the corresponding chlorides:

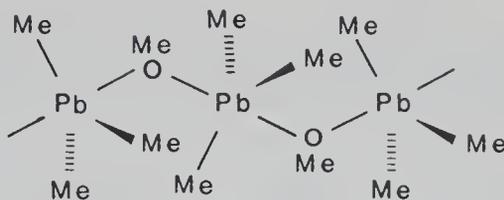


$R_2Pb(OH)_2$, which prevails in the region $8 < \text{pH} < 10$, is **amphoteric**. At $\text{pH} > 10$ $[R_2Pb(OH)_3]^-$ is encountered, whereas at $5 < \text{pH} < 8$ $[R_2Pb(OH)]_2^{2+}$ and at $\text{pH} < 5$ $[R_2Pb(aq)]^{2+}$ are the dominating species. Dications $[R_2Pb(\text{solv})]^{2+}$ are generated from R_2PbCl_2 in other media as well; the group R_2Pb^{2+} , like the isoelectronic moieties R_2Te^+ and R_2Hg , has a **linear** structure. The condensation of organolead hydroxides to form

plumboxanes occurs only sluggishly, it requires the continuous removal of water from the equilibrium mixture by distillation or by reaction with sodium metal:

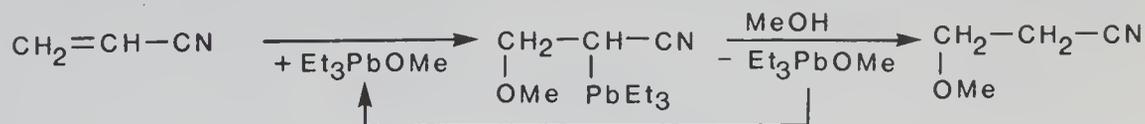


Conversely, plumboxanes undergo ready solvolytic cleavage; with alcohols, **organolead alkoxides** are obtained which form polymer chains in the solid state:

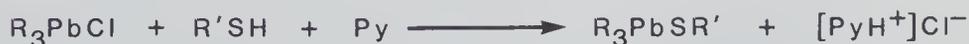
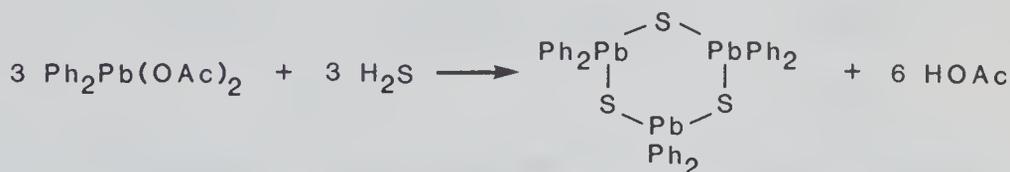
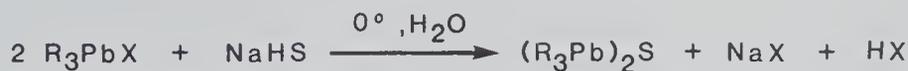


Polymer chains of $[(CH_3)_3PbOMe]_n$

Organolead alkoxides add to polar C=C double bonds (**oxyplumbation**, Davies, 1967). Methanolysis of this adduct regenerates R_3PbOMe ; therefore, in the addition of MeOH to C=C double bonds R_3PbOMe acts as a catalyst:

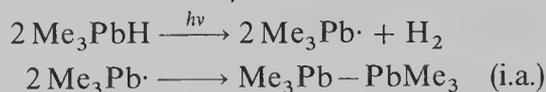


Lead, like tin, has a high affinity for sulfur; Pb-S bonds are stable in water:

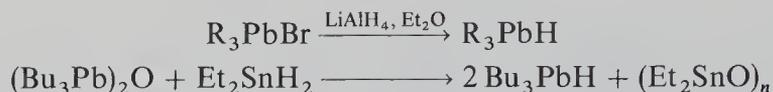


Organolead hydrides R_nPbH_{4-n} clearly demonstrate the gradation of chemical properties displayed by analogous Sn- and Pb compounds. Whereas Me_3SnH is indefinitely stable

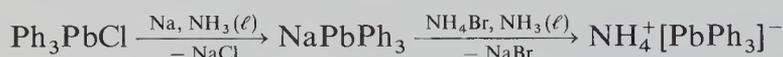
in an inert environment at room temperature, Me_3PbH decomposes at -40°C into Pb , H_2 , CH_4 and $\text{Me}_3\text{Pb}-\text{PbMe}_3$, decay being accelerated by light:



Molecules with larger alkyl substituents like Bu_3PbH are somewhat more stable thermally, they all share the high sensitivity to air and light, however. Methods for their preparation include the following reactions:



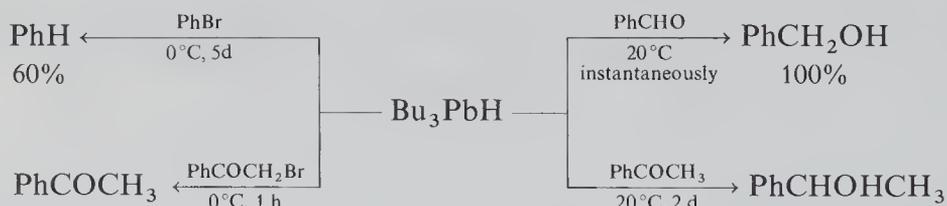
The treatment of **organoplumbyl anions** R_3Pb^- with proton donors does **not** lead to organolead hydrides:



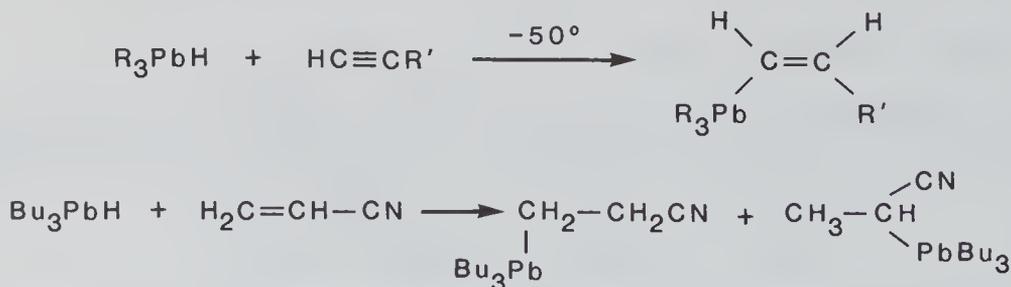
From this and related reactions of the lighter homologues, the following order of decreasing **proton affinity** can be derived:



The high reactivity of the $\text{Pb}-\text{H}$ bond is apparent from the mild conditions under which the reduction of organo halogen- and carbonyl compounds by means of R_3PbH proceeds:



For the reactions with organic halides, radical mechanisms are assumed; in the case of the reduction of carbonyl groups, polar mechanisms cannot be excluded. **Hydroplumbation** of alkynes and of conjugated alkenes takes place under mild conditions as well:



Medium

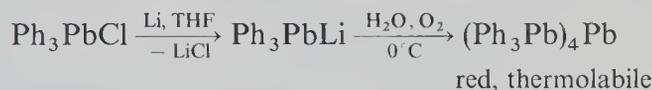
Mechanisms

Et_2O , 0°C	radical	92	:	8 %
BuCN , 20°C	polar	24	:	76 %

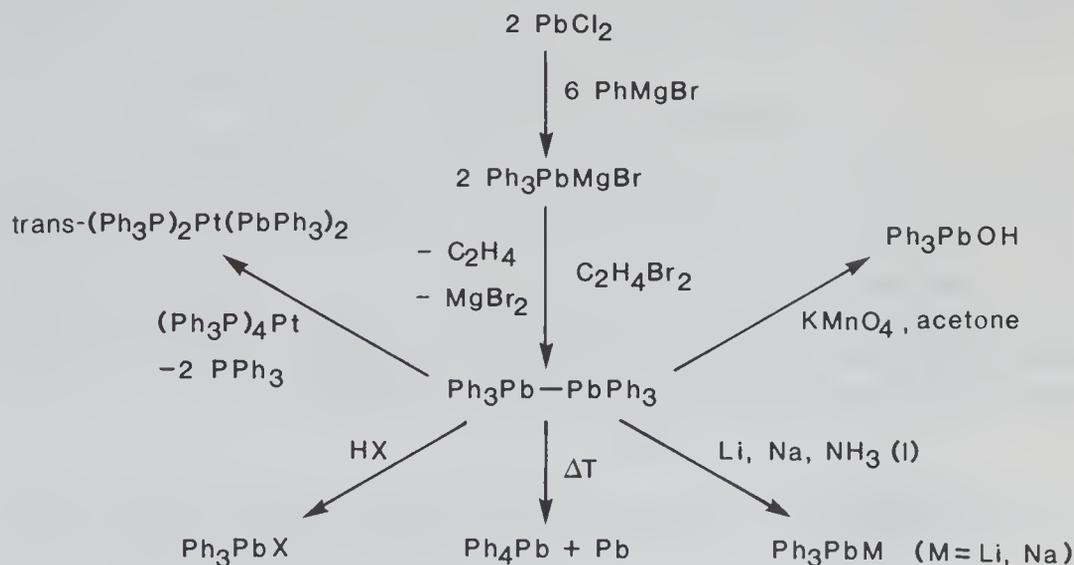
As this comparison shows, changing the medium may induce the transition from a radical to a polar reaction mechanism with concomitant change in product composition. The homolytic hydroplumbation does not require the addition of a radical generating reagent, since initiation is effected by the homolysis of the Pb–H bond, which at 0°C is already appreciable. Bu₃SnH, on the other hand, in the absence of an initiator (5 h, 0°C) does not cause hydrostannation of H₂C=CHCN. This once again demonstrates the higher stability of organotin hydrides as compared to their lead counterparts.

8.4.2 Pb^{III}- and Pb^{II} Organyls

Organolead compounds, in which lead is in an oxidation state lower than four, are the organoplumbyl radicals R₃Pb·, the organoplumbanes R(R₂Pb)_nR and the plumbylenes R₂Pb. Because of the low Pb–Pb bond energy, compounds with **Pb_n chains** have been well characterized only in a few cases. Besides the aforementioned diplumbanes R₃Pb–PbR₃, the propane- and neopentane analoga (*c*-Hex)₈Pb₃ (Dräger, 1986) and (Ph₃Pb)₄Pb deserve a mention. The latter is formed in an obscure reaction:

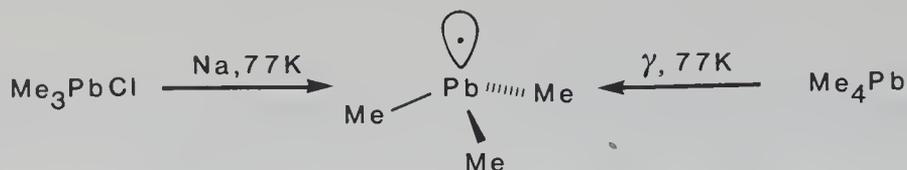


Hexaaryldiplumbanes, which are easily accessible from PbCl₂ and Grignard reagents (van der Kerk, 1970 R), undergo a variety of secondary reactions which lead into many classes of organolead compounds:



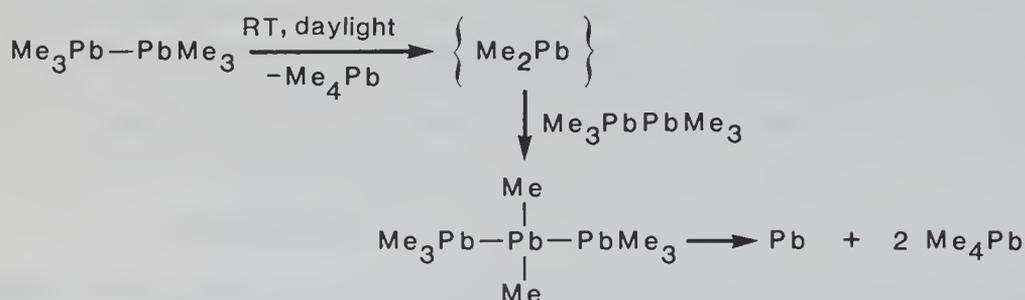
Despite the weakness of the Pb–Pb bond, evidence for the establishment of a dissociation equilibrium $\text{R}_3\text{Pb}-\text{PbR}_3 \rightleftharpoons 2 \text{R}_3\text{Pb}\cdot$ is absent; hexa(mesityl)diplumbane, dissolved in biphenyl, remains diamagnetic up to the temperature of decomposition ($\approx 300^\circ\text{C}$). This finding may be traced to small repulsion of the substituents in the dimer which possesses a long Pb–Pb bond and to ineffective resonance stabilization of the monomer.

Organoplumbyl radicals $R_3Pb\cdot$ may, however, be generated in different ways and studied at low temperature by means of ESR spectroscopy:

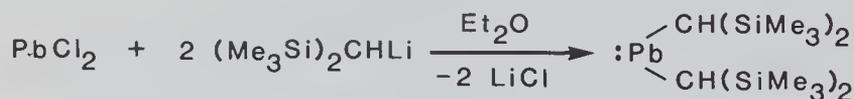


Like the corresponding radicals $Me_3E\cdot$ ($E = Si, Ge, Sn$), but unlike methyl radicals $R_3C\cdot$, $Me_3Pb\cdot$ has a pyramidal structure (cf. p. 120).

Apart from two exceptions **Plumbylenes** R_2Pb only occur as reactive intermediates as in the case of (organo)oligoplumbane decomposition:

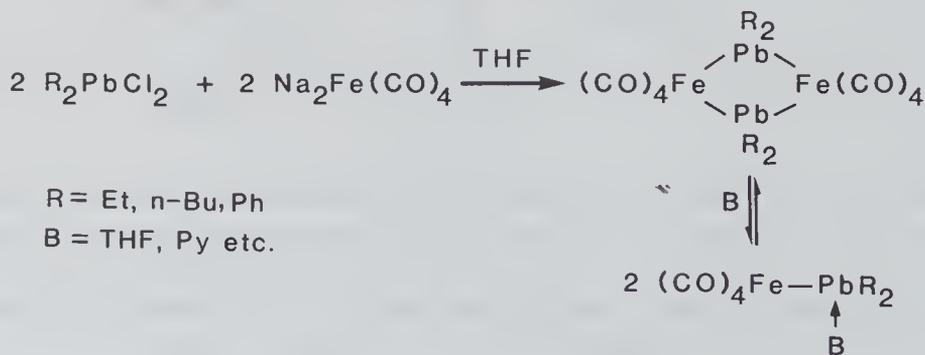


The first exception concerns $[(Me_3Si)_2CH]_2Pb$, the only plumbylene with σ -bonded alkyl groups which is stable at room temperature (Lappert, 1976):



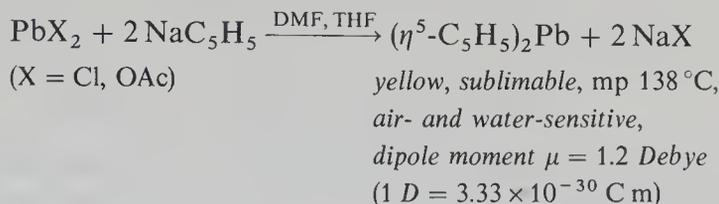
purple red, mp 44°C, diamagnetic

Like the corresponding tin species, this plumbylene may be coordinated to transition metals (example: $[(Me_3Si)_2CH]_2Pb-Mo(CO)_5$). More graceful plumbylenes occur as complexing ligands only in the bridging mode or, if terminally bonded, as Lewis base adducts. In both cases, lead is four-coordinate (Marks, 1973):

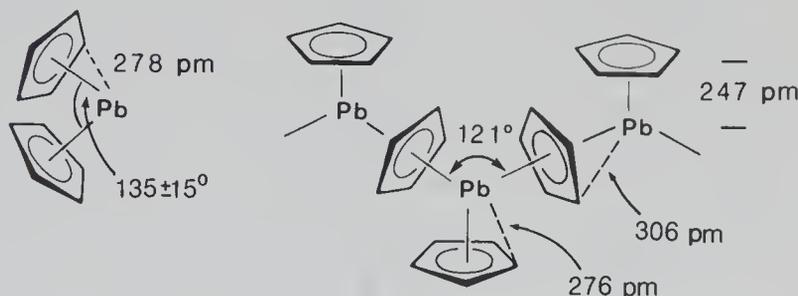


Transition-metal complexes containing bridging plumbynes were already described by Hein in 1947 (example: $[\text{Et}_2\text{PbFe}(\text{CO})_4]_2$).

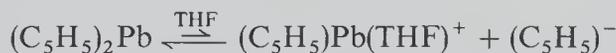
The second exception is represented by the plumbocenes (E. O. Fischer, 1956):



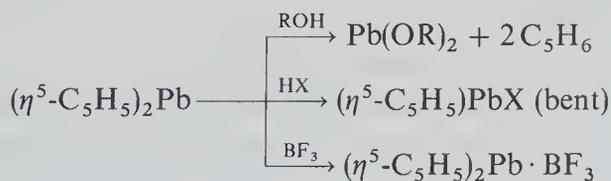
For isolated plumbocene molecules, a tilted structure similar to that of stannocene follows from dipole-moment measurements in solution as well as from electron-diffraction experiments in the gas phase. In the solid state, on the other hand, a polymeric chain structure is realized (X-ray diffraction).



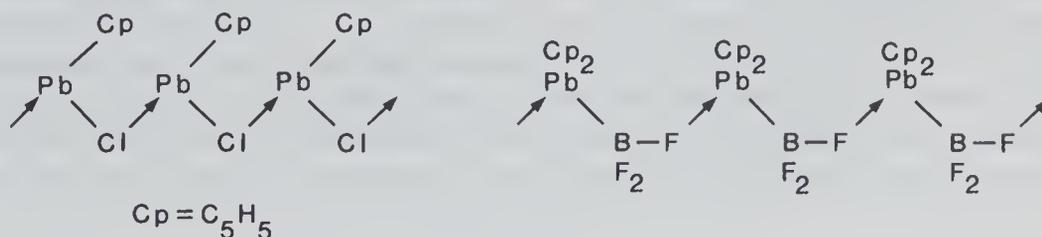
Decamethylplumbocene is monomeric even in the crystal (cf. p. 47). Solutions of plumbocene in THF display electrical conductivity, pointing to partial dissociation (Strohmeier, 1962):



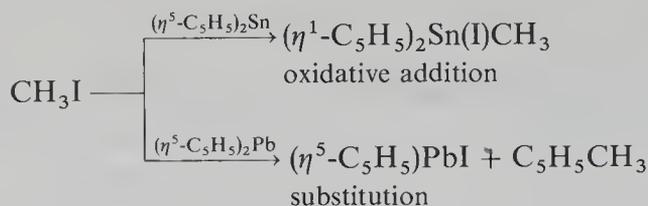
The cation in this equilibrium corresponds to the half-sandwich cations $(\text{C}_5\text{Me}_5)\text{M}^+$ (M = Ge, Sn, p. 119, 136) which, for the lighter homologues of Pb, could be isolated in quantity, albeit with other counterions. In its reactions plumbocene resembles stannocene:



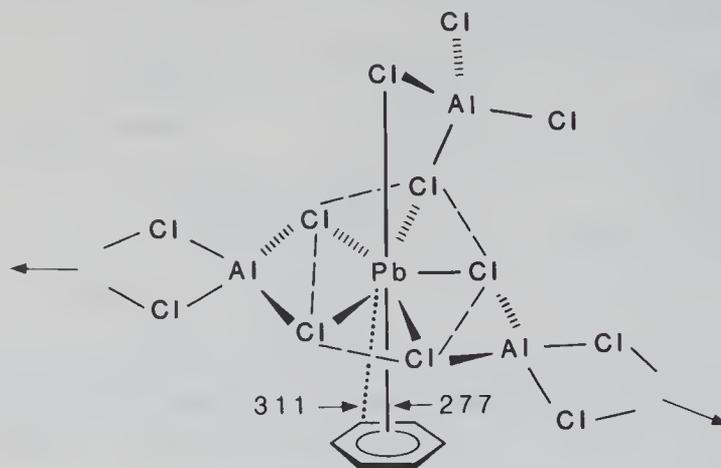
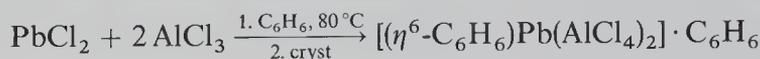
As in the case of $(\text{C}_5\text{H}_5)_2\text{Pb} \cdot \text{BF}_3$, the high melting point of $(\text{C}_5\text{H}_5)\text{PbCl}$ (mp 330 °C) suggests a highly associated structure (Puddephatt, 1979):



The preference for the lower oxidation state Pb^{II} manifests itself in the disparate behavior of stannocene and plumbocene in the reaction with methyl iodide:



η^6 -Coordination of arenes, which is weak for main-group metals (cf. p. 89 f), could also be demonstrated for Pb^{II} (Amma, 1974):



The structure consists of a chain of alternating Pb^{II} ions and AlCl_4^- tetrahedra; the coordination sphere of lead is completed by an additional bidentate AlCl_4^- ion and an $\eta^6\text{-C}_6\text{H}_6$ ligand. The $\text{Pb}-\text{C}$ distance, which is larger here as compared to plumbocene, signals a rather weak Pb -arene interaction. The second C_6H_6 molecule of the empirical formula resides outside the coordination sphere of lead.

Organolead compounds in vivo

In principle, lead organyls share a number of applications with organotin compounds. However, the toxicity of organolead compounds seriously impedes their use as biocides or as stabilizers for plastics. These draw-backs were ignored in the case of gasoline additives and it is only recently that restrictive measures have been adopted.

As in the case of Hg (p. 54 f) and Sn (p. 137), maximal toxicity is exhibited by the highly alkylated organolead cations R_2Pb^{2+} and R_3Pb^+ . These species are generated via **biomethylation** of inorganic lead compounds and as metabolites of lead organyls in the organism. R_3Pb^+ inhibits oxidative phosphorylation as well as the action of glutathione transferases. R_2Pb^{2+} blocks enzymes which possess neighboring thiol groups. Inorganic Pb^{2+} , conversely, is accumulated in bone, where it replaces Ca^{2+} . **Chelate therapy** is ill-suited for the excretion of organolead compounds since complexing ligands like diethylenetriamine pentaacetate or penicillamine only mobilize Pb^{2+} ions bound in skeletal materials.

9 Organoelement Compounds of the Nitrogen Group (Group 15)

The broadly encompassing term “organoelement chemistry” is justified for group 15 in particular since the organic chemistry of the nonmetal phosphorus, the metalloids, arsenic and antimony and the metal bismuth is intimately related. As far as practical and synthetic applications are concerned, the chemistry of As-, Sb- and Bi-organyls is overshadowed by the organometallics of groups 13 and 14. The attention the pharmacological activity of organoarsenic compounds received at the beginning of this century, has dissipated since the discovery of antibiotics. Other conceivable applications are seriously hampered by the high **toxicity of As-, Sb- and Bi organyls**. Addition of organoelement hydrides to unsaturated systems, which as hydroboration, hydroalumination and hydrostannation has proved invaluable in organic synthesis, knows no counterpart in group 15 since the organoelement hydrides of P, As, Sb and Bi are highly labile compounds. The organyls of group 15 are of considerable importance, however, as **σ -donor/ π -acceptor ligands in transition-metal complexes**. Another topic of recent interest is the incorporation of P, As, Sb, Bi into **$E=E(p_\pi-p_\pi)$ and $E=C(p_\pi-p_\pi)$ multiple bonds**. Limited practical utility, combined with a large variety of structural and bonding peculiarities have developed the study of group 15 organometallics into what one may call “chemistry for chemists”.

The structural multiplicity is a consequence of the fact that in group 15, **two oxidation states E^{III} and E^V** both form extensive series of organoelement compounds, whereas in groups 13 and 14 the element organyls of the respective lower oxidation states are species of somewhat exotic nature. Additional features are the variability of the coordination number, the existence of compounds with a mixed ligand sphere (e.g. $R_nE^VX_{n-5}$, $n = 1-4$) and the accompanying isomerisms, as well as the formation of oligomers or polymers by means of Lewis acid/base interaction or via condensation reactions. An inconsistent nomenclature (e.g. $AsH_3 =$ arsane, arsine, arsenic hydride) adds to the unwieldiness of the field.

As is the organoelement chemistry of groups 13 and 14, that of group 15 is governed by the decrease in energy of homonuclear ($E-E$) as well as of heteronuclear bonds ($E-C$, $E-H$) in the order $E = P > As > Sb > Bi$ (cf. p. 11). In the same order $E-C$ bond polarity increases.

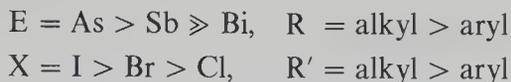
Structural elucidation of organoantimony compounds has profited from **^{121}Sb -Mössbauer spectroscopy**. **^{75}As -NMR** (100%, $I = 3/2$) has as yet only been applied sporadically.

At variance with groups 13 and 14, the organyls of As, Sb, Bi will be discussed jointly; organophosphorus compounds will only be mentioned where interesting parallels to the chemistry of the heavier homologues arise.

and quaternary compounds $R_3R'R''E$ as follows:



In additions of alkyl halides $R'X$ to R_3E , the following orders of reactivity are observed:



The addition of aryl halides ArX is promoted by $AlCl_3$.

STRUCTURES AND PROPERTIES

The pentaorganyls are thermally rather stable:



Compared to organoarsanes and -stibanes (R_3As and R_3Sb), the air-sensitivity of organoarsoranes and -stiboranes (R_5As and R_5Sb) is considerably attenuated.

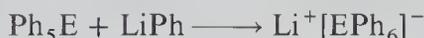
The pentaalkyl derivatives are easily hydrolyzed, however:



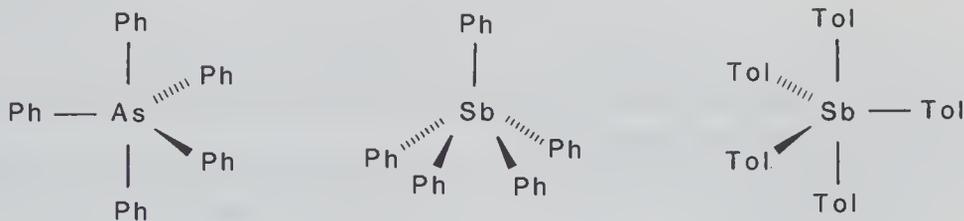
A characteristic feature of the species R_5E is the ready formation of **onium ions**:



and of **ate complexes**:



Of the two complementary geometries of coordination number 5, in the crystal the trigonal bipyramid is adopted by R_5E almost exclusively, an exception being pentaphenylstiborane Ph_5Sb :



The fact that pentaphenylstiborane, as opposed to trigonal-bipyramidal penta(*p*-tolyl)stiborane, assumes a square-pyramidal structure demonstrates, however, that the two complementary geometries differ in energy only marginally. The observation that in the 1H -NMR spectrum of $(CH_3)_5Sb$ even at $-100^\circ C$ all protons appear equivalent, points in the same direction. Obviously, the exchange between axial and equatorial environments of the trigonal

bipyramid, which only requires changes in bond angles (**pseudorotation, Berry mechanism**), is a process equipped with a low activation barrier.

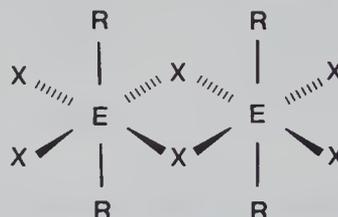
As expected, the onium ions R_4E^+ have tetrahedral and the ate-complex anions R_6E^- octahedral geometry.

9.1.2 Organoelement Derivatives R_nEX_{5-n}

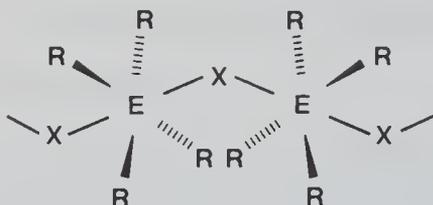
If arsoranes and stiboranes, in addition to organic residues, contain groups X (X = Hal, OH, OR etc.) which possess lone pairs of electrons, the structural picture becomes more complicated. Methods of preparation for the case X = halogen have already been mentioned. Species R_nEX_{5-n} realize at least four different structural variants which reflect the nature of E, R and X:



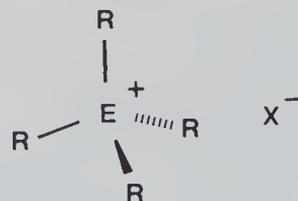
covalent monomeric, trigonal bipyramids, electronegative groups at axial positions, example: Me_3AsCl_2



covalent dimeric, edge sharing octahedra, organic groups at axial position, example: Ph_2SbCl_3



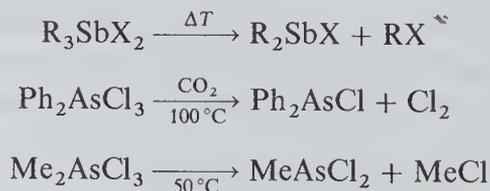
covalent polymeric, vertex sharing octahedra, halide at bridging position, example: Me_4SbF



*ionic, tetrahedra, examples: $[Ph_4As]^+I^-$
 $[Me_4Sb]^+[SbCl_6]^-$
 $\equiv (Me_2SbCl_3)_2$*

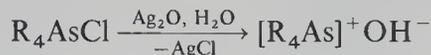
Besides X-ray structural analyses, ^{121}Sb -Mössbauer spectra have furnished information concerning the coordination geometry at antimony. Chiral arsonium- and stibonium ions $[RR'R''R'''E]^+$ are **configurationally stable**.

The thermal stability of compounds R_nEX_{5-n} decreases with decreasing n . Thermally induced cleavages are reverse reactions of the additions introduced in a preparative context in section 9.1.1:

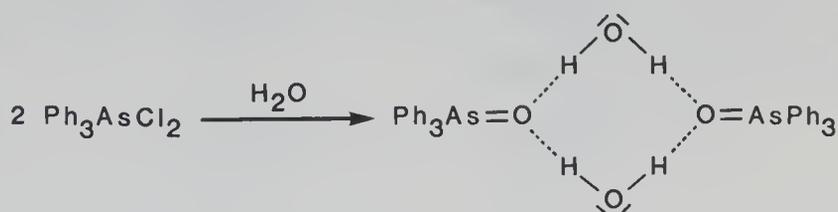


The more labile organoelement halides may, however, be stabilized as Lewis base adducts (example: MeSbCl_4 pyridine).

Solvolysis of species $\text{R}_n\text{EX}_{5-n}$ by water, alcohols, amines etc. leads to several classes of organoelement compounds. Thus, hydrolysis of R_4AsCl yields strongly basic, extensively dissociated **arsonium hydroxides**:

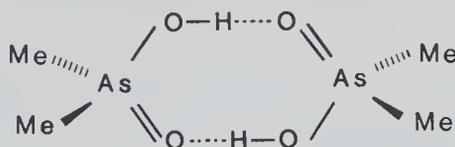
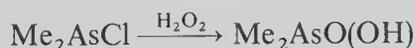
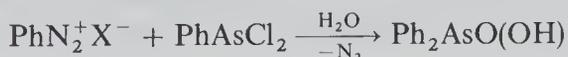


The tetraphenylarsonium ion Ph_4As^+ is frequently used to precipitate large anions from aqueous solution. The arsenobetain $\text{Me}_3\text{As}^\oplus\text{CH}_2\text{COO}^\ominus$ has been detected in the abdominal muscle of the rock lobster *Panulirus longipes cygnus* George (Cannon, 1977). Hydrolysis of the dichloride Ph_3AsCl_2 affords a triphenylarsane oxide hydrate which has an interesting dimeric structure:



In view of this participation of Ph_3AsO in strong hydrogen bonding, it comes as no surprise that triphenylarsane oxide forms stable adducts with a number of Lewis acids [example: $(\text{Ph}_3\text{AsO})_2\text{NiBr}_2$].

Hydrogen bridge bonding is also responsible for the dimeric nature of **arsinic acids** $\text{R}_2\text{AsO}(\text{OH})$ which can be prepared by a combination of oxidation and hydrolysis, starting from As^{III} -compounds:



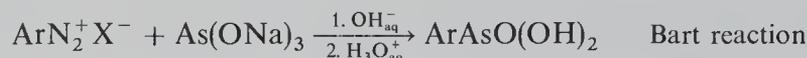
The dimerization of arsinic acids $\text{R}_2\text{AsO}(\text{OH})$ by means of hydrogen-bridge bonding resembles that of carboxylic acids.

Arsinic acids are amphoteric:



Stibinic acids $\text{R}_2\text{SbO}(\text{OH})$, which are polymeric, are accessible analogously to arsinic acids; they are also obtained via hydrolysis of R_2SbCl_3 .

Among the organoelement-oxygen compounds of group 15, it is the arsonic- and stibonic acids which have been studied most extensively. This is an outcome of the discovery by Thomas in 1905 that *p*-aminophenylarsonate, *p*-H₂NC₆H₄AsO(OH)ONa (Atoxyl) is effective in the chemotherapy of sleeping sickness by fighting the trypanosomes. Even today, certain substituted arylarsonic acids on a limited scale serve as herbicides, fungicides and bactericides. **Arsonic acids** RAsO(OH)₂ – like arsenic acids R₂AsO(OH) – are prepared from As^{III}-compounds. The following reaction may formally be described as an oxidative addition of ArX to As^{III} and subsequent hydrolysis:



Arsonic acids are acids of medium strength, they are highly resistant towards oxidation and form polymeric anhydrides (RAsO₂)_{*n*}. In analytical chemistry, phenylarsonic acid is utilized as a reagent for the **precipitation** of high-valent metal ions (Sn^{IV}, Zr^{IV}, Th^{IV}). **Stibonic acids** RSbO(OH)₂ which are accessible in a way similar to that for RAsO(OH)₂, may be reversibly converted into RSbCl₄:



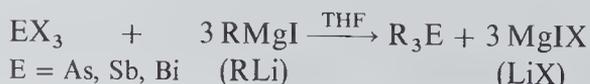
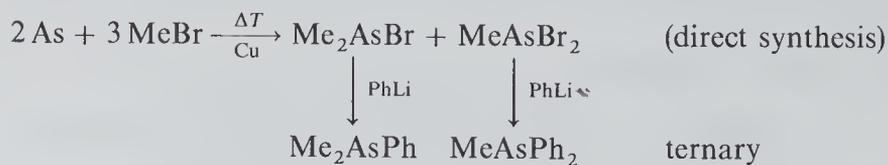
9.2 Element^{III} Organyls (E = As, Sb, Bi)

For the oxidation state E^{III}, the number of classes of compounds R_{*n*}EX_{3-*n*} is, of course, smaller than for the oxidation state E^V where the variability of *n* is greater. Furthermore, Lewis acidity is weak for compounds containing E^{III}; therefore, ate-complexes of the type R₄E⁻ are not encountered.

On the other hand, the species R₃E possess pronounced σ-donor and π-acceptor properties, which has led to their proliferation in coordination chemistry. Another characteristic is the existence of organoelement hydrides R_{*n*}EH_{3-*n*} having no counterpart in E^V chemistry. Selected examples of E^{III} organyls are listed on p. 153.

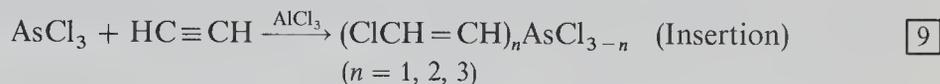
9.2.1 Trisorganoelement Compounds R₃E

PREPARATION

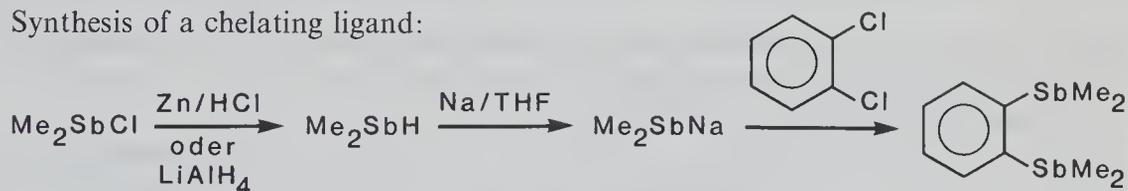


Selected examples of E^{III} organyls (X = Hal, OH, OR, 1/2 O, H):

	As ^{III}	Sb ^{III}	Bi ^{III}
R ₃ E	Ph ₃ As (CF ₃) ₃ As (η ¹ -C ₅ H ₅) ₃ As Arsane (Arsine)	Ph ₃ Sb (<i>n</i> -C ₃ H ₇) ₃ Sb (CH ₂ =CH) ₃ Sb Stibane (Stibine)	Ph ₃ Bi Me ₃ Bi Bismuthane (Bismuthine)
[R ₂ E] ⁻	[Me ₂ As]K	[Ph ₂ Sb]Na	[Ph ₂ Bi]Na
R ₂ EX or condensation product	Ph ₂ AsCl Me ₂ AsOR (Ph ₂ As) ₂ O Me ₂ AsH	Ph ₂ SbF (Me ₂ Sb) ₂ O Me ₂ SbH	Me ₂ BiBr Me ₂ BiH
REX ₂ or condensation product	PhAsCl ₂ MeAs(OR) ₂ (MeAsO) _n MeAsH ₂	MeSbCl ₂ MeSb(OR) ₂ (PhSbO) _n PbSbH ₂	PhBiCl ₂



Synthesis of a chelating ligand:

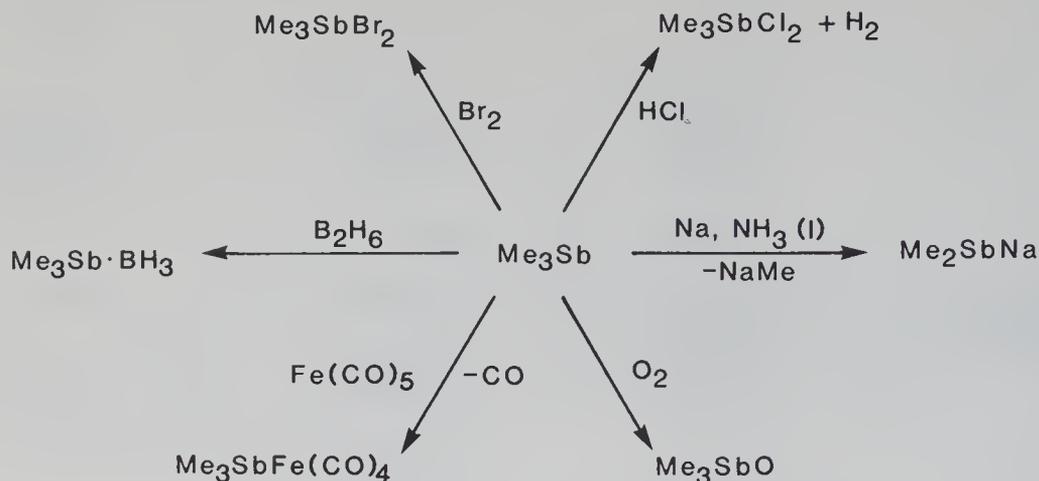


STRUCTURES AND PROPERTIES

The element trisalkyls R₃E, liquids at room temperature if R is small (Me₃As, bp 50 °C), differ from the pentaalkyls R₅E in their increased air-sensitivity; trisalkylstibanes R₃Sb and -bismuthanes R₃Bi are even pyrophoric. The element aryls Ph₃E, solids at room temperature, are considerably more resistant; their oxidation to Ph₃EO calls for the action of KMnO₄ or H₂O₂. The sensitivity towards oxidation increases in the order R₃As < R₃Sb < R₃Bi. Water does not attack trisorganoelement compounds R₃E.

Symptoms of poisoning in rooms which were decorated with wall-paper containing the pigment “Schweinfurter Grün” [3 Cu(AsO₂)₂ · Cu(CH₃COO)₂] were traced back to gaseous organoarsenic compounds generated by the mold *Penicillium brevicaulis* (Gosio, 1897). It was not until 1932 that Challenger identified trimethylarsane Me₃As as the active component of “Gosio gas”. His fundamental studies concerning the **biomethylation** of inorganic ions were subsequently extended to many other elements (cf. Hg p. 55, 203; Pb p. 146, Se p. 171).

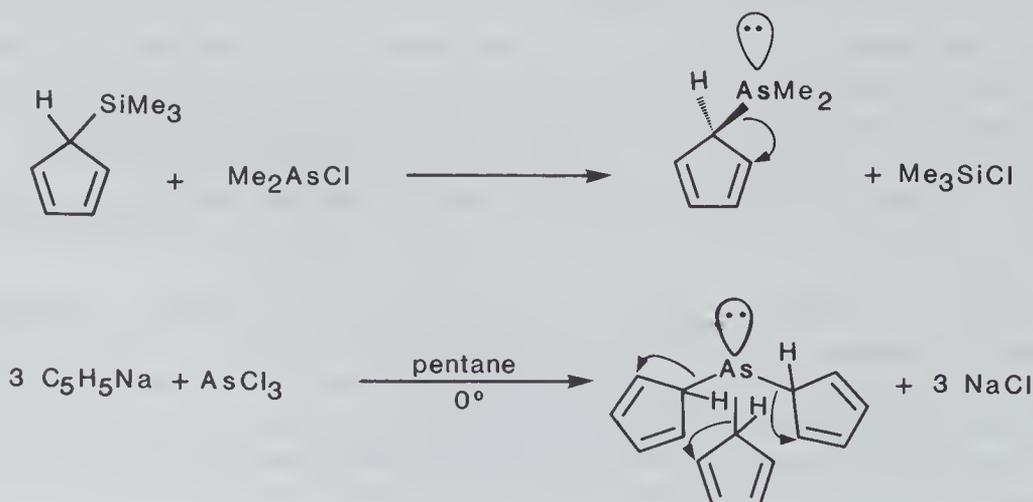
Some typical reactions of the element trisalkyls R_3E are presented in the following scheme, using trimethylstibane as an example:



Based on their distinctive σ -donor/ π -acceptor character, the species R_3E have found extensive use as ligands for transition metals, complex stability decreasing in the order $R_3P > R_3As > R_3Sb > R_3Bi$.

Trisorganoarsanes, -stibanes, and -bismuthanes R_3E have pyramidal structures; the bond angles $C-E-C$ exceed the angles $H-E-H$ of the respective hydrides EH_3 ; they decrease according to $R_3As > R_3Sb > R_3Bi$ [example: $(p-ClC_6H_4)_3E$, angle $C-E-C = 102^\circ, 97^\circ, 93^\circ$ respectively]. Chiral molecules $RR'R''E$ are configurationally stable; for $Me(Et)PhAs$ the inversion barrier amounts to 177 kJ/mol.

As in the case of the species $Me_3M(\eta^1-C_5H_5)$ ($M = Si, Ge, Sn$, cf. p. 99), **metallotropic 1, 2 shifts** are also observed for the compounds $Me_2E(\eta^1-C_5H_5)$ ($E = As, Sb$). They have the effect that at a characteristic temperature, the ring protons become equivalent on the 1H -NMR time-scale.



In the triscyclopentadienyl compounds $(\eta^1\text{-C}_5\text{H}_5)_3\text{E}$ (E = As, Sb, Bi) – highly sensitive species prone to polymerization – this dynamic process involves all three ligands; for $(\text{C}_5\text{H}_5)_3\text{As}$ it is slow at $T < -30^\circ$. For $(\text{C}_5\text{H}_5)_3\text{Sb}$ and $(\text{C}_5\text{H}_5)_3\text{Bi}$, the slow exchange region has not yet been reached by lowering the temperature. This concords with the barrier of 1,2-migration decreasing in the order $\text{As} > \text{Sb} > \text{Bi}$, which reflects decreasing E–C bond energy.

9.2.2 Organoelement Derivatives $\text{R}_n\text{EX}_{3-n}$

For organoelement^{III} halides a number of special **preparative methods** must be mentioned in addition to the general procedures introduced in section 9.2.1. Partial alkylation requires controlled reaction conditions and sterically demanding groups:



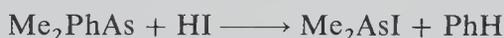
The following transfer of organic residues from silicon compounds to arsenic- or antimony halides is driven by the energy of the silicon-halogen bonds formed:



Halomethyl derivatives of arsenic arise from carbene insertion:



Compounds of the type R_2EX are also obtained according to:



Upon the action of BF_3 on $(\text{C}_5\text{Me}_5)_2\text{AsF}$, an **arsenocenium cation** is formed which – like the isoelectronic decamethylgermanocene (p. 119) – has a tilted sandwich structure (Jutzi, 1983):

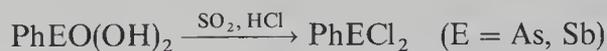


Compounds REX_2 are rationally prepared via E–C cleavage by hydrogen halide:

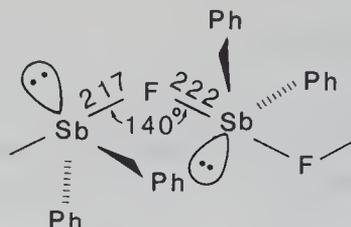


This selective cleavage of the As–Ph bond is surprising in view of the relative strengths of As–C bonds [$E(\text{As}–\text{Ph}) = 280\text{ kJ/mol}$, $E(\text{As}–\text{Me}) = 238\text{ kJ/mol}$]. Apparently, it is the group with the superior carbanion stabilization which is preferentially eliminated.

The reduction of arsonic acids or stibonic acids in the presence of a hydrogen halide also leads to species REX_2 :

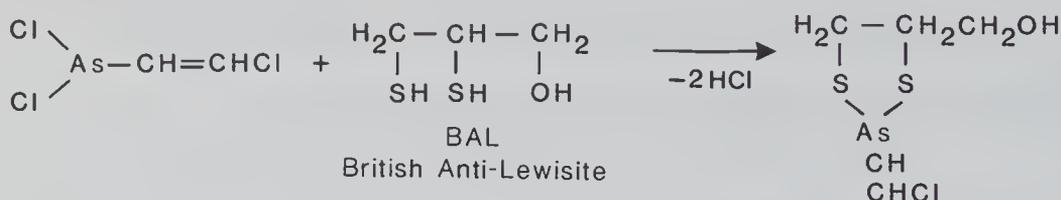


Like the binary compounds R_3E and EX_3 , the organoelement halides R_nEX_{3-n} ($X = \text{Cl}, \text{Br}, \text{I}; n = 1, 2$) are pyramidal; they usually crystallize in molecular lattices. Ph_2SbF is an exception:



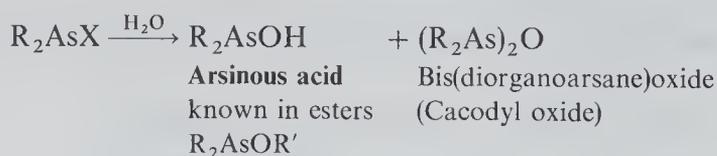
In the crystal, Ph_2SbF exhibits a chain structure which is caused by strong $\text{Sb}-\text{F} \rightarrow \text{Sb}$ bridges. Four bonding and one lone pair of electrons create a distorted trigonal-bipyramidal environment at antimony (Sowerby, 1979).

(2-Chlorovinyl)dichloroarsane (Lewisite) which is produced from $\text{HC}\equiv\text{CH}$ and AsCl_3 in the presence of AlCl_3 , was used as a chemical warfare agent in the First World War. Detoxification is effected by the reaction with 1,2-dithiols:

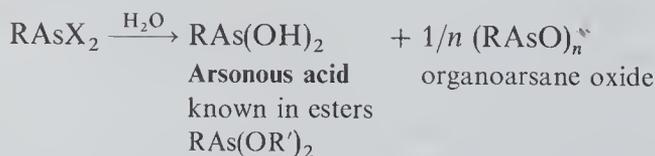


Other organoarsenic halides, which served similar abhorrent purposes, include Ph_2AsCl (Clark I) and Ph_2AsCN (Clark II).

The hydrolysis of organoelement^{III} halides leads to ill-characterized hydroxo compounds, which undergo further reactions:

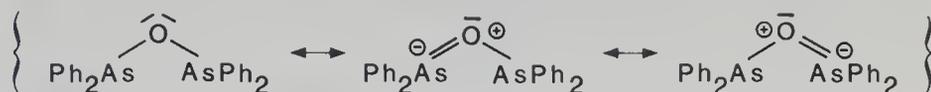


analogously: Stibinous acid + Bis(diorganostibane)oxide



analogously: Stibonous acid + Organostibane oxide

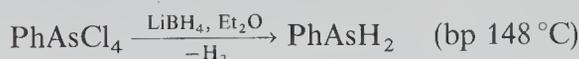
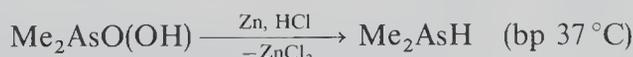
The polymeric structure of organoarsane oxides $(RAsO)_n$, which contrasts with the monomeric nature of nitroso compounds RNO , reflects the unfavorable energetics of a $p_\pi-p_\pi$ bond in monomeric $R-As=O$. In the case of $d_\pi-p_\pi$ interactions, orbital overlap is more effective. The large bond angle $As-O-As$ (137°) in bis(diphenylarsane)oxide argues for the participation of canonical forms with $As=O$ ($d_\pi-p_\pi$) bonds:



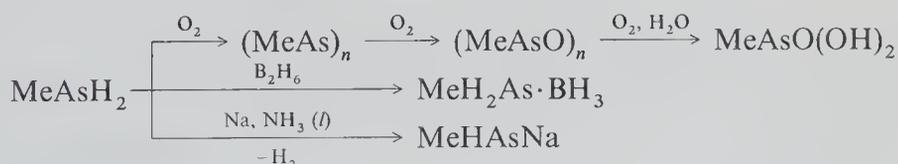
Organoelement^{III} hydrides R_nEH_{3-n} are highly reactive, air-sensitive compounds, whose stabilities decrease according to $E = As > Sb > Bi$, $R = \text{alkyl} > \text{aryl}$ and $n = 2 > 1$. Due to the low polarity of the $E-H$ bonds, they are stable towards hydrolysis, however. A general way of access consists in the substitution of X by H :



The reduction of organoelement^V compounds also leads to the respective hydrides:



A few typical reactions of the compounds R_nEH_{3-n} will be illustrated for the case of MeAsH_2 :

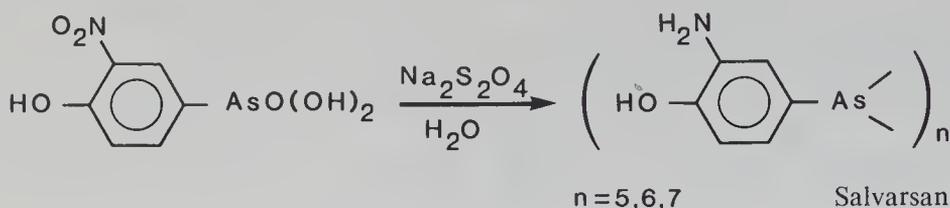


Organoelement hydrides of group 15 add to $>C=C<$ multiple bonds; these reactions are of no practical importance, however.

9.3 Chains and Rings containing E–E Single Bonds

A glance at the energies of homonuclear single bonds between elements of group 15 reveals that no great stability accrues to chains and rings of the heavier elements. The trend in bond energies for E_4 molecules is a case in point $E(\text{P-P}) = 201$,

$E(\text{As}-\text{As}) = 146$, $E(\text{Sb}-\text{Sb}) \approx 120$ kJ/mol. Nevertheless, compounds possessing As_n -rings were already known at the beginning of this century (Bertheim, 1908), and even served a good purpose:



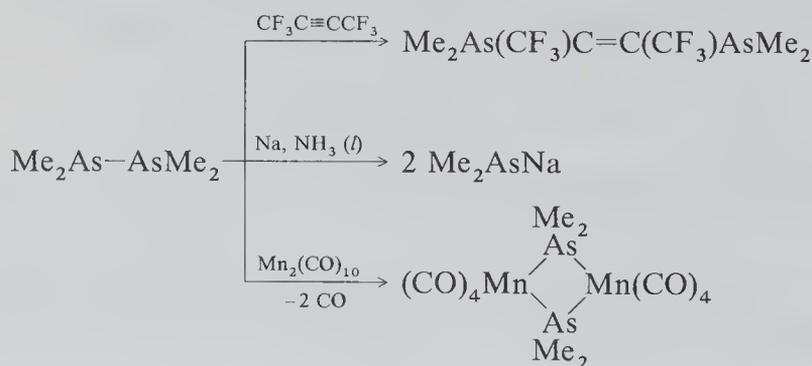
Salvarsan® is effective against *Treponema pallidum*, the microorganism which causes syphilis (P. Ehrlich, 1909).

This reaction yields rings of varying size which differ only slightly in energy. Since the discovery of antibiotics, chemotherapeutics based on organoarsenic compounds have, however, lost their importance.

The simplest species containing E–E bonds are the hydrazine analogues $\text{R}_2\text{E}-\text{ER}_2$. Tetramethyldiarsane, the principal component of Cadet's fuming liquid (p. 1), is prepared more deliberately by means of coupling reactions:

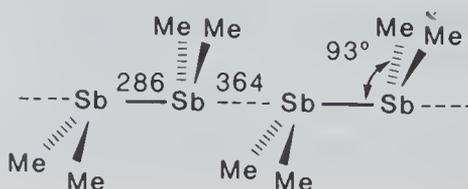


The weakness of the As–As bond accounts for numerous reactions:

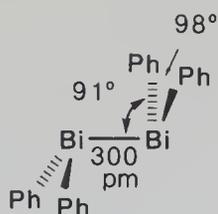


μ -dimethylarsenido bridges

Tetramethyldistibane $\text{Me}_2\text{Sb}-\text{SbMe}_2$, first described by Paneth in 1934, is a pyrophoric compound which decomposes more or less rapidly at room temperature in a closed vessel. Me_4Sb_2 is thermochromic (pale yellow in the solid state at -18°C , red at $+17^\circ\text{C}$ (mp), pale yellow again in the molten state or in solution). In the crystal, chains with intermolecular Sb–Sb interactions are encountered (Ashe, 1984):

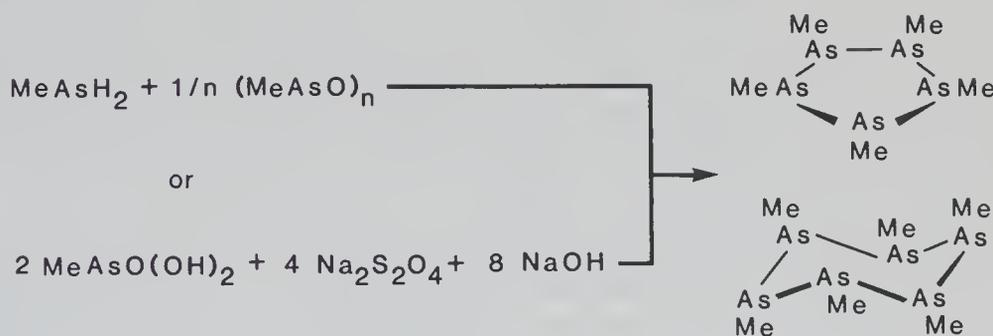


The first well-characterized dibismuthane also is of recent origin (Calderazzo, 1983):

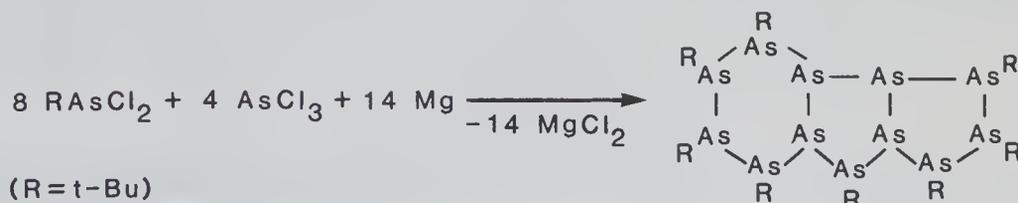


Tetraphenyldibismuthane Ph_4Bi_2 is an orange compound which decomposes at 100°C . Judging from the bond angles, the orbitals used by bismuth for bonding to carbon are essentially $6p$ orbitals; the lone pair at Bi therefore almost exclusively possesses $6s$ character.

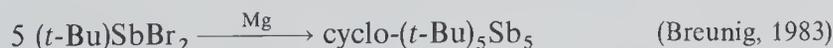
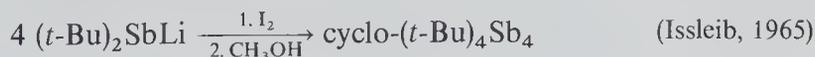
Longer chains between the elements of group 15 result from condensation reactions or from the reduction of compounds which contain RAs^{III} - or RAs^{V} units, the formation of homocyclic rings being strongly favored:



Recently, polycyclic organoarsanes have also been prepared. Example (Baudler, 1985):



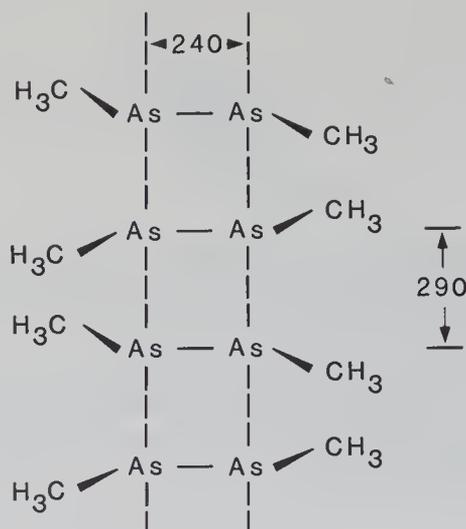
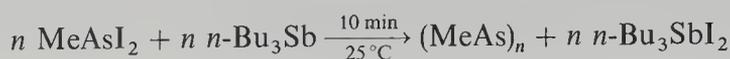
As for antimony, the weakness of the Sb–Sb bonds in stibacycles $(\text{RSb})_n$, $n = 3-6$, calls for their protection by bulky groups:



Polyarsinidene $(\text{RAs})_n$ chains of high molecularity are obtained from MeAsH_2 and MeAsI_2 after prolonged reaction times (Rheingold, 1973):

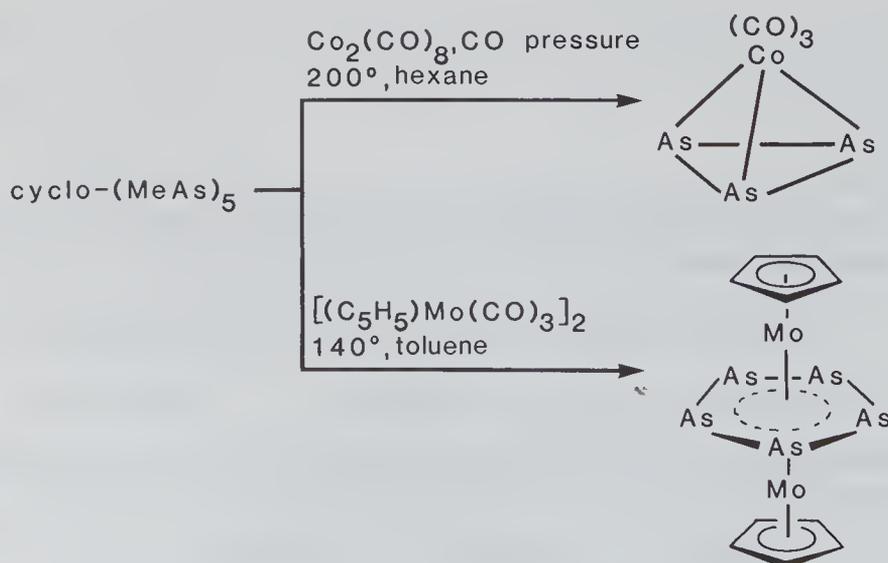


or, more quickly, via reduction by R_3Sb :



$(\text{MeAs})_n$ arises as purple-black crystals and forms a novel type of ladder structure displaying differing As–As distances. The distances at the “steps” correspond to regular As–As single bonds [cf. $d(\text{As}–\text{As}) = 243 \text{ pm}$ in As_4], the distances along the bars point to a bond order of about 0.5. This material has semiconducting properties.

(Pentamethyl)cyclopentaarsane $(\text{MeAs})_5$ can be converted into unsubstituted As_n rings ($n = 3, 5$) which are part of transition-metal clusters (chapter 16). The bonding situation in $(\text{cyclo-As}_3)\text{Co}(\text{CO})_3$ (Dahl, 1969) may be rationalized on the basis of the isolobal properties (p. 396) of the fragments As^\cdot and $(\text{CO})_3\text{Co}^\cdot$. For the triple-decker complex $(\text{cyclo-As}_5)[\text{Mo}(\text{C}_5\text{H}_5)]_2$ (Rheingold, 1982), discussions of the bonding condition are more involved:



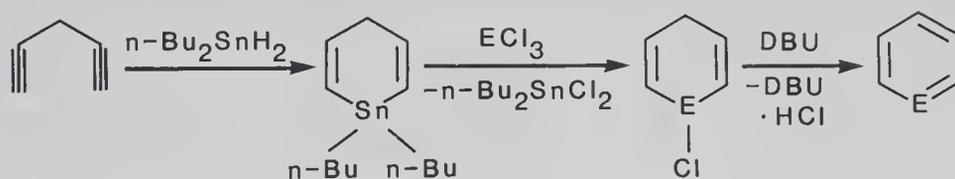
The bond distance $d(\text{Mo}-\text{Mo}) = 276 \text{ pm}$ argues for a long $\text{Mo}=\text{Mo}$ double bond which “permeates the As_5 ring”. In this context, compare the compounds $(\text{cyclo-P}_6)[\text{Mo}(\text{C}_5\text{Me}_5)]_2$ (p. 378) and $(\text{cyclo-P}_5)\text{Fe}(\text{C}_5\text{Me}_5)$ (p. 379).

9.4 E=C and E=E Multiple Bonds

Successful strategies for the generation of segments which contain $\text{E}=\text{C}(p_\pi-p_\pi)$ and $\text{E}=\text{E}(p_\pi-p_\pi)$ interactions for the heavier elements of group 15, are analogous to those used for group 14: incorporation of the respective multiple bond into conjugated systems, protection of the vulnerable bonding region by bulky groups and coordination to transition metals.

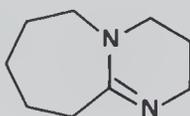
9.4.1 E=C($p_\pi-p_\pi$) Bonds

The heteroarenes $\text{C}_5\text{H}_5\text{E}$ ($\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$) form a complete series of homologous compounds which allows a systematic study of their properties. The parent molecules are prepared by means of the following reaction sequence (Ashe, 1971):



$\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$

DBU = Diazabicycloundecene
(a special deprotonating agent)



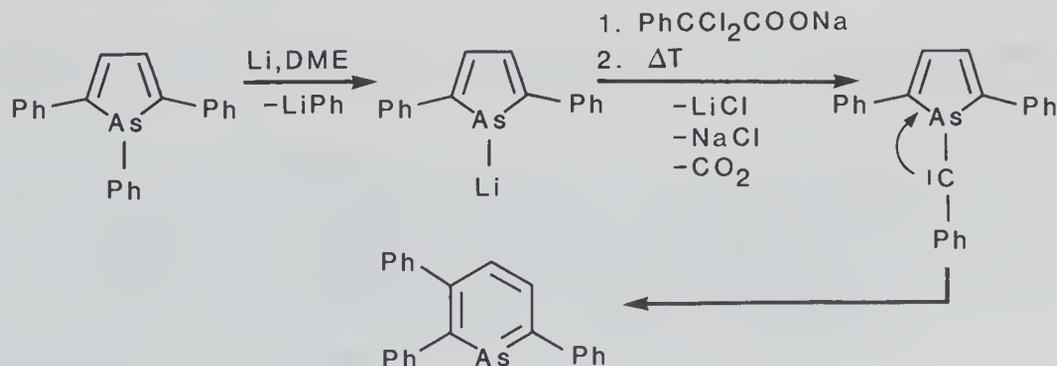
Phosphabenzene (Phosphinine)

Arsabenzene (Arsenine)

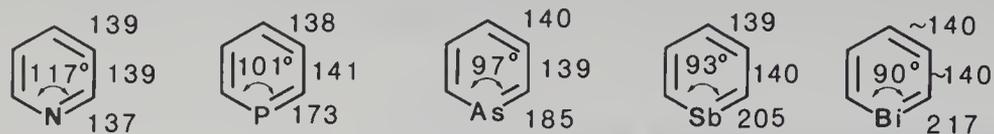
Stibabenzene

Bismabenzene

Substituted derivatives of arsabenzene are also accessible via carbene insertion followed by ring expansion (Märkl, 1972):



With increasing atomic number of E, the distortion of the six-membered rings increases:



According to spectroscopic data, these heterocycles are aromatic. Chemical evidence concerning their aromaticity is unavailable because the monomeric species C_5H_5E ($E = P, As, Sb, Bi$) are prone to oxidation and increasingly thermolabile. The phenyl-substituted derivatives are somewhat more stable. Stability decreases in the order $P > As > Sb > Bi$: arsabenzene is handled comparatively easily, stibabenzene as yet has only been characterized by spectroscopic techniques or as a Diels-Alder adduct:



Stibabenzene and bismabenzene at $0^\circ C$ engage in a monomer/dimer equilibrium:

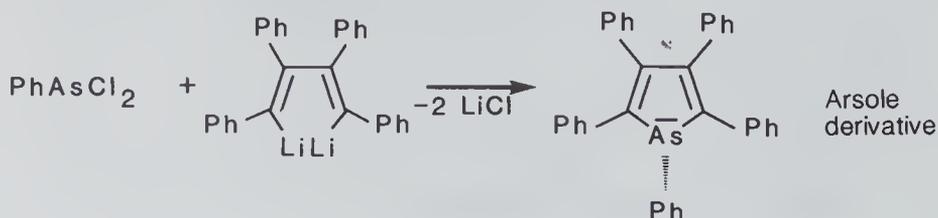


In view of the exceedingly high reactivity of silabenzene (p. 109) the properties of phosphabenzene – e.g. indefinitely stable at room temperature in the absence of air – are surprising. Evidently, $p_\pi-p_\pi$ bonds to phosphorous (>C=PR) are more resistant against addition reactions than $p_\pi-p_\pi$ bonds to silicon (>C=SiR_2). For the fictitious process

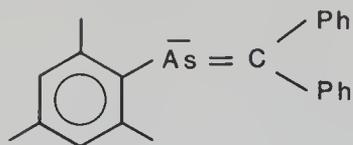


quantum-chemical calculations yield the reaction enthalpy $\Delta H = -92$ kJ/mol (Borden, 1987).

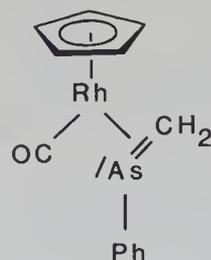
The elements of group 15 have also been incorporated into unsaturated five-membered rings:



Arsaalkenes (alkylidenearsanes) with isolated $\text{As}=\text{C}(p_\pi-p_\pi)$ bonds are stable as monomers only if sterically protected or coordinated to a transition metal:

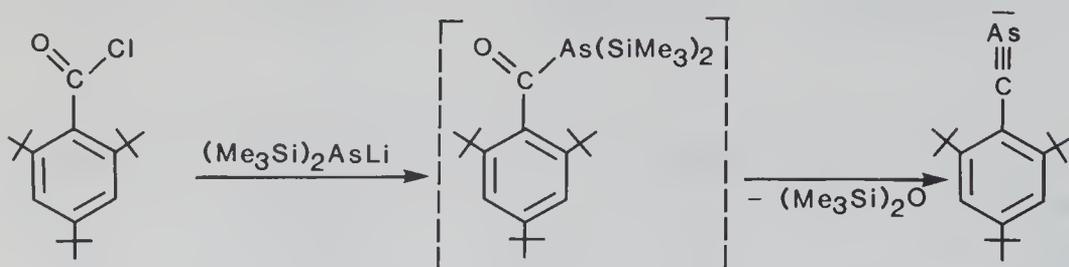


F. Bickelhaupt (1979)

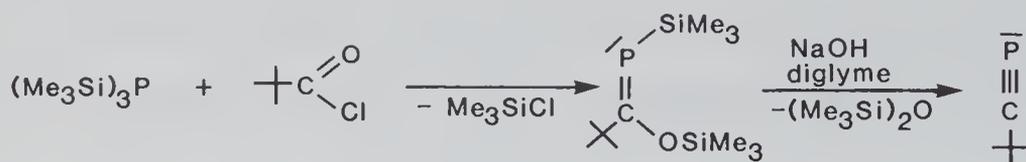


H. Werner (1984)

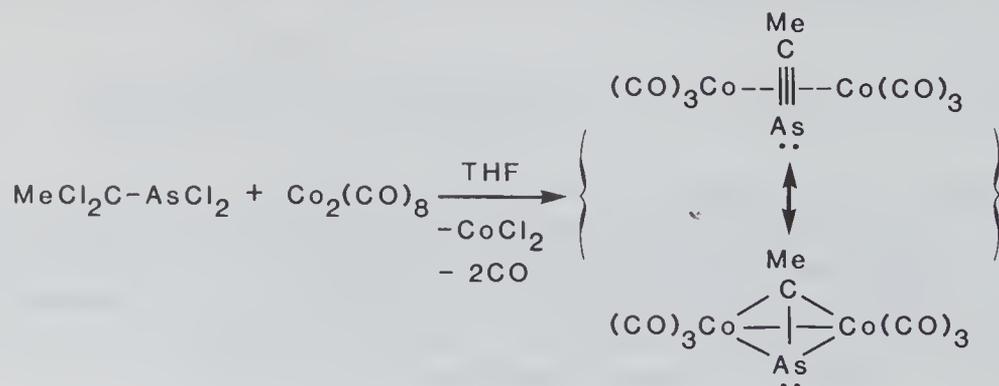
Arsaalkynes (alkylidynearsanes) could also be obtained in the presence of bulky substituents or as transition-metal complexes; the first molecule boasting a $-\text{C}\equiv\text{As}$ triple bond was only prepared very recently (Märkl, 1986):



For the sake of completeness, a phosphaethyne, which has been known somewhat longer, should be mentioned (Becker, 1981):



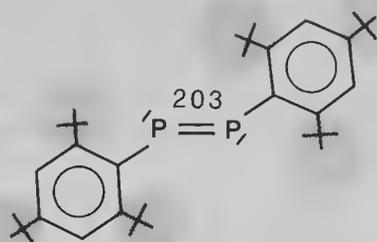
Arsaalkynes can also be generated in the coordination sphere of a transition metal (Seyferth, 1982):



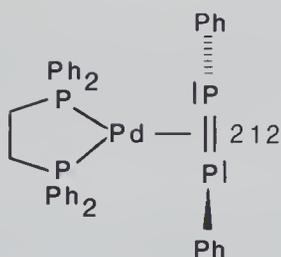
The bonding in the Co_2CA s core resembles the situation in transition-metal carbonyl complexes with bridging alkyne ligands (see chapter 15.2).

9.4.2 E=E ($p_\pi-p_\pi$) Bonds

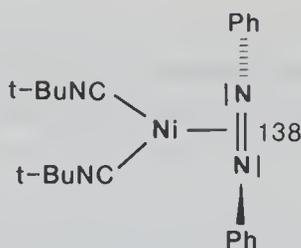
The realization of molecules containing E=E multiple bonds, which are homologues of the azo compounds $\text{RN}=\text{NR}$, also requires steric protection or metal coordination. The element phosphorus led the way:



Bis(aryl)diphosphene, Yoshifuji (1981)
compare P_4 : $d(\text{P}-\text{P}) = 223 \text{ pm}$

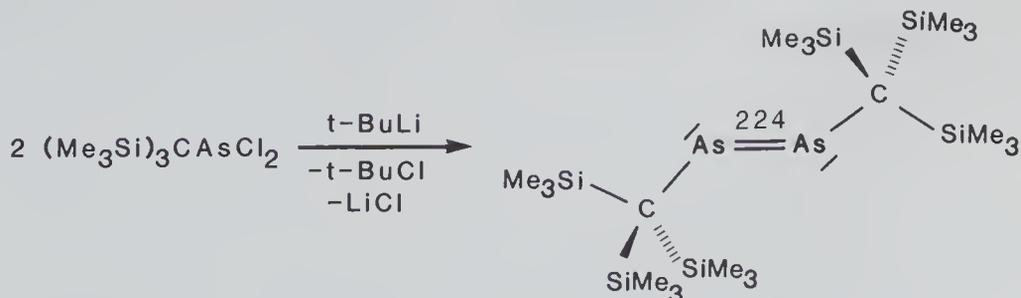


Diphosphene π -complex (Chatt, 1982)



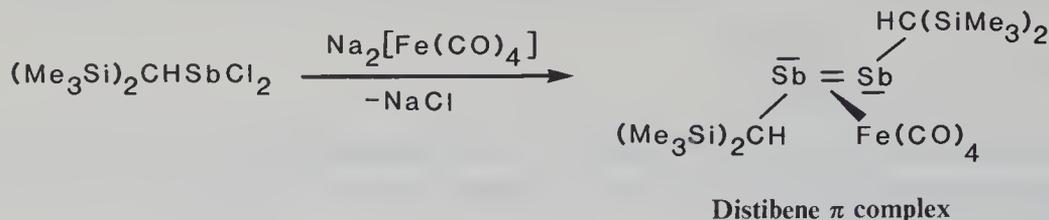
compare: *Diazene π -complex* (Ibers, 1972)

Recently, molecules possessing $-\text{As}=\text{As}-$ and $-\text{Sb}=\text{Sb}-$ double bonds have been reported (Cowley, 1985):



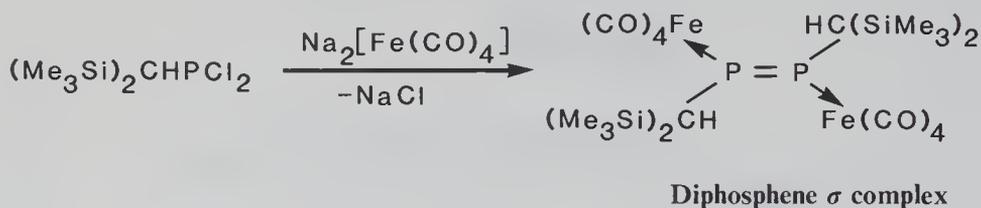
Bis[tris(trimethylsilyl)methyl]diarsene
compare As_4 : $d(\text{As}-\text{As}) = 245 \text{ pm}$

As of yet, stabilization of $-\text{Sb}=\text{Sb}-$ double bonds demands both types of protective measure (Cowley, 1985):



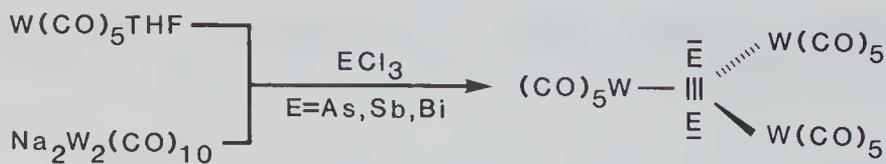
Bonding in the Sb_2Fe segment can be described in analogy to the interaction of olefins with transition metals. In this way, the double bond character of the $\text{Sb}=\text{Sb}$ bond is partially reduced (see pp. 257–258).

If instead of the stibane, the analogous phosphane is used, a product is obtained in which the $\text{Fe}(\text{CO})_4$ -fragments form σ -bonds to both phosphorus atoms (Power, 1983):



This disparate behavior is typical: lone pairs at phosphorus possess higher p -character and therefore more pronounced σ -donor properties than lone pairs at the heavier atoms of group 15, which are almost pure s -electrons [compare the decreasing Brønsted basicity in the series $\text{NH}_3 \gg \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$].

Species E_2 with an $\text{E}\equiv\text{E}$ triple bond contain no further groups – they are not organometallics. In the context of this section it is remarkable, however, that molecules E_2 ($\text{E} = \text{As}, \text{Sb}, \text{Bi}$) which contrary to N_2 are unstable, can be attached to metal carbonyl fragments (Huttner, 1982):



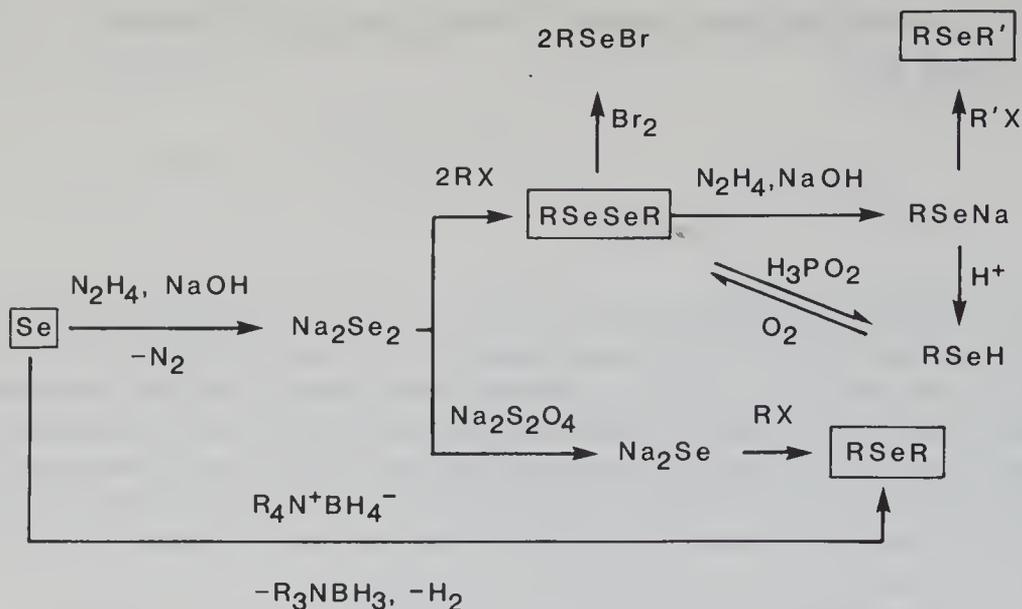
10 Organoelement compounds of Selenium and Tellurium (Group 16)

Organometallic chemistry of group 16 is confined to the elements selenium and tellurium, since oxygen and sulfur are typical non-metals, and the strong α -radiation of the nucleus $^{210}_{84}\text{Po}$ would rapidly destroy an organic ligand sphere. Since the discovery that organoselenium oxides readily undergo *syn*-eliminations (Reich, Sharpless, 1973), selenium organyls have gained considerable importance in organic synthesis. From the coordination chemists point of view, the stabilization of highly reactive molecules like selenoformaldehyde ($\text{H}_2\text{C}=\text{Se}$) or tellurocarbonyl ($\text{C}\equiv\text{Te}$) in transition-metal complexes is of interest (p. 238, 272). Another impetus was provided by the observation that the organic radical cation salt bis(tetramethyl-tetraselenafulvalene)perchlorate at 1.5 K changes from a metallic into a superconducting state (Bechgaard, 1981).

Very recently, thin layers of cadmium telluride CdTe have been produced from mixtures of $(\text{CH}_3)_2\text{Cd}$ and $(\text{C}_2\text{H}_5)_2\text{Te}$ by means of metal organic chemical vapor deposition (MOCVD). These layers, grown by photoepitaxy, show considerable promise as semiconducting materials in electronic devices (Irvine, 1987 R).

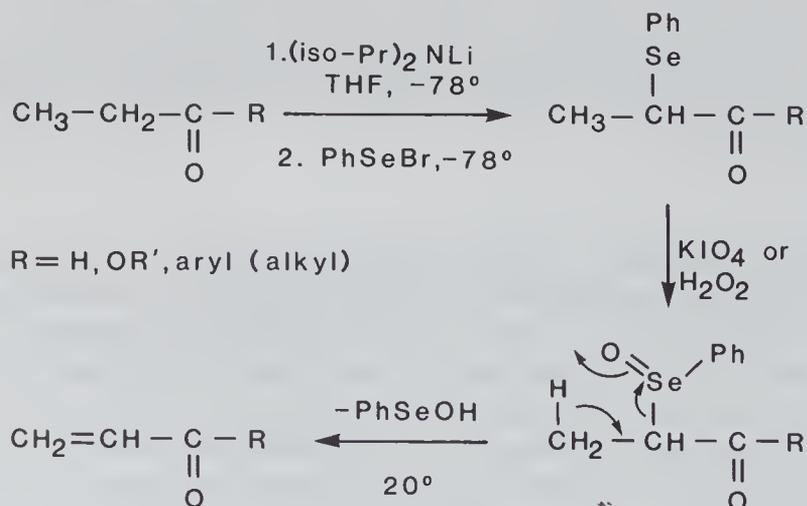
*Contrary to sulfur, selenium offers an isotope which is well-suited for NMR spectroscopy: ^{77}Se (7.5%, $I = 1/2$) features a receptivity which exceeds that of ^{13}C by a factor of three and carries no quadrupole moment. Chemical shifts δ in ^{77}Se -NMR spectra of selenium organyls cover a range of 2500 ppm, which is six times the range pertinent to ^{13}C -NMR. As expected, the values of the coupling constants $^1J(^{77}\text{Se}, ^{13}\text{C})$ correlate with the *s* character of the Se – C bond [Example: $\text{MeSe} - \text{CH}_2\text{CH}_2\text{Ph}$ 62 Hz, $\text{MeSe} - \text{CH} = \text{CHPh}$ 115 Hz, $\text{MeSe} - \text{C}\equiv\text{CPh}$ 187 Hz].*

Organoselenium compounds in their chemical behavior bear strong resemblance to organosulfur compounds. Synthetically important reactions for selenoorganyls usually proceed under milder conditions, a fact which is relevant in natural-product transformations. Compared to sulfur, selenium prefers lower oxidation states. Hence, organoselenium chemistry is dominated by the oxidation states Se^{II} and, to a lesser extent, Se^{IV} . In fact, many important reactions of organoselenium compounds are driven by the elimination of an organoselenium^{II} species from a selenium^{IV} precursor. Selenoles RSeH are more acidic than thiols RSH , yet selenides RSe^- are more nucleophilic than sulfides RS^- . Selenyl halides RSeX are more electrophilic than the corresponding sulfenyl halides RSX . As starting materials for many conversions, organoselenides (organoselenanes) R_2Se and organodiselenides (organodiselenanes) RSeSeR are employed; they are obtained as follows:



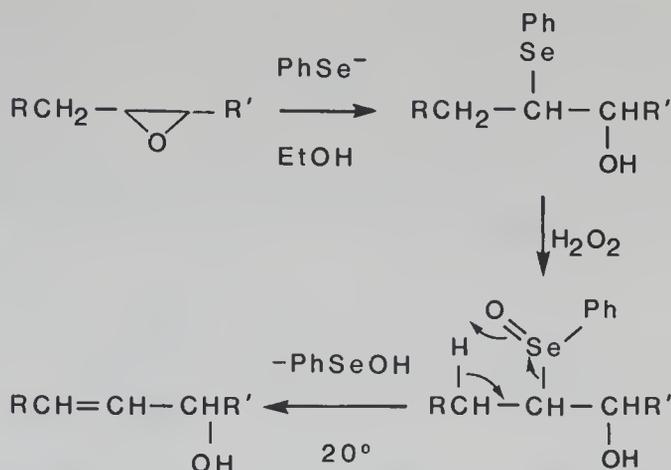
From RSeR and RSeSeR , respectively, a large variety of oxo-, hydroxo- and halo-organoselenium compounds can be prepared. Only a few examples are given here, which illustrate the most popular applications of selenium organyls in organic synthesis:

- β -Ketoselenium oxides via **syn-elimination of RSeOH** form α, β -unsaturated carbonyl compounds (Reich, Sharpless, 1973):



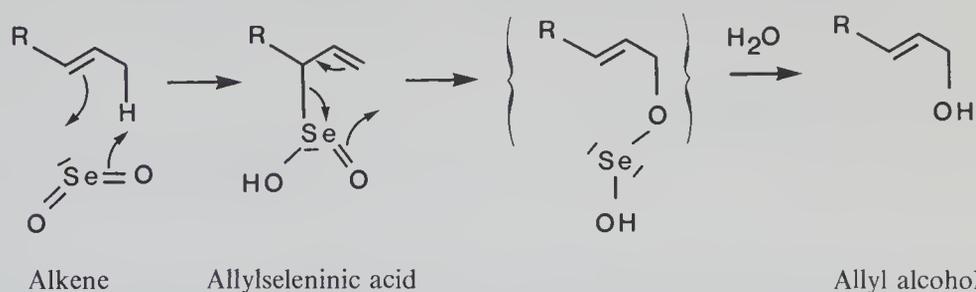
This is probably the mildest method for the **preparation of enones** from aldehydes, ketones or esters.

- In a related fashion, the conversion of **epoxides into allyl alcohols** is achieved:

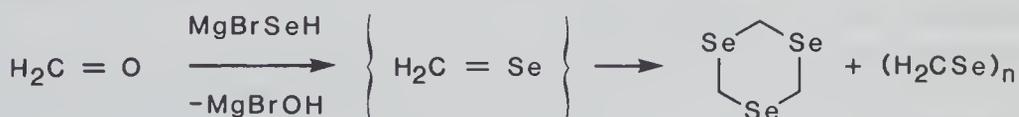


This reaction sequence may serve to regenerate a C=C double bond which was protected as an epoxide.

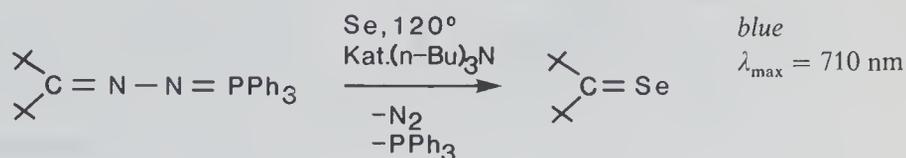
- The proven **oxidation of alkenes** to allyl alcohols by means of **selenium dioxide** is also thought to proceed via organoselenium intermediates (Sharpless, 1973):



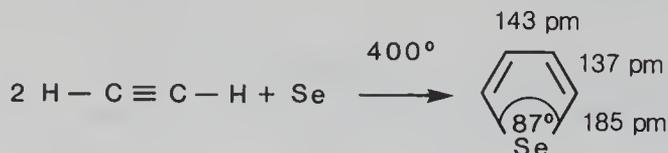
Of more academic interest is the question as to the existence of $p_\pi - p_\pi$ bonds between carbon and selenium or tellurium, respectively. Monosubstituted selenocarbonyl compounds oligomerize, whereby the >C=Se double bond is eliminated. Example (Mortillaro, 1965):



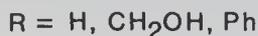
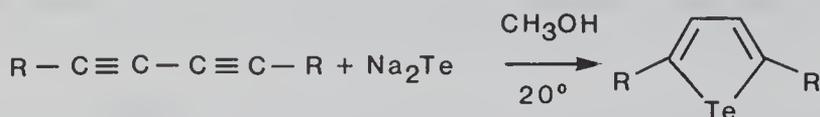
A selenoketone (selenone) with two bulky substituents was shown to be stable as a monomer, however (D. H. R. Barton, 1975):



Selenocarbonyl $C\equiv Se$, which is formed from CSe_2 in a high frequency discharge, polymerizes at temperatures as low as $-160^\circ C$; it can only be identified from the products of trapping reactions (Steudel, 1967) or as a ligand in transition-metal complexes (p. 238). In this context, the relative stability of monomeric CSe_2 is noteworthy. The propensity of the group 16 elements to engage in $p_\pi - p_\pi$ bonding to carbon should also be apparent from the extent of conjugation and the derived molecular properties of the heterocyclopentadienes C_4H_4E ($E = Se, Te$). **Selenophene** (Peel, 1928) and **Tellurophene** (Mack, 1966) are fairly easily accessible and well-characterized compounds:



The structural parameters of selenophene stem from the microwave spectrum (Magdesiava, 1969). The $Se-C$ bond length should be compared with the length of a genuine single bond, $d(Se-C) = 193 \text{ pm}$.



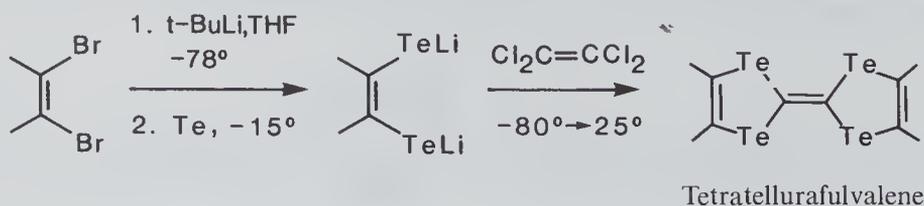
Cyclohydrotelluration

Judging from chemical evidence (electrophilic substitution dominates over addition) as well as from physical criteria (bond distances, $^1\text{H-NMR}$ spectra, diamagnetic susceptibility) aromatic character must be ascribed to selenophene and tellurophene. The following **order of decreasing aromaticity** has been derived (Marino, 1974):



The aromatic nature of selenophene C_4H_4Se contrasts with the diolefin character of isoelectronic arsole C_4H_4AsH (p. 163).

Two selenium atoms per five-membered ring are contained in the tetraselenafulvalenes which have already been mentioned with regard to their interesting electrical properties. Fairly recently, the corresponding tellurium compounds have also been prepared (Wudl, 1982):



Organoselenium Compounds in vivo

For higher organisms, selenium is an essential trace element (Schwarz, 1957); an Se-free diet leads to malfunction of the liver and to hemolytic processes. Since selenium has been detected in the retina, it is likely that this element also plays an important role in vision. The human organism stores 10–15 mg of selenium; a daily uptake exceeding 1 μg Se/g food is toxic but an uptake of less than 0.2 μg Se/g food causes a deficiency syndrome. Selenium plays its biochemical role as a component of glutathione peroxidase, an enzyme which is responsible for the protection of essential SH-groups and for the decomposition of peroxides, thereby acting as an **antioxidant** (Rotruck, 1973). The selenium-containing section of glutathione peroxidase is the amino acid selenocysteine $(\text{HSe})\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ (Stadtman, 1984). Other selenium organyls detected in living organisms include selenomethionine $\text{MeS}(\text{CH}_2)\text{CH}(\text{NH}_2)\text{COOH}$, trimethylselenonium salts $\text{Me}_3\text{Se}^+ \text{X}^-$, and dimethylselenide Me_2Se , a component with a garlic-like odor in the breath of organisms which suffer from selenium poisoning. The formation of Me_2Se from inorganic selenium compounds apparently aids in detoxification: Me_2Se is less toxic than the oxoanions SeO_3^{2-} (selenite) and SeO_4^{2-} (selenate) or elemental Se. This contrasts with mercury, where the problems of environmental contamination are aggravated by biomethylation (p. 55).

11 Organometallics of Copper, Silver and Gold (Group 11)

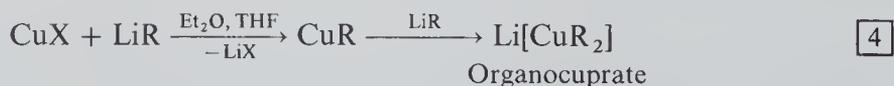
The metals copper, silver and gold clearly belong to the transition elements. The discussion of their chemistry at this particular point follows an established tradition in that it smoothly leads into the organometallic chemistry of the *d*-block elements (Chapters 12–17).

11.1 Copper- and Silver Organyls

The interest which chemists took in organocopper compounds was hitherto mainly confined to their use in organic synthesis. Points of departure were the study of reactions of copper organyls with organic halides (Gilman, 1936) and the observation that Cu^{I} ions catalyze the 1,4-addition of Grignard reagents to conjugated enones (Kharash, 1941). The intermediacy of organocopper compounds in these additions was demonstrated by House in 1966. Yet, the isolation of pure organocopper species and their characterization by diffraction methods was only achieved during the last decade. Problems arise from the high sensitivity of binary molecules MR ($\text{M} = \text{Cu}, \text{Ag}$) to H_2O and O_2 and from their lack of solubility in inert solvents. An aggravating factor is the tendency to form non-stoichiometric adducts like $[(\text{CuR})_x \cdot (\text{CuBr})_y]$ or solvates of varying composition, depending on the method of preparation. The organometallic chemistry of **Cu** and **Ag** is exclusively that of the **oxidation state + I**. In this section, only σ -organyls will be treated; π -complexes of the elements **Cu**, **Ag** and **Au** are deferred to sections which review the respective ligands (Chapters 12–17).

PREPARATION

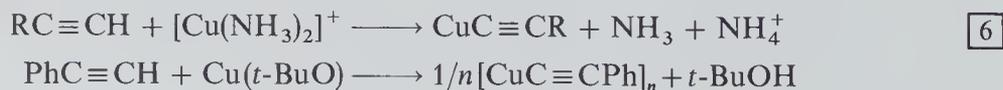
Copper Organyls



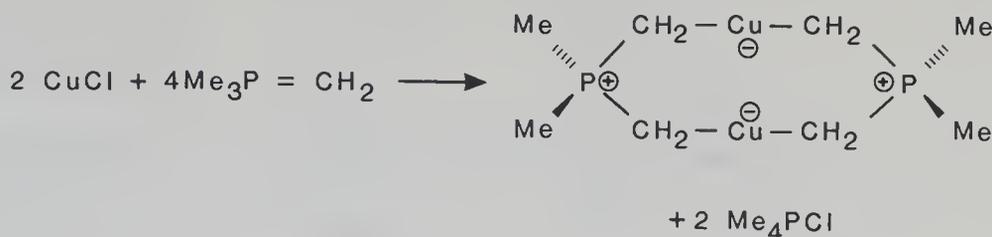
The usual designation “*organocuprate*” for compounds of the composition MCuR_2 is misleading because – contrary to experimental evidence (p. 175) – it suggests an ionic structure $\text{M}^+[\text{CuR}_2]^-$.



A good source for CuX is the compound $[(n\text{-Bu}_3\text{P})\text{CuI}]_4$. Alkynylcopper compounds are prepared by means of metallation:



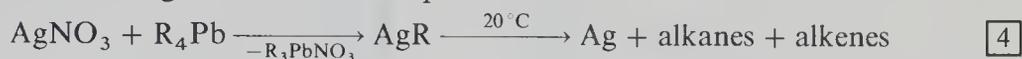
Copper acetylides (copper alkynyls) are inert towards hydrolysis, their association in the solid state is a result of π -complexation of copper to neighboring $-C\equiv CR$ units (p. 208). A particularly stable, sublimable organocopper compound is formed from Cu^I chloride and (trimethyl)methylenephosphorane via transylidation (Schmidbaur, 1973):



The inert character of this complex, containing bridging phosphoniodylid ligands, may be traced back to the absence of β -hydrogen atoms (cf. p. 199).

Silver Organyls

Compared to organocopper compounds, silver organyls are considerably less stable, decomposition setting in at ambient temperature.



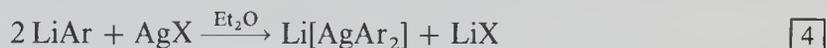
The corresponding perfluoroalkyl derivatives $R_F Ag$ are somewhat more stable (cf. p. 204):



Pure phenylsilver was first obtained in 1972; diphenylzinc proved to be a convenient arylating agent here (van der Kerk, 1977):



In the presence of an excess of $LiAr$, **organoargentates** are formed:

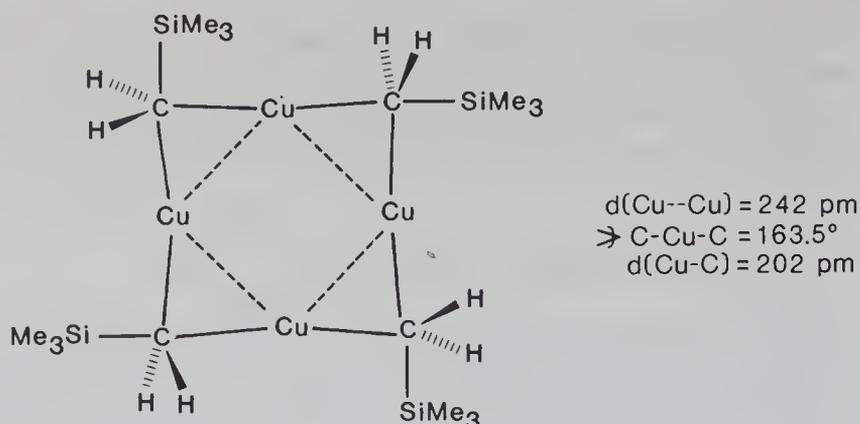


Silver alkynyls can be prepared via metallation in the presence of an auxiliary base:

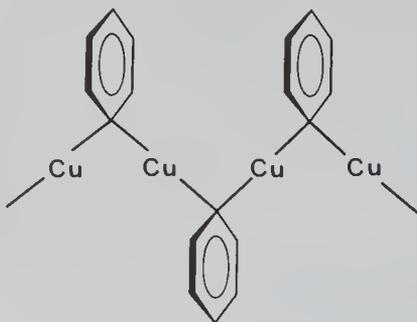


PROPERTIES OF SELECTED Cu- AND Ag ORGANYLs

Compound	Decomposition/ $^\circ C$	Degree of Association
CuMe	> -15 (explosive)	
AgMe	-50	
CuPh	100	polymer
CuC ₆ F ₅	220	tetramer
AgPh	74	polymer
CuCH ₂ SiMe ₃	78 (mp.)	tetramer
CuC \equiv CR	200	polymer
AgC \equiv CR	100–200	polymer
Li[CuMe ₂]		dimer

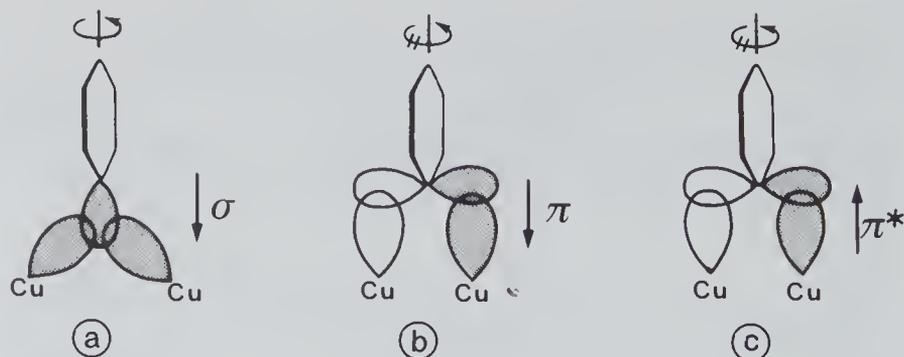


Structure of $[\text{CuCH}_2\text{SiMe}_3]_4$: Cu^1 adopts its preferred coordination number 2 (linear). For the tetramer, this leads to a planar Cu_4 ring. The $\text{Cu}-\text{C}-\text{Cu}$ bridges may be regarded as $2e3c$ bonds which arise from the interaction of $\text{C}(sp^3)$ - with $\text{Cu}(sp)$ hybrid orbitals (Lappert, 1977). Compare: $d(\text{Cu}-\text{Cu}) = 256 \text{ pm}$ (bulk Cu); $r(\text{Cu}^+) = 96 \text{ pm}$ (ionic radius).



$[\text{CuPh}]_x$, which has not yet been obtained as single crystals, is assumed also to be associated by means of $\text{Cu}-\text{C}-\text{Cu}$ $2e3c$ bridges.

Bonding in the $\text{Cu}-\text{C}-\text{Cu}$ bridge probably resembles the situation discussed for Al_2Ph_6 (p. 79); the access to $\text{Cu}(3d)$ electrons may, however, render additional interactions possible:



$\text{Cu}-\text{Cu}$ interaction:
Rotational barrier for
the phenyl ring:

bonding

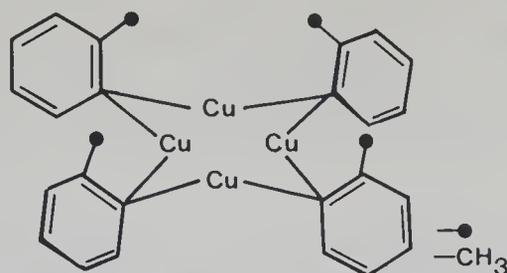
no

antibonding

yes

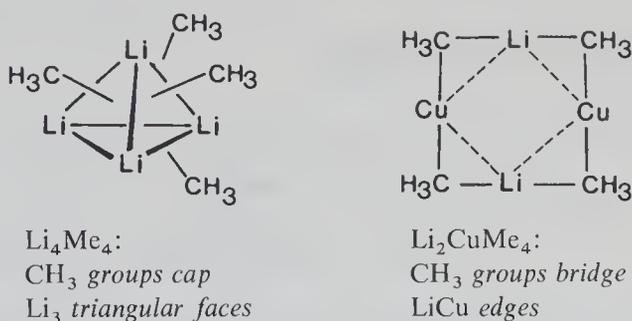
antibonding

yes

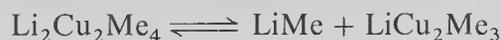


For $[(2\text{-tolyl})\text{Cu}]_4$ $^1\text{H-NMR}$ spectroscopy at low temperature reveals the presence of stereoisomers. Therefore, a barrier to rotation around the $\text{Cu}-\text{C}$ axis must be assumed. This finding argues for contributions of the types (b) and (c) to $\text{Cu}-\text{C}-\text{Cu}$ bridge bonding (Noltes, 1979).

The dimeric nature of the organocuprates, $[\text{Li}(\text{CuMe}_2)]_2 \equiv \text{Li}_2\text{Cu}_2\text{Me}_4$, would lead one to assume that their structure, in analogy to Li_4Me_4 , is tetrahedral. It is highly likely, however, that a Li_2Cu_2 ring with a trans disposition of the metals is formed instead (R. G. Pearson, 1976):



In solution, $^7\text{Li-NMR}$ evidence points to an equilibrium of three species (Lipshutz, 1985):



APPLICATION OF COPPER ORGANYLs IN ORGANIC SYNTHESIS

① Nucleophilic Substitution ($\text{S}_{\text{N}}2$) at Organic Halides (Cross coupling)

The organocuprate $\text{Li}[\text{CuR}_2]$ (Gilman reagent, 1952) is prepared in situ and converted into unsymmetrical coupling products:

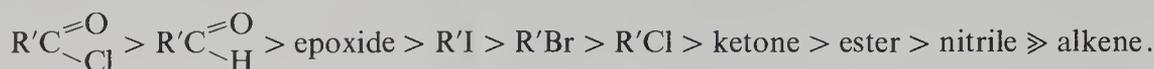


R = Alkyl, Alkenyl, Aryl, Heteroaryl

R' = Acyl, Alkyl, Alkenyl, Aryl, Heteroaryl

Lithium organocuprates $\text{Li}[\text{CuR}_2]$ are **less nucleophilic** than the parent lithium organyls LiR ; therefore, they react **more selectively** with organic substrates. In general, the follow-

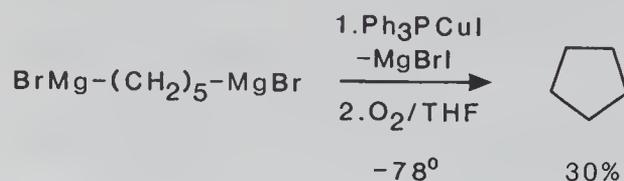
ing order of decreasing reactivity towards $\text{Li}[\text{CuR}_2]$ is observed:



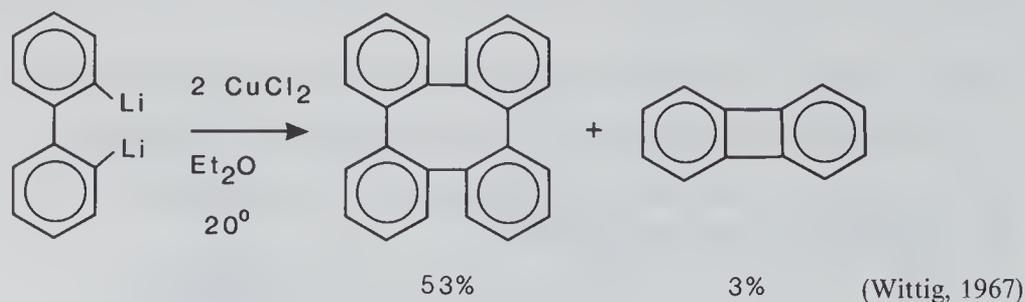
Competing reactions like metal/halogen exchange or elimination play a diminished role for $\text{Li}[\text{CuR}_2]$ as compared to LiR . During the formation of the incipient C–C bond, the configuration of the attacking group R is retained, that of the group R' in the substrate R'X is inverted. If R'X is an alkenyl halide, its configuration is preserved during the substitution:



② Oxidative Coupling via Copper Organyls



An important application of oxidative coupling is the preparation of **symmetrical bisaryls** and of **conjugated diynes**:

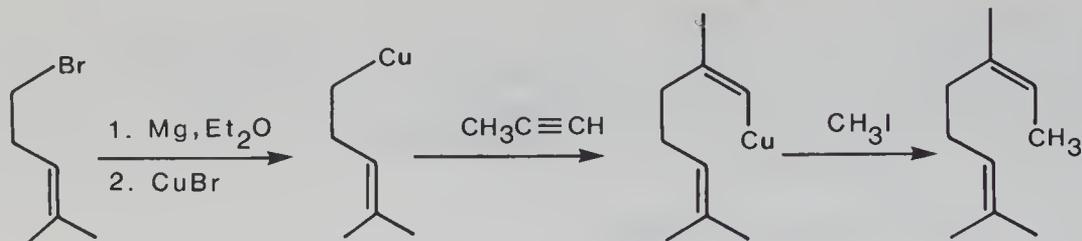


In this variant the use of Cu^{II} obviates the introduction of an additional oxidizing agent.

The following example portrays the synthesis of [18]annulene, a key compound in discussing the concept of aromaticity (Sondheimer, 1962):

With regard to yield and stereoselectivity, the stoichiometric use of organocuprates is generally superior to the variant which operates with Grignard reagents in the presence of catalytic quantities of $\text{Cu}^{\text{I,II}}$ salts (p. 172).

⑤ Addition to Terminal Alkynes (Carbocupration)



This synthesis of a terpene is highly stereospecific (99.9% *syn* addition). The actual organocopper compound here probably is the **heterocuprate** $\text{MgBr}[\text{RCuBr}]$. If lithium is used instead of magnesium, the **homocuprate** $\text{Li}[\text{CuR}_2]$ is formed, which at the terminal alkyne effects metallation rather than addition (Normant, 1976 R).

⑥ Cu^{I} and Ag^{I} also play an important role in **transition-metal catalyzed valence isomerizations** (p. 415).

11.2 Gold Organyls

The chemistry of gold is defined by the oxidation states Au^{I} and Au^{III} . Inorganic compounds of $\text{Au}^{\text{I}}(d^{10})$ usually assume the coordination number 2 with a linear geometry and a 14 VE configuration. Less abundant are Au^{I} complexes, possessing the coordination number 3 (trigonal planar, 16 VE) or 4 (tetrahedral, 18 VE). $\text{Au}^{\text{III}}(d^8)$ complexes are four-coordinate (square planar, 16 VE), the $\text{Au}(6p_z)$ orbital remaining unoccupied. For purely inorganic complexes of Au^{III} , the coordination numbers 5 and 6 are also encountered.

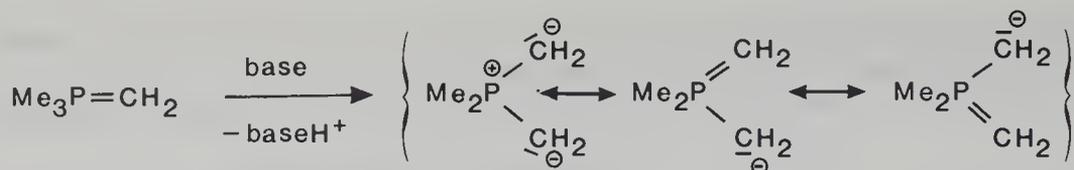
In organogold chemistry, the cases Au^{I} , **coordination number 2** (linear) and Au^{III} , **coordination number 4** (square planar) are typical. In this section, only gold σ -organyls will be discussed.

Au^{I} Organyls

Simple binary compounds AuR are as yet unknown; Au^{I} organyls are, however, obtained as **adducts** LAuR ($\text{L} = \text{PR}_3, \text{RNC}$) and as **organoaurates** $\text{M}[\text{AuR}_2]$, the latter exhibiting low stability (Kochi, 1973):



Organoaurates become significantly more stable if the cation M^+ is converted into a complex ion (Tobias, 1976): $[\text{Li}(\text{PMDT})][\text{AuMe}_2]$ only decomposes at 120°C (PMDT

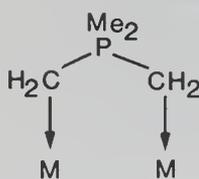


If the ylid itself serves as the base, the proton transfer is termed **transylation**:

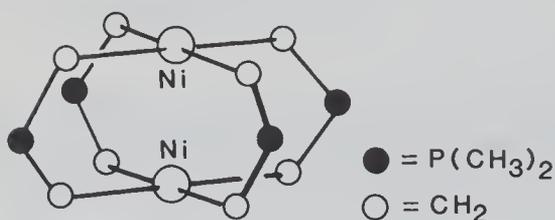
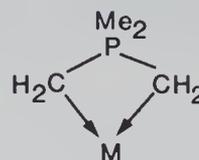


Coordination modes of phosphoniodiylids:

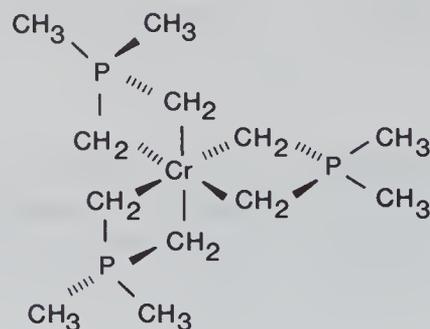
bridging



chelating



Decomposition at 87 °C



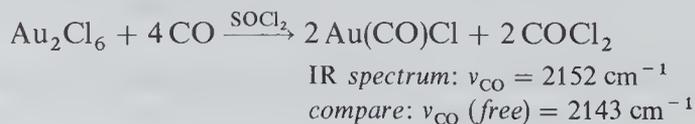
Sublimation at 30 °C (HV)

The bridging variant leads to σ -organometallics, especially of the coinage metals (Cu, Ag, Au), which display surprisingly high stability.

Au^I-Carbonyl Complexes

Binary metal carbonyls $\text{Au}_n(\text{CO})_n$ are unstable under ambient conditions. The compounds $\text{Au}(\text{CO})$ and $\text{Au}(\text{CO})_2$, which have been obtained by means of metal-atom ligand-vapor cocondensation (p. 255), decompose above 20 K.

Ternary carbonyl-gold halides are accessible, however:



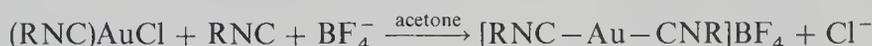
The position of the stretching band ν_{CO} suggests that the backbonding contribution $\text{Au} \rightarrow \text{CO}$ for $\text{Au}(\text{CO})\text{Cl}$ is insignificant (Calderazzo, 1977). This is what would be expected for an $\text{M}(d^{10})$ complex (see p. 190).

Au^{I} -Isocyanide and Au^{I} -Carbene Complexes

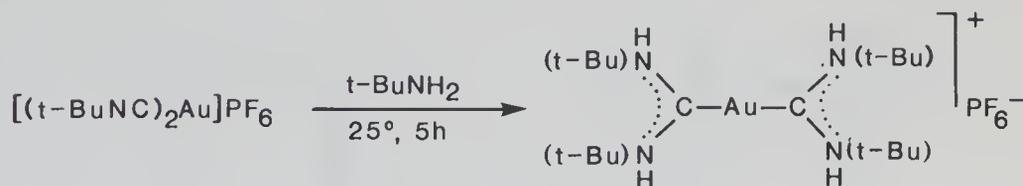
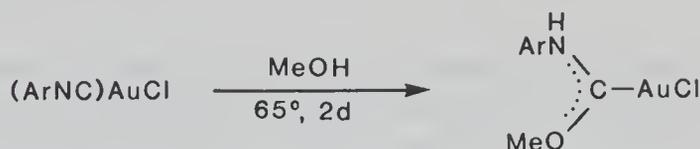
Isocyanides RNC as ligands at gold have more to offer than the related ligand CO (cf. p. 240). A considerable number of Au^{I} -isocyanide complexes are known; these species can be converted into carbene complexes. Neutral $(\text{RNC})\text{Au}^{\text{I}}$ species are best obtained via substitution of dimethylsulfide by isocyanide (Bonati, 1973):



Bis(isocyanide)gold^I cations can be isolated as salts with non-coordinating anions:



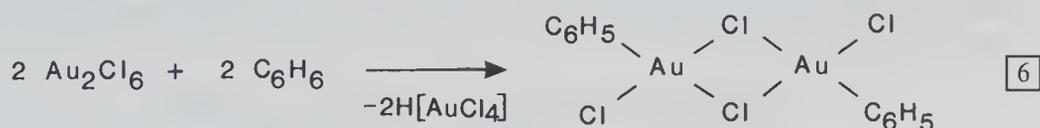
Conversion into (carbene)gold^I complexes is effected by the addition of molecules bearing OH - or NH_2 groups (cf. p. 240):



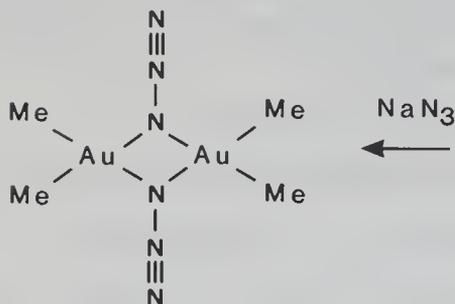
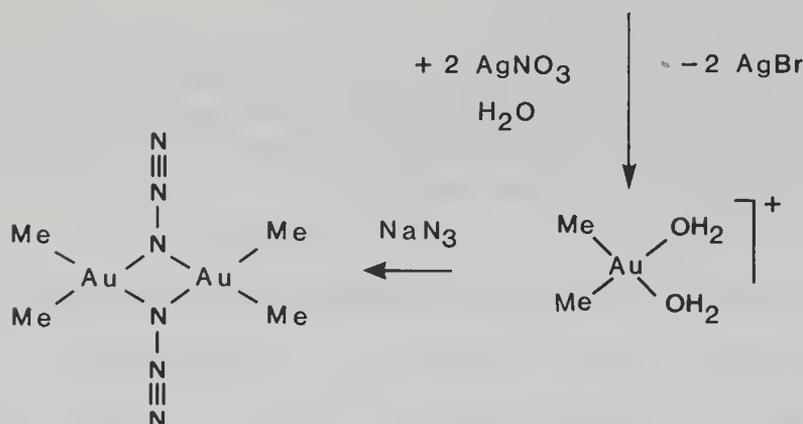
(McCleverty, 1973)

Au^{III} Organyls

A traditional way of access to organogold^{III} compounds is the **auration** reaction (Kharash, 1931):

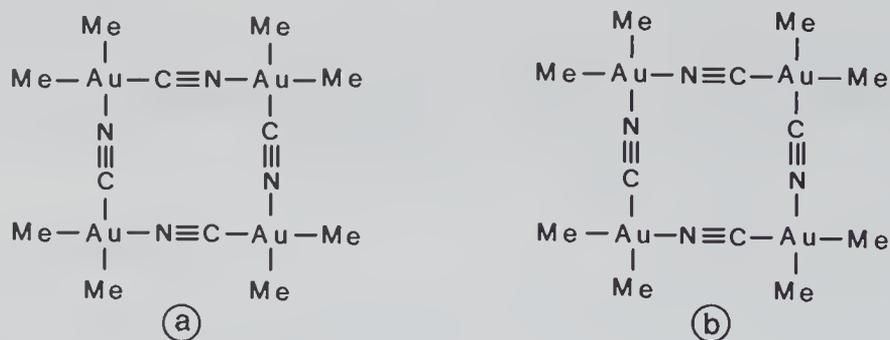


In these binuclear complexes, gold has a square planar environment.

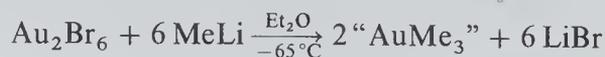


The unit
 $[\text{Me}_2\text{Au}(\text{H}_2\text{O})_2]^+$
 is surprisingly stable.

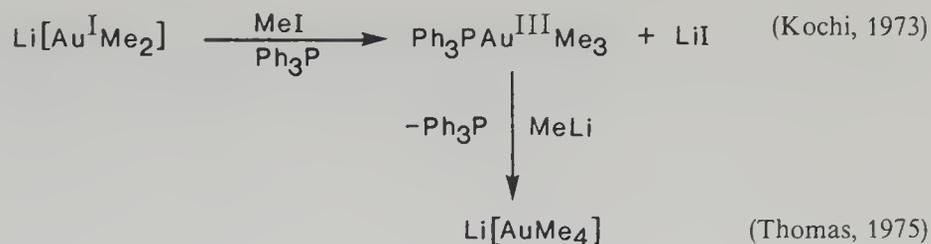
Bis(alkyl)gold^{III} cyanides – as opposed to bis(alkyl)gold^{III} azides – are tetrameric since the ligand $\text{C}\equiv\text{N}^-$ only forms linear bridges. In the ¹H-NMR spectrum, four signals are observed instead of the two anticipated signals for the CH_3 protons. Obviously, in addition to form (a) (identical orientation of the CN bridges) the disordered form (b) is also present:



The inclination of Au^{III} to participate in $\text{Au}-\text{C}-\text{Au}$ ($2e\ 3c$) bonding appears to be small; hence, rather than through dimerization to Au_2Me_6 (compare: Al_2Me_6), AuMe_3 prefers to achieve coordination number four with the help of additional ligands. The ill-characterized compound trimethylgold, which was obtained in solution by Gilman in 1948, decomposes at $T > -40^\circ\text{C}$:



The triphenylphosphane adduct $\text{Ph}_3\text{PAuMe}_3$, prepared via oxidative addition of MeI to $\text{Li}[\text{AuMe}_2]$, is stable up to 115°C (mp, decomp.), however:



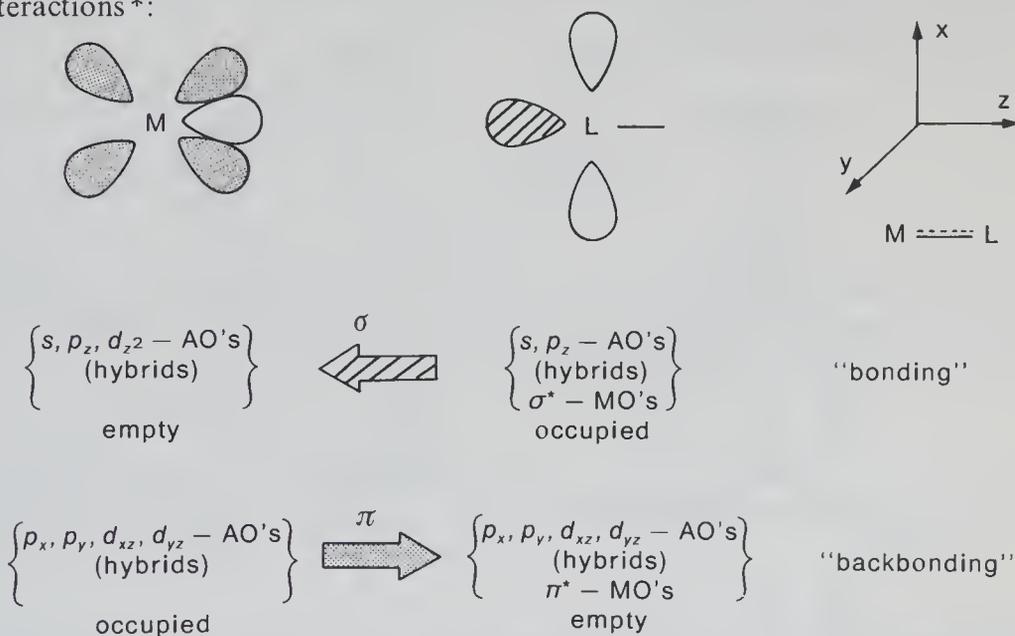
The expulsion of the ligand Ph_3P upon the addition of methyllithium implies that the tetramethylaurate^{III} ion is coordinatively saturated with a 16 VE configuration. This is a typical feature of $\text{M}(\text{d}^8)$ complexes of the late transition metals (p. 189) which we will encounter several times in the following discussion of organotransition-metal chemistry.

ORGANOMETALLIC COMPOUNDS OF THE TRANSITION ELEMENTS

The full variety of organometallic chemistry presents itself in the realm of transition metals. Contributing factors include:

- *extended possibilities for the formation of metal-carbon bonds. While it is rare for main-group elements to use nd orbitals in addition to ns and np orbitals in chemical bonding, for transition metals, the $(n - 1) d$, ns and np orbitals must all be regarded as **regular valence orbitals**. Partial occupation of these orbitals gives transition metals both electron-donor and electron-acceptor properties, which in conjunction with donor/acceptor ligands like CO, isonitriles, carbenes, olefins and arenes allows for considerable variation of the metal-ligand bond order $M \equiv L$ (**σ -donor/ π -acceptor synergism**). This principle is prevalent in large areas of transition-metal organometallic chemistry.*

Interactions*:



- *various forms of **metal-metal multiple bonding** with or without additional bridging ligands. This leads to the formation of cluster compounds which are of interest from a structural as well as from a theoretical point of view (see Chapter 16).*
- *the ability to **change the coordination number**. Together with the lability of metal-carbon σ -bonds this phenomenon offers possibilities for organometallic catalysis (see Chapter 17).*

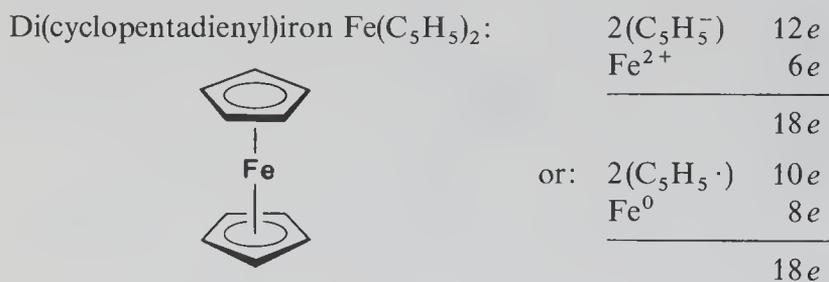
* The shaded areas in this drawing indicate orbital occupation rather than phase.

12 The 18 Valence Electron (18 VE) Rule

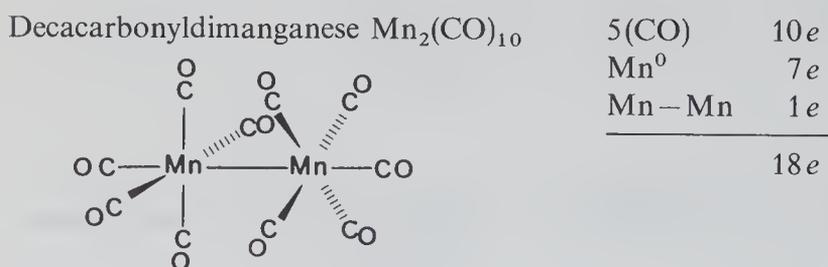
The 18 electron rule and the concept of σ -donor/ π -acceptor synergism (“bonding and backbonding”) represent the most rudimentary basis for discussing structure and bonding in organotransition-metal compounds.

The 18 electron rule (Sidgwick, 1927) is based on the valence bond (VB) formalism of localized metal-ligand bonds; it states that thermodynamically stable transition-metal organometallics are formed when the sum of the metal d electrons plus the electrons conventionally regarded as being supplied by the ligands equals 18. In this way, the metal formally attains the electron configuration of the next higher noble gas [18 VE rule, also paraphrased as “inert gas rule”, “effective atomic number (EAN) rule”]. When applying the 18 VE rule the following conventions should be considered:

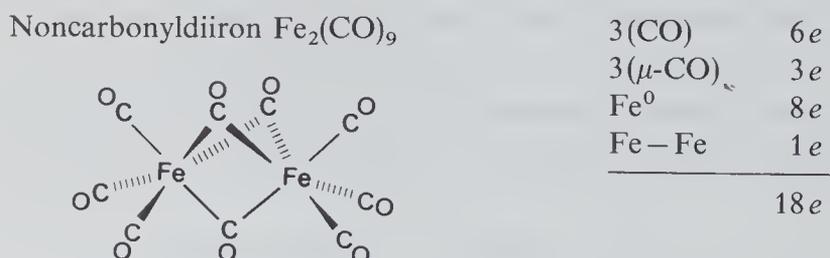
- ① The intramolecular partitioning of the electrons has to ensure that the total complex charge remains unchanged:



- ② A metal-metal bond contributes *one* electron to the count on each metal:



- ③ The electron pair of a bridging carbonyl ligand donates *one electron to each* of the bridged metals:



In the following table, ligands commonly encountered in organotransition-metal chemistry are listed together with the respective numbers of electrons relevant to the application of the 18 VE rule:

Neutral	Positive	Negative	Ligand L
1	0	2	alkyl, aryl, hydride, halide (X)
2	—	—	ethylene, monoolefin, CO, phosphane etc.
3	2	4	π -allyl, enyl, cyclopropenyl, NO
4	—	—	diolefin
4	—	6	cyclobutadiene (C_4H_4 or $C_4H_4^{2-}$)
5	—	6	cyclopentadienyl, dienyl
6	—	—	arene, triolefin
7	6	—	tropylium ($C_7H_7^+$)
8	—	10	cyclooctatetraene (C_8H_8 or $C_8H_8^{2-}$)

The 18 VE rule has considerable predictive value in that the composition of many transition-metal complexes may be anticipated from combinations of sets of ligands with transition metals of appropriate *d* electron count. For organometallics of the *f* elements (lanthanides and actinides) this procedure is not applicable (see p. 364).

A perspective view at coordination chemistry (p. 188) suggests a division into three classes:

Class	Number of valence electrons	18 VE rule
I	... 16 17 18 19 ...	not obeyed
II	... 16 17 18	not exceeded
III	18	obeyed

How does the nature of the central atom as well as the ligands determine whether a complex belongs to class I, II or III?

GUIDING PRINCIPLES:

- | | | |
|------------------------|---------------|------------|
| – bonding orbitals | should be | } occupied |
| – nonbonding orbitals | may be | |
| – antibonding orbitals | should not be | |

COMMENTS:

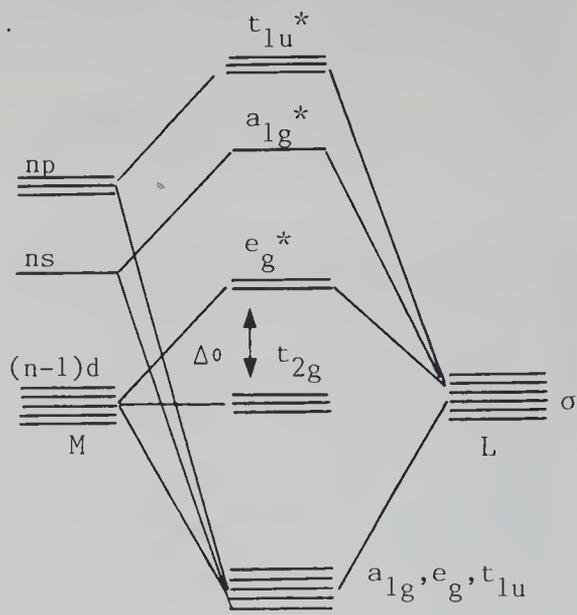
Class I: The splitting Δ_0 is relatively small for 3*d* metals as well as for ligands at the lower end of the spectrochemical series.

- t_{2g} is nonbonding and can be occupied by 0–6 electrons.
- e_g^* is weakly antibonding and can be occupied by 0–4 electrons.

Therefore, 12–22 valence electrons can be accommodated, i.e., the 18 VE rule is not obeyed. Due to their inherently-small splitting Δ_{tet} , tetrahedral complexes also belong to this class.

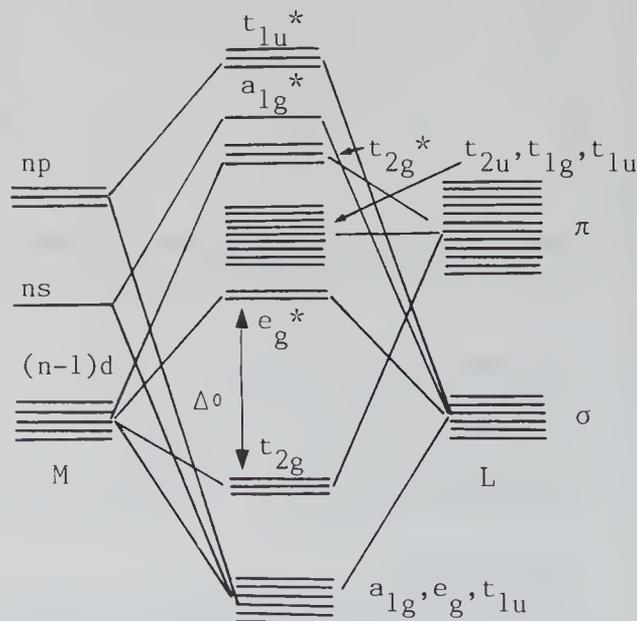
Typical transition-metal complexes and their assignment to classes I–III

Class I	$n(\text{VE}) \cong 18$	
	$n(d)$	$n(\text{VE})$
TiF_6^{2-}	0	12
VCl_6^{2-}	1	13
$\text{V}(\text{C}_2\text{O}_4)_3^{3-}$	2	14
$\text{Cr}(\text{NCS})_6^{3-}$	3	15
$\text{Mn}(\text{CN})_6^{3-}$	4	16
$\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$	5	17
$\text{Co}(\text{NH}_3)_6^{3+}$	6	18
$\text{Co}(\text{H}_2\text{O})_6^{2+}$	7	19
$\text{Ni}(\text{en})_3^{2+}$	8	20
$\text{Cu}(\text{NH}_3)_6^{2+}$	9	21
$\text{Zn}(\text{en})_3^{2+}$	10	22



Molecular orbital diagram for an octahedral complex (simplified), σ -bonding only

Class II	$n(\text{VE}) \leq 18$	
	$n(d)$	$n(\text{VE})$
ZrF_6^{2-}	0	12
WCl_6	0	12
WCl_6^-	1	13
WCl_6^{2-}	2	14
TcF_6^{2-}	3	15
OsCl_6^{2-}	4	16
$\text{W}(\text{CN})_8^{3-}$	1	17
$\text{W}(\text{CN})_8^{4-}$	2	18
PtF_6	4	16
PtF_6^-	5	17
PtF_6^{2-}	6	18
PtCl_4^{2-}	8	16



Molecular orbital diagram for an octahedral complex (simplified), σ - and π -bonding

Class III	$n = 18$		
	$n(d)$	$n(L)$	$n(\text{VE})$
$\text{V}(\text{CO})_6^-$	6	12	18
$\text{CpMn}(\text{CO})_3$	7	11	18
$\text{Fe}(\text{CN})_6^{4-}$	6	12	18
$\text{Fe}(\text{PF}_3)_5$	8	10	18
$\text{Fe}(\text{CO})_4^{2-}$	10	8	18
$\text{CH}_3\text{Co}(\text{CO})_4$	9	9	18
$\text{Ni}(\text{CNR})_4$	10	8	18
$\text{Fe}_2(\text{CO})_9$	8	10	18
$[\text{CpCr}(\text{CO})_3]_2$	6	12	18

adapted from P. R. Mitchell, R. V. Parish, *J. Chem. Ed.* 46 (1969) 811.

Class II: Δ_0 is larger for 4*d* and 5*d* metals (especially in high oxidation states), and for σ ligands in the intermediate and upper ranges of the spectrochemical series.

- t_{2g} is essentially nonbonding and can be occupied by 0–6 electrons.
- e_g^* is more strongly antibonding and thus no longer available for occupancy.

Consequently, the valence shell contains 18 VE or less. A similar splitting Δ_0 (t_{2g} , e_g^*) is also observed for complexes of the 3*d* metals with ligands possessing extremely high ligand field strength (e.g. CN^-).

Class III: Δ_0 is largest for ligands at the uppermost end of the spectrochemical series (good π -acceptors like CO, PF_3 , olefins, arenes).

- t_{2g} becomes bonding due to the interaction with π orbitals of the ligands and should be occupied by 6 electrons.
- e_g^* is strongly antibonding and remains empty.

Therefore the 18 VE rule is obeyed, unless steric reasons prevent the attainment of an 18 VE shell [$\text{V}(\text{CO})_6$ (17 VE), WMe_6 (12 VE)].

Organometallic compounds of the transition metals almost exclusively belong to class III.

THE PARTICULAR CASE OF $\text{M}(d^8)$ AND $\text{M}(d^{10})$ COMPLEXES

For elements at the end of the transition series (“late transition metals”) 16- or 14 VE configurations are favored over 18 VE configurations.

Examples:	$\text{M}(d^8)$	
$[\text{Ni}(\text{CN})_4]^{2-}$	16 VE	
$[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$	16 VE	square planar, C.N. 4
$[\text{AuCl}_4]^-$	16 VE	

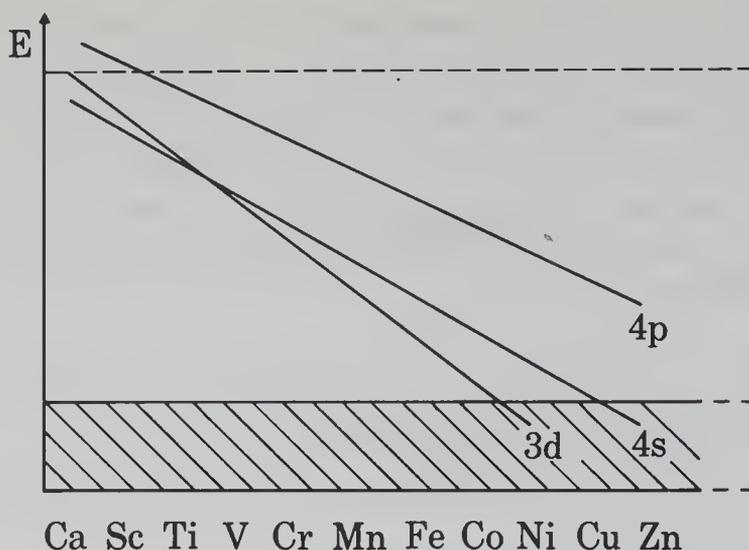
According to the 18 VE rule, a coordination number (C.N.) of 5 would have been expected. This is found for “earlier transition metals” with a d^8 electron configuration:

$\text{Fe}(\text{CO})_5$, $(\eta^4\text{-C}_6\text{H}_8)(\eta^6\text{-C}_6\text{H}_6)\text{Ru}$, $[\text{Mn}(\text{CO})_5]^-$.

Examples:	$\text{M}(d^{10})$	
$[\text{Ag}(\text{CN})_2]^-$	14 VE	linear, C.N. 2
R_3PAuCl	14 VE	

A qualitative explanation takes into account:

- (1) the electroneutrality principle (Pauling, 1948)
- (2) the π -acceptor character of the ligands
- (3) the change in energetic separation between $(n-1)d$, ns and np orbitals within a transition series



The increase in atomic number is accompanied by a decrease in orbital energies because additional valence electrons only partially screen the higher nuclear charge. For $(n-1)d$ orbitals, the decrease in energy is more pronounced than for ns and np orbitals, as d electrons show less interelectronic repulsion than s and p electrons. Moreover, a positive charge on the metal also serves to increase the separation between s , p and d orbitals. Thus, Ca^0 possesses the ground configuration $[\text{Ar}]4s^2$, while that of the isoelectronic ion Ti^{2+} is $[\text{Ar}]3d^2$. A more refined treatment is offered by F. L. Pilar (1978): “ $4s$ is *always* above $3d$!”.

ARGUMENTATIVE EXAMPLES BASED ON POINTS (1)–(3) (p. 189)

- $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{CNR})_5$
 $\text{Fe}^0(d^8)$, 18 VE

The energies of the d , s and p orbitals are still rather close; effective backbonding $\text{Fe} \rightarrow \text{CO}$ from the relatively large $\text{Fe}^0(3d)$ orbitals leads to an equilibration of charge thereby fulfilling the electroneutrality principle.

- $\text{Ni}(\text{CO})_4$
 $\text{Ni}^0(d^{10})$, 18 VE, C.N. 4

but



The lower π -acceptor properties of PR_3 , compared to CO , and the low energy of the d orbitals in the $\text{Ni}^0(d^{10})$ configuration (low π -donor properties) limit the extent of backbonding, leading to an equilibrium between C.N. 4 and C.N. 3.

- $[\text{Ni}(\text{CN})_5]^{3-} \rightleftharpoons [\text{Ni}(\text{CN})_4]^{2-} + \text{CN}^-$
 $\text{Ni}^{\text{II}}(d^8)$, 18 VE, C.N. 5 $\text{Ni}^{\text{II}}(d^8)$, 16 VE, C.N. 4

The equilibrium strongly favors the 16 VE complex, although CN^- is a good π -acceptor and steric crowding is absent. The increase in nuclear charge $\text{Ni}^0 \rightarrow \text{Ni}^{2+}$ effects a strong

decrease in the energy of $3d$ relative to $4s$ and $4p$. The possibility to attain electroneutrality through $\text{Ni}(3d_n) \rightarrow \text{CN}_\pi$ interaction is limited.

With the ligand Cl^- , which is lower in the spectrochemical series, only the 16-VE complex $[\text{NiCl}_4]^{2-}$ is realized.

A further increase in the separation of the $(n-1)d$, ns and np orbitals is observed when an $\text{M}(d^{10})$ configuration *also* has a positive nuclear charge, as in Cu^I , Ag^I , Au^I and Hg^{II} . 14 VE complexes are now favored with C.N. 2 (linear). Bonding in these complexes is best described in terms of $\text{M}(d_{z^2}s)$ rather than $\text{M}(sp)$ -hybrids (Orgel, 1960 R). The energetically higher $\text{M}(p)$ orbitals thus remain uninvolved.

Excursion

Can the VSEPR concept (valence shell electron-pair repulsion, Gillespie-Nyholm model) be applied to transition-metal complexes?

The structures of simple compounds of the main-group elements can often be predicted by counting bonding and non-bonding valence electron pairs. An important role is played by the stereochemically active lone pairs of electrons. The transfer of this principle to transition-metal complexes is generally not possible (see p. 192).

- *The common occurrence of coordination number 6, independent of the number of valence electrons* (see class I, S. 187) shows that for transition-metal complexes electrostatic ligand-ligand interaction and the ratio $r_{\text{anion}}/r_{\text{cation}}$ are of structural significance in addition to covalent interactions.
- *For 18 VE complexes, structures are observed which would also have been predicted by VSEPR theory. In the case of $\text{M}(d^4)$, C.N. 7, the two complementary structures “pentagonal bipyramid” (e.g. $[\text{Mo}(\text{CN})_7]^{5-}$) and “monocapped trigonal prism” (e.g. $[(t\text{-BuNC})_7\text{Mo}]^{2+}$) both occur. For $\text{M}(d^8)$, C.N. 5 as well, complementary structures are encountered: $[\text{Ni}(\text{CN})_5]^{3-}$ (square pyramid) and $\text{Fe}(\text{CO})_5$ (trigonal bipyramid).*

- *For species with less than 18 valence electrons, structural predictions by means of VSEPR theory are successful only in the case of $\text{M}(d^{10})$ complexes (example: $\text{Ni}(\text{CO})_3$, trigonal planar).*
- *For species with less than 18 valence electrons and an incomplete $\text{M}(d^n)$ valence shell ($n < 10$), VSEPR theory is inapplicable. Qualitative predictions can, however, be made as follows:*
 - (a) *Start with the corresponding 18 VE complex and successively remove the ligands together with their σ -bonding electron pairs.*
 - (b) *Leave the structure of the remaining fragment unchanged [example: $\text{Cr}(\text{CO})_6 \rightarrow \text{Cr}(\text{CO})_5 \rightarrow \text{Cr}(\text{CO})_4 \rightarrow \text{Cr}(\text{CO})_3$].*

In a phenomenological vein, vacant coordination sites play the same role for transition metals as lone pairs do for main-group elements. This, however, is only true for ligands with modest steric demand.

More subtle explanations are provided by ligand field theory, molecular orbital theory and the angular overlap model.

VSEP	Main-group elements					
	7	6	5	4	3	2
7						
6						
5						
4						
3						



d^n	Transition elements				
	Pentagonal bipyramid or monocapped trig. prism	Distorted octahedron, eg $Ti(CO)_6^*$			
d^4					
d^6		 $Cr(CO)_6$	 $Cr(CO)_5^*$	 $Cr(CO)_4^*$	 $Cr(CO)_3^*$
d^8			 $Fe(CO)_5$	 $Ni(CN)_4^{2-}$	 $Rh(PR_3)_3^+$
d^{10}				 $Ni(CO)_4$	 $Ni(CO)_3^*$

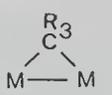
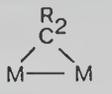
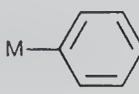
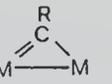
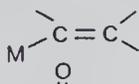
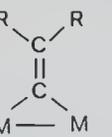
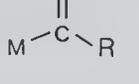
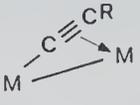
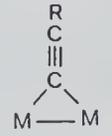
* detectable by matrix isolation only

18 VE

adapted from
D. M. P. Mingos
in COMC 3
(1982) 14

13 σ -Donor Ligands

As mentioned earlier in Chapter 2, it is convenient to classify organometallic compounds of the transition elements according to their respective ligands. The following table lists the more important organic ligands containing at least two carbon atoms, which coordinate to the transition metal through σ bonds:

Carbon Hybridization	Ligand	
	terminal	bridging
sp ³	M—CR ₃ Alkyl	 3-Center μ_2 -alkyl
		 μ_2 -Alkylidene
		 μ_3 -Alkylidyne
sp ²	M—  Aryl	 3-Center μ_2 -aryl
	M=CR ₂ Carbene or alkylidene	 μ_2 -Alkylidyne
	 Vinyl	 μ_2 -Vinylidene
	 Acyl	
sp	M \equiv CR Carbyne or alkylidyne	 $\mu_2(\sigma, \pi)$ -Alkynyl
	M—C \equiv CR Alkynyl	
	M=C=CR ₂ Vinylidene	 3-Center μ_2 -alkynyl

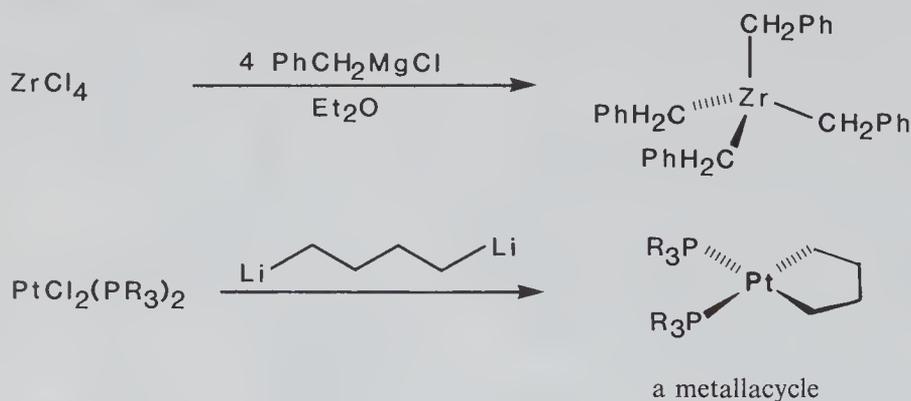
Depending on the capability of the ligand to form multiple bonds, the pure σ bond (M–C single bond) can be supplemented by various degrees of π interaction (M \equiv C multiple bond). The discussions found in this and the following chapters are roughly ordered according to the degree of increasing π -acceptor properties of the ligand, beginning with transition-metal alkyls (“ σ complexes”) and ending with transition-metal complexes of cyclic conjugated π ligands (“ π complexes”).

13.1 Preparation of Transition-Metal Alkyls and -Aryls

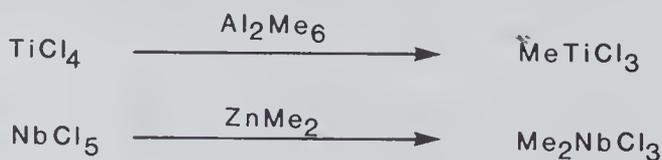
Several preparative methods mentioned in Chapter 4 (methods [1] – [12]) for main-group organometallics are applicable to transition metals as well. Additional methods [13] – [15] for transition-metal organometallics use metal complexes in low oxidation states as starting materials (ligand = CO, PR_3 , olefins etc.); complexes of this kind do not exist for main-group elements.

Metal halide + organolithium (Mg, Al) reagent

Metathesis [4]



Apart from the strongly carbanionic alkyllithium- and Grignard reagents, other main-group organometallics, namely those of Al, Zn, Hg, and Sn, can also be used. Their attenuated alkylating power can be utilized if only partial exchange of halide ligands is desired.



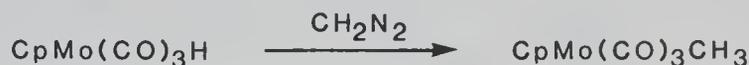
Metal hydride + alkene

Alkene insertion
(Hydrometallation) 8

1,4 addition, cis and trans

The insertion of an olefin into the M–H bond is also the decisive step in certain homogeneous catalytic processes (see Chapter 17).

Metal hydride + carbene

Carbene insertion 10

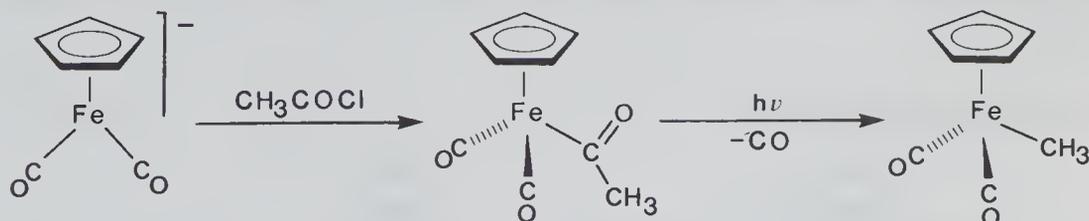
Carbonylate anion + alkyl halide

Metallate alkylation 13

A common side reaction is the elimination of HX from RX, caused by the nucleophilic carbonylate anions.

Carbonylate anion + acyl halide

Metallate acylation

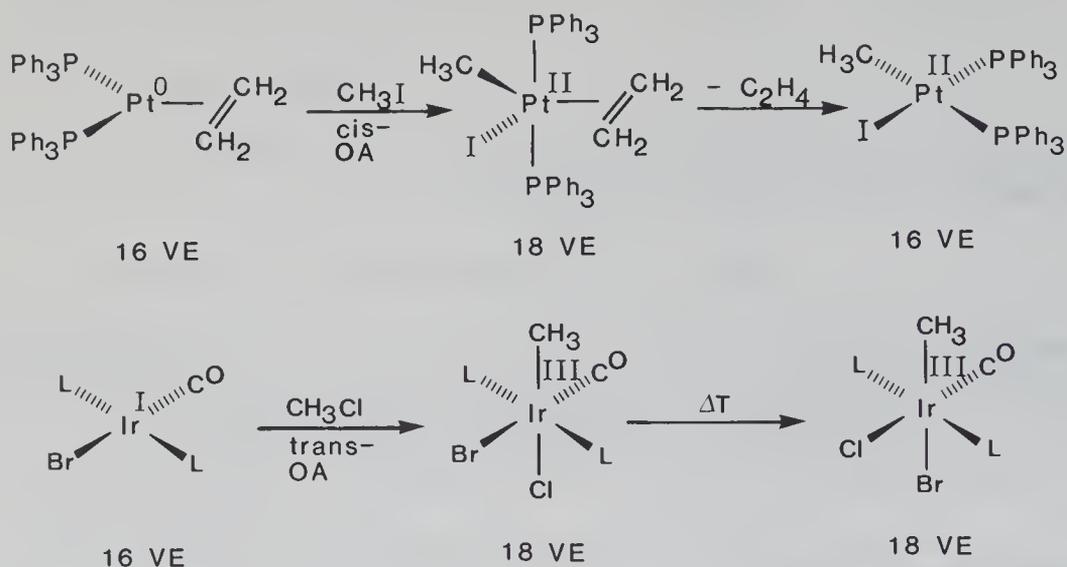


Many metal acyl complexes eliminate one molecule of CO on heating or after photochemical irradiation (see p. 359). This reaction is often reversible.

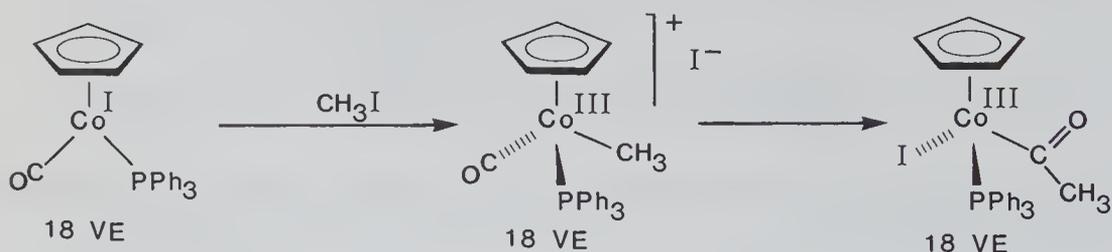
16 VE metal complex + alkyl halide

Oxidative addition [14]

Many complexes with 16 valence electrons, in which the metal has either a d^{10} or d^8 configuration, react with alkyl halides. This raises the formal oxidation state and the coordination number of the metal by +2. The process is called oxidative addition; it can lead to either cis or trans addition.



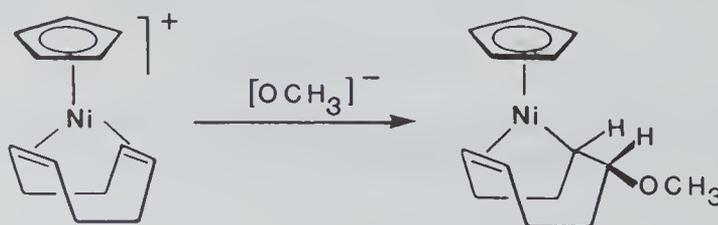
This type of reaction is also observed for 18 VE complexes with a basic metal:



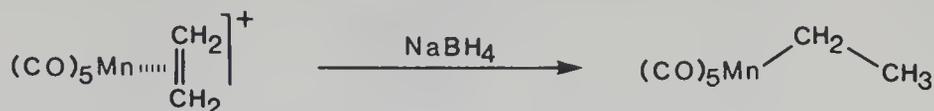
Complexes with high electron density on the central atom and the propensity to increase their coordination number are sometimes referred to as “metal bases” (see H. Werner, 1983 R).

Olefin complex + nucleophile

Addition [15]



Upon nucleophilic addition to an η^2 -ligand, a π/σ -rearrangement is observed. A further example:

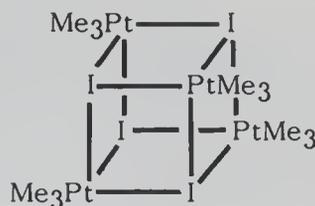


13.2 Selected Properties of Transition-Metal σ Organometallics

13.2.1 Thermodynamic Stability versus Kinetic Lability

Earlier attempts to prepare binary transition-metal alkyls or -aryls like diethyliron or dimethylnickel showed that such complexes could not be made under normal laboratory conditions, although they possibly existed as solvates at low temperatures.

Known compounds with transition-metal-carbon σ bonds invariably contained additional ligands, notably η^5 - C_5H_5 , CO, PR_3 or halides:



heterocubane type



Further examples: $\text{CpFe}(\text{CO})_2\text{CH}_3$, $\text{CH}_3\text{Mn}(\text{CO})_5$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). This led to the assumption that transition-metal $\text{TM}-\sigma\text{C}$ bonds generally are weaker than main-group element $\text{MGE}-\sigma\text{C}$ bonds, a hypothesis that today is on longer tenable.

A comparison of force constants for the metal-carbon stretching frequency shows that $\text{MGE}-\sigma\text{C}$ and $\text{TM}-\sigma\text{C}$ bonds can be of comparable strength:

$\text{M}(\text{CH}_3)_4$	Si	Ge	Sn	Pb	Ti
force constants					
$k(\text{M}-\text{C})/\text{N cm}^{-1}$	2.93	2.72	2.25	1.90	2.28

Thermochemical data for transition-metal organometallics point in the same direction and it is currently assumed that the bond energy of $\text{TM}-\sigma\text{C}$ bonds lies between 120–350 kJ/mol. It should be noted, however, that the following data are mean values $\bar{E}(\text{M}-\text{C})$ rather than individual bond dissociation energies (cf. p. 12). Values found at the lower end of this scale should be considered more representative:

Compound	$\bar{E}(\text{M}^{\sigma}\text{-C})/\text{kJ/mol}$	Compound	$\bar{E}(\text{M}^{\sigma}\text{-C})/\text{kJ/mol}$
Cp_2TiPh_2	330	WMe_6	160
$\text{Ti}(\text{CH}_2\text{Ph})_4$	260	$(\text{CO})_5\text{MnMe}$	150
$\text{Zr}(\text{CH}_2\text{Ph})_4$	310	$(\text{CO})_5\text{ReMe}$	220
TaMe_5	260	CpPtMe_3	160

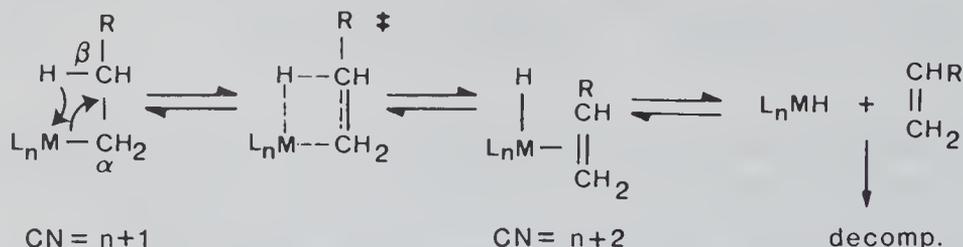
Despite the fundamental importance of $\text{M}^{\sigma}\text{-C}$ bond energies, their quantitative assessment is still a matter of debate. Inconsistencies may arise from the various experimental methods by which these data are obtained (thermochemistry, photochemistry, equilibrium constants, kinetic measurements etc., see Halpern, 1982 R) Even if a reliable value for $\bar{E}(\text{M}-\text{C})$ is available, it remains questionable whether this value can be transferred to other organometallic fragments (Dias, 1987).

With regard to the $\text{TM}-\text{C}$ bond, it can nevertheless be stated with confidence that:

- the $\text{TM}-\text{C}$ bond is weaker than the bond of TM to other main-group elements (F, O, Cl, N)
- its energy (in contrast to $\text{MGE}-\text{C}$) increases with increasing atomic number
- steric effects must be taken into account (e.g. TaMe_5 , WMe_6).

Further, it is now generally recognized that the difficulties in handling binary transition-metal alkyls are not due to particularly low **thermodynamic stability**, but rather to high **kinetic lability** (Wilkinson, 1970). An effective strategy to prepare such compounds must therefore aim at blocking possible decomposition pathways.

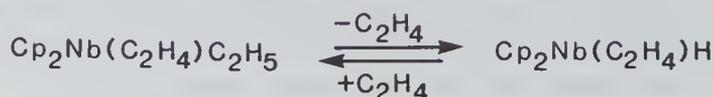
One general decomposition mechanism involves **β -elimination**, resulting in a metal hydride and an olefin:

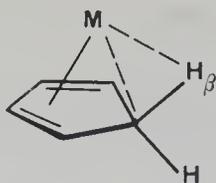


Experimental proof for this mechanism is provided by the formation of copper deuteride in the following thermolysis:



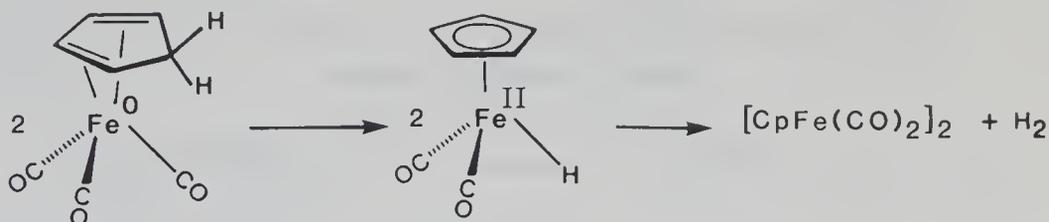
β -Eliminations can also be reversible:





In this context, the facile loss of hydrogen from η^4 -cyclopentadiene complexes is readily understood. This reaction proceeds via the intermediate formation of a cyclopentadienyl hydride [cf. C–H \rightarrow M (2e 3c) bonds, p. 267].

The first step can be regarded as an intramolecular oxidative addition:

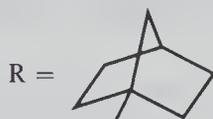


β -Elimination can be suppressed, i.e. TM $^{\sigma}$ -alkyls become **inert**, when

- the formation of an olefin is either sterically or energetically unfavorable
- the organic ligand is void of hydrogen in the β -position
- the central atom is coordinatively saturated

Examples:

- Double bonds to bridgehead carbon atoms are unfavorable (Bredt's rule):**

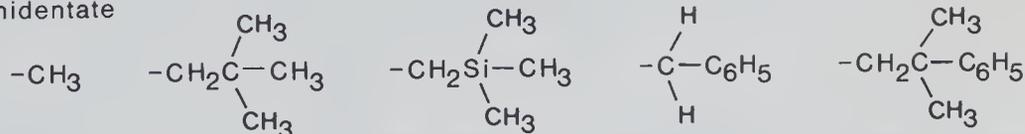


In binary complexes MR_4 , the norbornyl group stabilizes the rare oxidation states Cr^{IV} , Mn^{IV} , Fe^{IV} and Co^{IV} .

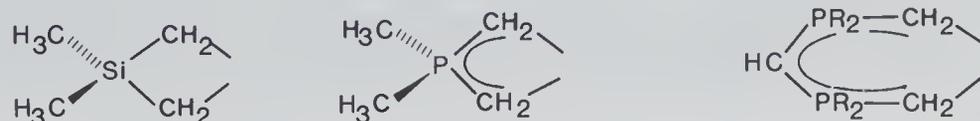
- Absence of β -H:**

C-ligands without β -hydrogens

unidentate



bidentate



The silaneopentyl group ($R = \text{CH}_2\text{SiMe}_3$) forms rather inert $\text{TM}^\sigma\text{-C}$ bonds (VOR_3 , mp 75°C , CrR_4 , mp 40°C).

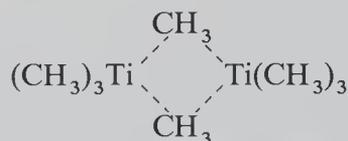
Furthermore, compare the thermal stability of the neopentyl complex $\text{Ti}[\text{CH}_2\text{C}(\text{CH}_3)_3]_4$, (mp 90°C) with the analogous alkyl complexes $\text{Ti}(\text{CH}_3)_4$ (decomp. -40°C) and $\text{Ti}(\text{C}_2\text{H}_5)_4$ (decomp. -80°C). This also holds for the corresponding zirconium complexes; while $\text{Zr}(\text{Ph})_4$ cannot be isolated and $\text{Zr}(\text{CH}_3)_4$ decomposes above -15°C , tetra-benzylzirconium is stable up to the melting point (132°C).

(c) Absence of free coordination sites:

This aspect is illustrated by the differing properties of $\text{Ti}(\text{CH}_3)_4$ and $\text{Pb}(\text{CH}_3)_4$:

$\text{Ti}(\text{CH}_3)_4$	$\text{Pb}(\text{CH}_3)_4$
decomp. -40°C	distills at $110^\circ\text{C}/1$ bar (despite a smaller force constant of the $\text{Pb}^\sigma\text{-C}$ bond, cf. p. 197!)

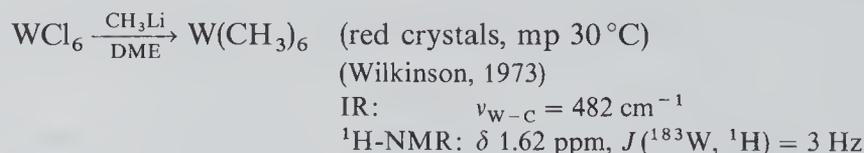
The decomposition of $\text{Ti}(\text{CH}_3)_4$ possibly proceeds via a bimolecular mechanism:



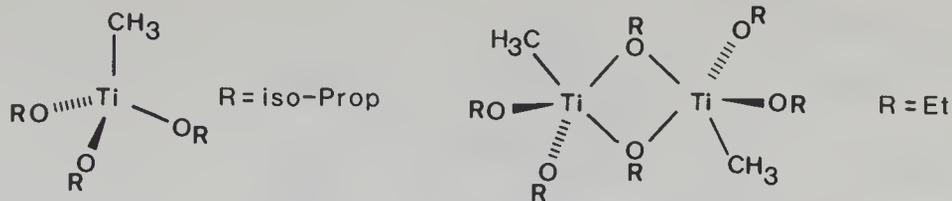
This dimerisation should effect a weakening of the $\text{Ti}-\text{C}$ ($2e2c$) bond by converting it into a three center bond $\text{Ti}-\overset{\curvearrowright}{\text{C}}-\text{Ti}$ ($2e3c$).

For $\text{Pb}(\text{CH}_3)_4$, an analogous decomposition pathway would be unfavorable, since the main-group element lead has only high-energy d orbitals at its disposal for extending the coordination shell.

Tetramethyltitanium in the form of its bipyridyl adduct $(\text{bipy})\text{Ti}(\text{CH}_3)_4$ is thermally much more stable (blockage of free coordination sites, suppression of bimolecular decomposition). Bidentate ligands like bis(dimethylphosphino)ethane (dmpe) are particularly suitable. The inert nature of 18 VE $\text{TM}^\sigma\text{-C}$ alkyls, which contain cyclopentadienyl ligands, is explained in a similar manner. The labile, coordinatively unsaturated species $\text{Ti}(\text{CH}_3)_4$ contrasts with the relatively inert, sterically shielded molecule $\text{W}(\text{CH}_3)_6$:

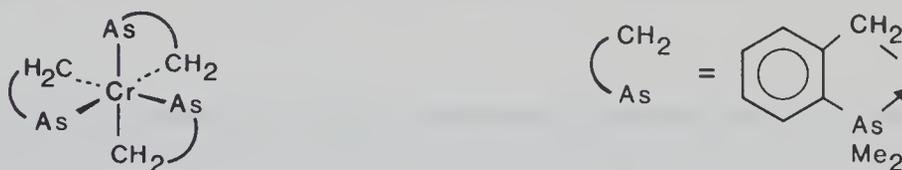


A further variant of coordinative saturation and thus kinetic stabilization is realized in complexes of the general type CH_3TiX_3 ($X = \text{halide, OR, NR}_2$). Cryoscopic measurements on $\text{CH}_3\text{Ti}(\text{OR})_3$ show only a small degree of association for $\text{CH}_3\text{Ti}(\text{OCHMe}_2)_3$, while in solution $\text{CH}_3\text{Ti}(\text{OC}_2\text{H}_5)_3$ exists almost exclusively as a dimer with alkoxy bridges:



In addition, He(II)-photoelectron spectra suggest considerable mixing between empty titanium orbitals and the doubly occupied orbitals of the oxygen atoms. This π -donor effect is also important in other complexes RTiX_3 , its strength increasing in the order $\text{X} = \text{Cl} < \text{OR} < \text{NR}_2$.

If all three criteria (a)–(c) are fulfilled, a compound with remarkable thermal stability results:



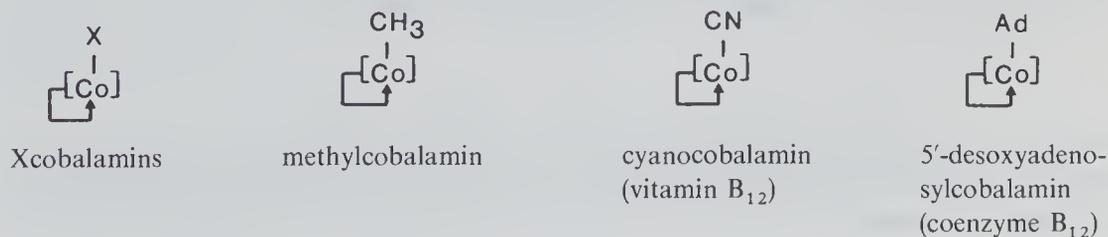
stable up to 350°C !
(Wilkinson, 1970)

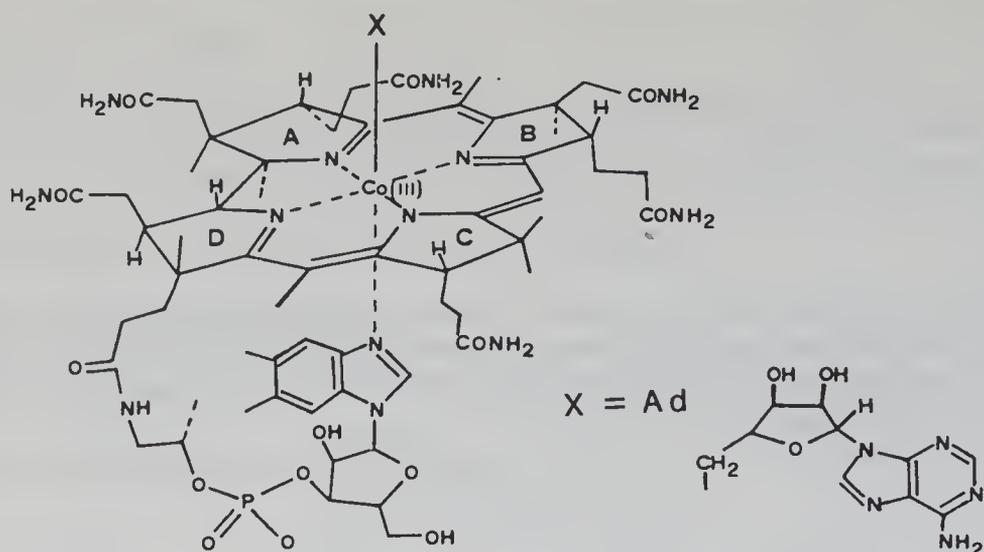
$\text{TM}-\text{C}$ bonds can even occur in complexes of the classical Werner type, in so far as these complexes are kinetically inert. This is encountered in the cases of $\text{Cr}^{\text{III}}(d^3)$, $\text{Co}^{\text{III}}(d^6)$ and $\text{Rh}^{\text{III}}(d^6)$.

Examples: $[\text{Rh}(\text{NH}_3)_5\text{C}_2\text{H}_5]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_5\text{CHCl}_2]^{2+}$.

13.2.2 Transition-Metal σ Complexes in vivo

With the possible exception of cytochrome P 450 (Ortiz de Montellano, 1982 R), the **cobalamins** are the only naturally-occurring compounds known to date which contain $\text{TM}-\text{C}$ σ bonds. They consist of a central cobalt atom, a substituted corrin ring which acts as an equatorial tetradentate ligand, an axial ligand X, and a 5,6-dimethylbenzimidazole base that is linked to the side chain of a pyrrole ring through ribose and phosphate units. The various cobalamins differ in the nature of the ligand X:





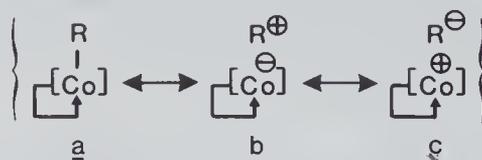
Coenzyme B₁₂, of which the adult human body contains 2–5 mg, is stable in a neutral, aqueous medium and resists oxidation by air. Methylcobalamin (isolable from microorganisms) releases methane and ethane only above 180 °C as result of a homolytic cleavage of the Co–C bond. This homolysis can also be initiated by photochemical irradiation. In the **isomerase reaction**, coenzyme B₁₂ catalyses 1,2-shifts of alkyl groups:



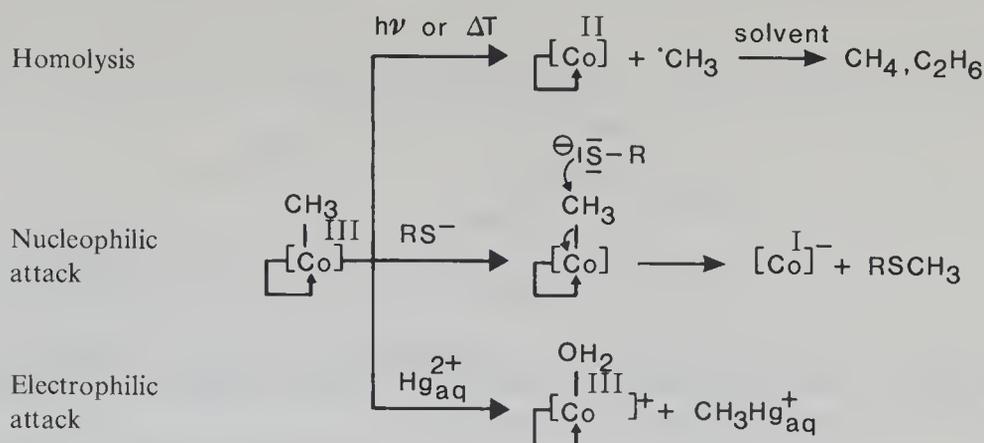
With the intention to clarify the mechanism of this and other reactions, an extensive organometallic chemistry of the cobalamins and their model systems, the cobaloximes, has been developed (Schrauzer, Dolphin, 1976 R).

The chemical versatility of the cobalamins is founded upon the following aspects:

- The largely covalent Co–C bond can be represented by three resonance structures:

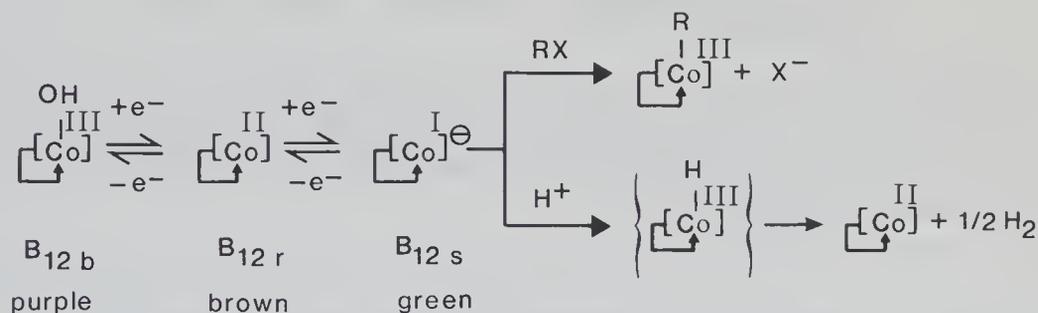


Depending on the reaction conditions and the nature of the attacking reagent, three possible modes of Co–C bond cleavage can be envisaged. They are all supported by experimental evidence:



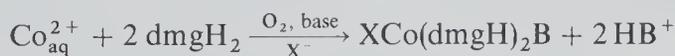
In the latter transalkylation, the methyl group is transferred as a carbanion (cf. p. 54f).

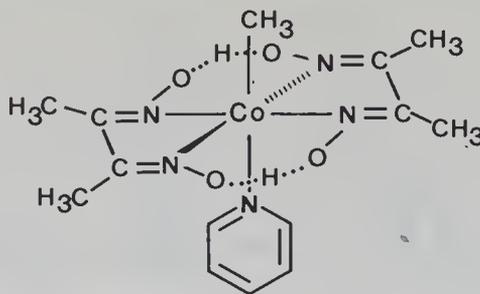
- **Changes of the oxidation state of the cobalt atom** in cobalamins can be induced in vitro by electrochemical means (Savéant, 1982 R) as well as by chemical reducing agents:



Vitamin B_{12s} is oxidized by O_2 , but metastable under physiological pH conditions. It represents an extraordinarily strong reducing agent. By means of oxidative addition of alkylating agents to B_{12s} , several cobalamin derivatives may be obtained. Hydridocobalamin is unstable in aqueous solution. The reduced form B_{12s} apparently plays an important role in enzyme reactions, catalysed by coenzyme B_{12} . These reactions have not been clarified in detail, but mechanistic patterns of organometallic chemistry may help in proposing reasonable schemes.

Many properties of the natural cobalamins are mimicked by the **cobaloximes**, which are easily prepared from Co^{II} salts, dimethylglyoxime, a base and an alkylating agent (Schrauzer, 1964).





Bis(dimethylglyoximate)(methyl)(pyridine)cobalt, *methylcobaloxime*. In this synthetic model compound the bond lengths $d(\text{Co}-\text{N}_{\text{eq}})$ and $d(\text{Co}-\text{C})$ are identical to those of coenzyme B_{12} . The ligand field strengths of the original and its model are also very similar.

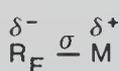
13.2.3 Transition-Metal Perfluorocarbon σ Complexes

Transition-metal organometallics $\text{R}_\text{F}-\text{M}$ with perfluorinated ligands, in comparison with the corresponding complexes $\text{R}_\text{H}-\text{M}$, very often show increased thermal stability which may be traced to a combination of thermodynamic and kinetic factors. Example:

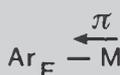


Due to the high lattice energy of metal fluorides (the likely products of decomposition), $\text{R}_\text{F}-\text{M}$ complexes are thermodynamically less stable than $\text{R}_\text{H}-\text{M}$ species. Therefore, the higher thermal stability of perfluorinated organometallics probably reflects the increased bond dissociation energy $D(\text{M}-\text{R}_\text{F})$.

Possible reasons for $D(\text{M}-\text{R}_\text{F}) > D(\text{M}-\text{R}_\text{H})$:

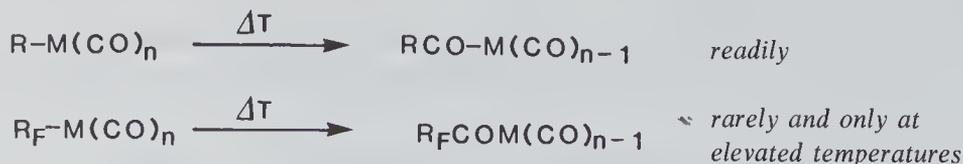


The high partial charge $\text{M}^{\delta+}$ generates contracted metal orbitals, whereby metal-carbon overlap is increased.



Low-lying π^* molecular orbitals in perfluorosubstituted arenes effectively lend themselves to $\text{Ar} \leftarrow \text{M}$ backbonding thereby increasing the metal-carbon bond strength.

The high bond energy of the $\text{M}-\text{R}_\text{F}$ bond may also be responsible for the fact that insertions of CO molecules into $\text{M}-\text{C}$ bonds are unfavorable:



Suitable methods for the **preparation** of perfluoroalkyl- and perfluoroarylmethyl complexes include coupling reactions, oxidative additions and insertions, but, compared to hydrocarbon complexes, certain peculiarities have to be taken into consideration.

Perfluoroacyl halides on reaction with carbonylate ions readily form perfluoroacyl-metal complexes, from which the perfluoroalkyl derivatives are easily prepared by decarbonylation:



Perfluoroalkyl chlorides are unreactive; the corresponding iodides in reactions with metal carbonyl anions display reversed polarity $\text{R}_F^{\delta-} - \text{I}^{\delta+}$:



With neutral metal carbonyls, R_FI undergoes oxidative addition, thus behaving like a pseudo-interhalogen compound:



Cyclic perfluoroolefins and -arenes are highly susceptible to nucleophilic substitution of F^- by metal carbonyl anions:



In contrast, the less nucleophilic neutral metal carbonyls are subject to oxidative addition in reactions with unsaturated fluorocarbons, the degree of fluorination being maintained:



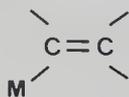
Alternatively, insertion of a perfluoroolefin into a metal-metal bond is observed:



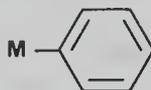
14 σ -Donor/ π -Acceptor Ligands

14.1 Transition-Metal Alkenyls

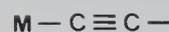
Complexes containing the structural elements



-alkenyl
(vinyl complexes)



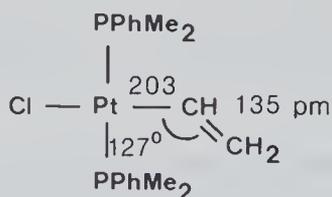
-phenyl
(aryl complexes)



-alkynyl
(acetylide complexes)

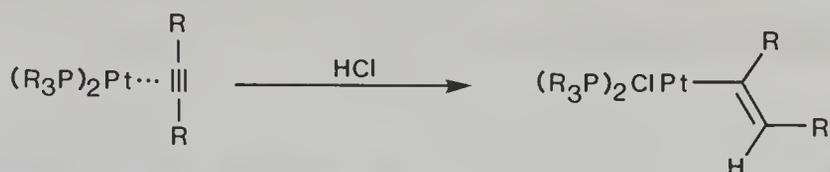
occupy a position between the complexes with pure σ -donor ligands (transition-metal alkyls) and the large class of σ -donor/ π -acceptor complexes ($L = \text{CO}$, phosphane etc.). Although alkenyl-, alkynyl- and aryl ligands have empty π^* orbitals which, in principle, are suitable for interaction with occupied d orbitals, structural data suggest that the $M-C$ interaction has little double-bond character. If the $M-C$ distances were shorter than the sum of the covalent radii, then some π -bonding would be indicated. The structural data of the following platinum complexes are a case in point:

	Pt-C	$r_{\text{cov}} \text{Pt}^{\text{II}}$	$r_{\text{cov}} \text{C}$ in pm
<i>trans</i> -[PtCl(CH ₂ SiMe ₃)(PPhMe ₂) ₂]	208	131	77 (sp^3)
<i>trans</i> -[PtCl(CH=CH ₂)(PPhMe ₂) ₂]	203	131	67 (sp^2)
<i>trans</i> -[PtCl(C≡CPh)(PPhMe ₂) ₂]	198	131	60 (sp)



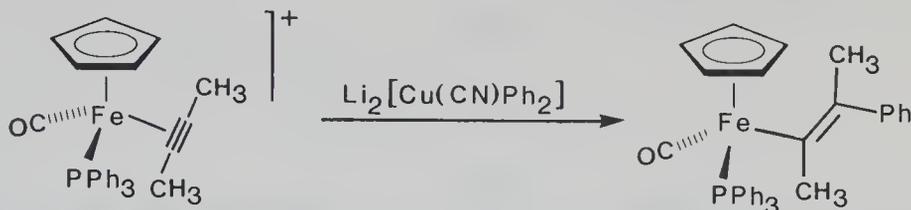
In all three examples, the distances $\text{Pt}-\text{C}$ are *not* shorter than the sum of the covalent radii of Pt^{II} and C (in the respective hybridization state). They therefore give no indication of π -bonding between platinum and carbon. If considerable back bonding $\text{Pt}(d_{\pi}) \rightarrow \text{C}(p_{\pi}^*)$ occurred, one would also expect a lengthening of the $\text{C}-\text{C}$ bond, which is not observed.

Apart from the usual methods of preparation, which have been shown also to be applicable to transition-metal alkyls (cf. p. 194f), one possible route to **transition-metal σ -vinyl complexes** is the oxidative addition of HX to η^2 -alkyne complexes:

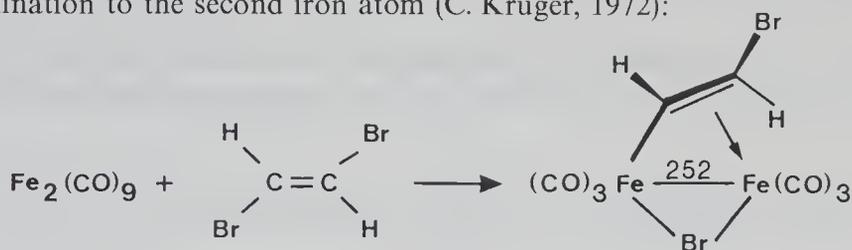


In this case, the proton enters cis to the metal, which may reflect prior protonation of the metal.

Transition-metal σ -alkenyls can also be obtained by means of nucleophilic addition to cationic alkyne complexes. The *trans* stereochemistry of the product indicates that the nucleophile attacks from the non-coordinated side of the ligand:

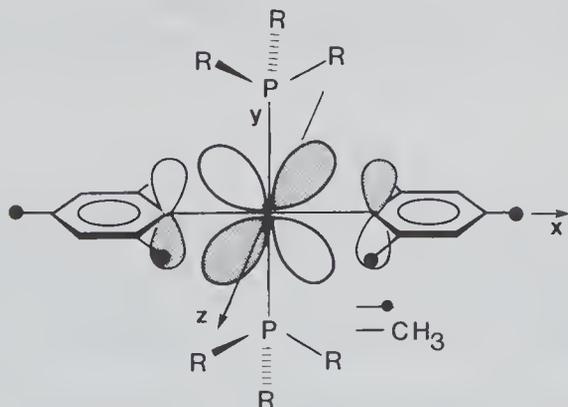


Vinyl groups occasionally act as bidentate σ/π -bridging ligands, as the olefinic double bond remains unchanged by σ -coordination. Alternatively, this can be regarded as ferra-allyl coordination to the second iron atom (C. Krüger, 1972):

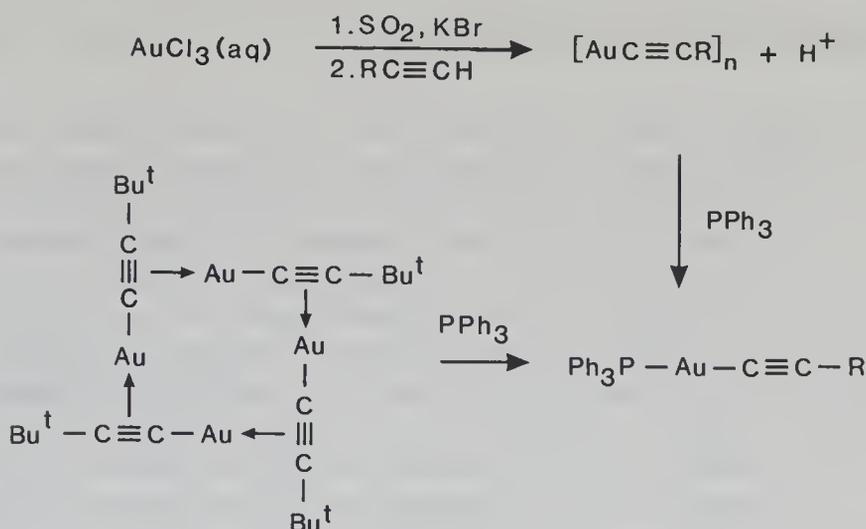


Compared to the number of metal alkynyls discussed in the next chapter, metal alkenyls are relatively rare.

Transition-metal σ -aryl complexes are not necessarily more stable than the analogous alkyl complexes. TiPh_4 decomposes above 0°C to give TiPh_2 and biphenyl. Exceptional stability is encountered in the square-planar nickel, palladium and platinum complexes $(\text{mesityl})_2\text{M}(\text{PR}_3)_2$. The corresponding alkyl and phenyl complexes are quite labile.

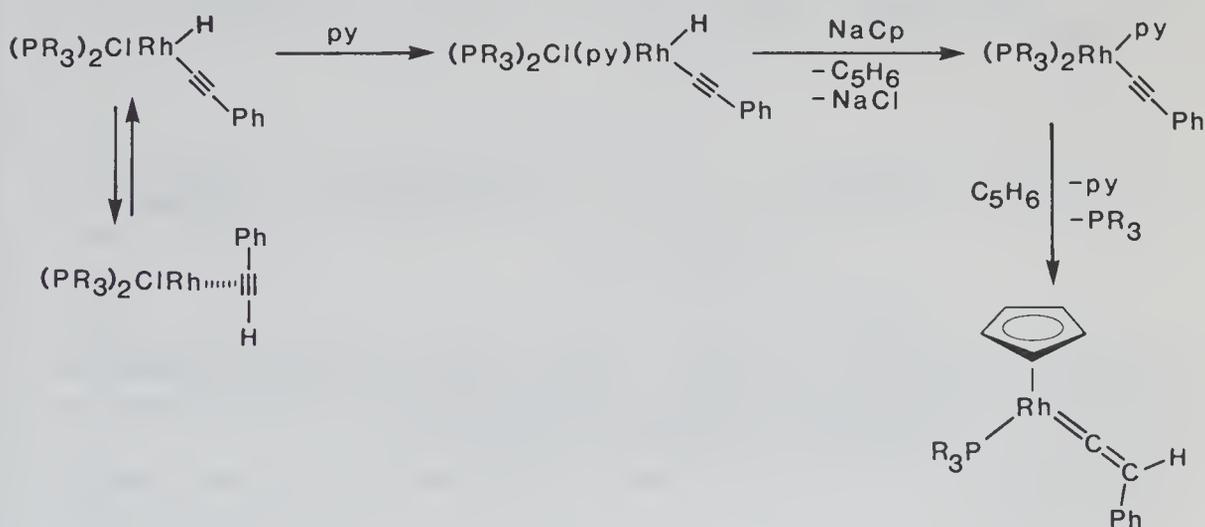


The *ortho*-substituents prevent rotation of the aryl group, forcing it into a conformation that ensures optimal overlap $\text{Pt}(d_{xy})\text{-Aryl}(\pi^*)$. A further role of the *ortho*-substituents, in addition to preventing β -elimination, may be to sterically inhibit the attack of ligands along the *z*-axis.



The relative ease of depolymerization of alkynyl-gold complexes by Lewis bases may be associated with the reluctance of gold(I) to exceed coordination number 2. As implied by the weakness of the gold-olefin bond and the non-existence of binary gold carbonyls (Chapter 14.5), the σ -acceptor/ π -donor synergism is only weakly established in the “late transition-metal ion” $\text{Au}^{\text{I}}(d^{10})$.

Transition-metal σ -alkynyls occur as intermediates in the rearrangement of 1-alkyne to vinylidene ligands (Werner, 1983):



The phenylalkyne π complex equilibrates with its σ -alkynyl(hydrido) isomer. Upon addition of pyridine, this equilibrium is shifted, strongly favoring the σ -alkynyl(hydrido) species. The hydrogen migration from metal to carbon is thought to proceed via a two-step intermolecular elimination/addition mechanism (see also vinylidene complexes p. 217).

14.3 Transition-Metal Carbene Complexes

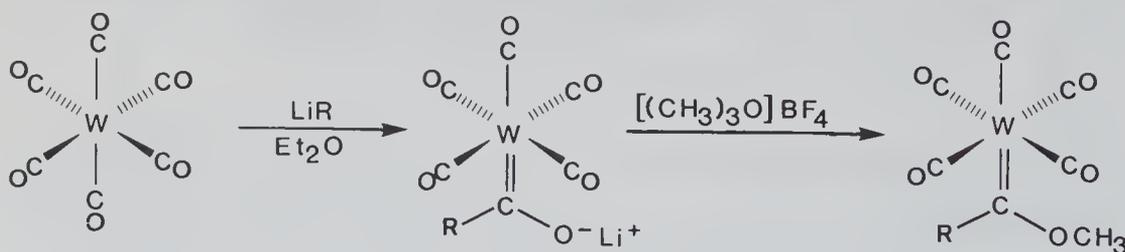
Compounds containing metal-carbon double bonds are generally called metal-carbene complexes. If no heteroatoms are directly bound to the carbene carbon atom, they are referred to as metal-alkylidene complexes. The terms "Fischer carbene complexes" (heteroatom substituted) and "Schrock carbene complexes" (C, H substituted) are also used occasionally. Complexes with metal-carbon triple bonds are designated metal-carbyne or metal-alkylidyne complexes. The first carbene complex was prepared in 1964, the first carbyne complex in 1973. Since then, this class of compounds has developed into an important branch of organometallic chemistry. The role carbene complexes assume as intermediates in olefin metathesis (p. 419) has further contributed to their current relevance. The synthesis of the dichlorocarbene complex (tetraphenylporphyrin)- $\text{Fe}(\text{CCl}_2) \cdot \text{H}_2\text{O}$, prepared from CCl_4 , is regarded as a model reaction for the degradation of chlorohydrocarbons in the liver as catalyzed by the enzyme system cytochrome P-450 (Mansuy, 1978).

PREPARATION

There are many routes to carbene complexes. The following examples also portray typical reactions of the respective starting materials.

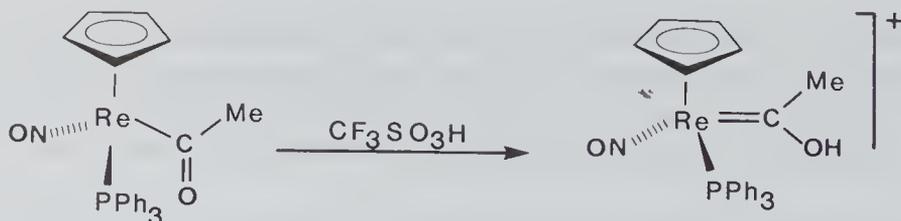
1. Addition of alkyllithium to $\text{M}-\text{CO}$

(E. O. Fischer, 1964)



This reaction is concordant with quantum-chemical calculations (Fenske, 1968), which have shown that the carbon atom in coordinated CO should bear a larger positive charge than in free CO. Nucleophilic attack should therefore be favorable.

A variant of this procedure is the protonation (alkylation) of neutral acyl complexes (Gladysz, 1983):



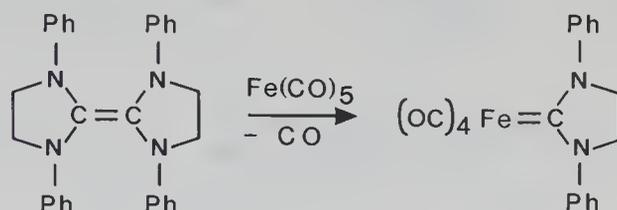
2. Addition of ROH to isocyanide complexes

(Chatt, 1969)



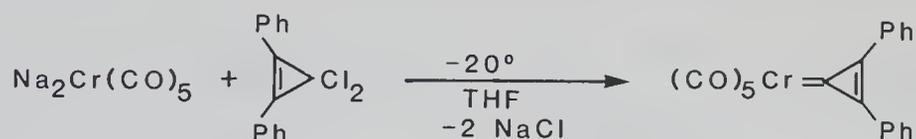
3. From electron-rich olefins

(Lappert, 1971)



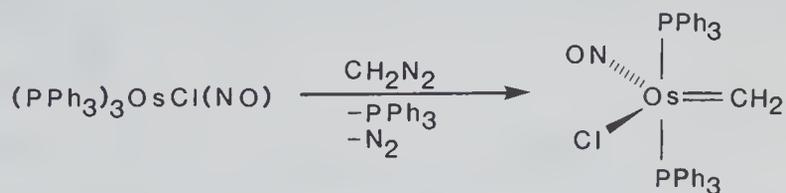
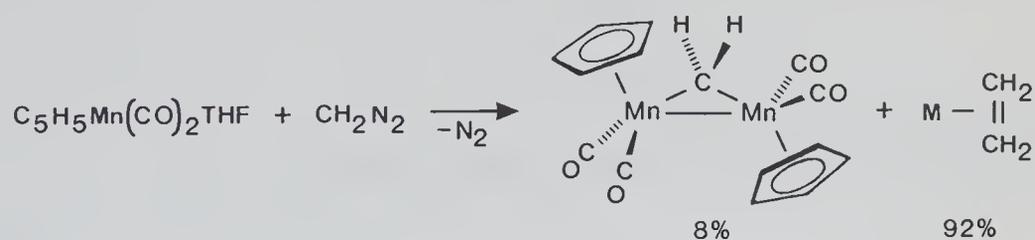
4. From carbonyl metallates and geminal dichlorides

(Öfele, 1968)



5. Interception of free carbenes

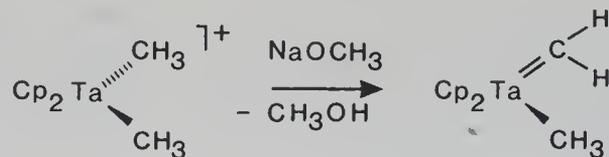
(Herrmann, 1975)



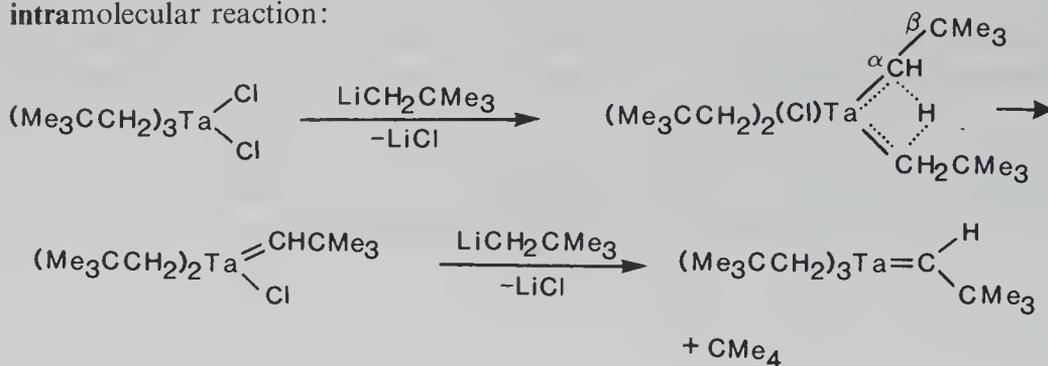
(Roper, 1983)

6. α -Deprotonation of an M-alkyl group intermolecular reaction:

(Schrock, 1975)

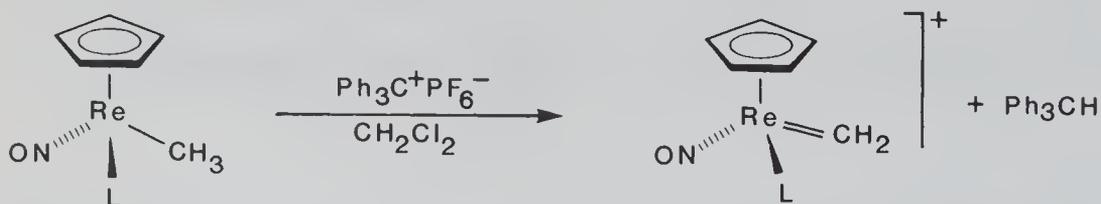


intramolecular reaction:



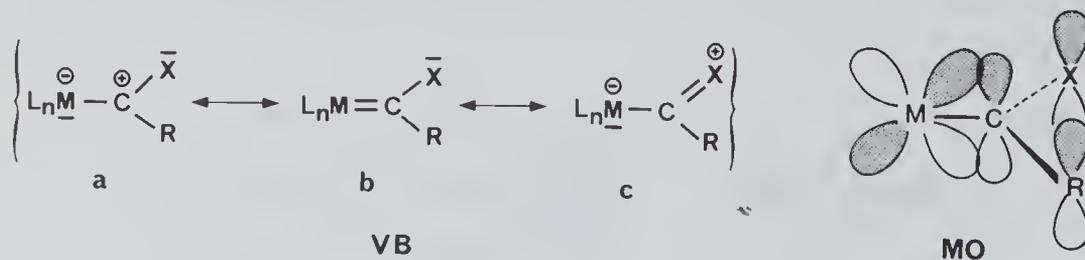
7. Hydride abstraction from an M-alkyl group

(Gladysz, 1983)



STRUCTURE AND BONDING

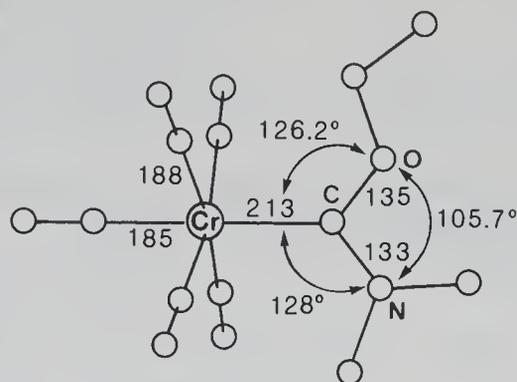
The metal-carbene bond can be described by several resonance forms:



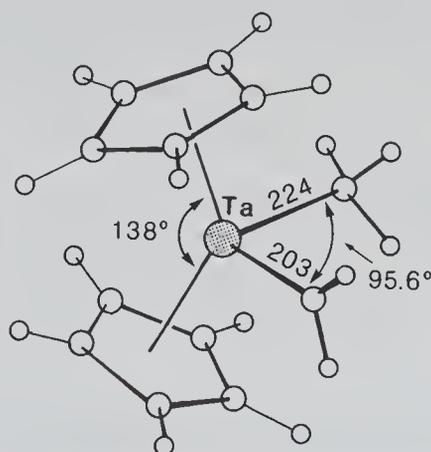
The relative contributions of the individual resonance forms **a**, **b** and **c** depend on the π -donor properties of the substituents M, X and R at the carbene carbon atom. From

structural studies of various carbene complexes, the following characteristics can be deduced:

- the coordinated carbene has trigonal planar geometry, carbon hybridization is approximately sp^2 .
- The bond $M-C(\text{carbene})$ is significantly shorter than an $M-C$ single bond, but longer than the bond $M-C(\text{CO})$ in metal carbonyls. This points to the importance of resonance form **b** [$M(d_\pi) \rightarrow C(p_\pi)$ contribution].
- The bond $C-X$ ($X = \text{heteroatom}$) is shorter than a single bond. A contribution of the resonance form **c** [$C(p_\pi) \leftarrow X(p_\pi)$ interaction] is thereby implied.



Structure of $(\text{CO})_5\text{CrC}(\text{OEt})\text{NMe}_2$. The atoms Cr, C, O, N are coplanar, the O-C-N moiety is staggered with respect to the $\text{Cr}(\text{CO})_5$ unit (Huttner, 1972).



Structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CH}_2)\text{CH}_3$. This complex allows a comparison of bond parameters of the groups $M=\text{CH}_2$ and $M-\text{CH}_3$ in an identical environment (Schrock, 1975).

Spectroscopic characteristics:

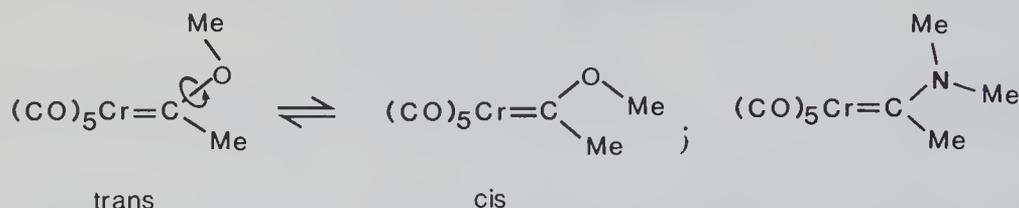
$\text{Cr}(\text{CO})_6$: $\nu_{(\text{CO})}$ stretching frequency (Raman): 2108 cm^{-1}
 $(\text{CH}_3\text{O})\text{CH}_3\text{C}=\text{Cr}(\text{CO})_5$: $\nu_{(\text{CO})}$ trans to carbene: 1953 cm^{-1}

These **IR data** imply that the carbene carbon atom is a weaker π -acceptor and/or a stronger σ -donor than CO. This is in agreement with the dipole moment

$(\text{CO})_5\text{Cr}^{\delta-} - \text{C}^{\delta+}$ of 4 Debye, whose direction indicates a significant positive charge on the carbene carbon atom (resonance form **a**) and suggests electrophilic reactivity of this site.

^{13}C -NMR	δ (ppm)	reacts as:	<i>The ^{13}C-NMR signals of coordinated carbene carbon atoms are spread over a large shift range; as with the signals of organic carbenium ions, they appear at low field (compare Ph_3C^+: δ 212 ppm, Me_3C^+: δ 336 ppm). The compounds $(t\text{-BuCH}_2)_3\text{Ta}=\text{C}(t\text{-Bu})\text{H}$ and $(\text{CO})_5\text{Cr}=\text{C}(\text{NMe}_2)\text{H}$ demonstrate that reliable predictions of nucleophilic or electrophilic behavior cannot be made on the basis of ^{13}C-NMR spectra.</i>
$\text{Cp}_2(\text{Me})\text{Ta}=\text{CH}_2$	224	Nu	
$(t\text{-BuCH}_2)_3\text{Ta}=\text{C}^{\text{-}t\text{-Bu}}\text{H}$	250	Nu	
$(\text{CO})_5\text{Cr}=\text{C}^{\text{-}N(\text{CH}_3)_2}\text{H}$	246	El	
$(\text{CO})_5\text{Cr}=\text{C}^{\text{-}OCH_3}\text{Ph}$	351	El	
$(\text{CO})_5\text{Cr}=\text{C}^{\text{-}Ph}\text{Ph}$	399	El	

^1H -NMR spectral data, however, offer definite proof for the significance of $\text{M}=\text{C}$ as well as $\text{C}=\text{X}$ double-bond character in the $\text{MC}(\text{X})\text{R}$ fragment:

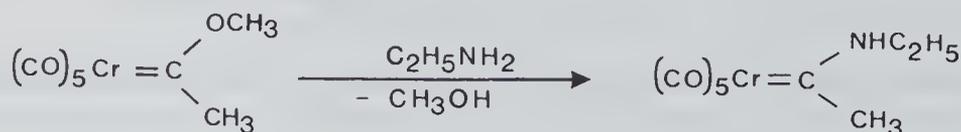


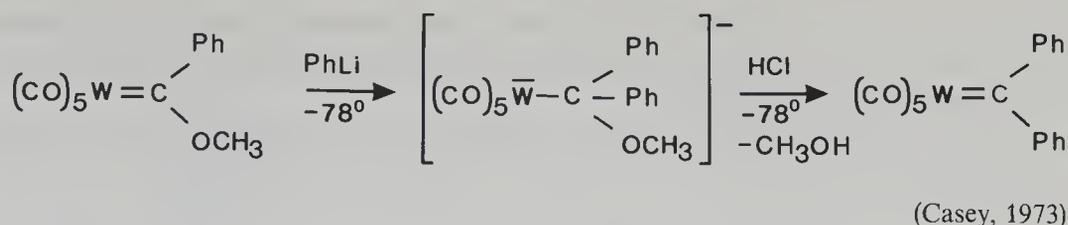
In the solid state, the methoxy(methyl)carbene complex is in its *trans*-conformation. In solution at -40°C , both *cis* and *trans* forms occur (four ^1H -NMR signals). Raising the temperature leads to pairwise coalescence of the ^1H -NMR signals, caused by the rotation around the $\text{C}-\text{O}$ bond axis ($E_a = 52$ kJ/mol, Kreiter, 1969). For the dimethylamino complex, the rotational barrier is higher so that three signals for the non-equivalent methyl groups are observed at room temperature.

The $\text{M}=\text{CR}_2$ bond in alkylidene complexes of the Schrock type is particularly rigid; considerable $\text{M}=\text{C}$ double-bond character must be present here (p. 213). Thus, the non-equivalence of the methylene protons in the ^1H -NMR spectrum of $\text{MeCp}(\text{Cp})\text{Ta}(\text{CH}_2)\text{CH}_3$ remains unchanged up to $T = 100^\circ\text{C}$ (decomp.), which indicates an activation energy for methylene rotation of $\Delta G^\ddagger > 90$ kJ/mol.

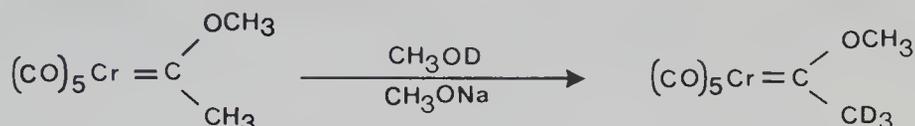
REACTIONS OF TRANSITION-METAL CARBENE COMPLEXES

The **heterocarbene complexes**, prepared by methods 1–3, are relatively inert, as the vacant orbital at the carbene carbon atom can be filled by π -interaction with heteroatom lone pairs as well as with occupied metal d orbitals. Nevertheless, this **carbene carbon** atom still shows **electrophilic character** (resonance form **a**, p. 212) and reacts with a variety of nucleophiles, e.g. amines and alkyllithium reagents, forming other carbene complexes.

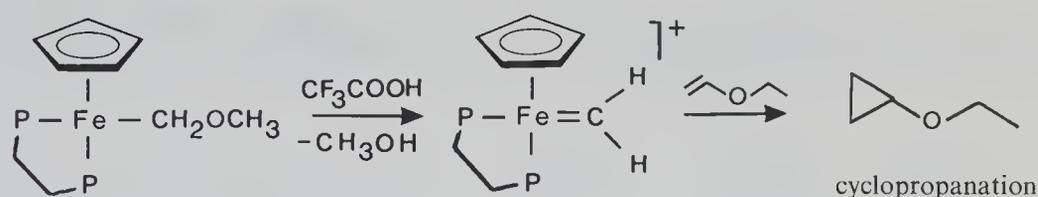




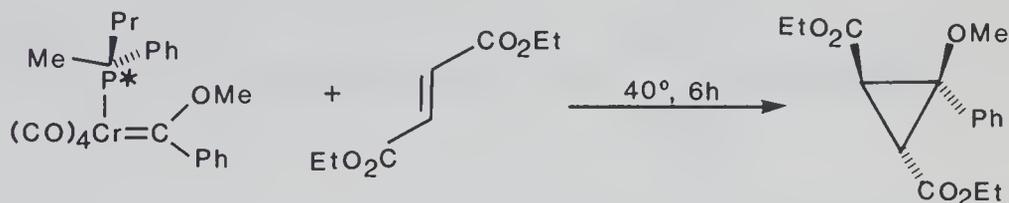
The acidity of a neighboring methyl group is markedly enhanced:



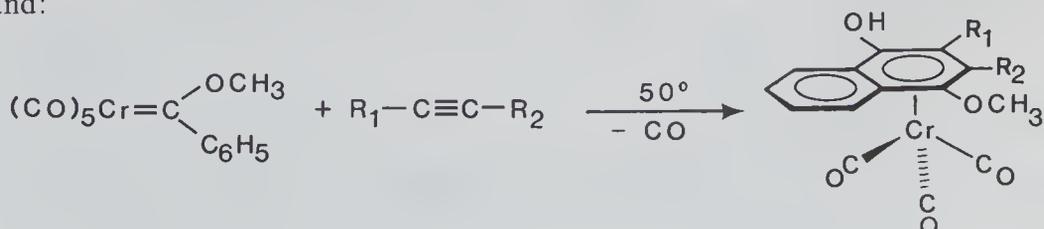
Carbene complexes in general are poor sources of free carbenes. In specific cases they can, however, be used as **carbene transfer agents**. An example is the cationic carbene complex $[\text{CpFe}(\text{CH}_2)\text{L}_2]^+$, which is generated and used *in situ* (Brookhart, 1987 R):



The following chiral carbene complex reacts with diethyl fumarate under *chirality transfer* to yield an optically active cyclopropane (E. O. Fischer, 1973). This reaction most likely proceeds via initial loss of one CO ligand and coordination of the olefin to the vacant coordination site. Intramolecular cycloaddition then forms a metallacyclobutane intermediate (see Chauvin mechanism, p. 420).

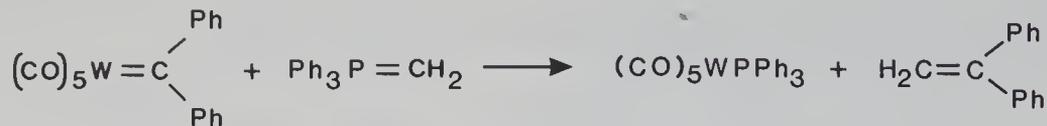


A further use of carbene complexes in organic synthesis is their reaction with alkynes. This method utilizes the bifunctionality of carbonyl carbene complexes. Pentacarbonyl-[methoxy(phenyl)carbene]chromium reacts under mild conditions with a number of non-heteroatomsubstituted alkynes to form 4-methoxy-1-naphthols, which are π -bonded to $\text{Cr}(\text{CO})_3$ fragments. The unsubstituted naphthol ring and the $\text{C}(\text{OCH}_3)$ unit of the second ring originate from the carbene ligand, while the group $\text{C}(\text{OH})$ is derived from a carbonyl ligand:



This cyclization reaction, which can be applied to other carbonyl carbene complexes as well, has been used for the synthesis of certain natural products, e.g. derivatives of Vitamin E and K (Dötz, 1984 R).

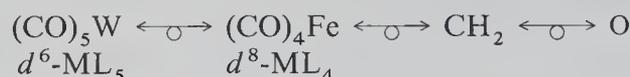
Like organic carbonyl derivatives, carbene complexes can undergo a type of Wittig reaction (Casey, 1973):



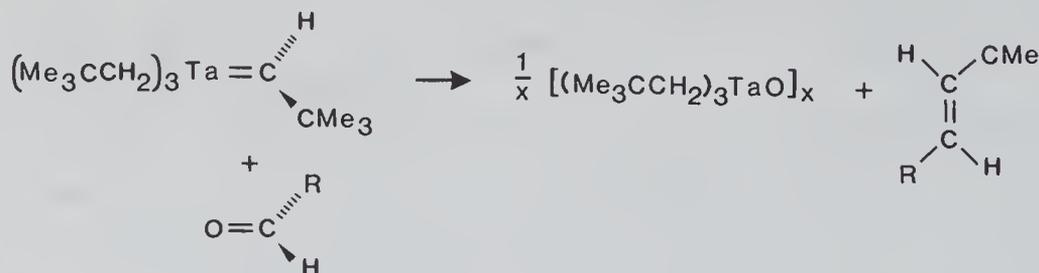
compare:



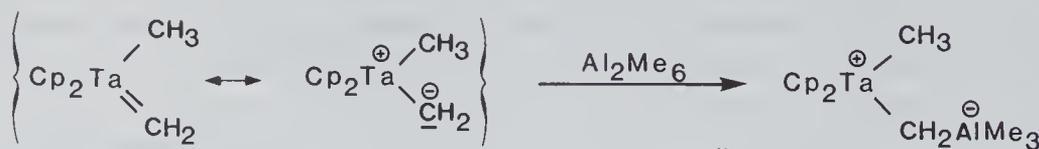
The similarity between these two reactions can be rationalized on the basis of the following isolobal analogy (p. 396):



Alkylidene complexes prepared by method 6, which are void of heteroatom stabilization, are considerably more reactive. They are primarily formed with transition metals in high oxidation states bearing ligands which are weak π -acceptors. In these complexes, the **alkylidene carbon atom** is **nucleophilic** and electrophiles may be added:



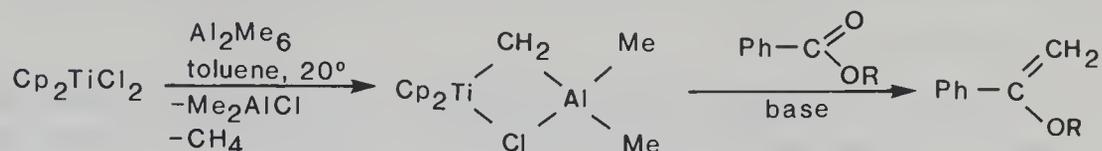
Alkylidene complexes therefore react like metal ylides:



compare:

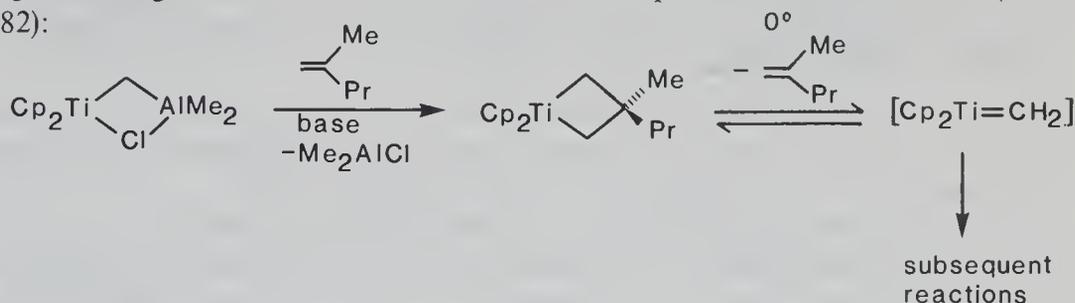


A useful preparative application of this analogy is found in **Tebbe's reagent**, an alternative to the classical Wittig reagents (Grubbs, 1980):



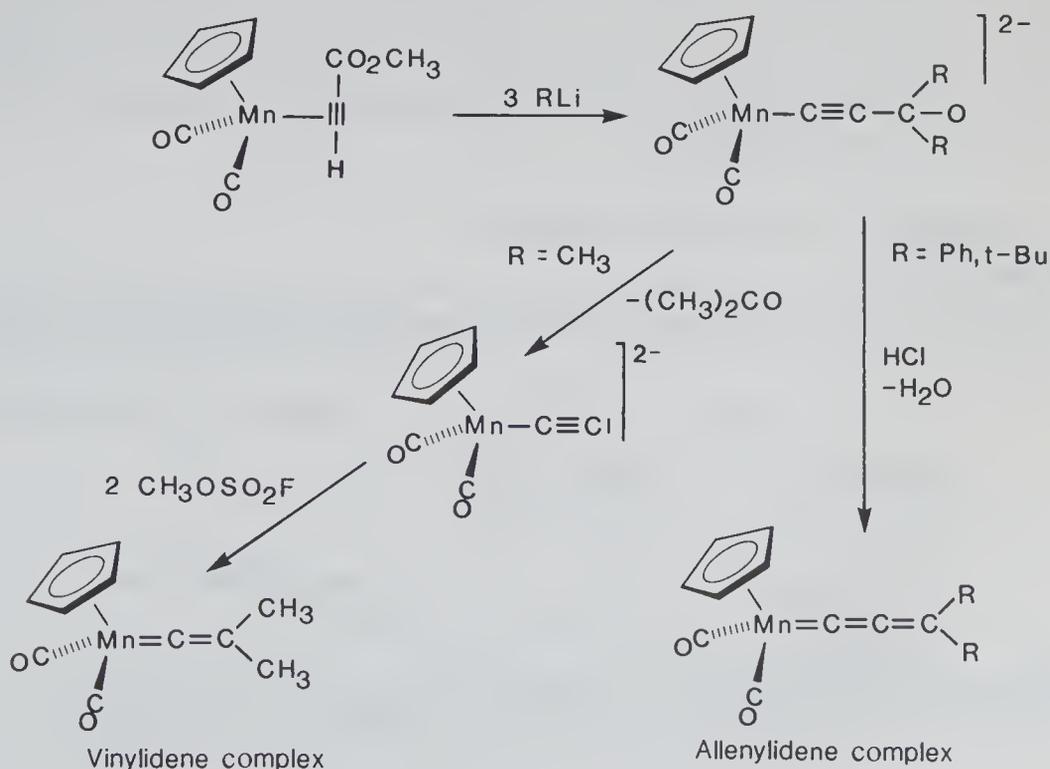
The actual **methylene transfer reagent** in this reaction is the alkylidene complex $\text{Cp}_2\text{Ti}=\text{CH}_2$, formed from Tebbe's reagent by loss of Me_2AlCl . For this conversion of an ester into an alkoxy olefin, conventional Wittig reagents are not suitable.

A variation of this method proceeds via a metallacycle, which is generated from Tebbe's reagent through the reaction with an olefin in the presence of a Lewis base (Grubbs, 1982):



In contrast to the $\text{Ti}(\text{CAlCl})$ reagent, the $\text{Ti}(\text{CCC})$ derivative can be handled in air for brief periods. Its use as a methylene transfer reagent does **not** require the presence of base.

Carbene complexes with cumulated double bonds are formed by protonation or by alkylation of σ -alkynyl complexes which are generated *in situ* (Berke, 1980):



The vinylidene ligand is one of the strongest π -acceptors, surpassed in this respect only by the ligands SO_2 and CS .

POST SCRIPTUM

The distribution of the reactivity patterns “nucleophilic” and “electrophilic” among the two classes of carbene complexes $\text{M}=\text{C}(\text{X})\text{R}$ may seem paradoxical to the reader: why should Fischer carbene complexes (central atom in low oxidation state, π -donor substituents X) exhibit electrophilic behavior, whereas Schrock complexes (central metal atom in high oxidation state, substituents R void of π -donor character) show nucleophilic behavior? A survey of factors which govern the character of the carbene carbon center shows, however, that a simple answer is not to be expected:

- electron configuration and shielding characteristics of the central metal atom,
- inductive and conjugative effects of the ligands L and of the substituents R and X
- overall charge of the carbene complex.

Furthermore, chemical reactions can proceed either by charge control or by frontier orbital control. In the latter case, a negative partial charge on the carbene carbon atom does not necessarily lead to nucleophilic behavior (Roper, 1986 R).

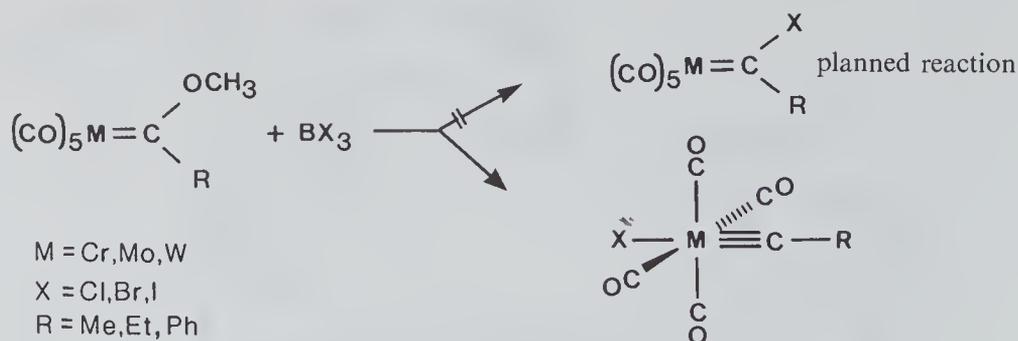
If, notwithstanding these ambiguities, a qualitative explanation is still desired, one could argue that the **electrophilic nature** of the carbene carbon atom in Fischer complexes is due to the combined effect of the π -acceptor ligands on the metal and the inductive effects of the electronegative heteroatoms on the carbene center. The **nucleophilic nature** of Schrock complexes, however, may be due to the strong $\text{M} \rightarrow \text{C}(\text{carbene})$ backbonding and the absence of $-I$ substituents on the carbene.

An alternative explanation ascribes electrophilic behavior to those carbene complexes, in which the respective free carbene possesses a singlet ground state and nucleophilic character to those complexes, where the free carbene has a triplet ground state (Hall, 1984). It is best, however, to avoid such strict classifications and discuss the relation between bonding and reactivity in each individual case according to judicious consideration of the various factors involved.

14.4 Transition-Metal Carbyne Complexes

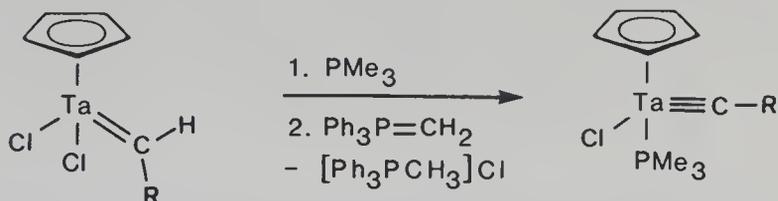
PREPARATION

1. The first examples of this class of compounds emerged serendipitously (E. O. Fischer, 1973):

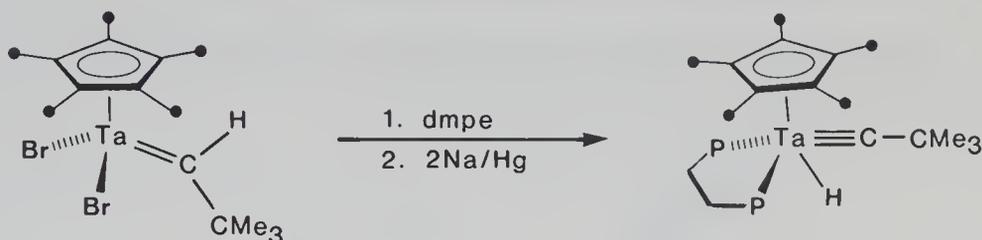


Substitution always involves the carbonyl group *trans* to the carbene ligand.

2. Another route, applicable only to compounds of the early transition metals in high oxidation states, is α -deprotonation of a carbene ligand (Schrock, 1978):



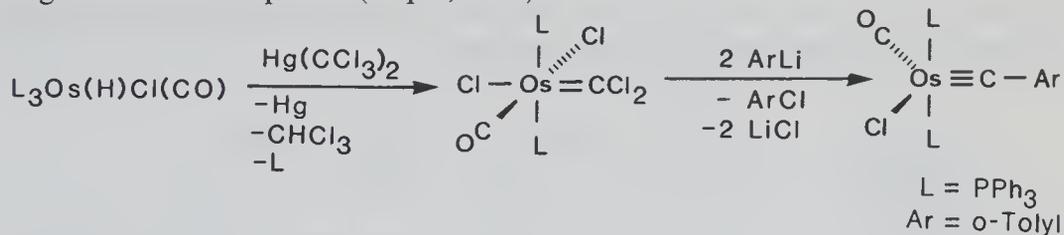
A related reaction is α -H elimination, in which an α -hydrogen atom of a coordinated alkylidene is transferred to the metal atom (Schrock, 1980):



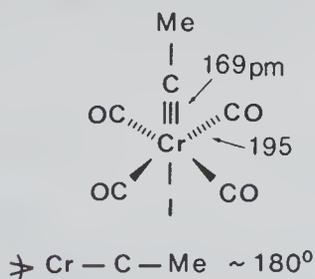
3. Transition-metal alkylidyne complexes can also be prepared from hexa(*t*-butoxy)-ditungsten and alkynes under mild conditions via a **metathesis reaction** (Schrock, 1982):



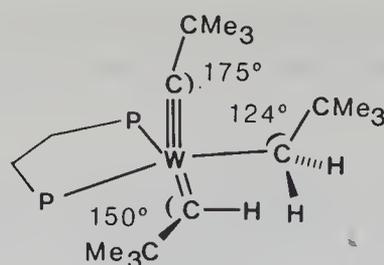
4. A further method is the treatment of a reactive dichlorocarbene complex with an organolithium compound (Roper, 1980):



STRUCTURE AND BONDING

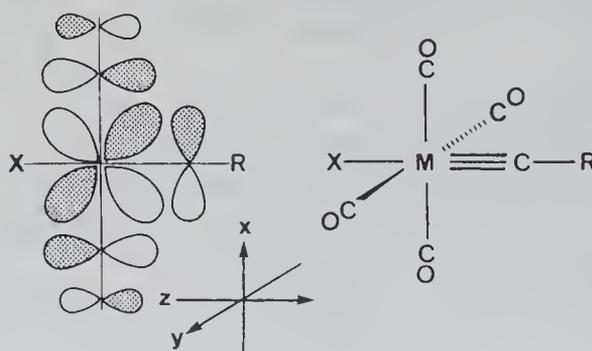


The M-C(carbyne) bond is usually shorter than the corresponding distance M-C(carbonyl). The bond axis M \equiv C-R is linear or nearly linear.



Structural data for the compound $(\text{dmpe})\text{W}(\text{CH}_2\text{CMe}_3)(\text{CHCMe}_3)\text{CCMe}_3$ allow a direct comparison of the lengths of formal W–C single, W=C double and W \equiv C triple bonds (Churchill, 1979): $d(\text{W-alkyl}) = 225 \text{ pm}$; $d(\text{W-alkylidene}) = 194 \text{ pm}$; $d(\text{W-alkylidyne}) = 178 \text{ pm}$.

The M–C bond in carbyne complexes is best described as a combination of one σ -donor bonding and two π -acceptor backbonding interactions:



π -interaction (backbonding) of the $\text{M}(d_{xz})$ orbital with the p_x orbital of the carbyne ligand and two π^* molecular orbitals of two CO ligands. The same interaction occurs in the yz -plane.

As in the case of carbene complexes, an electron-rich heteroatom substituent can also contribute to the stabilization of carbyne complexes.



Instead of a triple bond to **one** metal, the ligand $\text{RC}\dot{\text{C}}$ can also form three single bonds to **three** metals, thereby becoming the triple-bridging μ_3 -alkylidyne **building block** in transition-metal clusters. Details concerning the use of carbene and carbyne complexes in cluster synthesis are deferred to Chapter 16.5.

14.5 Metal Carbonyls

Transition-metal carbonyls are among the longest known classes of organometallic compounds. They are common starting materials for the synthesis of other low-valent metal complexes, especially clusters (see Chapter 16). The carbonyl ligand can not only be substituted for a large number of other ligands (Lewis bases, olefins, arenes), but the

remaining CO groups stabilize the molecule against oxidation or thermal decomposition. Metal carbonyl derivatives play an important role as intermediates in homogeneous catalysis (see Chapter 17).

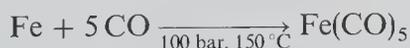
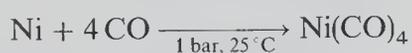
Carbonyl groups are also useful probes for determining the electronic and molecular structure of organometallic species by spectroscopic methods.

Neutral, binary metal carbonyls:

4	5	6	7	8	9	10	11
Ti	V(CO) ₆	Cr(CO) ₆	Mn ₂ (CO) ₁₀	Fe(CO) ₅ Fe ₂ (CO) ₉ Fe ₃ (CO) ₁₂	Co ₂ (CO) ₈ Co ₄ (CO) ₁₂ Co ₆ (CO) ₁₆	Ni(CO) ₄	Cu
Zr	Nb	Mo(CO) ₆	Tc ₂ (CO) ₁₀ Tc ₃ (CO) ₁₂	Ru(CO) ₅ Ru ₃ (CO) ₁₂ Ru ₆ (CO) ₁₈	Rh ₂ (CO) ₈ Rh ₄ (CO) ₁₂ Rh ₆ (CO) ₁₆	Pd	Ag
Hf	Ta	W(CO) ₆	Re ₂ (CO) ₁₀	Os(CO) ₅ Os ₃ (CO) ₁₂	Ir ₄ (CO) ₁₂ Ir ₆ (CO) ₁₆	Pt	Au

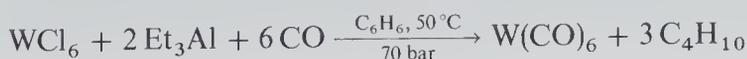
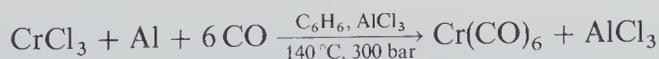
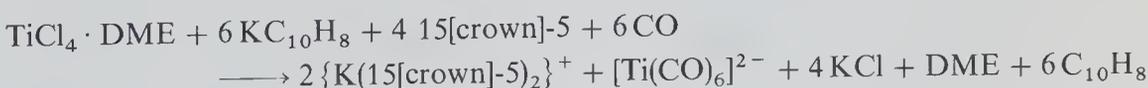
14.5.1 Preparation, Structure and Properties

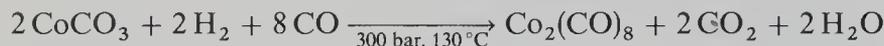
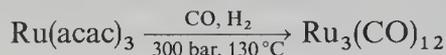
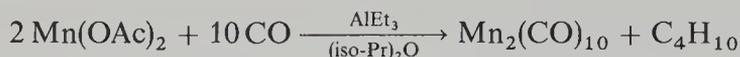
1. Metal + CO



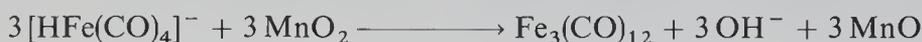
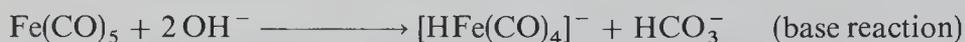
Pure iron (void of surface oxides) reacts with CO at room temperature and a pressure of 1 bar.

2. Metal salt + reducing agent + CO





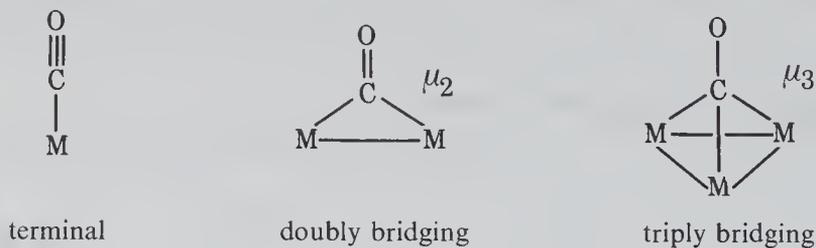
3. Miscellaneous methods



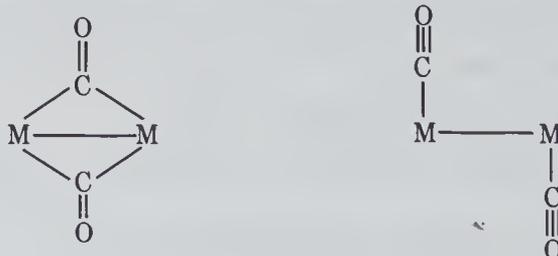
Structures of various binary metal carbonyls are shown on p. 224.

14.5.2 Variants of CO Bridging

The three principal coordination modes of the CO ligand are:



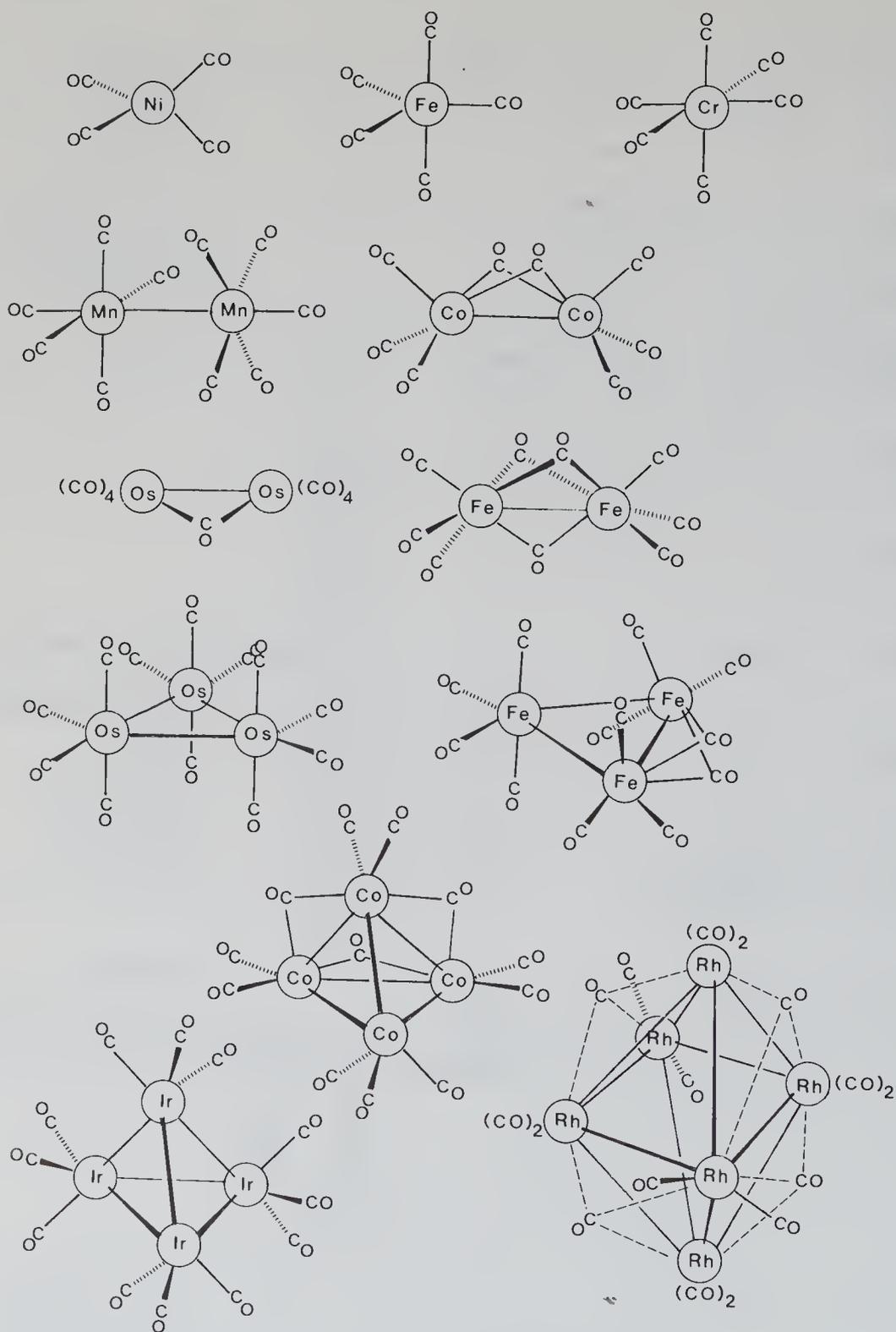
Doubly bridging carbonyl groups are quite common, especially in polynuclear clusters; they appear almost exclusively in conjunction with metal-metal bonds:



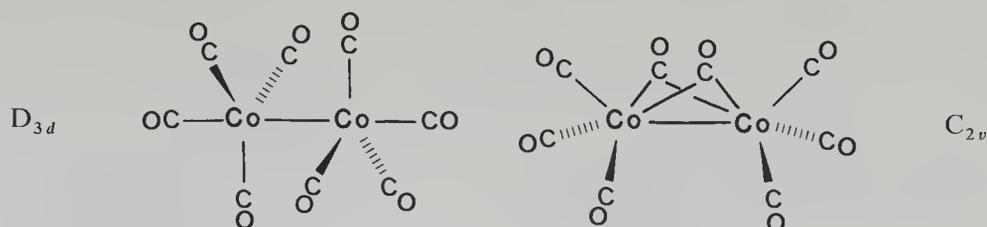
CO bridges often occur in pairs and can be in dynamic equilibrium with the non-bridging mode. For example, octacarbonyldicobalt in solution consists of a mixture of at least two structural isomers (see p. 225 above).

Physical Properties of Selected Metal Carbonyls

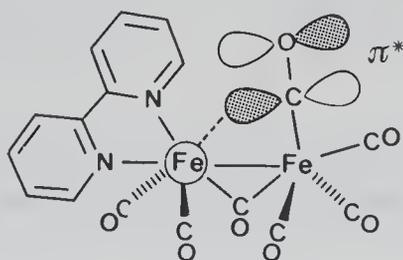
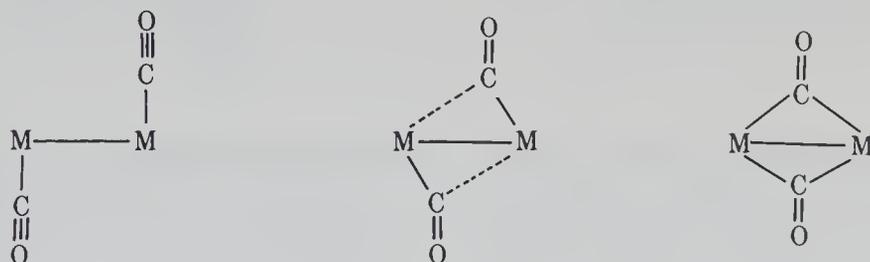
Compound	Color	mp. in °C	Symmetry	IR ν_{CO} in cm^{-1}	Miscellaneous
$\text{V}(\text{CO})_6$	green-black	70(<i>d</i>)	O_h	1976	paramagnetic, $S = 1/2$
$\text{Cr}(\text{CO})_6$	white	130(<i>d</i>)	O_h	2000	$d(\text{Cr}-\text{C}) = 192 \text{ pm}$ $\Delta_0 = 32'200 \text{ cm}^{-1}$
$\text{Mo}(\text{CO})_6$	white	– (subl)	O_h	2004	$d(\text{Mo}-\text{C}) = 206 \text{ pm}$ $\Delta_0 = 32'150 \text{ cm}^{-1}$
$\text{W}(\text{CO})_6$	white	– (subl)	O_h	1998	$d(\text{W}-\text{C}) = 207 \text{ pm}$ $\Delta_0 = 32'200 \text{ cm}^{-1}$
$\text{Mn}_2(\text{CO})_{10}$	yellow	154	D_{4d}	2044(m) 2013(s) 1983(m)	$d(\text{Mn}-\text{Mn}) = 293 \text{ pm}$
$\text{Tc}_2(\text{CO})_{10}$	white	177	D_{4d}	2065(m) 2017(s) 1984(m)	
$\text{Re}_2(\text{CO})_{10}$	white	177	D_{4d}	2070(m) 2014(s) 1976(m)	
$\text{Fe}(\text{CO})_5$	yellow	–20	D_{3h}	2034(s) 2013(vs)	bp 103 °C, highly toxic $d(\text{Fe}-\text{C}_{\text{ax}}) = 181 \text{ pm}$ $d(\text{Fe}-\text{C}_{\text{eq}}) = 183 \text{ pm}$
$\text{Ru}(\text{CO})_5$	colorless	–22	D_{3h}	2035(s) 1999(vs)	unstable; forms $\text{Ru}_3(\text{CO})_{12}$
$\text{Os}(\text{CO})_5$	colorless	–15	D_{3h}	2034(s) 1991(vs)	very unstable; forms $\text{Os}_3(\text{CO})_{12}$
$\text{Fe}_2(\text{CO})_9$	gold-yellow	<i>d</i>	D_{3h}	2082(m) 2019(2) 1829(s)	$d(\text{Fe}-\text{Fe}) = 246 \text{ pm}$
$\text{Co}_2(\text{CO})_8$	orange red	51(<i>d</i>)	C_{2v} (solid) D_{3d} (solution)	2112 2071 2059 2044 2031 2001 1886 1857	$d(\text{Co}-\text{Co}) = 254 \text{ pm}$
$\text{Ni}(\text{CO})_4$	colorless	–25	T_d	2057	bp 34 °C, highly toxic $d(\text{Ni}-\text{C}) = 184 \text{ pm}$ easily decomposes to Ni and 4 CO



Structures of binary metal carbonyls:

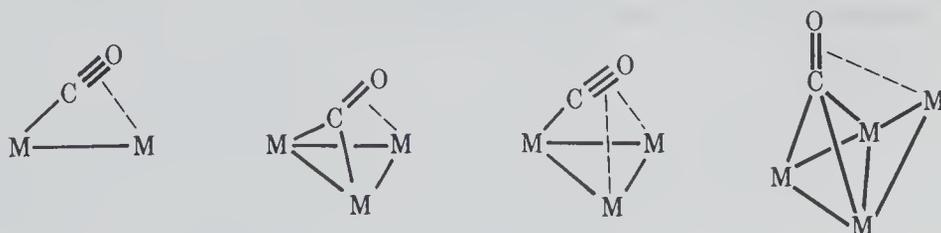


Larger metals prefer the unbridged form (compare the structures of $\text{Fe}_2(\text{CO})_9$ vs $\text{Os}_2(\text{CO})_9$ or of $\text{Fe}_3(\text{CO})_{12}$ vs $\text{Os}_3(\text{CO})_{12}$). Presumably, in the case of larger metal atoms, the bond distance $\text{M}-\text{M}$ and the angle $\text{M}-\text{C}-\text{M}$ of a CO-bridge are incompatible. Apart from the symmetrical bridge, unsymmetrically **semibridging** μ_2 -CO groups are also occasionally encountered. They can be regarded as being intermediate between terminal and bridging carbonyls.

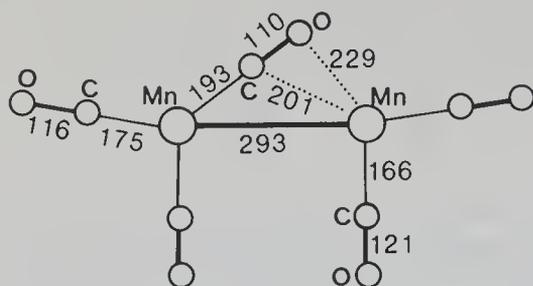


Substitution of two CO groups in $\text{Fe}_2(\text{CO})_9$ for 2,2'-bipyridyl (bipy) leads to considerable structural change in the bridging region. The superior σ -donor and inferior π -acceptor character of bipy as compared to CO would entail an uneven charge distribution over the Fe atoms. The higher negative charge density on Fe may, however, be reduced by means of a **semibridging** CO unit which towards Fe exhibits π -acceptor character exclusively, the σ -donor action being restricted to Fe.

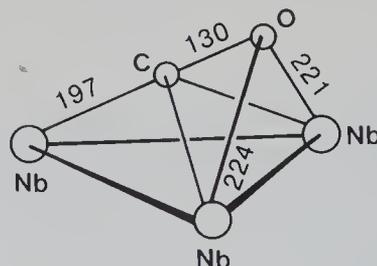
In a further unsymmetrical form, the σ/π -bridge, CO acts as a four- or six-electron donor displaying side-on coordination which is uncommon in mononuclear carbonyl complexes (this coordination mode is reminiscent of vinyl complexes, p. 207):



Examples for σ/π -bridging CO:



The $\text{Mn}_2(\text{CO})_5$ core in
 $(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2\text{Mn}_2(\text{CO})_5$



The $\text{Nb}_3(\mu\text{-CO})$ core in
 $[\text{CpNb}(\text{CO})_2]_3(\mu\text{-CO})$

14.5.3 Bonding in Metal Carbonyls, Theory and Experimental Evidence

ELECTRONIC STRUCTURE OF THE M–CO BOND

The description of the transition metal-CO bond as a resonance hybrid



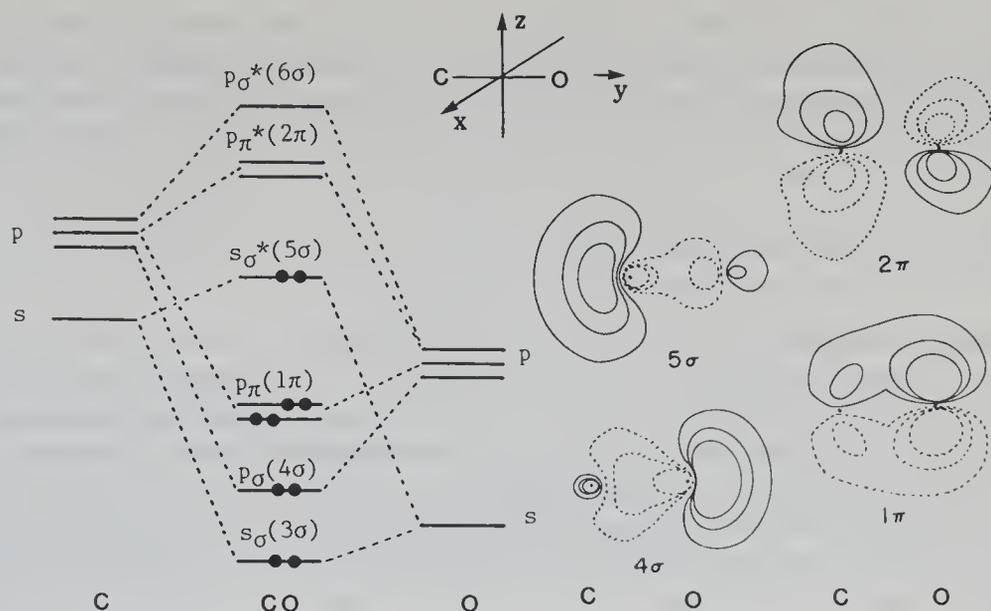
(Pauling, 1935)

leads to a bond order between 1 and 2 for the M–C bond, between 2 and 3 for the C–O bond and to less charge separation which satisfies the electroneutrality principle. Because of its prevalence in organometallic chemistry, a closer look at the carbonyl ligand is warranted, however.

The character of the frontier orbitals of CO may be derived from the following experimental evidence:

Species	Configuration	$d(\text{C}-\text{O})/\text{pm}$	$\nu_{\text{CO}}/\text{cm}^{-1}$	Conclusion
CO	$(5\sigma)^2$	113	2143	
CO^+	$(5\sigma)^1$	111	2184	5σ is weakly antibonding
CO^*	$(5\sigma)^1(2\pi)^1$	S 124	1489	2π is strongly antibonding
		T 121	1715	

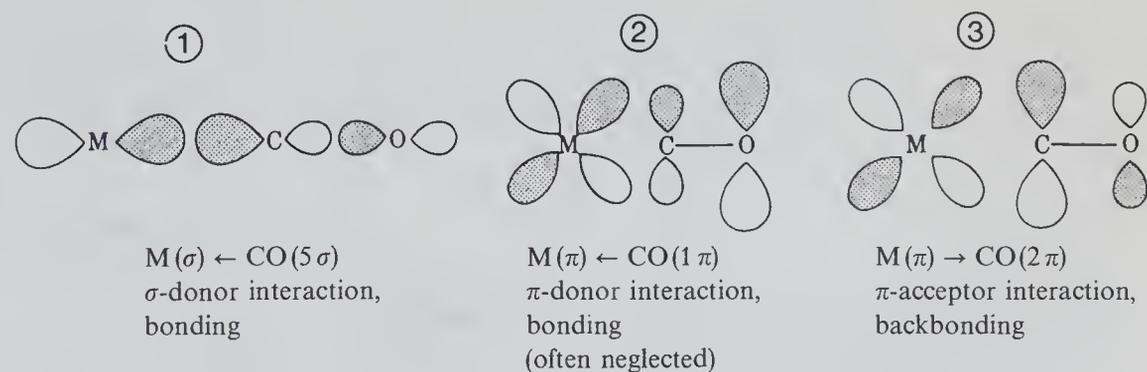
(Johnson, Klemperer, 1977) S = singlet state, T = triplet state



This rudimentary **energy-level diagram** for CO can be refined by inclusion of s, p_y -mixing. Even in its simplest form, the nature of the HOMO (σ^* , antibonding) and the LUMO (π^* , antibonding) is depicted correctly. The symbols in brackets refer to the energetic sequence of the molecular orbitals, which results if all atomic orbitals, including C(1s) and O(1s), are considered.

Based on quantum-chemical calculations, **contour lines** for the MO's of free CO may be drawn. They portray the shape of the ligand molecular orbitals which are relevant for M–C–O bonding. Solid and broken lines indicate opposite phase. The absolute values (0.3, 0.2 and 0.1) decrease with increasing radial distance.

These data for CO in the ground state, the electronically excited state (CO*) and as the cation (CO⁺) contribute to an understanding of the changes this molecule undergoes on coordination to a transition metal. Consider a single moiety M–C–O:



Bond order M–C:	increases	increases	increases
Bond order C–O:	increases	increases	decreases
Stretching frequency ν_{CO} :	increases	increases	decreases

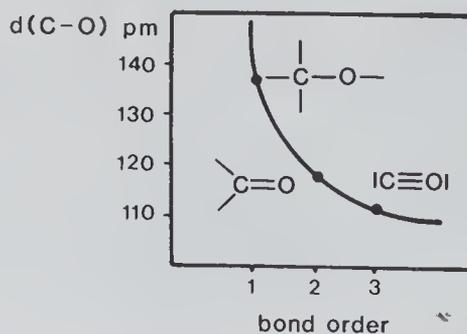
Quantum-chemical calculations suggest that the most important contribution to $M-CO$ bonding is furnished by interaction ①. The electroneutrality principle is fulfilled by minor contributions from interaction ③. This is apparent from the contour-line diagrams which show that for bonds of comparable strength the $M d(\pi) \rightarrow CO(2\pi)$ interaction leads to more extensive charge transfer than the $M(d\sigma) \leftarrow CO(5\sigma)$ interaction. From the data $d(C-O)$ and ν_{CO} for free $CO^* (5\sigma)^1(2\pi)^1$, it can be further deduced that even a small participation of the vacant ligand MO 2π in $M-C-O$ bonding is sufficient to bring about considerable change in the $C-O$ bond order.

Experimental evidence (bond lengths, stretching frequencies or force constants) reflects the sum of effects caused by the interactions ①–③. A partitioning into individual contributions ①–③ or even the question as to the legitimacy of such a separation is controversial since the interactions are not independent of each other (synergism, p. 185). The correlation between the change a ligand experiences either by raising it into an electronically excited state or by coordinating it to a transition metal remains a useful concept, however. It can be applied when discussing the bond parameters of olefin complexes and in explanations of the chemical activation of molecules by complex formation.

The transition from a fragment $M-C-O$ to a real molecule, e.g. $M(CO)_6$, does not raise any new aspects concerning the nature of the $M-CO$ bond, but is an application of the MO approach to larger molecules. The separation of the interactions into σ (octahedron: a_{1g}, e_g, t_{1u}) and π (octahedron: t_{2g}) is facilitated by symmetry considerations.

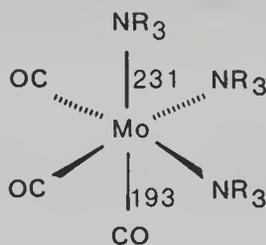
EXPERIMENTAL EVIDENCE FOR MULTIPLE BONDING $M \cdots C \cdots O$

The most conclusive indications of the bond order in metal carbonyls are provided by **crystal structure determinations and by vibrational spectra**. As backbonding from the metal to CO increases, the $M-C$ bond should become stronger (shorter) and the $C-O$ bond correspondingly weaker (longer).



For the discussion of bond orders, the *distance* $d(C-O)$ is ill-suited since bonds of orders 2 and 3 vary only marginally in their lengths. For bonds of orders 1 and 2, $d(C-O)$ differs substantially, however. In free carbon monoxide, $d(C-O)$ amounts to 113 pm while in metal carbonyls $d(C-O) = 115$ pm is generally found.

More revealing is an inspection of the *distance* $d(\text{M}-\text{C})$; here the progression from $\text{M}-\text{C}$ to $\text{M}=\text{C}$ is accompanied by a shortening of 30–40 pm. However, a quantitative assessment is again difficult, as reference values $d(\text{M}-\text{C}, \text{single bond})$ often are unavailable for zerovalent metals.



Estimation of $d(\text{M}-\text{C}, \text{single bond})$:

The covalent radius for Mo^0 can be inferred by subtracting the covalent radius of nitrogen (sp^3 , 70 pm) from the $\text{Mo}-\text{N}$ distance (231 pm). This difference (161 pm) added to the covalent radius of carbon (sp , 72 pm) leads to the distance $d(\text{Mo}-\text{C}, \text{single}) = 233$ pm. The smaller value $d(\text{Mo}-\text{C}) = 193$ pm found in $(\text{R}_3\text{N})_3\text{Mo}(\text{CO})_3$ therefore indicates significant double-bond character for the molybdenum-carbon bond.

The discussion of chemical bonding in metal carbonyls profits from the consideration of **infrared spectra**: To a first approximation, $\text{C}-\text{O}$ stretching vibrational frequencies, in contrast to $\text{M}-\text{C}$ stretching frequencies, can be regarded as being independent from other vibrations in the molecule. Therefore a relation between CO stretching vibrational frequency and CO bond order can be established.

(a) Bonding modes of the carbonyl group

The change in vibrational stretching frequencies ν_{CO} is quite characteristic:

	Free	Terminal	μ_2 -CO	μ_3 -CO
$\nu_{\text{CO}} (\text{cm}^{-1})$	2143	1850–2120	1750–1850	1620–1730

Example: $\text{Cr}(\text{CO})_6$ $\nu_{\text{CO}} = 2000 \text{ cm}^{-1}$, $k = 17.8 \text{ N cm}^{-1}$
Bond order $\text{C}-\text{O} \approx 2.7$.

(b) Charge on the complex

	$\nu_{\text{CO}}/\text{cm}^{-1}$	
d^{10}	$\text{Ni}(\text{CO})_4$	2060
	$\text{Co}(\text{CO})_4^-$	1890
	$\text{Fe}(\text{CO})_4^{2-}$	1790
d^6	$\text{Mn}(\text{CO})_6^+$	2090
	$\text{Cr}(\text{CO})_6$	2000
	$\text{V}(\text{CO})_6^-$	1860
	CO_{free}	2143

Increasing negative charge leads to expansion, increasing positive charge to contraction of the metal d orbitals with attendant increase or decrease in the overlap $\text{M}(d, \pi) - \text{CO}(\pi^*)$, respectively. The charge of the complex therefore influences the extent of backbonding, which manifests itself in the value of ν_{CO} .

In the adduct $\text{H}_3\text{B}^\ominus - \oplus\text{CO}$, boron can be regarded as a central atom void of π -donor character. Backbonding effects are therefore absent and the CO stretching frequency is shifted to a **higher** wave number ($\nu_{\text{CO}} = 2164 \text{ cm}^{-1}$), in accordance with the nature of the donor orbital $\text{CO}(5\sigma)$, which is slightly antibonding with respect to the intra-ligand bond (p. 226).

(c) Symmetry of the molecule

The number and intensities of carbonyl stretching bands in the vibrational spectra largely depend on the local symmetry around the central atom (p. 231). Quite often, the symmetry of a metal carbonyl complex is determined simply by counting the number of infrared bands. The expected number of IR-active bands can be derived by means of group theory.

(d) π -Acceptor and σ -donor properties of other ligands

Ligands in mutual *trans* position compete for the electrons of a particular metal d orbital. Two CO groups therefore weaken each other's bond to the same central atom. By replacing a CO group with a ligand which is a weaker π -acceptor, the $\text{M}-\text{CO}$ bond in the *trans* position is strengthened and the $\text{C}-\text{O}$ bond weakened.



This notion is exemplified by a comparison of CO stretching frequencies in a series of complexes of the general composition $\text{L}_3\text{Mo}(\text{CO})_3$ (Cotton, 1964):

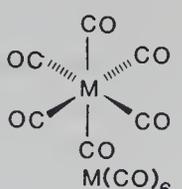
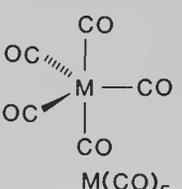
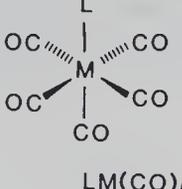
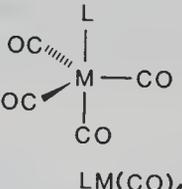
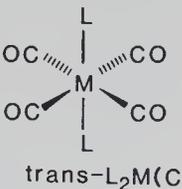
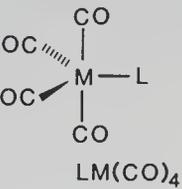
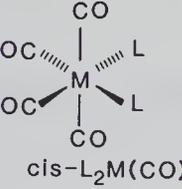
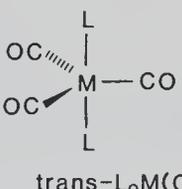
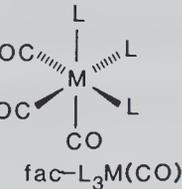
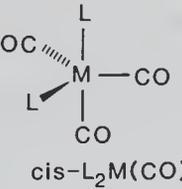
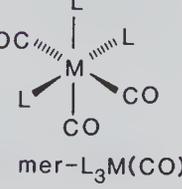
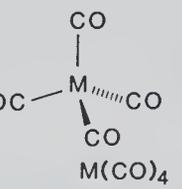
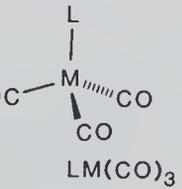
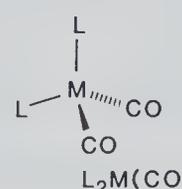
Complex	$\nu_{\text{CO}} \text{ cm}^{-1}$
$(\text{PF}_3)_3\text{Mo}(\text{CO})_3$	2055, 2090
$(\text{PCl}_3)_3\text{Mo}(\text{CO})_3$	1991, 2040
$[\text{P}(\text{OMe})_3]_3\text{Mo}(\text{CO})_3$	1888, 1977
$(\text{PPh}_3)_3\text{Mo}(\text{CO})_3$	1835, 1934
$(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3$	1783, 1915
$(\text{dien})\text{Mo}(\text{CO})_3$	1758, 1898
$(\text{Py})_3\text{Mo}(\text{CO})_3$	1746, 1888

In this series, PF_3 is the better π -acceptor (backbonding into d orbitals of phosphorus, electron-withdrawing substituents); pyridine and the tridentate ligand diethylenetriamine (dien) have poor or no π -acceptor character and behave as σ -donors exclusively.

Based on the ν_{CO} stretching frequencies in complexes with a mixed ligand sphere, the following **order of π -acceptor strength** can be proposed:



Number and Modes of IR-active bands (ν_{CO}) in carbonyl complexes, depending on the local symmetry of $\text{M}(\text{CO})_n$

Complex	Number and Modes of IR-active Bands ν_{CO}	Point Group	Complex	Number and Modes of IR-active Bands ν_{CO}	Point Group
	1 T_{1u}	O_h		2 $A_2'' + E'$	D_{3h}
	3 $2A_1 + E$	C_{4v}		3 $2A_1 + E$	C_{3v}
	1 E_u	D_{4h}		4 $2A_1 + B_1 + B_2$	C_{2v}
	4 $2A_1 + B_1 + B_2$	C_{2v}		1 E'	D_{3h}
	2 $A_1 + E$	C_{3v}		3 $2A' + A''$	C_s
	3 $2A_1 + B_2$	C_{2v}		1 T_2	T_d
	2 $A_1 + E$	C_{3v}		2 $A_1 + B_1$	C_{2v}

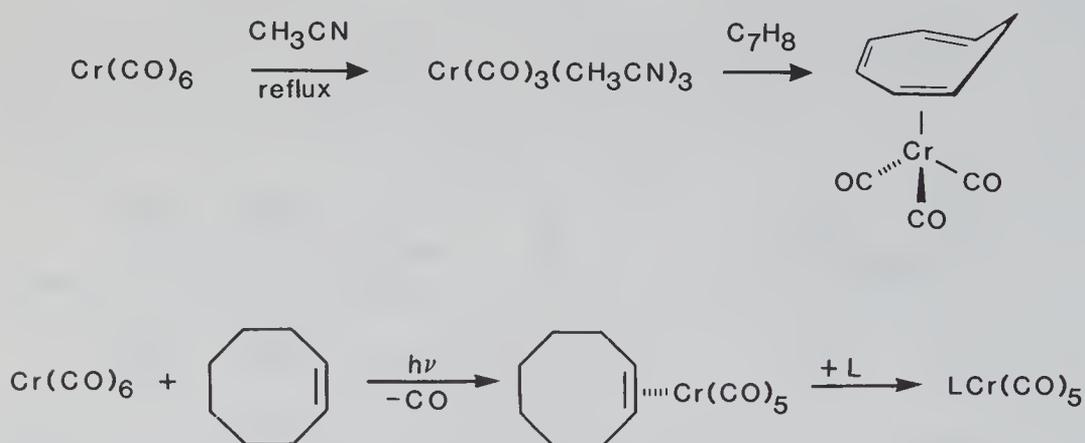
14.5.4 Principal Reaction Types of Metal Carbonyls

CO is such a common ligand that a chapter covering reactions of metal carbonyls would necessarily cover a substantial part of organometallic chemistry. Here, only a small survey will be given, with references to other relevant sections of the text.

① Substitution

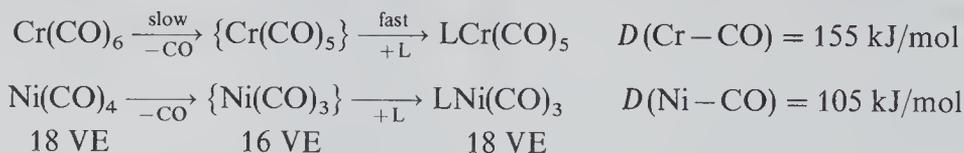
CO groups can be substituted thermally as well as photochemically (cf. p. 244) for other ligands (Lewis bases, olefins, arenes). This general method is a standard procedure for the synthesis of low-valent metal complexes. A complete substitution of all carbonyl groups is rarely accomplished.

One variant frequently employed is the intermediate introduction of a ligand whose bond to the metal is labile. This ligand can then be replaced by other ligands under mild conditions:



Other M(CO)_x transfer agents are the complexes $(\text{THF})\text{Mo(CO)}_5$, $(\text{CH}_2\text{Cl}_2)\text{Cr(CO)}_5$ and $(\text{cyclooctene})_2\text{Fe(CO)}_3$ (Grevels, 1984).

Carbonyl substitutions at **18 VE complexes** proceed by a dissociative mechanism (**D**), that is *via* an intermediate of lower coordination number (or its solvate):



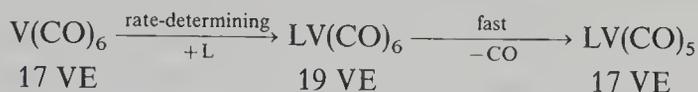
Ni(CO)_4 reacts faster than Cr(CO)_6 , the activation enthalpies ΔH^\ddagger of these reactions being virtually identical to the bond energies $D(\text{M}-\text{CO})$.

For reasons yet unexplained, the rate of substitution is highest for the central element in each group:

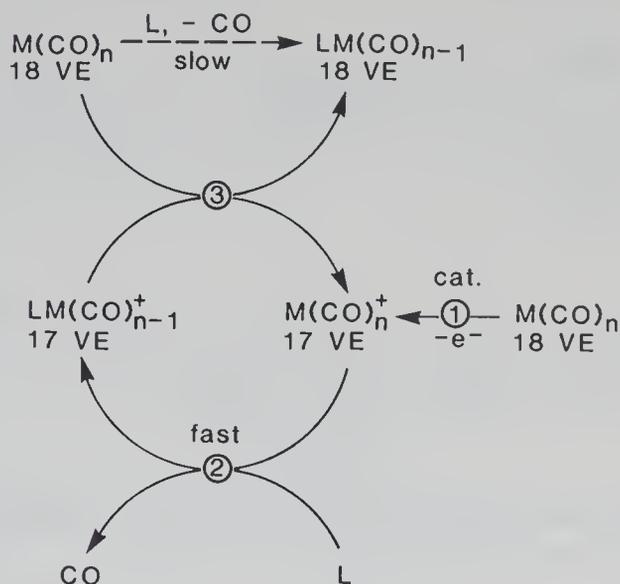
$\text{Cr} < \text{Mo} > \text{W}$
$\text{Co} < \text{Rh} > \text{Ir}$
$\text{Ni} < \text{Pd} > \text{Pt}$

Carbonyl metal complexes with a **17 VE shell** undergo substitution *via* an associative mechanism (**A**); it can be shown that the formation of a 19 VE intermediate is accompa-

nied by a gain in bond energy (Poë, 1975):



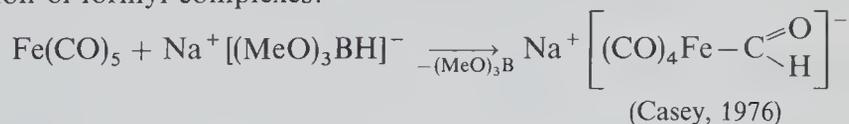
The 17 VE complex $\text{V}(\text{CO})_6$ reacts 10^{10} times faster than the 18 VE complex $\text{Cr}(\text{CO})_6$! The accelerated substitution of a 17 VE as compared to an 18 VE complex is utilized in **electron transfer (ET) catalysis**. This principle will be explained for the case of ET catalysis initiated by oxidation (Kochi, 1983):



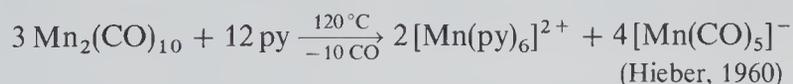
The labile species $\text{M}(\text{CO})_n^+$ must be generated chemically or electrochemically in catalytic amounts only, step ①. A necessary requirement is that the redox potentials allow step ③ to proceed spontaneously. ET catalyses can also be initiated by reduction ($18 \text{ VE} \rightarrow 19 \text{ VE}$).

② Addition of nucleophiles to η -CO

- Formation of carbene complexes (p. 210)
- Formation of carbonylmetallates (p. 234)
- Formation of formyl complexes:



③ Disproportionation

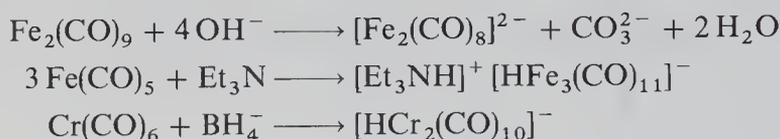
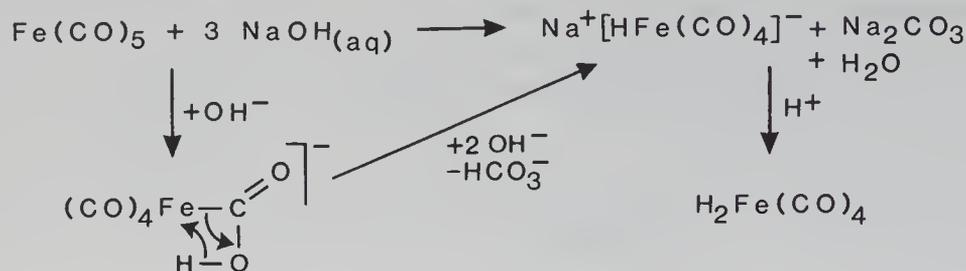


This type of disproportionation is also observed for $\text{Co}_2(\text{CO})_8$; it can be effected photochemically (Tyler, 1985 R).

④ Oxidative decarbonylation (p. 237, 336)

14.5.5 Carbonylmetallates and Carbonyl Metal Hydrides

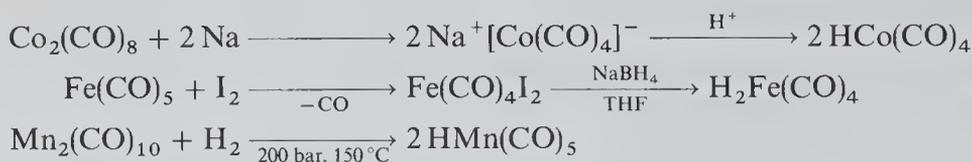
The classical route to metal carbonyl anions (**carbonylmetallates**) is the reaction of metal carbonyls with strong bases (base reaction, W. Hieber, 1895–1976, the pioneer of metal carbonyl chemistry). In this reaction, the base OH^- attacks the carbonyl carbon atom (cf. the analogous reaction with alkyllithium reagents, p. 210) and the initial addition product decomposes, presumably by β -elimination, to give the carbonylmetallates:



The initially formed formyl complex $[(\text{CO})_5\text{Cr}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}]^-$ has a half-life of $\tau_{1/2} \approx 40$ min at room temperature (Casey, 1976).

Carbonylmetallates are formed by most metal carbonyls. Their protonation generally (but not always) leads to metal carbonyl hydrides (Examples: $\text{Mn}(\text{CO})_5^-$, $\text{Fe}(\text{CO})_4^{2-}$, $\text{Co}(\text{CO})_4^-$).

Other methods to generate **transition-metal carbonyl hydrides**:



Properties of some metal carbonyl hydrides:

Complex	mp °C	Decomp. °C	IR $\nu_{\text{M-H}}$	¹ H-NMR δ ppm	pK _a	Acidity comparable to
HCo(CO) ₄	-26	-26	1934	-10	1	H ₂ SO ₄
H ₂ Fe(CO) ₄	-70	-10		-11.1	4.7	CH ₃ COOH
[HFe(CO) ₄] ⁻					14	H ₂ O
HMn(CO) ₅	-25	stab. RT	1783	- 7.5	7	H ₂ S

The term “hydride” for these complexes is based on the assignment of formal oxidation states (hydrogen has a higher electronegativity than most transition metals, cf. p. 8) and

should not be equated with chemical reactivity. The properties of transition-metal hydrides vary considerably; they range from hydridic through inert to acidic in character.

M–H functioning as a hydride donor:

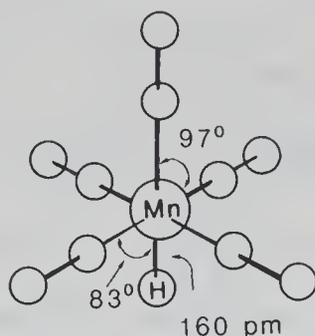


M–H functioning as a proton donor:

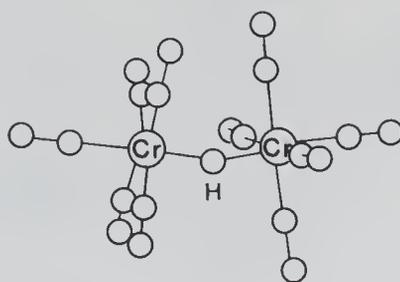


Structural elucidation of metal hydrides by means of X-ray diffraction is difficult (the atomic scattering factors are proportional to the square of the atomic number; light atoms have high amplitudes of thermal vibration). Neutron diffraction is preferable. Typical values for the bond parameters in transition-metal hydrides:

$$d(\text{M}-\text{H}) = 150\text{--}170 \text{ pm} \quad E(\text{M}-\text{H}) \approx 250 \text{ kJ/mol}$$



The hydride ligand occupies a definite position in the coordination polyhedron. $\text{Mn}(\text{CO})_5\text{H}$ has the structure of a slightly distorted octahedron. The $\text{Mn}-\text{H}$ distance approximates the sum of the covalent radii. With increasing bulk the ancillary ligands (e.g. PPh_3) may dominate the overall geometry of the complex, however.



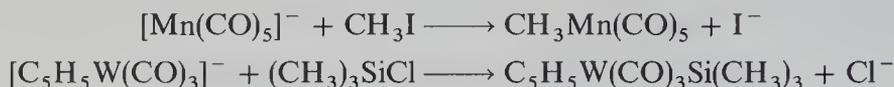
The localization of a bridging hydride ligand ($\text{M}-\text{H}-\text{M}$) is especially difficult because of the proximity of two strongly scattering metal atoms. The position of the hydride ligand in $[\text{Et}_4\text{N}]^+ [\text{HCr}_2(\text{CO})_{10}]^-$ was determined by neutron diffraction.

The bonding situation in the $\text{M}-\text{H}-\text{M}$ bridge is similar to that in the moiety $\text{B}-\text{H}-\text{B}$ (“open” $2e\ 3c$ bond) encountered in boranes.

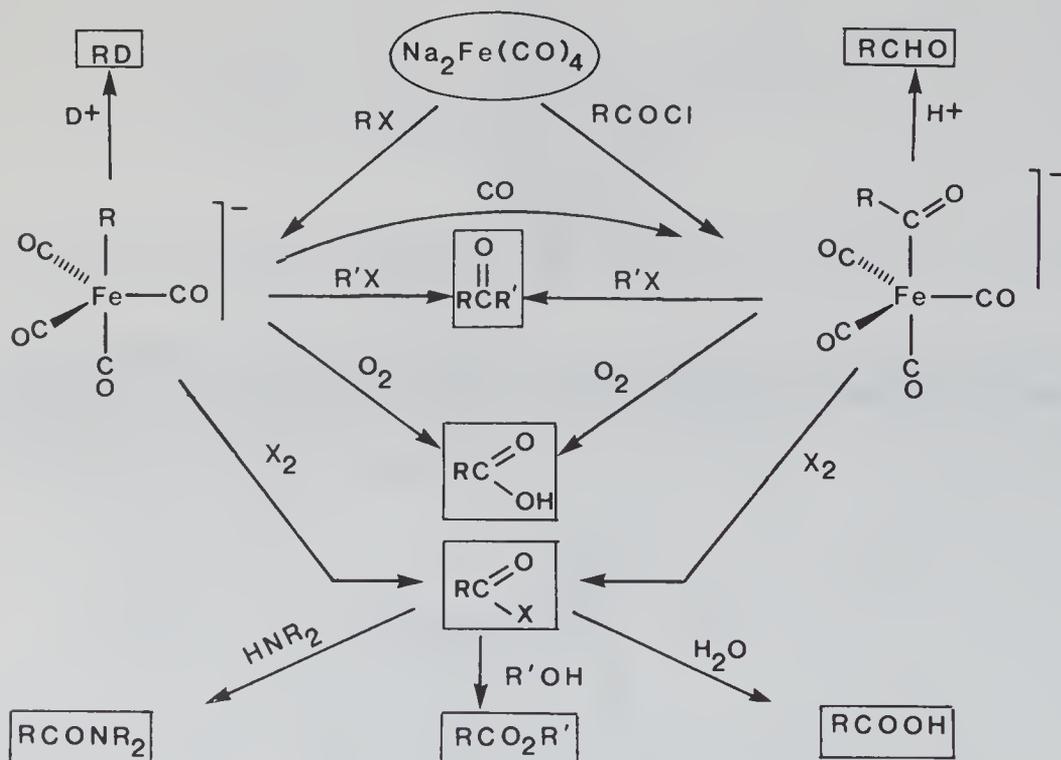
$\text{M}-\text{H}$ units are easily detected by large high-field shifts of their ^1H -NMR signals (see also p. 306). This shielding cannot be directly related to structure and reactivity of these

complexes, though. The absence of a high-field NMR signal ($0 > \delta > -50$ ppm) does not necessarily imply that an M–H moiety is absent. More reliable indications of the presence of direct M–H bonds are found in the **coupling constants**, e.g. $^1J(^{103}\text{Rh}, ^1\text{H}) = 15\text{--}30$ Hz, $^1J(^{183}\text{W}, ^1\text{H}) = 28\text{--}80$ Hz, $^1J(^{195}\text{Pt}, ^1\text{H}) = 700\text{--}1300$ Hz.

In addition to **protonation**, other important reactions of carbonylmetallates include **alkylation** and **silylation**:



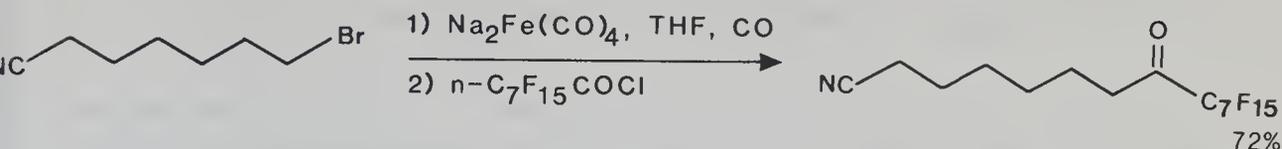
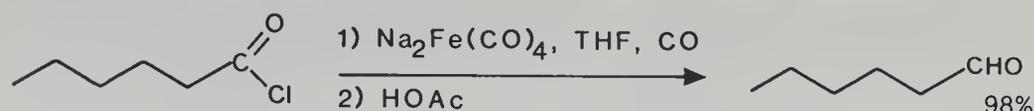
Carbonylmetallates have also found application in organic synthesis ($\text{Na}_2\text{Fe}(\text{CO})_4$, “**Collman’s reagent**”). Organic halogen compounds can be functionalized in many ways via intermediary reaction with disodium tetracarbonylferrate:



Advantages: high yields (70–90%), other functional groups need not be protected since the organoiron anions do not add to carbonyl or nitrile groups.

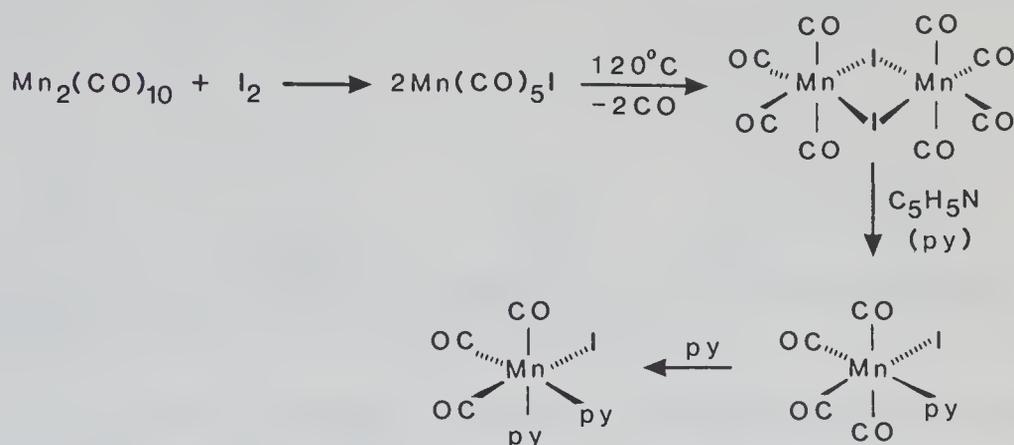
Limitations: $\text{Fe}(\text{CO})_4^{2-}$ is a strong base and, with tertiary halogen compounds, effects HX-elimination.

Examples:



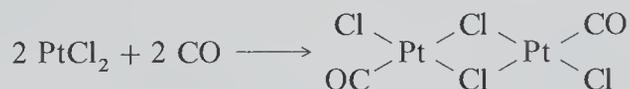
14.5.6 Carbonyl Metal Halides

Carbonyl metal halides are known for most transition metals. They are formed by reaction of metal carbonyls with halogens or by reaction of metal salts with CO:

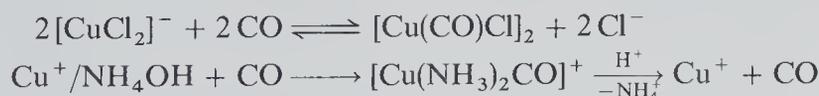


The formation of the *fac*-substitution product results from the *trans* effect of the CO ligands.

The late transition metals copper, palladium, platinum, and gold, while not forming stable binary carbonyls, do give carbonyl metal halides:



The reversible fixation of CO to Cu(I) serves to remove carbon monoxide from gases:



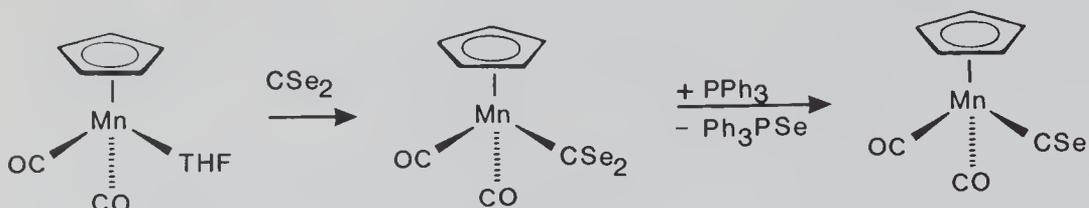
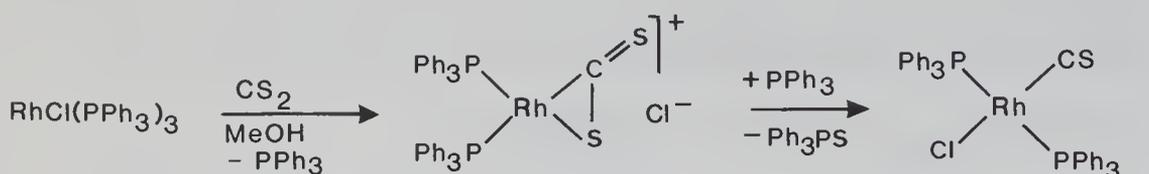
The corresponding complex $[\text{Cu}(\text{en})\text{CO}]\text{Cl}$ of the chelating ligand ethylenediamine (en) can be isolated, although it is rather unstable.

Carbonyl metal halides are suitable precursors for the formation of **metal-metal bonds**:

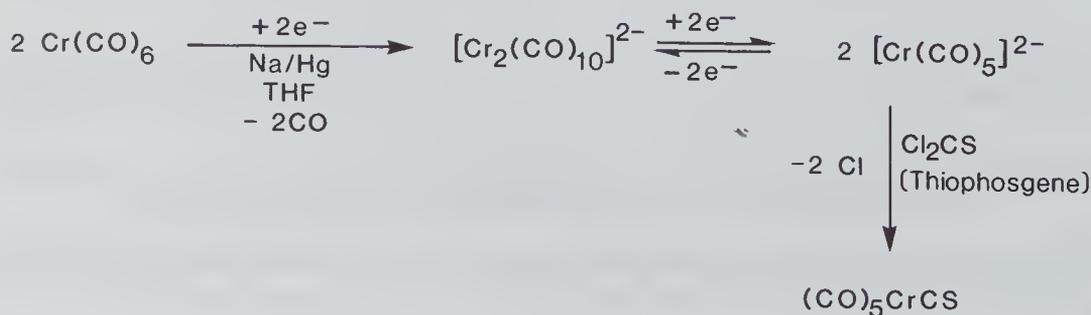
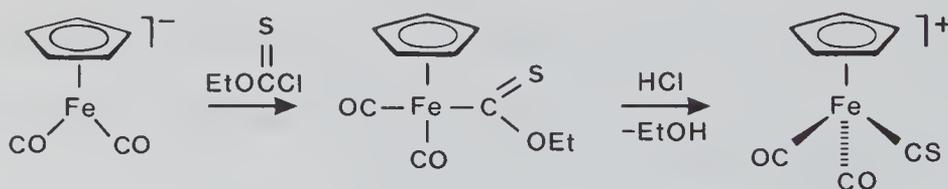


14.6 Thio-, Seleno-, and Tellurocarbonyl Metal Complexes

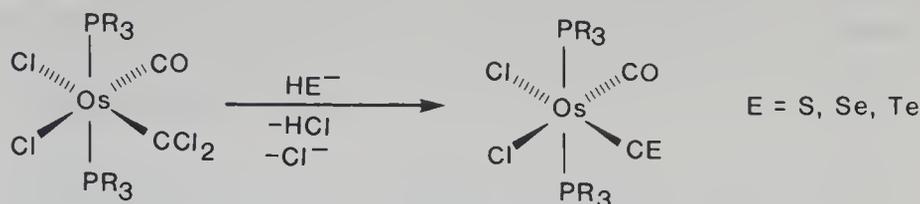
Although the molecules CS, CSe, and CTe as monomers are unstable at room temperature, they can be generated in the coordination sphere of a transition metal. The most common source for CS is CS₂, which itself is first coordinated as an η^2 -ligand to the metal. The η^2 -CS₂ unit is then attacked by triphenylphosphine to yield the η^1 -thiocarbonyl complex and triphenylphosphanesulfide (Wilkinson, 1967):



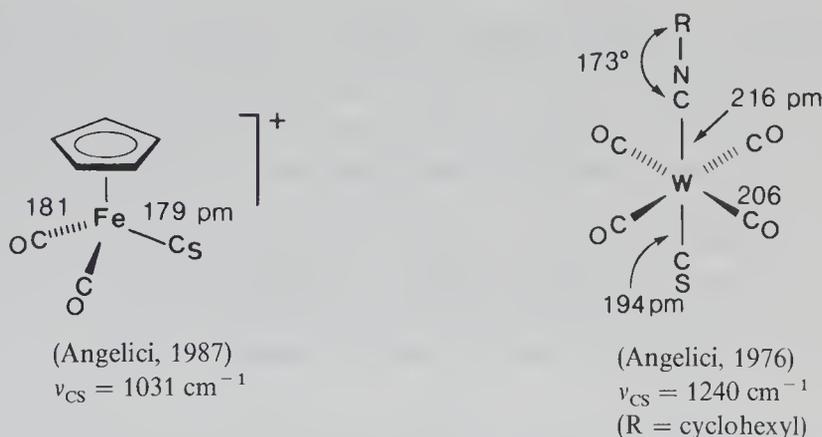
Other sources for CS are ethylchlorothioformate or thiophosgene (Angelici, 1977 R):



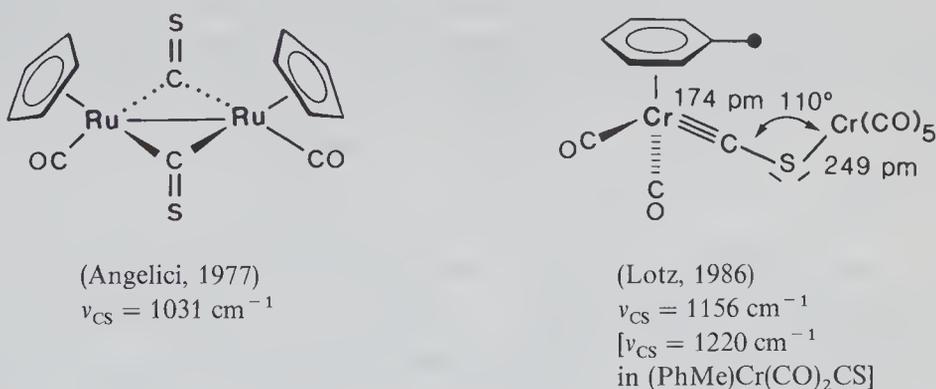
An additional approach is the substitution of two chlorine atoms in a dichlorocarbene complex by E^{2-} (Roper, 1980):



The M–C–S segment is usually linear, the M–CS bond being shorter and therefore stronger than an M–CO bond in the same coordination sphere:



Bridging CS ligands are also known; apparently CS is even more inclined to serve as a bridging ligand and in this function more versatile than CO:



Note the preference of μ -CS bridging over μ -CO bridging in $[(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})\text{CS}]_2$ and the bridging mode M–C–S–M in $(\text{PhMe})\text{Cr}(\text{CO})_2\text{SCr}(\text{CO})_5$. For the ligand CO, bridging of the type M–C–O–M has only been observed in a few exceptional cases (Trogler, 1985).

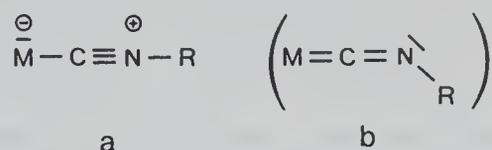
The valence electron formula used above is in agreement with the bond angle CSCr and with the very short $\text{Cr}\equiv\text{C}$ bond, which is reminiscent of the bond length in carbyne complexes (p. 219).

- Compared to metal carbonyls, metal isonitriles have a greater tendency to occur in higher oxidation states (M^I , M^{II}) and a reduced ability to stabilize low oxidation states (M^0 , M^{-I}).
- Metal coordination of CO without exception results in a lowering of the stretching frequency ν_{CO} . For isonitriles, shifts of ν_{CN} to higher as well as to lower wave numbers are observed upon coordination:

L = p-CH ₃ C ₆ H ₄ NC	L	L ₄ Ni	L ₄ Ag ⁺
ν_{CN}/cm^{-1}	2136	2065	2186 (sh)
			2177
		2033	2136 (w)

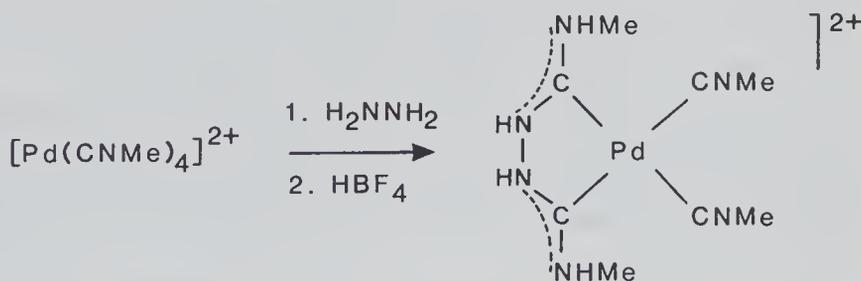
Compared with CO, isonitriles CNR display **stronger σ -donor** and **weaker π -acceptor** character, the latter being influenced by the nature of the group R.

Contrary to what might be anticipated from the contribution of canonical form b, backbonding does not lead to a bent structure for the isonitrile ligand.



Whereas strict adherence to the octet rule (a VB concept) for b would necessitate placing a lone pair of electrons on the nitrogen atom with concomitant ligand bending, the use of vacant antibonding orbitals π^* of linear CNR for the backbonding interaction circumvents a "violation" of the octet rule. Note that the concept of antibonding molecular orbitals and their engagement in chemical bonding is alien to the valence bond formalism.

From the large number of reactions of metal isonitriles, only the addition of compounds with active hydrogen (alcohols, phenols, amines, hydrazines) are mentioned here:



This type of reaction constitutes a general route for preparing aminocarbene complexes (cf. Chapter 14.3).

The fact that the chemistry of metal isonitriles has long been overshadowed by that of metal carbonyls is not due to a lack of interesting reactions, but rather to the repulsive smell of the free ligands.

Excursion

Photochemical Reactivity of Organotransition Metal Complexes

Absorption of a photon converts a molecule into an excited electronic state, which constitutes a new chemical species with altered molecular and electronic structure and therefore different chemical behavior. Compared to the respective ground state, molecules in an electronically excited state may display different bond angles (formation of strained systems, p. 415), as well as drastic changes of the acidity constants and in the redox potentials. Most importantly, specific bond weakening in an excited state may cause greatly enhanced chemical reactivity. Thus, thermal substitution of CO in $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ requires high temperatures, whereas photochemically it proceeds at room temperature.

A thorough discussion of a photochemical reaction ideally includes a description of **photophysical aspects** (nature and life-time of the electronically excited state), **photochemical primary processes** (bond cleavage, bimolecular substitution, redox process) and of **synthetic utility**. In organometallic chemistry, this completeness is hardly ever achieved. Already, the problems begin with an unequivocal assignment of the excitation since the differentiation between metal-centered ($d-d$) and charge-transfer (CT) transitions, dear to the practitioner of ligand field spectroscopy, finds only limited applicability to organotransition-metal complexes, where covalent bond character dominates. Here **both** orbitals involved in an electronic transition usually contain metal- **and** ligand contributions, rendering criteria of assignment like solvatochromism or substitution effects inappropriate.

*In the simplified MO scheme of an octahedral complex, the various types of electronic excitation are defined. Correlation lines lead to the basis orbitals which dominate in the respective molecular orbitals. Source: N. Sutin, *Inorg. React. Meth.* **15** (1986) 260, J. J. Zuckerman, Ed.*

LF

Ligand-field transition between orbitals with dominant metal (nd) character.

Example: (piperidine)W(CO)₅, $\lambda = 403$ nm, $\epsilon = 3860$ (Wrighton, 1974).

This category also includes transitions $\sigma(\text{M}-\text{M}) \rightarrow \sigma^(\text{M}-\text{M})$ in oligonuclear complexes with metal-metal bonds.*

Example: Mn₂(CO)₁₀, $\lambda = 336$ nm, $\epsilon = 33700$ (Wrighton, 1975).

MLCT

Metal-to-ligand charge transfer, formally an intramolecular oxidation of the metal and reduction of the ligand(s).

Example: (4-formyl-pyridine)W(CO)₅, $\lambda = 470$ nm, $\epsilon = 6470$ (Wrighton, 1973).

LMCT

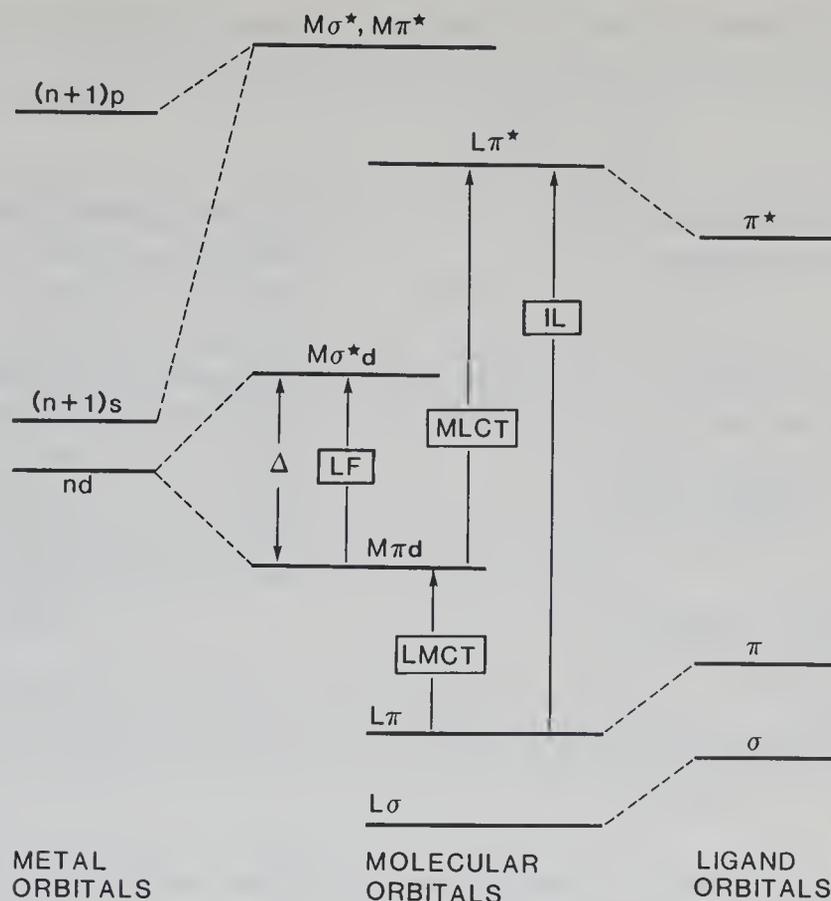
Ligand-to-metal charge transfer.

Example: [Cp₂Fe]⁺, $\lambda = 617$ nm, $\epsilon = 450$ (H. B. Gray, 1973 R).

IL

Intraligand transition, electronic excitation $n \rightarrow \pi^$ or $\pi \rightarrow \pi^*$, respectively, between orbitals which are predominantly centered on a ligand, counterpart to LF-transition.*

Example: (trans-4-styrylpyridine)W(CO)₅, $\lambda = 316$ nm, $\epsilon = 16300$ (Wrighton, 1973).



Additional excitations are:

IT **Intervence transition**, $M \rightarrow M'$ charge transfer in mixed valence oligonuclear complexes. Example: biferrocenyl⁺, $[(C_5H_5)Fe^{II}(C_5H_4-C_5H_4)-Fe^{III}(C_5H_5)]^+$, $\lambda = 1900$ nm, $\epsilon = 550$ (Cowan, 1973 R).

MSCT **Metal-to-solvent charge transfer**. Example: Cp_2Fe in CCl_4 , $\lambda = 320$ nm. Irradiation at the frequency of the MSCT band causes photo-oxidation of the substrate according to



For the photochemical primary processes which follow the initial absorption of light, the life-times of the electronically excited states are of critical importance. The photochemically active state of a molecule is not necessarily generated directly by the absorption of a photon:

The intensive red color of $[Fe(bipy)_3]^{2+}$ is due to an MLCT transition. However, the MLCT state is extremely short-lived ($\tau \leq 10^{-11}$ s) and rapid relaxation to a longer lived chemically active LF state occurs ($\tau = 10^{-9}$ s, Sutin, 1980). Note that direct generation of an LF state ($d-d$ transition) would be Laporte-forbidden.

Electronic excitations are usually accompanied by vibrational excitations (vertical transition, Franck-Condon principle). Excessive vibrational energy is rapidly dissipated into

the surrounding medium, though, resulting in a thermally equilibrated excited state ("thexi-state").

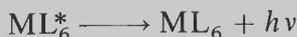
Depending on the energy and the life-time of the excited states, the following processes may succeed:

Unimolecular primary processes:

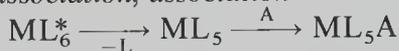
Radiationless deactivation



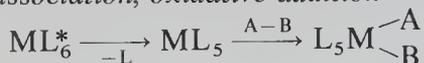
Luminescence



Dissociation, association



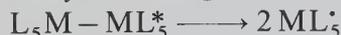
Dissociation, oxidative addition



Isomerization

cis/trans or d/l rearrangement

Homolytic cleavage



Reductive elimination



Bimolecular primary processes:

Collisional deactivation (thermal)



Energy transfer (electronic)



Electron transfer (after MLCT)



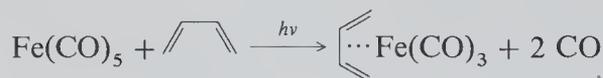
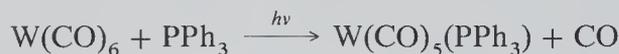
Association (after MLCT)



In the following sections, four photochemically initiated reaction types, which have gained preparative importance, will be discussed.

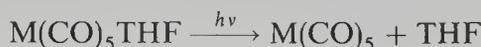
1. PHOTOCHEMICAL SUBSTITUTION AT METAL CARBONYLS

This is the best known and the most frequently executed photoreaction in organometallic chemistry. Examples:



The rate constant for the dissociation $\text{Cr}(\text{CO})_6 \rightarrow \text{Cr}(\text{CO})_5 + \text{CO}$, which precedes the entrance of a new ligand L, is increased upon photochemical excitation $\text{Cr}(\text{CO})_6 \xrightarrow{h\nu} \text{Cr}(\text{CO})_6^*$ by a factor of 10^{16} ! This effect may be traced to the ligand-field transition $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$ which leads to the depopulation of an M-CO bonding- and the population of an M-CO antibonding MO (see p. 188). In metal carbonyl complexes $\text{M}(\text{CO})_m\text{L}_n$ with a mixed coordination sphere, photochemical excitation causes dissocia-

tion of that ligand which is most weakly bonded in the ground state as well. This will be the ligand at the lowest position respectively in the spectrochemical series:

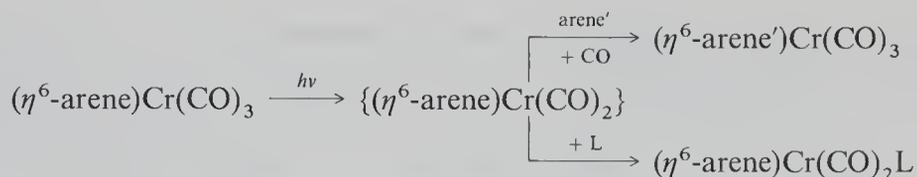


For this reason, the weakly bonded ligand THF can only be introduced once. Among ligands which form bonds of comparable strength, competitive reactions are observed:



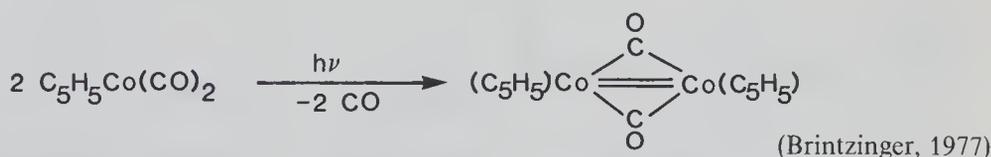
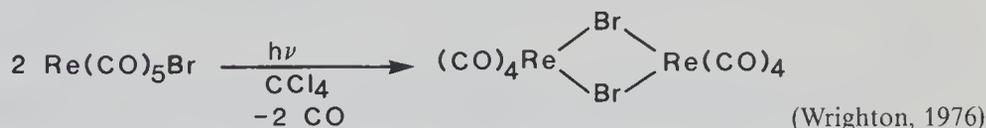
Thus, in the presence of an excess of trimethylphosphite, quantitative photochemical conversion of $\text{Mo}(\text{CO})_6$ into $\text{Mo}[\text{P}(\text{OMe})_3]_6$ can be achieved (Poilblanc, 1972).

In $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$, the arene as well as the carbonyl groups may be replaced:



Mo- and W-complexes undergo CO substitution less readily.

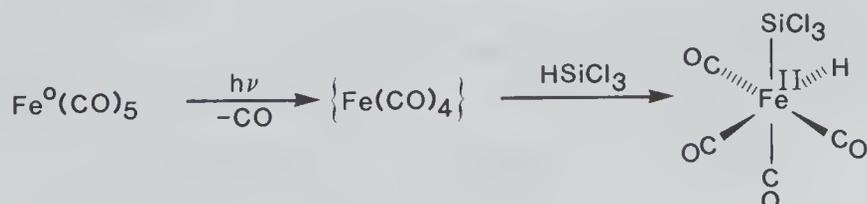
If suitable free ligands are absent, the gap in the coordination sphere, generated through photochemical dissociation of CO, may be closed by dimerization:



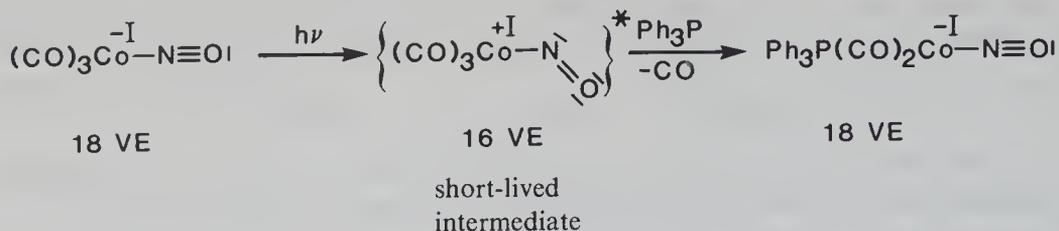
The gap may also be filled internally via $\sigma(\eta^1) \rightarrow \pi(\eta^3)$ rearrangement:



Another possibility of coordinative saturation is oxidative addition, as exemplified by hydrosilation (Graham, 1971):

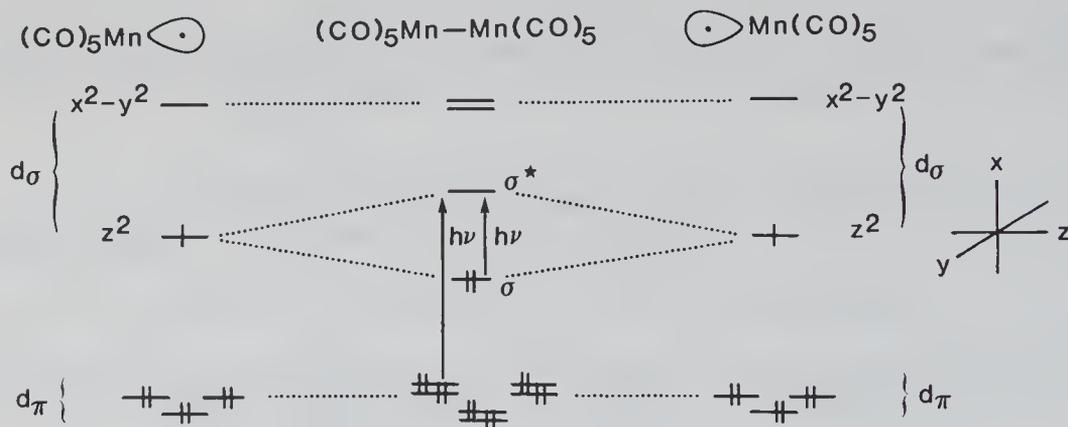


Whereas the previous examples of carbonyl substitution featured **dissociative activation**, the electronic peculiarities of the ligand NO permit an **associative mechanism** which is initiated by a preceding photochemical conversion of NO^+ (linear coordination) into NO^- (bent coordination) (Zink, 1981):



2. PHOTOCHEMICAL REACTIONS WITH CLEAVAGE OF METAL-METAL BONDS

Oligonuclear organotransition metal compounds may hold metal-metal bonds of the orders 1–4 (chapter 16). In the simplest case, two 17 VE fragments are linked by means of an M–M single bond. Examples: $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Co}_2(\text{CO})_8$.



In these dinuclear species, the M–M single bond is the weakest link. Photochemical excitation $\sigma \rightarrow \sigma^*$ reduces the bond order to zero and **homolytic cleavage** yields two organometallic radicals which undergo subsequent reactions:



From a study of competitive reactions for the halogen abstractions, the following reactivity sequence was derived (Abrahamson, 1978):

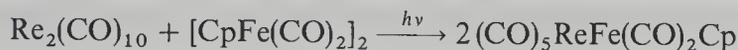


This series parallels the trend in the energetic splitting $E(\sigma, \sigma^*)$ which manifests itself in the optical spectra of the respective dimers.

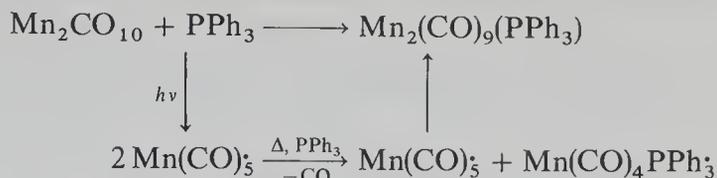
Other photolytic and follow-up reactions which are synthetically useful include:



Through co-photolysis heterometallic dinuclear complexes may be prepared:

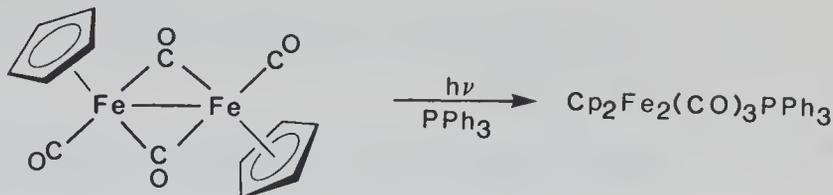


A few seemingly simple photochemically induced substitutions have been shown to proceed via an initial cleavage of the metal-metal bond (Wrighton, 1975):

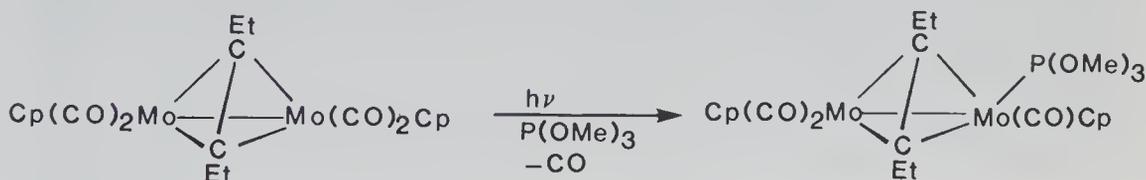


The 17 VE radical $\text{Mn}(\text{CO})_5$ is substitution-labile; replacement of CO by PPh_3 takes an **associative** path, that is without preceding expulsion of CO (T. L. Brown, 1985).

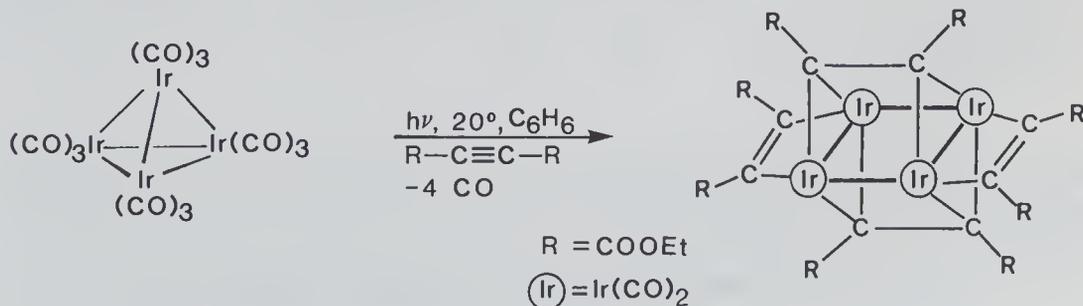
In $[\text{CpFe}(\text{CO})_2]_2$, however, the dimeric structure is maintained during the substitution process (T. J. Meyer, 1980):



This also applies to $\mu(\eta^2:\eta^2\text{-Et}_2\text{C}_2)[\text{CpMo}(\text{CO})_2]_2$ (Muetterties, 1980):



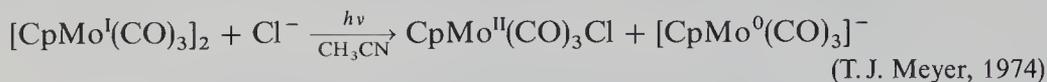
Obviously, bridging ligands in addition to metal-metal bonds obviate homolytic cleavage. If the cluster $\text{Ir}_4(\text{CO})_{12}$ is photolyzed in the presence of an alkyne, the aggregation Ir_4 is preserved, the metal frame changing from tetrahedral to planar geometry, however. The entrance of an electron-rich alkyne abates the electron deficiency of the Ir_4 -unit with concomitant **reduction of metal-metal connectivity** (B. F. G. Johnson, 1978):



On the other hand, the thermodynamic stability of certain organometallic clusters may also lead to the **generation of new metal-metal bonds** under photochemical conditions:



Occasionally, photoreactions of dinuclear metal carbonyls are accompanied by disproportionation:

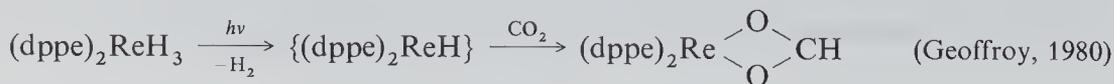
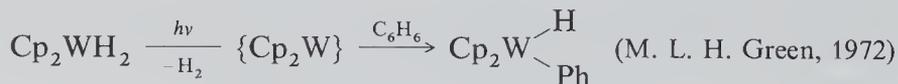
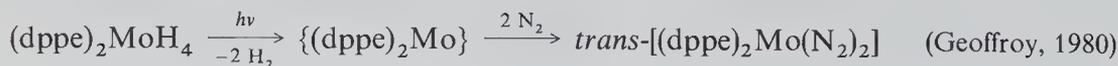


Mechanistically, these reactions may follow the sequence homolysis \rightarrow substitution \rightarrow electron transfer.

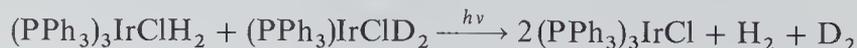
3. PHOTOCHEMICAL REACTIONS WITH CLEAVAGE OF METAL-HYDROGEN BONDS

While transition-metal hydrogen bond cleavage reactions do not strictly belong to the realm of organometallic chemistry, they are closely related to it.

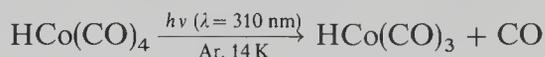
- In the case of **mononuclear di- and oligohydrides**, the primary reaction of the photochemically excited molecule usually is **reductive elimination of H₂** (Geoffroy, 1980 R). The electron-rich and sparsely coordinated species which are formed in this way are highly reactive. They combine even with relatively inert partners, which is of considerable preparative significance (see p. 440):



Evidently, elimination of H₂ proceeds in a concerted way, since HD is not formed in the following photolysis (Geoffroy, 1976):



- **Oligohydridometal clusters** like $\text{Re}_3\text{H}_3(\text{CO})_{12}$ resist photochemical H_2 elimination. Here, the hydride ligands are in metal bridging positions, which impedes the concerted elimination of an H_2 molecule. Instead, the photochemistry of these hydrido clusters is governed by metal-metal bond cleavage and by carbonyl substitution.
- In **monohydrido complexes** as well, photoinduced ligand substitution is the usual reaction, homolytic cleavage of transition-metal hydrogen bonds being the exception. This is plausible because the concerted loss of an H_2 molecule from a dihydride is a low energy reaction path, whereas the cleavage of a single metal-hydrogen bond in a monohydride is a high energy one. Photoinduced dissociation of a metal carbonyl hydride can be studied by means of IR spectroscopy in matrix isolation (Orchin, 1978):



In the presence of potential ligands, photosubstitution is effected:

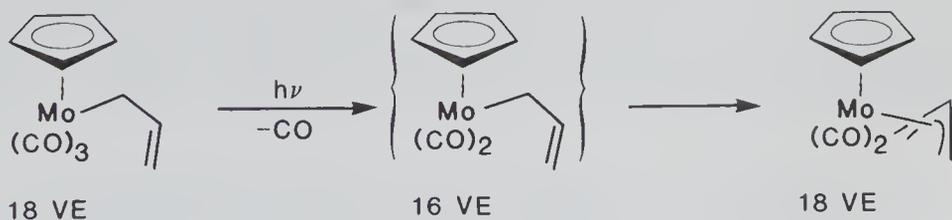


This reaction is much slower than photosubstitution of $\text{Re}_2(\text{CO})_{10}$, which was shown to proceed via $\text{Re}(\text{CO})_5$ radicals. Thus for $\text{HRe}(\text{CO})_5$, $\text{Re}-\text{H}$ homolysis as a primary process may confidently be excluded (T. L. Brown, 1977).

4. PHOTOCHEMICAL REACTIONS WITH CLEAVAGE OF TRANSITION METAL-CARBON BONDS

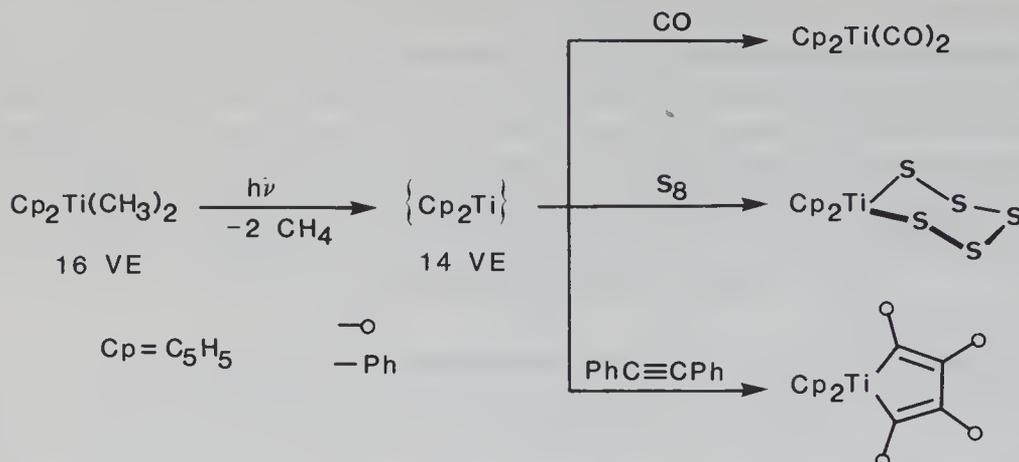
The study of photochemically initiated reactions of organometallics containing transition metal-carbon σ bonds is complicated by the fact that these molecules often have access to thermal pathways of decomposition like β -hydride elimination (p. 198). If one turns to thermally more stable complexes with a mixed ligand sphere (example: $\text{CpMo}(\text{CO})_3\text{CH}_3$), the photochemical reactivity of the metal-alkyl bond is complemented by the possibility of reactions in other segments of the molecule. This diversity clouds the mechanistic picture. Even more than in the preceding sections preparative utility will be stressed here.

- An early application of photochemical excitation in organometallic chemistry was the synthesis of π -allyl complexes via $\sigma \rightarrow \pi$ rearrangement (M. L. H. Green, 1963):

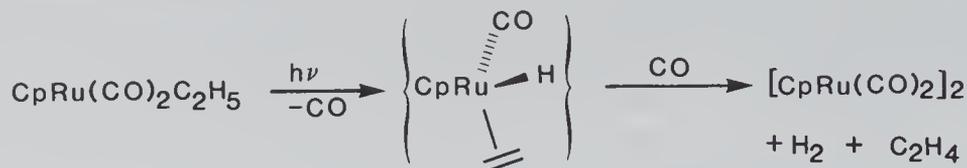


The primary photoreaction here is loss of a CO ligand, followed by the change in the bonding mode of the allyl group from η^1 (σ -complex) to η^3 (π -complex). According to this pattern, (η^5 -pentadienyl)metal moieties can also be generated (p. 290).

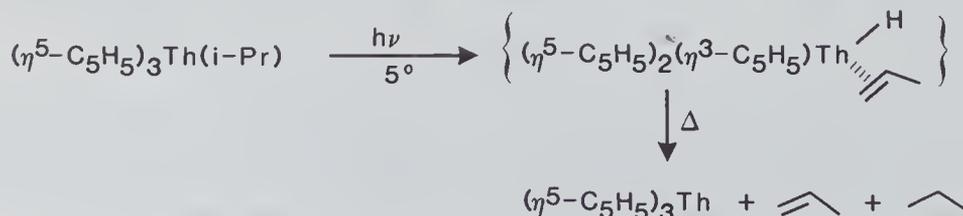
- **Photodealkylation**, a method for the formation of reactive organometallic intermediates, has found extensive preparative application. Example (Alt, 1984 R):



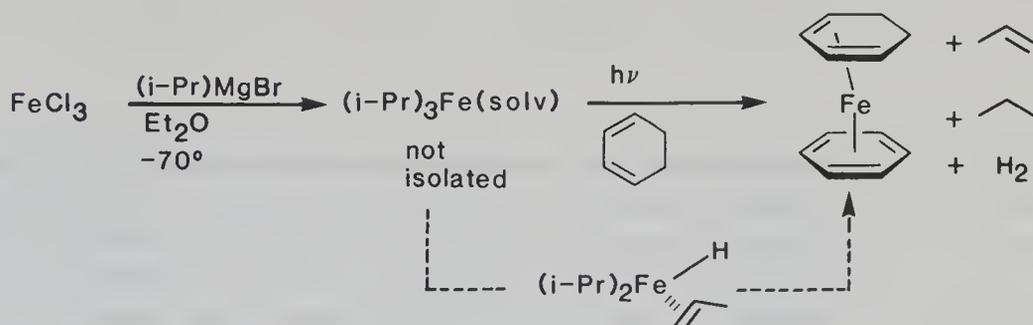
A remarkable aspect is the loss of CH_4 : labeling studies indicate that the hydrogen required is furnished by the C_5H_5 ligand. Only traces of C_2H_6 are observed; therefore, the intermediacy of CH_3 radicals is unlikely. Apparently, the photolysis of molecules with $\text{TM}^\sigma\text{-C}$ bonds differs fundamentally from that of organometallic dihydrides, where reductive elimination of H_2 dominates. In the absence of potential ligands, photodealkylations may be succeeded by dimerization of the organometal fragments (Wrighton, 1982):



Here as well, the initial step is photochemical loss of CO. An olefin(hydrido)complex intermediate is implied by the reaction products H_2 and C_2H_4 . A prerequisite for the β -elimination mechanism to occur is the initial generation of a vacant coordination site. If in addition to σ -bonded alkyl groups, the central metal atom carries only multidentate ligands, photochemical excitation may lead to bond weakening for one of these ligands, reducing its hapticity (e.g. $\eta^5 \rightarrow \eta^3$). The photochemical formation of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Th}$ from the thermally stable compound $(\eta^5\text{-C}_5\text{H}_5)_3\text{Th}(i\text{-Pr})$ is thought to follow this pattern (Marks, 1977):



- The **Fischer-Müller reaction**, a versatile method for the synthesis of arene- and olefin complexes is also based on the photochemical cleavage of $M^{\sigma}C$ bonds ($M = V, Cr, Fe, Ru, Os, Pt; R = i-Pr$). Example (E. O. Fischer, 1962):



Once again, the formation of C_3H_6 and C_3H_8 (1 : 1) suggests a β -hydride elimination mechanism with an olefin(hydrido)complex as an intermediate.

Despite numerous practical applications, a mechanistic understanding of the photochemistry of organometallics is still in its infancy. Significant advances are expected from the application of ultra-fast methods like laser flash photolysis, which explores the picosecond range (Peters, 1986 R). A particularly attractive aspect of photochemistry is the close symbiosis between spectroscopy and chemistry. After all, electron spectroscopic characterization of the educts in their ground states and photochemical generation of the new reactive species often are identical processes.

15 σ , π -Donor/ π -Acceptor Ligands

A common feature of the extensive class of π -complexes is the fact that the $L \rightarrow M$ donor- as well as the $L \leftarrow M$ acceptor interaction utilizes ligand orbitals which – with regard to the intra-ligand bond – have π -symmetry. The ligand-metal bond in π -complexes always contains an $L \leftarrow M$ π -acceptor component; the $L \rightarrow M$ donor contribution, as will be discussed for the various ligands, can have σ -symmetry (monoolefins) or σ - and π -symmetry (oligoolefins, enyl ligands, arenes and heteroarenes).

15.1 Olefin Complexes

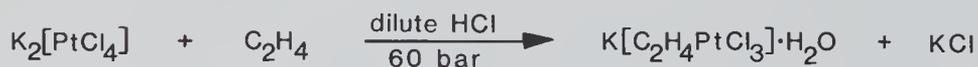
15.1.1 Homoalkene Complexes

Olefin complexes are widespread among the transition metals. These complexes play an important role in reactions that are catalyzed by organotransition-metal compounds, such as hydrogenation, oligomerization, polymerization, cyclization, hydroformylation, isomerization, and oxidation (see Chapter 17).

Conjugated oligoolefins form particularly stable complexes, as do nonconjugated diolefins with a sterically favorable arrangement of the double bonds (chelate effect).

PREPARATION

1. Substitution Reactions



This complex was prepared for the first time by Zeise in 1827 by boiling PtCl_4 in ethanol. The first preparation starting from ethylene was described by Birnbaum (1868). With SnCl_2 as a catalyst, this reaction proceeds in a few hours, given a C_2H_4 pressure of 1 bar.

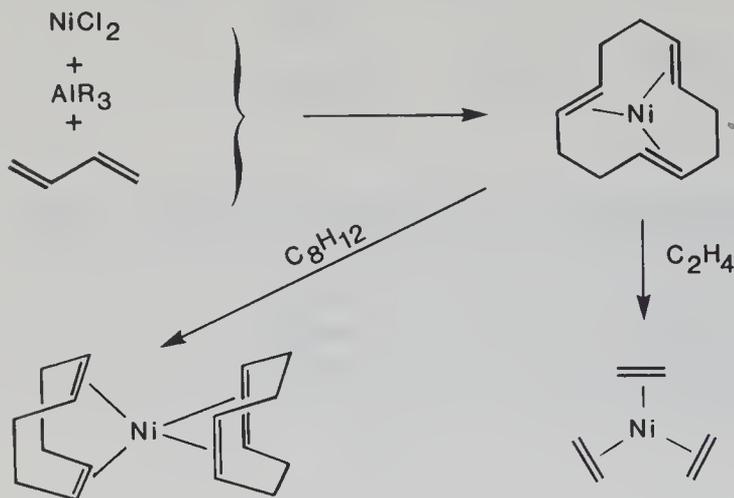
AlCl_3 facilitates the substitution of Cl^- by incorporating it into the $[\text{AlCl}_4]^-$ counterion:



The use of AgBF_4 leads to the precipitation of silver halide and the introduction of the noncoordinating anion BF_4^- (Caution: AgBF_4 is also a good oxidizing agent!):



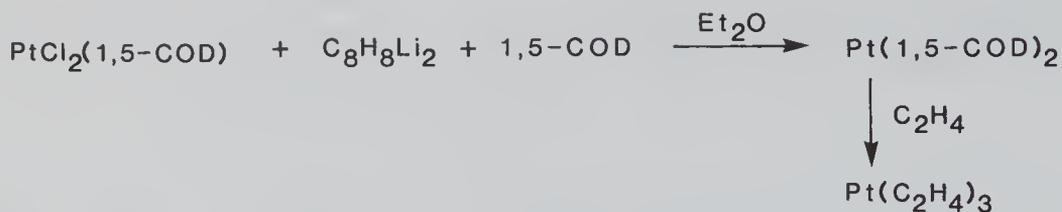
2. Metal Salt + Olefin + Reducing Agent



(*Trans-trans-trans-cyclododecatriene*)Ni⁰ (Wilke, 1961): The high reactivity of this complex is expressed in the term "naked nickel".

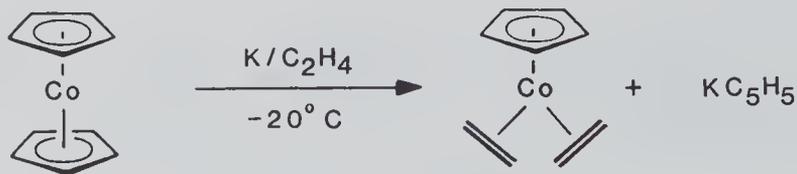
Ni⁰(COD)₂, a good source of Ni⁰ for further reactions.

The first binary metal-ethylene complex, colorless, stable up to 0°C (Wilke, 1973).

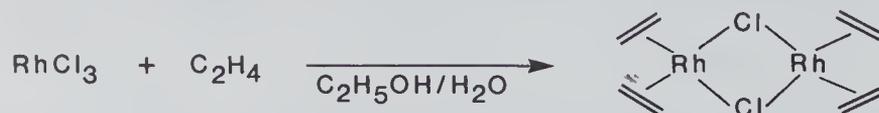


Trisethyleneplatinum is only stable under a C₂H₄ atmosphere (Stone, 1976).

A special variation of this reaction type is the reductive cleavage of metallocenes (Jonas, 1980):

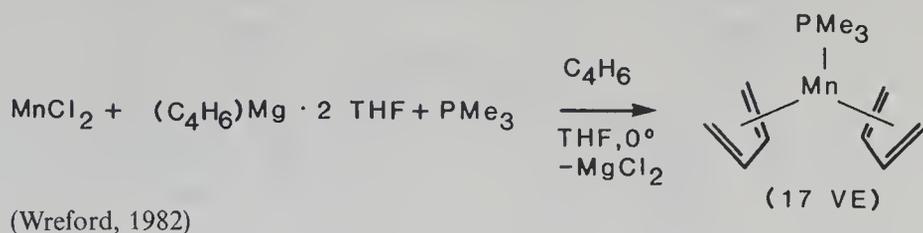


CpCo(C₂H₄)₂ is a useful reagent for the transfer of the half-sandwich unit CpCo.



In this reaction, Rh(III) is reduced by an excess of ethylene.

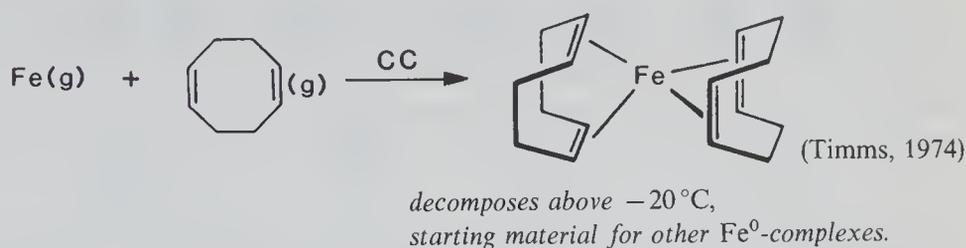
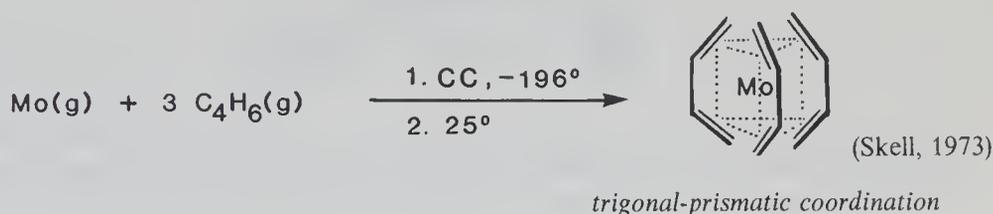
3. Butadiene Transfer by Means of Magnesium Butadiene (cf. p. 41)



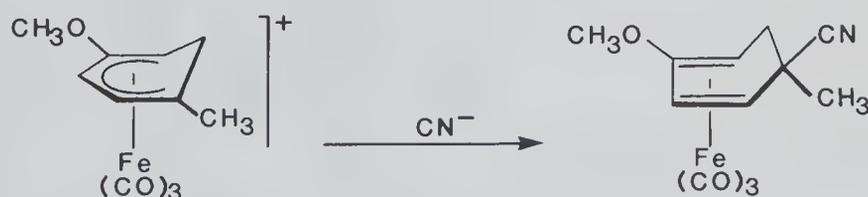
This procedure is also applicable to other transition-metal halides.

4. Metal-Atom Ligand-Vapor Cocondensation (CC)

In the cocondensation method (sometimes referred to as metal-vapor synthesis) metal vapors are condensed with the gaseous ligand on a cooled surface or into ligand solutions of low vapor pressure. On warming to room temperature, metal complexes are formed in competition with metal aggregation (Skell, Timms, Klabunde, M. L. H. Green). For a number of fundamental organometallics, cocondensation techniques currently represent the only way of access. Drawbacks to this method include the frequent low yields and the large amount of cooling agent required.

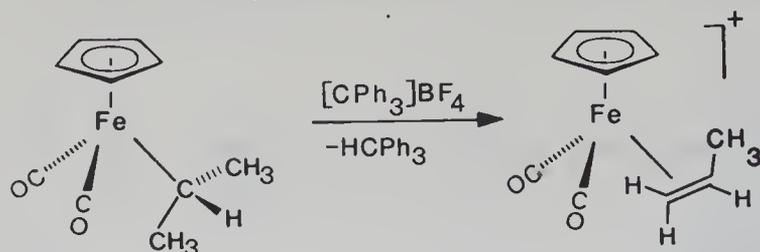


5. Transformation of Enyl Complexes



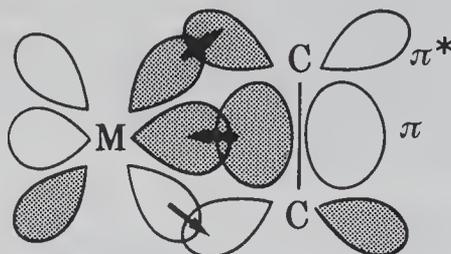
Such nucleophilic additions are generally regio- as well as stereoselective; the nucleophile attacks trans to the metal.

6. Hydride Abstraction from Alkyl Complexes



STRUCTURE AND BONDING OF MONOOLEFIN COMPLEXES

The coordination of a monoolefin to a transition metal provides the simplest example of a metal π -complex. The qualitative bonding description (Dewar, Chatt, Duncanson, 1953) is similar to that for the $M-\text{CO}$ moiety as far as the donor-acceptor synergism is concerned.



The donor component (from the ligand's viewpoint) is the interaction of the filled, π -bonding orbital of ethylene with vacant metal orbitals, the acceptor component that of filled metal orbitals with the vacant π^ -antibonding orbital of ethylene (shading indicates orbital phases.)*

The tendency to form olefin complexes is therefore also controlled by the σ -acceptor/ π -donor characteristics of the metal. Under the assumption that the σ -acceptor properties correlate with the **electron affinity EA** and the π -donor properties with the **promotion energy PE**, data for the free transition-metal atoms or ions can be used to evaluate their tendency to form complexes with olefins or with other donor/acceptor ligands (p. 257).

The ability of an olefin to function as a Lewis base as well as a Lewis acid in its bonding to a transition metal helps to fulfill the electroneutrality principle. In this context, consider the results of quantum-chemical calculations on some model compounds (Roos, 1977):

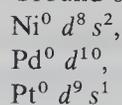
		Calculated charge on		
		Ni	C_2H_4	NH_2 or NH_3
$(\text{C}_2\text{H}_4)\text{Ni}(\text{NH}_2)_2$	"Ni(II) complex"	+0.83	+0.02	-0.43
$(\text{C}_2\text{H}_4)\text{Ni}(\text{NH}_3)_2$	"Ni(0) complex"	+0.58	-0.78	+0.11

Despite the different formal oxidation states, this quantitative treatment of the bonding leads to very similar charges on the central atom!

High electron affinity (EA) of the metal favors the $M \leftarrow \sigma$ olefin contribution, low promotion energy (PE) the $M \rightarrow \pi^*$ olefin contribution to chemical bonding: Ni^0 is a good π -donor, Hg^{2+} a good σ -acceptor; Pd^{2+} is a good π -donor and a good σ -acceptor. The donor/acceptor behavior of the metal towards the olefin is also influenced by ancillary ligands.

Source: R. S. Nyholm, *Proc. Chem. Soc.* (1961) 273

* Ground-state configurations:

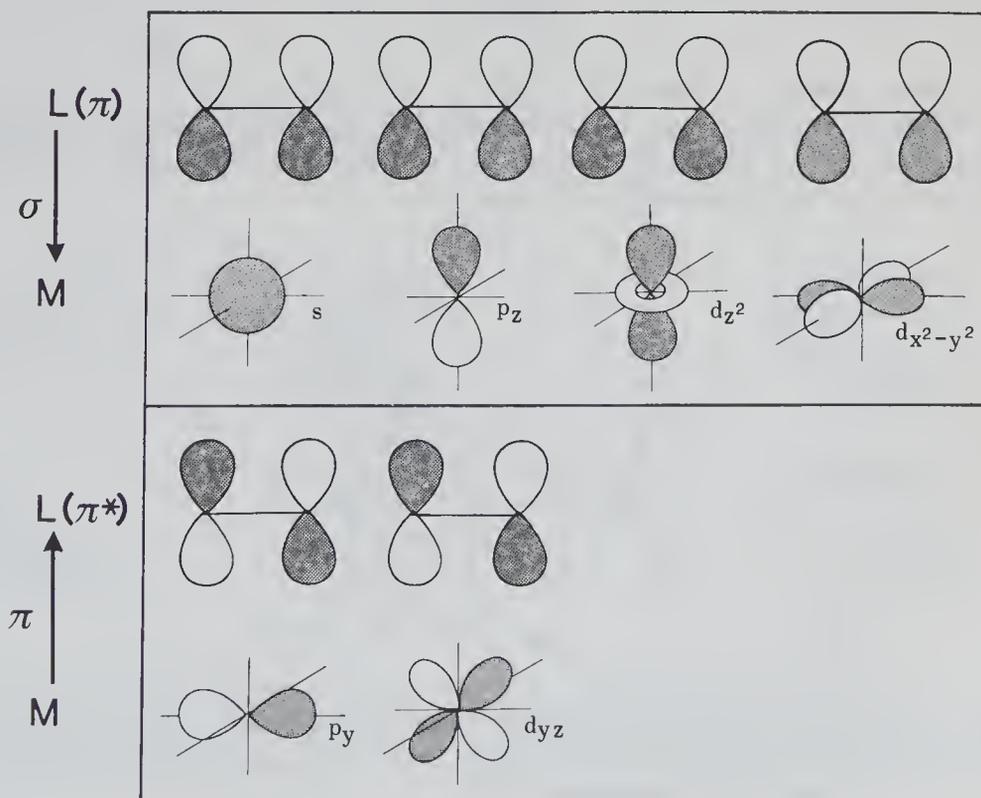


Atom or Ion	Electr. Config.	PE in eV	EA in eV
$Ni(0)^*$	d^{10}	1.72	1.2
$Pd(0)^*$	d^{10}	4.23	1.3
$Pt(0)^*$	d^{10}	3.28	2.4
$Rh(I)$	d^8	1.6	7.31
$Ir(I)$	d^8	2.4	7.95
$Pd(II)$	d^8	3.05	18.56
$Pt(II)$	d^8	3.39	19.42
$Cu(I)$	d^{10}	8.25	7.72
$Ag(I)$	d^{10}	9.94	7.59
$Au(I)$	d^{10}	7.83	9.22
$Zn(II)$	d^{10}	17.1	17.96
$Cd(II)$	d^{10}	16.6	16.90
$Hg(II)$	d^{10}	12.8	16.90

$$PE \begin{cases} nd^{10} \rightarrow nd^9 (n+1)p^1 \\ nd^8 \rightarrow nd^7 (n+1)p^1 \end{cases}$$

$$EA \begin{cases} nd^{10} \rightarrow nd^{10} (n+1)s^1 \\ nd^8 \rightarrow nd^8 (n+1)s^1 \end{cases}$$

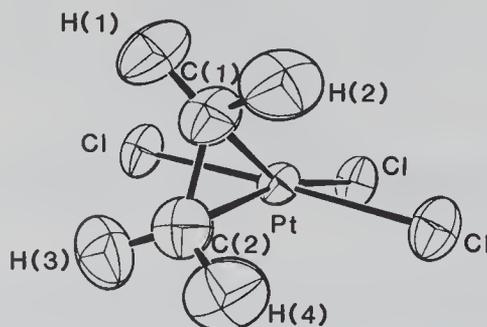
The MO treatment of the MC_2 fragment consists of symmetry-matched combinations of metal and ligand orbitals:



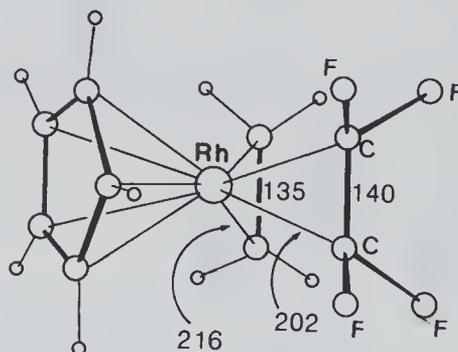
Both the $M \leftarrow \sigma$ olefin donor and the $M \rightarrow \pi$ olefin acceptor part of the interaction serve to weaken the intra-ligand C–C bond. In principle, this is evident from the phase relations in the $L(\pi)$ and $L(\pi^*)$ molecular orbitals, verification being provided by a comparison of the $\nu_{C=C}$ vibrational frequencies of free and coordinated ethylene:

Complex	$\nu_{C=C}/\text{cm}^{-1}$	Complex	$\nu_{C=C}/\text{cm}^{-1}$
$[(C_2H_4)_2Ag]BF_4$	1584	$(C_2H_4)Fe(CO)_4$	1551
$[(C_2H_4)_2Re(CO)_4]PF_6$	1539	$[CpFe(CO)_2C_2H_4]PF_6$	1527
$[C_2H_4PdCl_2]_2$	1525	$K[PtCl_3(C_2H_4)] \cdot H_2O$	1516
$CpMn(CO)_2(C_2H_4)$	1508	$[C_2H_4PtCl_2]_2$	1506
$CpRh(C_2H_4)_2$	1493	C_2H_4 , free	1623

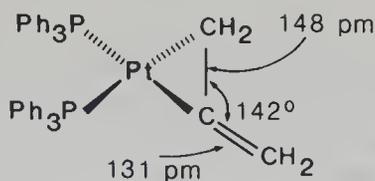
An important structural aspect is the **loss of planarity of the olefin upon coordination to a transition metal**. In substituted ethylenes C_2X_4 , this deformation increases with increasing electronegativity of X.



Structure (neutron diffraction) of $K[PtCl_3(C_2H_4)]$. The C–C bond length is 137 pm, similar to the uncomplexed olefin (135 pm). The olefin is oriented perpendicular to the $PtCl_3$ -plane. The Pt–Cl bond trans to the olefin is slightly elongated. The atoms H(1)–H(4), C(1) and C(2) are not coplanar. The dihedral angle between the CH_2 planes is 146° (Bau, 1975).

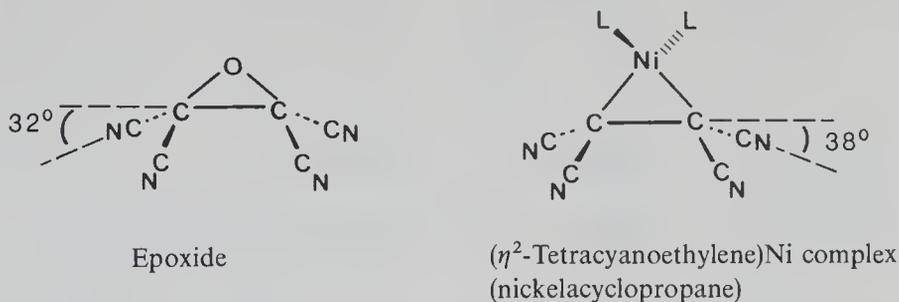


Structure (X-ray diffraction) of $(C_5H_5)Rh(C_2H_4)(C_2F_4)$. The carbon atoms of C_2F_4 are closer to the metal than those of C_2H_4 . The dihedral angle between the two CH_2 -planes in C_2H_4 is 138° , that of the CF_2 -planes in C_2F_4 is 106° (Guggenberger, 1972).



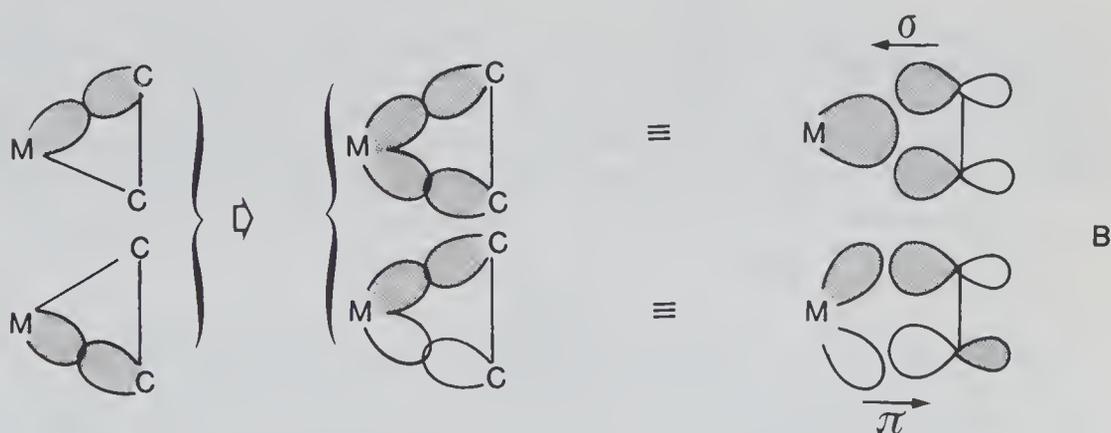
The coordination of allenes also leads to considerable distortion of the C_3 -unit, which is linear in the free state. A similar distortion is also experienced by CO_2 , coordinated side-on as a "diheteroallene" ligand in complexes of the type $(R_3P)_2Ni(\eta^2-CO_2)$ (Darensbourg, 1983 R).

There is a certain structural similarity between the fragment $(\eta^2\text{-alkene})M$ and an epoxide, warranting a metallacyclopropane description of the former:



At first sight, such a formulation seems to bear little resemblance to the Dewar-Chatt-Duncanson model. It can be shown, however, that the actual bonding situation is well in accordance with a description somewhere between these two borderline cases (R. Hoffmann, 1979):

Localized orbitals Linear combination Delocalized orbitals

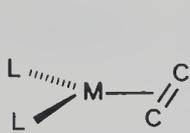


Metallacyclopropane description:
two localized $2e\ 3c$ MC σ -bonds, alkene acting as a bidentate ligand (non-planar)

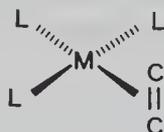
Dewar-Chatt-Duncanson model:
One delocalised $2e\ 3c$ MC_2 σ -bond, one delocalised $2e\ 3c$ MC_2 π -bond, alkene acting as a "monodentate" ligand (planar).

While in the alternative **B** (p. 259), the carbon atoms are sp^2 -hybridized (planar η^2 -ethylene), the percentage of p character in the hybrid orbital is higher in alternative **A** (non-planar η^2 -ethylene). The deviation from planarity of coordinated ethylene should therefore correlate with the tendency of carbon atoms to form hybrid orbitals with higher p character. This tendency grows with increasing electronegativity of the substituents (**Bent's Rule**, e.g. the $\text{CH}_3\cdot$ radical is planar, $\text{CF}_3\cdot$ is pyramidal).

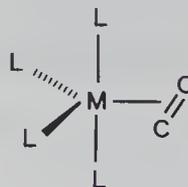
The conformation relative to the M-olefin axis depends on the coordination number of the metal as well as on the number of valence electrons:



C.N. 3, 16 VE

 L_2M (alkene) L_2M (alkyne)Examples: $(\text{PPh}_3)_2\text{NiC}_2\text{H}_4$ $\text{Pt}(\text{C}_2\text{H}_4)_3$ 

C.N. 4, 16 VE

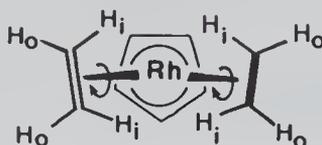
 L_3M (alkene)Examples: $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ 

C.N. 5, 18 VE

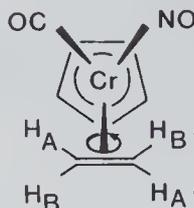
 L_4M (alkene)Examples: $(\text{PPh}_3)_2\text{IrBr}(\text{CO})\text{TCNE}$

TCNE = tetracyanoethylene

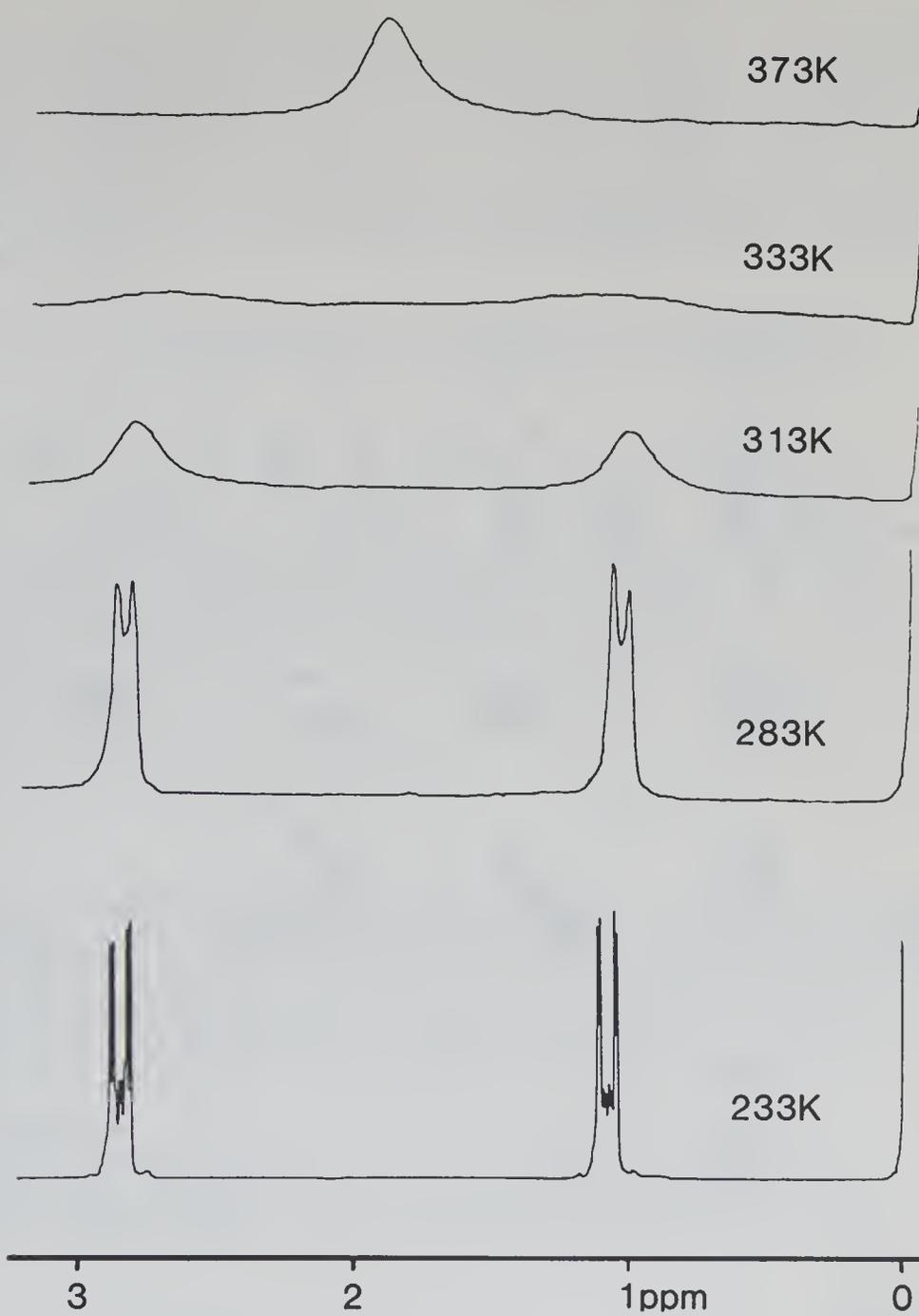
Hindered ligand rotation of coordinated alkenes (and alkynes) often occurs in a temperature range which is suitable for routine ^1H - and ^{13}C -NMR studies. This is demonstrated by the temperature-dependent ^1H -NMR spectrum of the fluxional molecule $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ (p. 261).



On fast rotation around the metal-ligand axis (the rotational frequency is higher than the signal separation in Hz), the inner (H_i) and the outer (H_o) protons appear equivalent. At low temperatures, this rotation can be "frozen", and an $\text{AA}'\text{XX}'$ spectrum is observed instead of a single signal (Cramer, 1969). That this rotation takes place around the metal-ligand axis rather than around the $\text{C}-\text{C}$ axis of ethylene is proved by the temperature-dependent ^1H -NMR spectrum of a chiral ethylene complex:



Upon raising the temperature, the spectrum of $\text{C}_5\text{H}_5\text{CrCO}(\text{NO})\text{C}_2\text{H}_4$ converts from an ABCD - to an $\text{AA}'\text{BB}'$ type; two pairs of diastereotopic protons are therefore retained. An additional rotation around the ethylene ($\text{C}-\text{C}$) axis would, however, result in an A_4 -type spectrum (Kreiter, 1974).



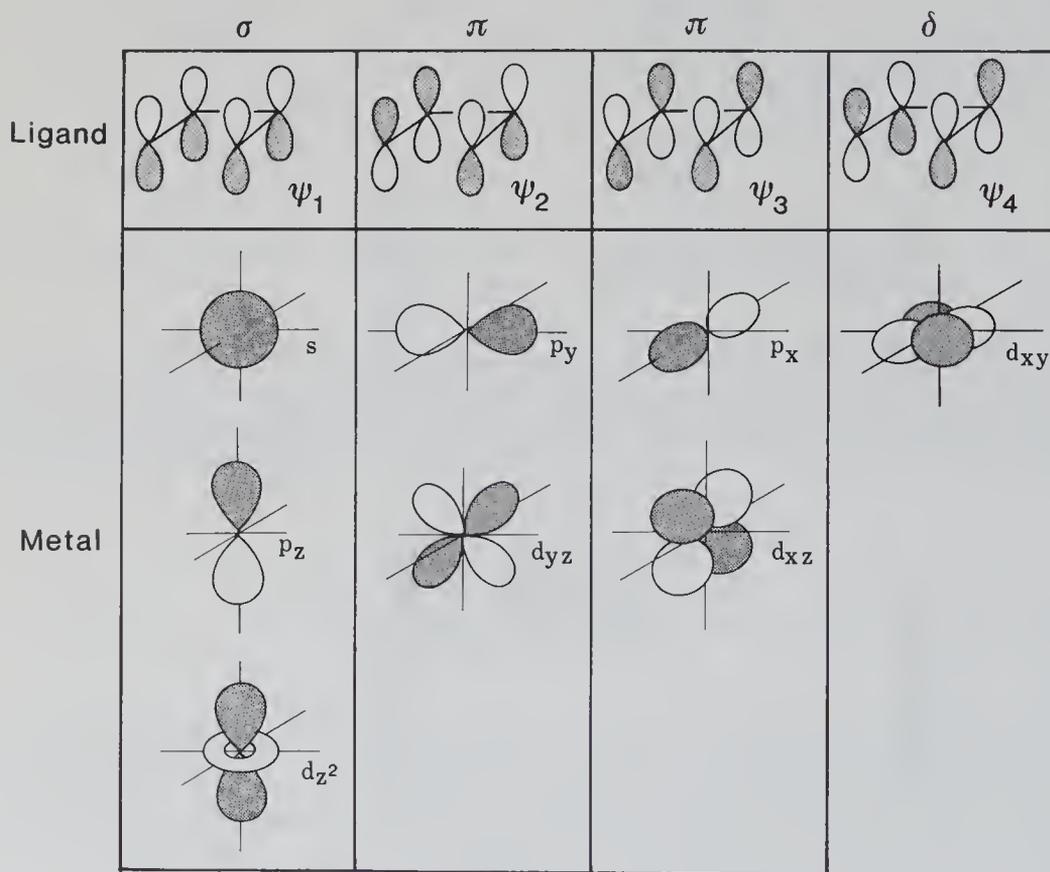
$^1\text{H-NMR}$ spectrum of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ (200 MHz).

If the ligands C_2H_4 and C_2F_4 are present in the same molecule (see structure p. 258), the rotation around the $\text{M}-\text{C}_2\text{F}_4$ axis ceases at a higher temperature than that around the $\text{M}-\text{C}_2\text{H}_4$ axis, a consequence of the different rotational barriers for the two ligands. Apparently the backbonding contribution $\text{M} \rightarrow \text{olefin}$, mainly responsible for the rotational barrier, is larger for C_2F_4 than for C_2H_4 .

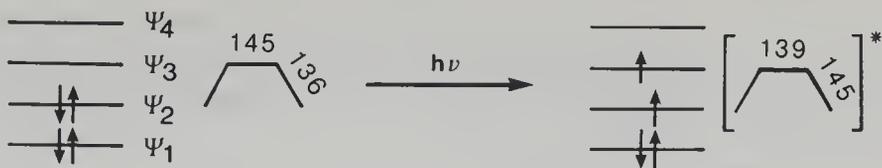
STRUCTURE AND BONDING OF DIOLEFIN COMPLEXES

Distinguishing between compounds with isolated diolefins and those with conjugated diolefins is justified in terms of bonding theory. The metal-ligand bonds in complexes with nonconjugated diolefins closely correspond to those in monoolefin-metal complexes. Conjugated di- and oligoolefins, however, have delocalized π -MO's of differing energies and symmetries. They offer a larger variety of combinations with the metal atomic orbitals, resulting in more stable metal-carbon bonds.

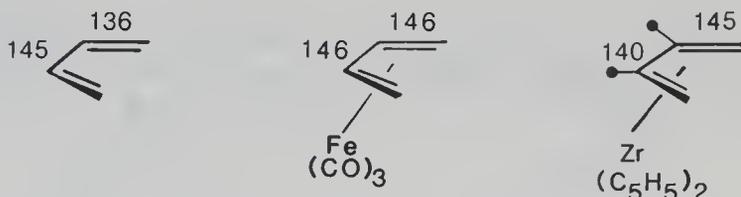
Metal-ligand interactions in butadiene complexes:



In an extension of the Dewar-Chatt-Duncanson model, the bonding situation in $(\eta^4\text{-C}_4\text{H}_6)\text{M}$ can be described by the components $\psi_1 \xrightarrow{\sigma} \text{M}$, $\psi_2 \xrightarrow{\pi} \text{M}$, $\psi_3 \xleftarrow{\pi} \text{M}$ and $\psi_4 \xleftarrow{\delta} \text{M}$. Both interactions $\text{M} \xrightarrow{\pi} \text{L}$ should result in a lengthening of the terminal C—C bonds and a shortening of the internal C—C bond. This is a consequence of the depopulation of ψ_2 , the population of ψ_3 and the nodal characteristics of these ligand orbitals. In this context, it should be mentioned that electronic excitation of free butadiene induces similar changes in bond lengths:



The following examples illustrate the influence of transition-metal coordination on the ligand parameters:



Apart from bond lengths, coupling constants $^1J(^{13}\text{C}, ^{13}\text{C})$ in ^{13}C -NMR spectra also argue for a change of bond orders within the η^4 -1,3-diene ligand. For the terminal carbon atoms, a hybridization state intermediate between sp^2 and sp^3 can be assumed on the basis of the observed coupling constants $^1J(^{13}\text{C}, ^1\text{H})$. This may be described by the two canonical forms:



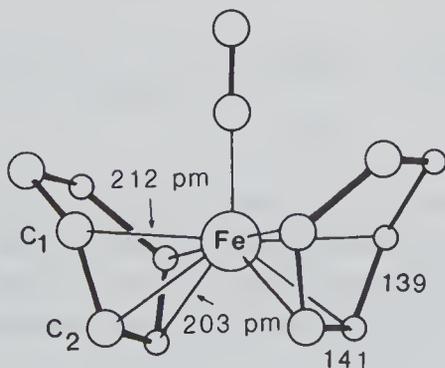
The relative weight of these two resonance forms can be discussed on the basis of the $\text{M}-\text{C}$ distances. While complexes of the “late” transition metals merit a description as π -complexes, corresponding compounds of the “early” transition metals are better designated as **metallacyclopentenenes**. In such generalizations, however, the nature of the substituents on the ligands should not be disregarded (cf. $\eta^2\text{-C}_2\text{X}_4$, p. 259).

“ π -Complex”

$(\eta^4\text{-cyclohexadiene})_2\text{Fe}(\text{CO})$

$\text{M}-\text{C}_1(\text{terminal}) = \text{long}$

$\text{M}-\text{C}_2(\text{internal}) = \text{short}$

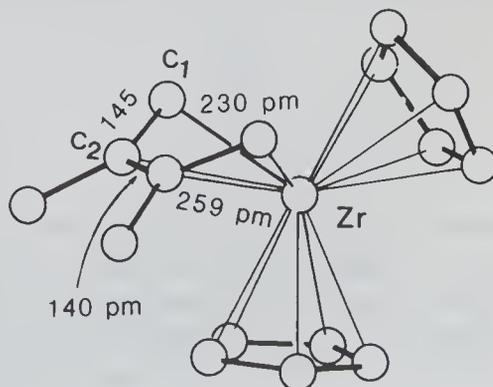


“Metallacyclopentene”

$(\eta^4\text{-dimethylbutadiene})\text{ZrCp}_2$

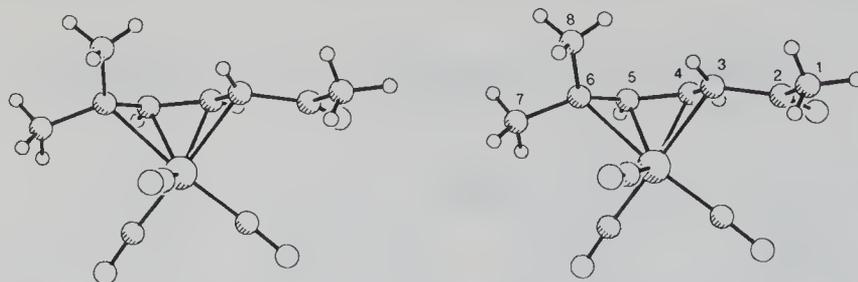
$\text{M}-\text{C}_1(\text{terminal}) = \text{short}$

$\text{M}-\text{C}_2(\text{internal}) = \text{long}$



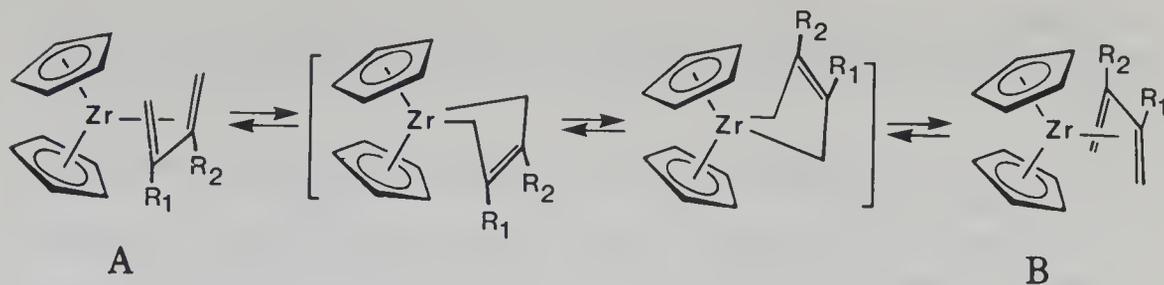
Further structural characteristics of (1,3-diene)Fe(CO)₃ complexes can be deduced from extensive X-ray diffraction studies and from spectroscopic data. This is discussed for the following representative example, the structure of tricarbonyl[3-6 η -(6-methylhepta-3,5-dien-2-one)]iron (Prewo, 1988):

(Guide to three-dimensional viewing: p. 71)

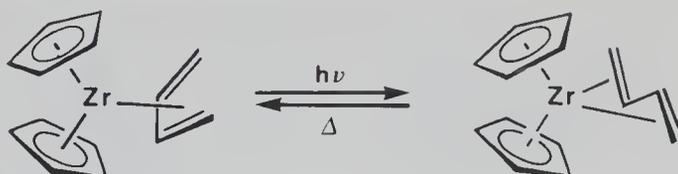


- The terminal substituents [e.g. C(7) and C(8)] are not coplanar with the coordinated carbon atoms C(3)–C(6). The deviation from planarity is 16.6° for the bond C(6)–C(7) and 52.4° for the bond C(6)–C(8). This is due to a strong **distortion of C(6)–C(8)** relative to C(3)–C(6), one result being that the overlap of the C(6) p_{π} -orbital with Fe(3d)-orbitals is altered.
- (1,3-diene)Fe(CO)₃ complexes are **conformationally labile**. Crystal structures disclose a nearly square-planar geometry, with the apical and two basal positions occupied by carbonyl groups. For a species of low symmetry like the iron carbonyl complex shown above, three signals for the three nonequivalent carbonyl groups would be expected in the ¹³C-NMR spectrum. At room temperature, however, only one signal is usually observed, indicating a rapid exchange process within the Fe(CO)₃ moiety. Upon lowering the temperature, the slow exchange region can be reached (Takats, 1976). The experimental data are most reasonably explained by an exchange process involving rotation of the Fe(CO)₃ moiety about its **pseudo-C₃** axis, whereby the olefin retains its planarity.
- (1,3-diene)Fe(CO)₃ complexes are **configurationally stable**. Prochiral diolefins form chiral complexes which can be resolved into enantiomers.

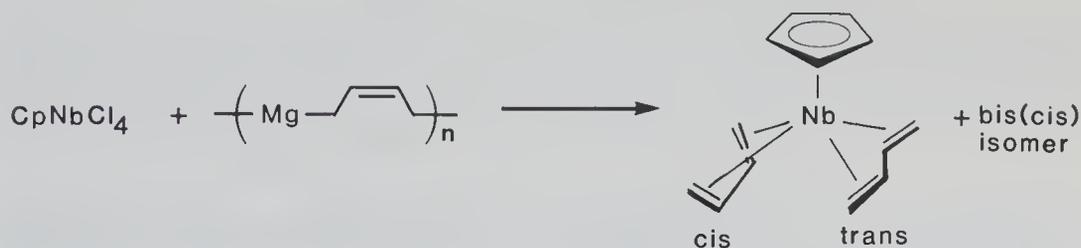
In contrast to the corresponding (diene)Fe(CO)₃ compounds, diolefin complexes of zirconium are **configurationally nonrigid**. The two cyclopentadienyl rings become equivalent through a rapid flipping movement of the diolefin (possibly via a purely σ -bonded metallacyclopentene intermediate). If R₁ and R₂ differ, then **A** and **B** are enantiomeric and the rearrangement effects racemization (Erker, 1982):



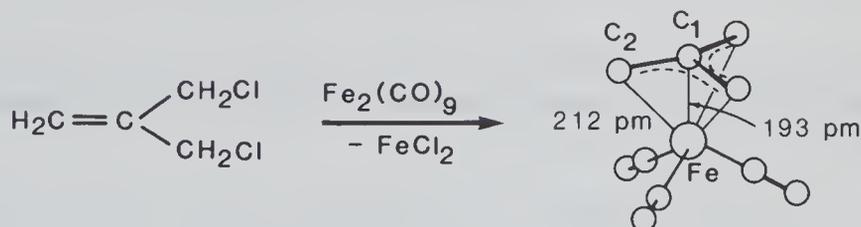
Among the organozirconium complexes, one also finds the only monomeric complexes in which butadiene adopts the *s-trans* configuration (Erker, 1982):



In $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\eta^4\text{-C}_4\text{H}_6)_2$, according to its 500 MHz $^1\text{H-NMR}$ spectrum, the *cis* and *trans* forms of butadiene even coexist in the same molecule (Yasuda, 1988):



Trimethylenemethane, a constitutional isomer of butadiene, is only stable if coordinated to a transition metal (Emerson, Pettit, 1966):



The different Fe–C distances reflect the reluctance of trimethylenemethane to sacrifice its planarity and thereby its *intra*-ligand π -conjugation.

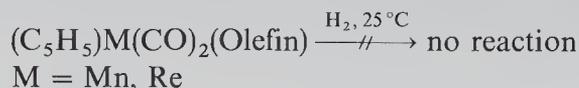
REACTIONS OF NONCONJUGATED OLEFIN COMPLEXES

The **thermodynamic stability** of these complexes is strongly influenced by the nature of the olefin:

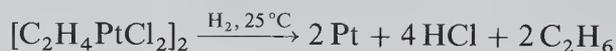
- *Electron-withdrawing substituents increase the stability whereas electron-donating substituents decrease it.*
- *In cases where **cis-trans isomerism** is possible, the more stable complex is invariably formed by the **cis-olefin**.*
- *Complexes of **ring-strained** cycloalkenes like cyclopropene, **trans-cyclooctene** and norbornene display surprising stability.*
- *As a consequence of the **chelate effect**, particularly high stability is shown by complexes in which isolated olefins are part of a carbocycle of favorable geometry. Examples:*



The **redox behavior** of olefin complexes is not easily generalized:



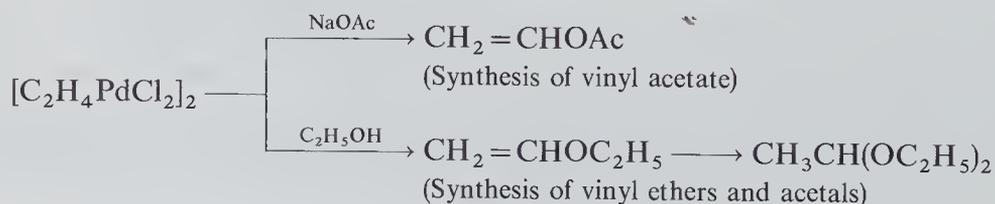
but



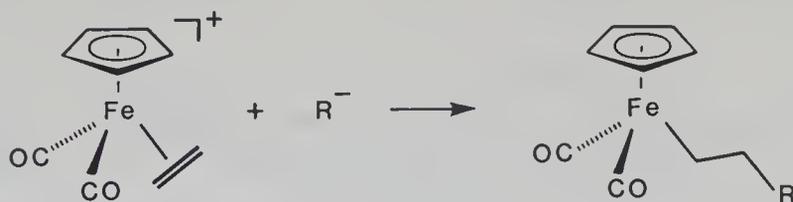
The most characteristic reaction of monoolefin complexes is **ligand substitution**, occurring in many cases under mild conditions, and providing an important method for the synthesis of metal complexes of low thermal stability:



Also of synthetic interest is the **behavior** of some metal-olefin complexes **towards nucleophilic reagents**. This reaction has been extensively studied for dimeric (olefin)palladium chlorides:



Complexes of the general type $[\text{CpFe}(\text{CO})_2(\text{olefin})]^+$ react with a variety of nucleophiles via a $\pi - \sigma$ rearrangement of the metal-ligand bond to give stable, neutral metal alkyls (Rosenblum):

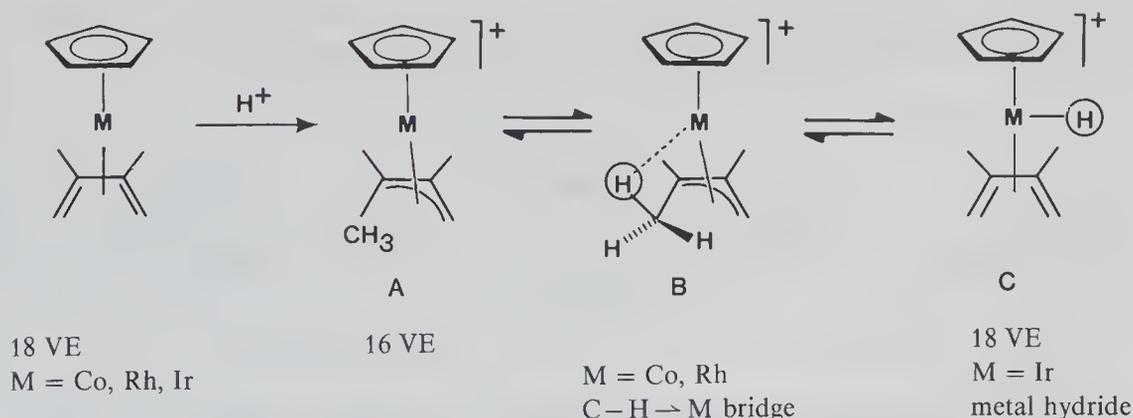


REACTIONS OF DI- AND OLIGOOLEFIN COMPLEXES

Metal-coordinated di- and oligoolefins are quite unreactive compared to the respective free olefin; they can neither be catalytically hydrogenated nor do they undergo Diels-Alder reactions. However, provided they are stable to oxidation, they can react with **electrophiles** such as strong acids. If the proton prefers addition to a coordinated carbon atom rather than to the metal, the valence shell has to be filled by an additional two-electron ligand like carbon monoxide:



An alternative way to compensate this electron deficit at the metal is the formation of a $\text{C}-\text{H} \rightarrow \text{M}$ bridge. Protonated diolefin complexes (form **A**) exist in a dynamic equilibrium with forms **B** and **C**. At low temperatures, for $\text{M} = \text{Co}$, Rh form **B** and for $\text{M} = \text{Ir}$ form **C** dominates (Salzer, 1987):



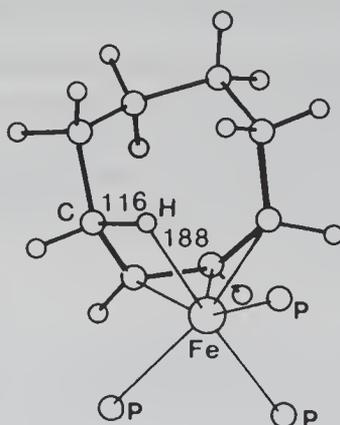
The C_5Me_5 congener of the rhodium complex is a fluxional molecule, whose dynamic ^{13}C -NMR spectrum is discussed on p. 304).

Such $2e3c$ bonds between the $\text{C}-\text{H}$ entity of a ligand and the central metal atom, for which M. L. H. Green has proposed the term “agostic”, strongly resemble the familiar $\text{B}-\text{H}-\text{B}$ bridges in borane chemistry. Agostic interactions model the attack of an unsat-

urated fragment L_nM at a C–H bond; they contribute to our understanding of C–H activation at transition-metal centers (p. 439). C–H \rightarrow M bridges have mainly been detected in complexes in which C–H bonds are positioned β to coordinated allyl and diolefin units (Brookhart, 1983 R).

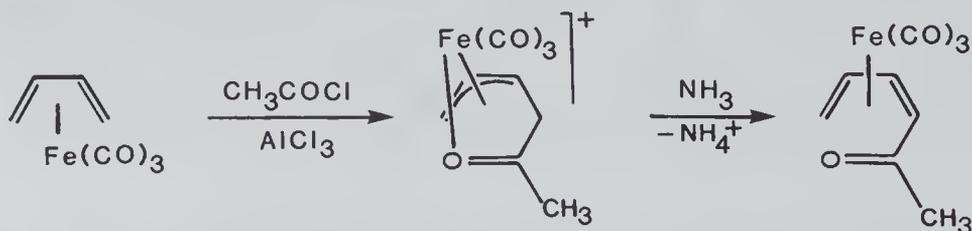
The existence of C–H \rightarrow M bridges can be deduced from

- structural data (especially those obtained from neutron diffraction)
- chemical shifts to high-field in the $^1\text{H-NMR}$ spectrum ($\delta = -5$ to -15 ppm)
- reduced coupling constants [$^1J(\text{C}, \text{H}) = 75-100$ Hz]
- vibrational frequencies at low wave numbers ($\nu_{\text{CH}} = 2700-2300$ cm^{-1}).

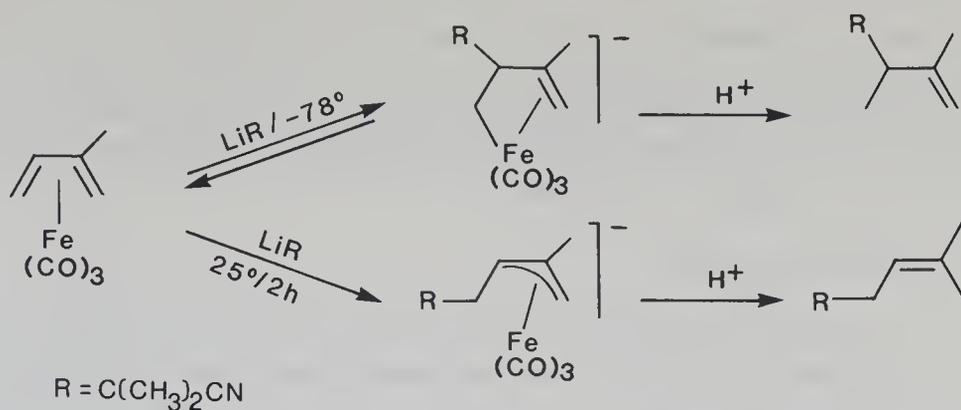


A typical example of a C–H \rightarrow M bridge is seen in the structure of $\{(\eta^3\text{-C}_8\text{H}_{13})\text{Fe}[\text{P}(\text{OMe})_3]_3\}\text{BF}_4$ (Stucky, Ittel, 1980).

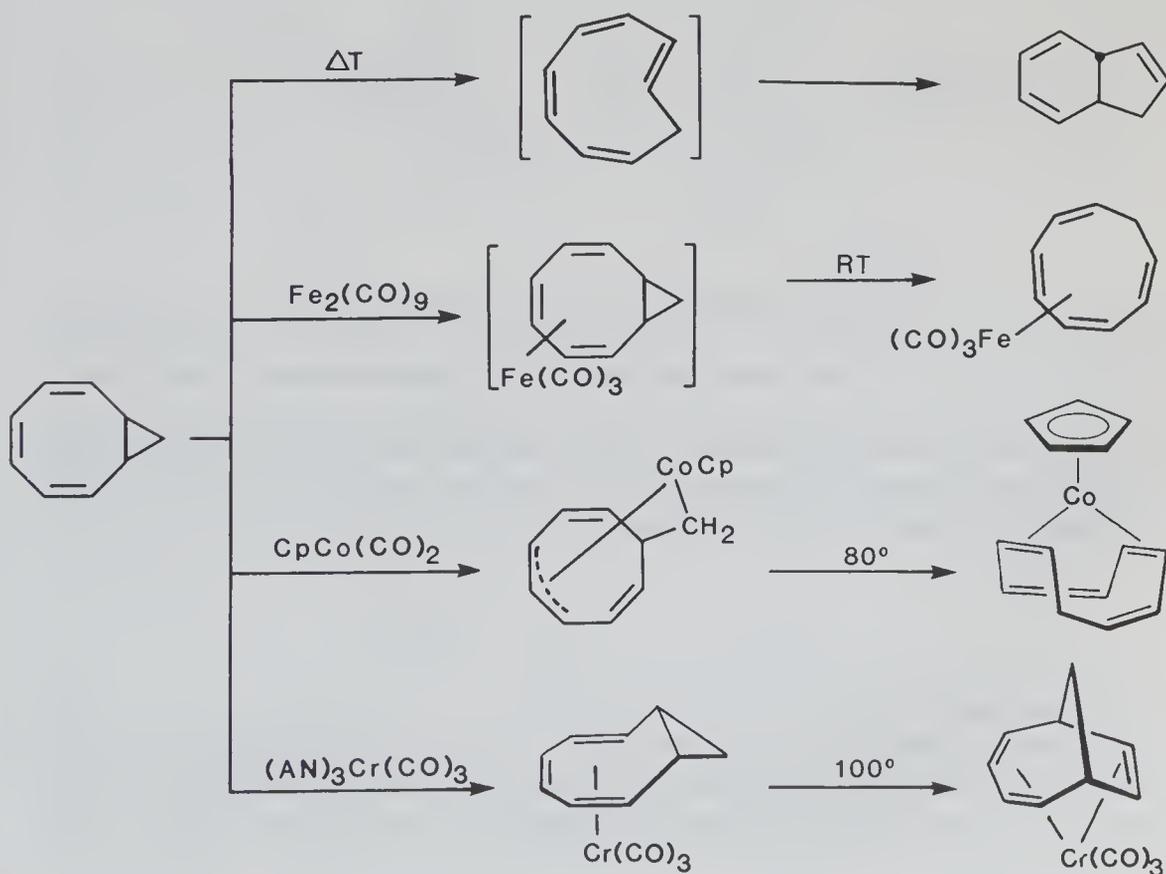
Friedel-Crafts acylations of (diene) $\text{Fe}(\text{CO})_3$ complexes are also initiated by an electrophilic attack at the terminal carbon atom of the ligand (Pauson, 1974):



Besides electrophilic additions, **nucleophilic additions** to coordinated olefins are of growing synthetic interest. At -78 $^\circ\text{C}$, alkyllithium reagents attack (isoprene) $\text{Fe}(\text{CO})_3$ exclusively at an internal unsubstituted carbon atom. Since this addition is kinetically controlled and reversible, warming to room temperature favors the formation of the thermodynamically more stable allyl complex. The anionic complexes are only stable in solution, so that their structures have to be deduced from product analysis after aqueous quenching (Semmelhack, 1984):



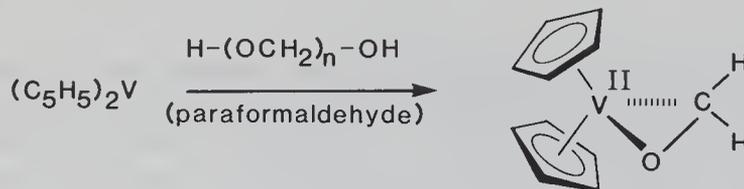
Metal-coordinated oligoolefins can undergo **valence isomerization** in a manner similar to the free olefins; the 'Woodward-Hoffmann rules' of organic chemistry are not applicable to these organometallics, however. Instead, the course of the reaction is mainly influenced by the respective organometallic fragment and its coordinative preference. Bicyclo[6.1.0]nonatriene and its metal complexes may serve as an illustrative example:



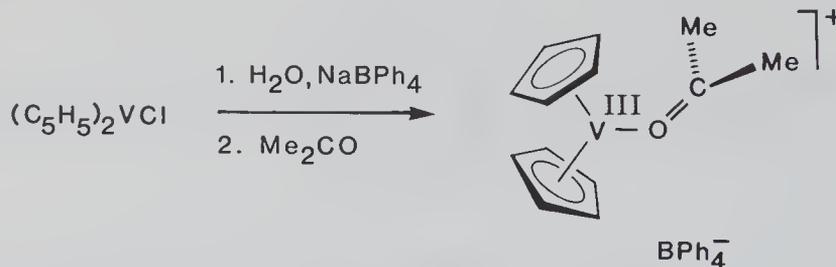
The iron and cobalt complexes contain the ligand cyclononatetraene, a molecule of low stability if uncomplexed. In the case of $\text{CpCo}(\text{CO})_2$, an intermediate displaying σ , π -coordination can be isolated, indicating prior insertion of the cobalt complex into the cyclopropane ring. The valence isomerization takes a different course when bicyclonona-triene is coordinated to a $\text{Cr}(\text{CO})_3$ moiety.

15.1.2 Heteroalkene Complexes

From the point of view of coordination chemistry it seems reasonable to regard organic carbonyl compounds as heteroalkenes (formaldehyde = oxaethene). The bonding modes η^1 -vinyl and η^2 -alkene of olefins then correspond to terminal (η^1 -O) and side-on (η^2 -C, O) coordination of carbonyl groups, respectively:



The IR vibrational frequency for this η^2 (C, O) formaldehyde complex ($\nu_{\text{CO}} = 1160 \text{ cm}^{-1}$) is strongly shifted to lower wave numbers (for free H_2CO : $\nu_{\text{CO}} = 1746 \text{ cm}^{-1}$) (Floriani, 1982).

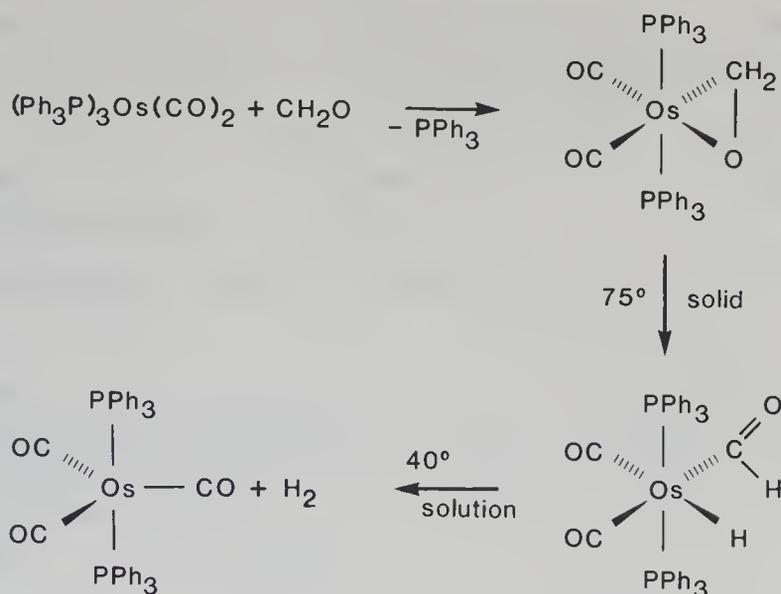


On the other hand, η^1 (O) coordination of the keto group to the electron-deficient $[(\text{C}_5\text{H}_5)_2\text{V}]^+$ ion weakens the $\text{C}=\text{O}$ double bond only moderately ($\nu_{\text{CO}} = 1660$ versus 1715 cm^{-1}), the reason being that backbonding $\text{M} \rightarrow \text{L}$ is absent here (Floriani, 1981).

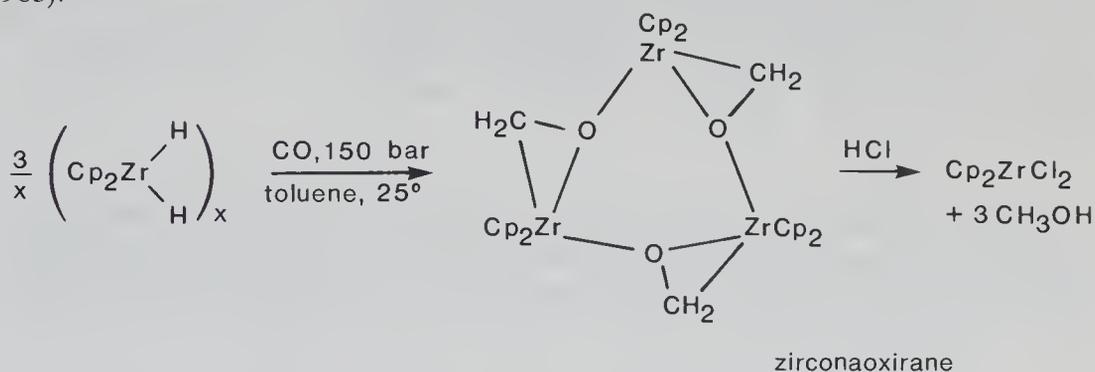
Because of their possible involvement in Fischer-Tropsch processes (see p. 430), formaldehyde and formyl complexes currently enjoy considerable interest. However, an essential step, the CO-insertion into an $\text{M}-\text{H}$ bond,



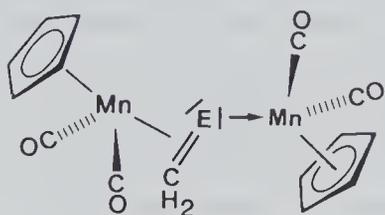
is thermodynamically unfavorable and does not usually proceed spontaneously (The formation of free formaldehyde from H_2 and CO is also endothermic, $\Delta H^0 = +26 \text{ kJ/mol}$). In fact, a reaction sequence discovered by Roper (1979) is the reversal of a Fischer-Tropsch process:



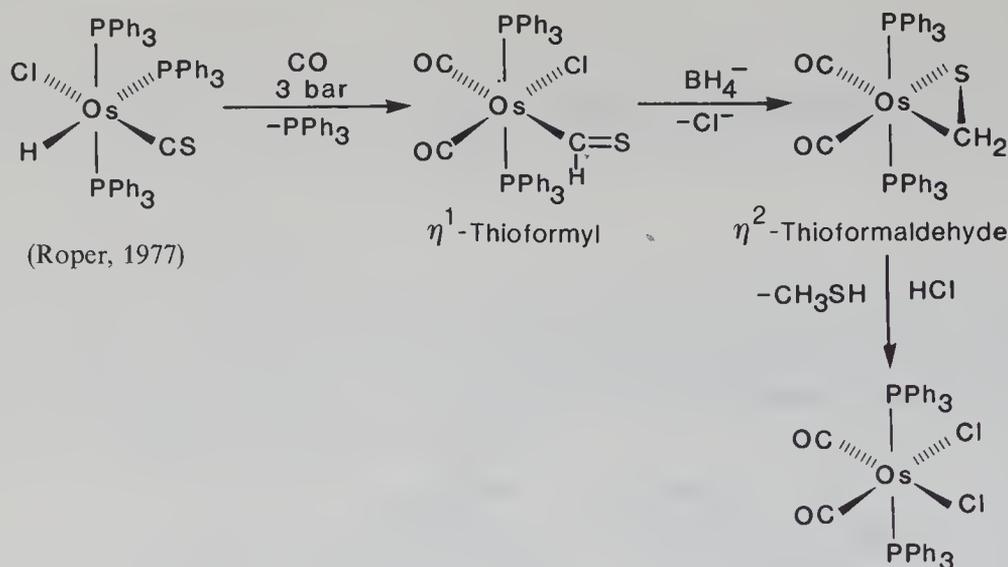
The formation of trimeric (η^2 -formaldehyde)zirconocene from zirconocene dihydride and carbon monoxide does proceed in the proper Fischer-Tropsch fashion (Erker, Krüger, 1983):



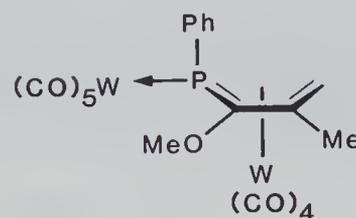
The work to formally split H_2 into H^+ and H^- – required for the formation of Cp_2ZrH_2 from Cp_2ZrCl_2 – has to be invested prior to the CO insertion described above, however. A typical example of the concept “stabilization of reactive molecules by complex formation” is supplied by the isolation of compounds containing **chalcogeno formaldehydes** $\text{H}_2\text{C}=\text{E}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) as ligands. These species are generated in the coordination sphere of the metal from the respective precursor ligands (Roper, 1977, see p. 272 above).



The ambidentate nature of chalcogeno formaldehydes becomes apparent in their function as **bridging ligands** in that the π -electron pair of the $\text{C}=\text{E}$ double bond as well as the lone pair on E engage in metal-ligand bonding ($\text{E} = \text{S}, \text{Se}, \text{Te}$) (Herrmann, Herberhold, 1983).



Another class of highly reactive small molecules is that of the phosphalkenes (cf. p. 161f). An achievement of recent vintage is the preparation of the first η^4 -1-phosphabutadiene complex of a transition metal. The reactivity of this ligand is apparent from the fact that for its stabilization, the coordination of the π -electron system as well as of the phosphorus lone pair to carbonyl tungsten fragments is essential (Mathey, 1987).

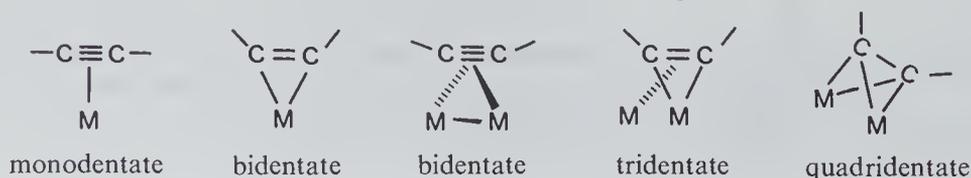


η^2 - CO_2 metal complexes which may formally be regarded as coordination compounds of the ligand dioxallene, have been alluded to on p. 259. They may play a role in transition-metal catalyzed carbon-carbon coupling between CO_2 and organic substrates (“ CO_2 activation”, Braunstein 1988 R).

15.2 Alkyne Complexes

The most important aspects pertaining to the organometallic chemistry of alkynes concern the **cyclooligomerization of acetylenes** and the amazing **product variety** found in the reactions between acetylenes and metal carbonyls. This is largely due to the following facts:

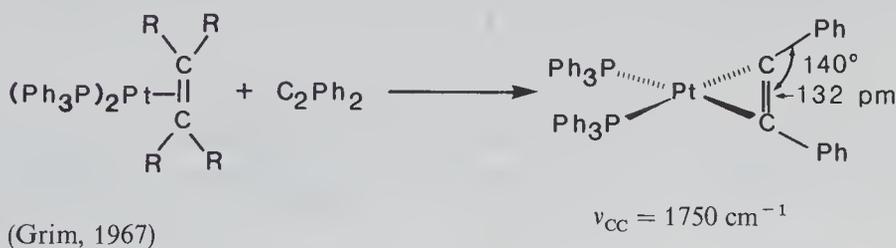
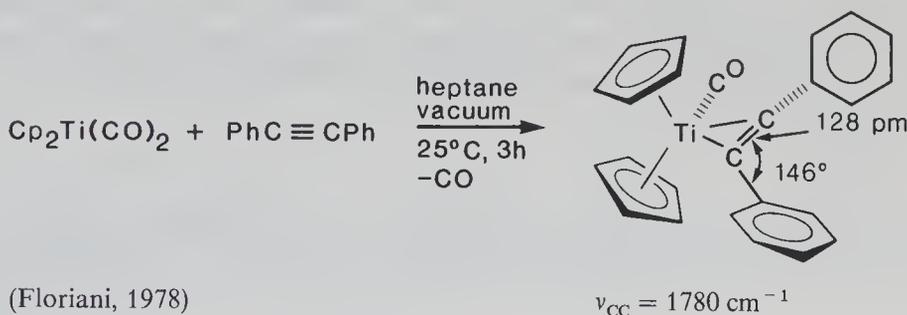
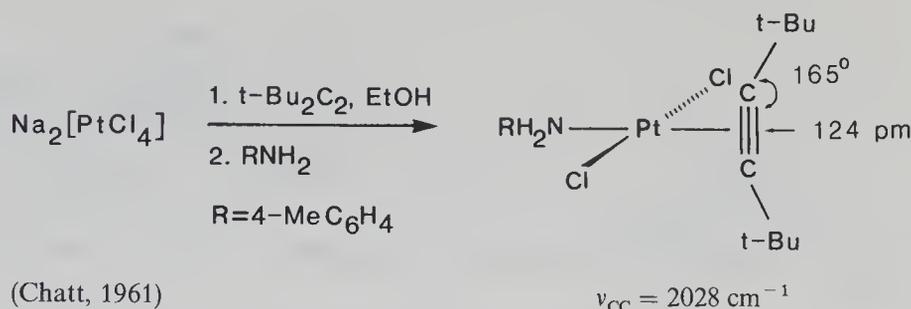
- The alkyne ligand can coordinate like two orthogonal alkene units.
- The alkyne ligand can formally occupy one or two (resp. three or four) coordination sites. The assignment of its denticity is closely associated with descriptions of the bond type:



- Alkyne ligands can be complexed in dimerized or trimerized form.
- Alkyne oligomerization can also involve the incorporation of carbonyl groups and/or the metal atom.

15.2.1 Homoalkyne Complexes

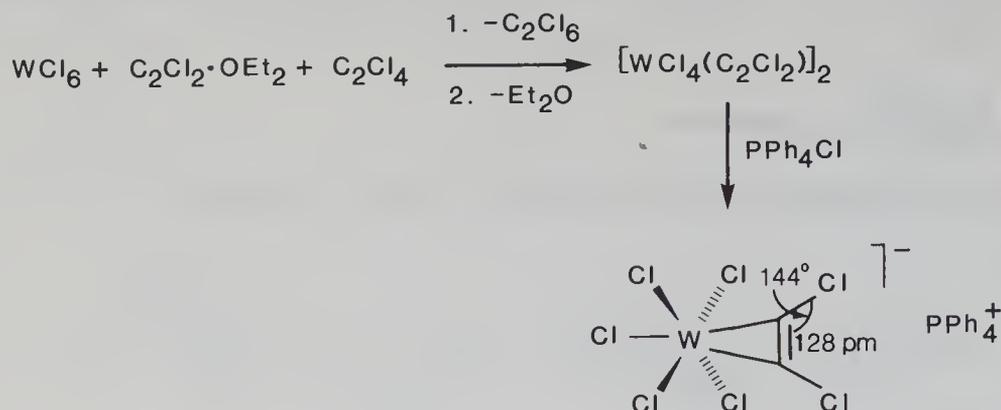
ALKYNES AS FORMAL MONO- OR BIDENTATE LIGANDS:



The C–C bond lengths in transition-metal coordinated alkynes cover almost the whole range between $d(\text{C}\equiv\text{C})_{\text{free}} = 120 \text{ pm}$ and $d(\text{C}=\text{C})_{\text{free}} = 134 \text{ pm}$. Notable here is the correlation between $d(\text{CC})_{\text{coord.}}$, the CCR bond angle and the stretching frequency ν_{CC} ($\nu_{\text{C}\equiv\text{C}, \text{free}} = 2190\text{--}2260 \text{ cm}^{-1}$, depending on the substituents). In fact, it seems appropriate to describe $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{C}_2)$ as a **metallacyclopropene** since the alkyne formally occupies two coordination sites.

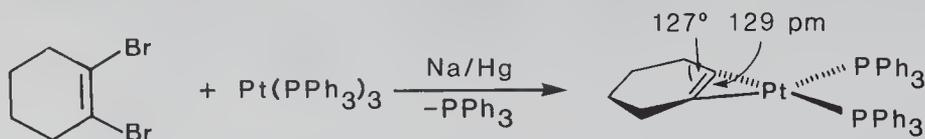
As with alkene complexes, the stability of alkyne complexes increases with increasing electron-withdrawing character of X in $\text{XC}\equiv\text{CX}$. Thus, halogen-substituted acetylenes,

which are highly explosive compounds in the uncomplexed state, may be stabilized by complex formation (Dehnicke, 1986):

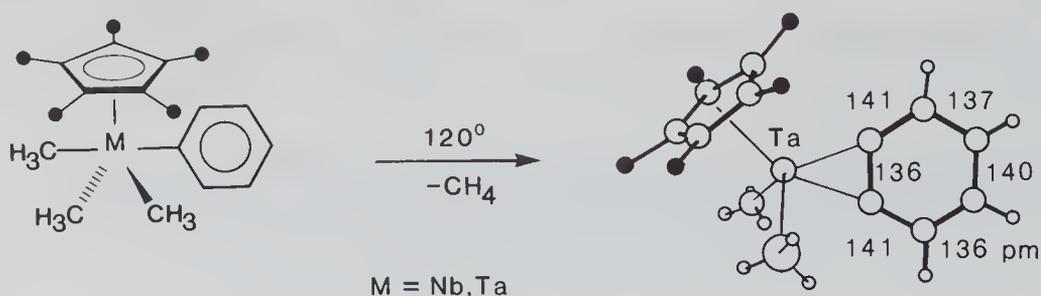


This example shows that alkynes can also be coordinated to transition metals in higher oxidation states.

Even cyclohexyne, unstable as a free molecule, is obtained in metal-coordinated form. This stabilization is due to the distortion from linearity which alkynes experience on coordination, and which in this case relieves ring strain (Whimp, 1971):



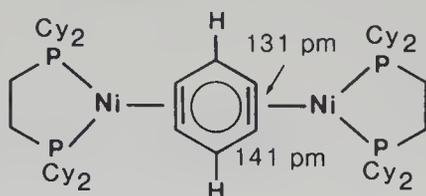
No less remarkable is the coordination of benzyne C_6H_4 , also not stable as a free molecule (Schrock, 1979):



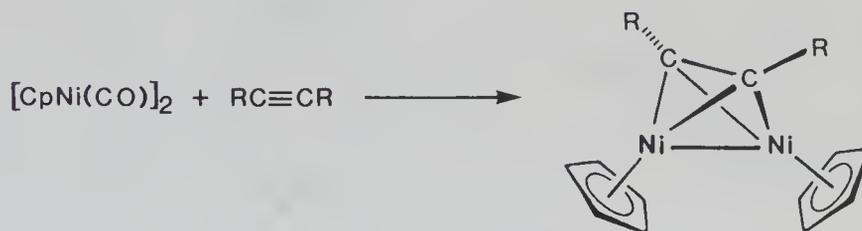
The aromatic ring of the η^2 -benzyne unit exhibits C–C bond-length alternation (symmetry D_{3h}); the bond length between the two coordinated carbon atoms is not significantly different from those of the other two short C–C bonds. The formulation of this complex as an aryne π -complex or as a metallabenzocyclopropene remains largely a matter of semantics.

Very recently, even benzdiyne C_6H_2 (tetrahydrobenzene) could be stabilized by means of coordination to two Ni(0) centers. The structural parameters of this unusual complex

indicate extensive localization of the π electrons in the region of the coordinated carbon atoms (Bennett, 1988):

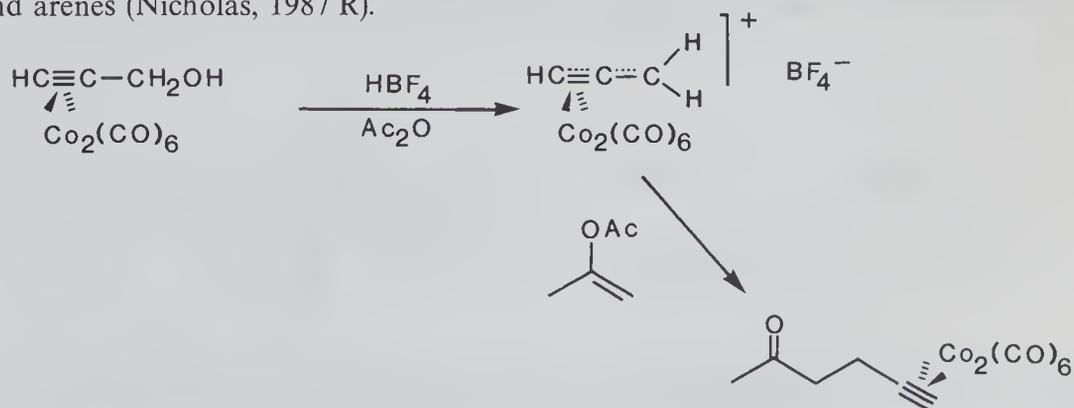


ALKYNES AS BRIDGING LIGANDS



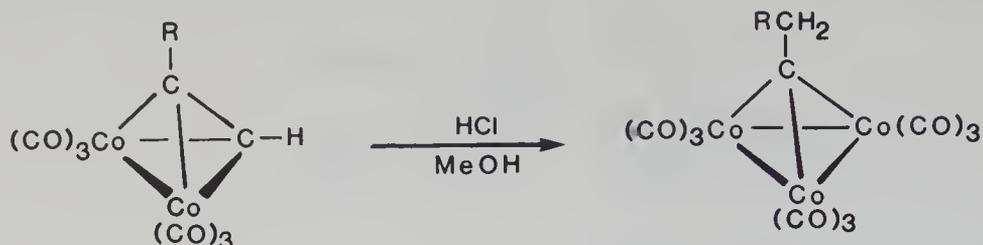
The classification of these and similar oligonuclear compounds as acetylene complexes is somewhat arbitrary; they could just as well be regarded as metal-carbon clusters (cf. Chapter 16).

The coordination of an alkyne to a $\text{Co}_2(\text{CO})_6$ moiety considerably reduces the reactivity of the $\text{C}\equiv\text{C}$ triple bond, allowing selective reactions at the functional groups of the coordinated alkyne to be carried out. For example, propargyl alcohols are converted by strong acids into **metal-stabilized propargyl cations**. Spectroscopic data speak for delocalization of the positive charge over the whole (alkyne) $\text{Co}_2(\text{CO})_6$ unit. Such complexes can be used as selective electrophilic alkylating agents in reactions with ketones, enol acetates and arenes (Nicholas, 1987 R).

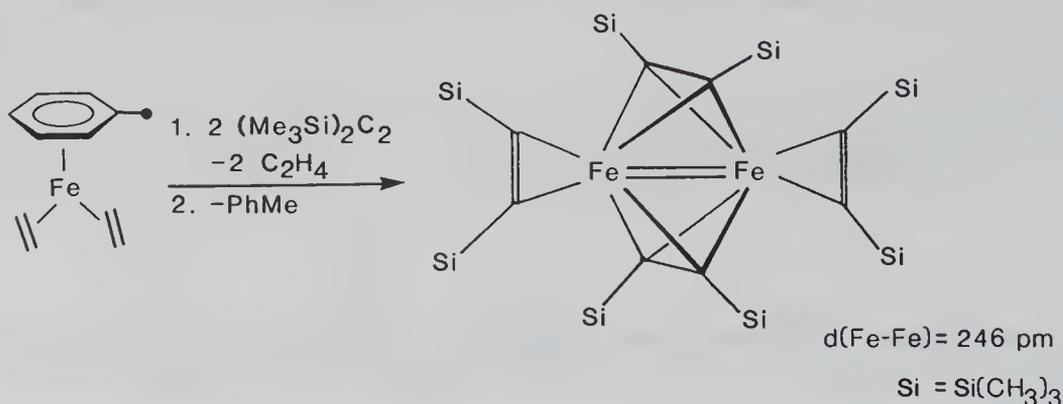


The free alkynes can be generated by oxidative decomplexation.

A further interesting reaction of the cobalt cluster (alkyne) $\text{Co}_2(\text{CO})_6$ is the conversion μ_2 -alkyne \rightarrow μ_3 -alkylidyne:

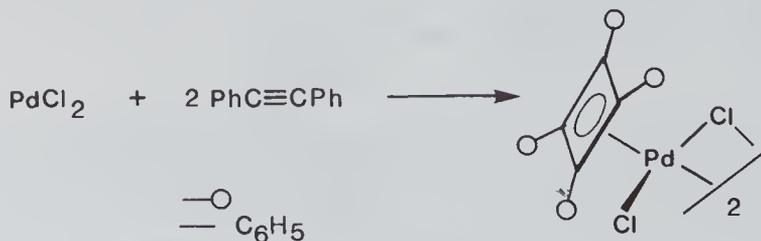


Two edge-sharing metallatetrahedrane clusters build the framework of the binary iron alkyne complex $(\text{Me}_3\text{SiC}_2\text{SiMe}_3)_4\text{Fe}_2$ which forms from the precursor (η^6 -toluene)ironbis(ethylene), the latter being accessible through metal-atom ligand-vapor cocondensation (Zenneck, 1988):

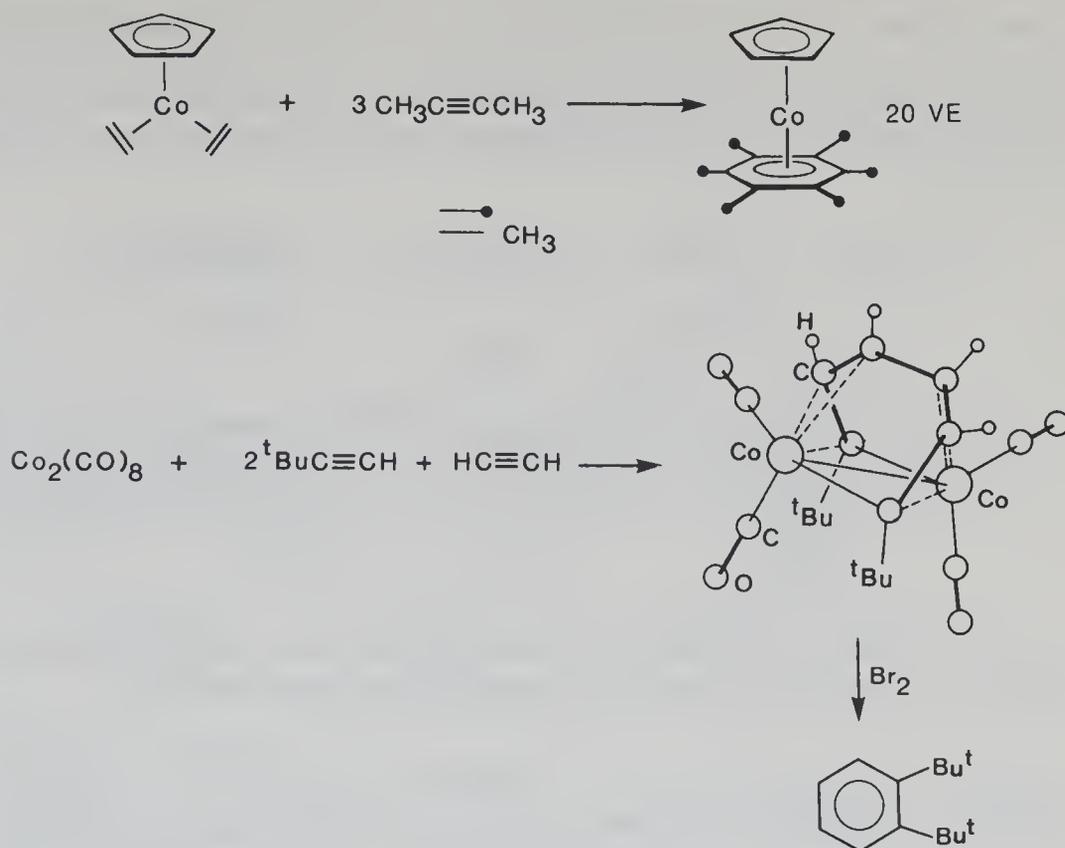


OLIGOMERIZATION OF ALKYNES

Reactions of alkynes with metal compounds can lead to di- tri- or tetramerization of the organic ligand. Not in all cases is an isolable metal complex formed, though (see Chapter 17). The reaction with palladium salts yields cyclobutadiene complexes in addition to alkyne complexes and benzene derivatives (Maitlis, 1976 R):

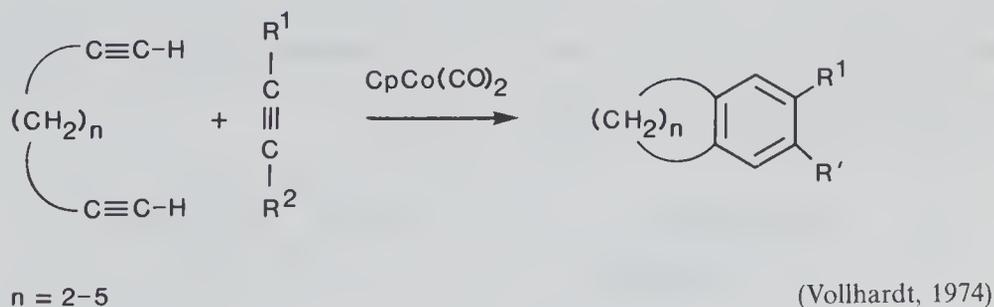
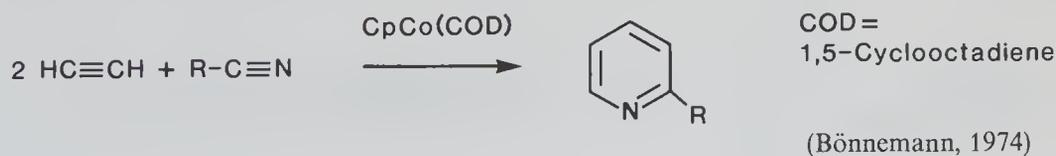


Certain organocobalt complexes have also proven suitable for the cyclotrimerization of alkynes, the isolation of arene complexes being possible in individual cases (Jonas, 1983):

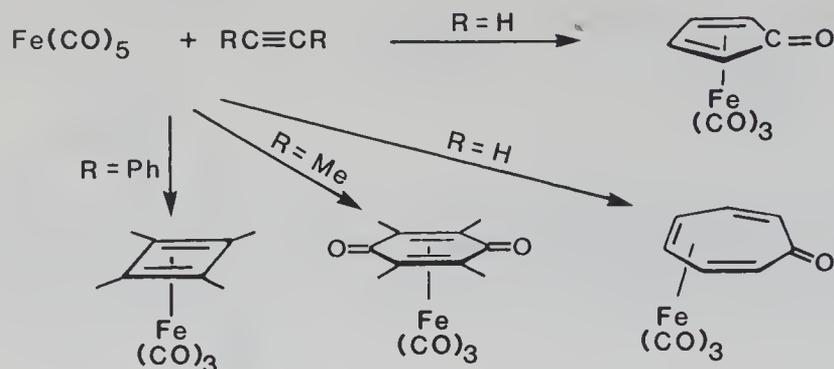


This binuclear complex with a “fly-over” ligand, formed by alkyne trimerization, contains Co(*d*⁷) centers which are η^1 -bonded to terminal carbons and η^3 -bonded to internal allyl units. Carbonyl ligands and a Co–Co bond complete the 18 VE shell.

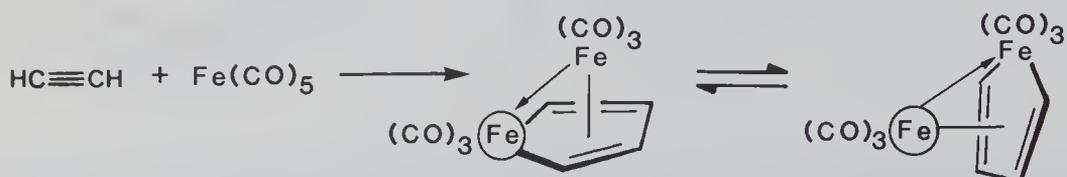
Of greater importance is the cobalt-catalyzed cotrimerization of alkynes and nitriles discovered by Yamazaki (1973) (see p. 375). Whereas this reaction has been extended by Bönnemann (1985 R) into a versatile pyridine synthesis, Vollhardt (1984 R) has placed the emphasis on synthesizing homocyclic systems:



The best catalysts for the cyclotetramerization of acetylenes to give cyclooctatetraene derivatives are labile Ni(II) complexes like Ni(acac)₂ or Ni(CN)₂ (Reppe, 1940f). This reaction forms the basis of an industrial process to produce cyclooctatetraene (see p. 421). Cyclooligomerizations can also be accompanied by incorporation of one or more molecules of CO:

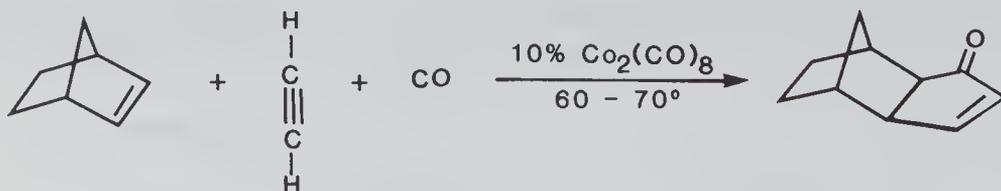


Among the possible products are dimeric complexes in which one $\text{Fe}(\text{CO})_3$ moiety is π -bonded, the other becoming part of a metallacyclopentadiene ("ferrole"):



The two $\text{Fe}(\text{CO})_3$ units are presumably linked by a metal-metal bond (249 pm), and, as labelling experiments have shown, are subject to intramolecular exchange. Chiral derivatives of these ferracyclopentadienes undergo rapid thermal racemization.

A related cyclization is the **Pauson-Khand reaction**, in which substituted cyclopentenones are formed in a single step from an alkyne, an alkene and CO, with $\text{Co}_2(\text{CO})_8$ acting as a catalyst.

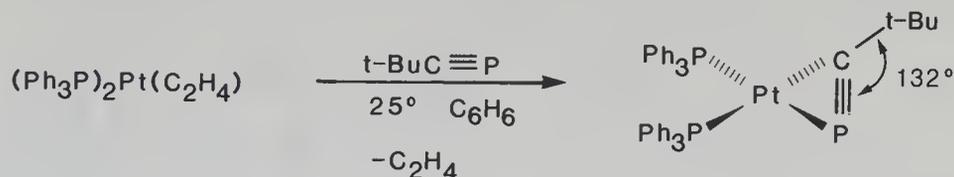


In most cases, however, this reaction is carried out by first isolating the (alkyne) $\text{Co}_2(\text{CO})_6$ complex, followed by its stoichiometric addition to the alkene. The CO group usually ends up adjacent to the bulkier substituent of the alkyne:

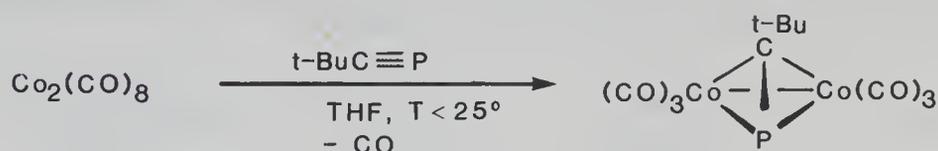


15.2.2 Heteroalkyne Complexes

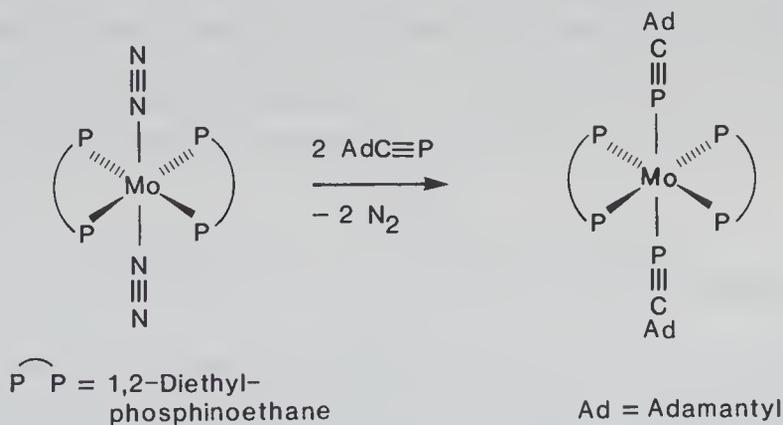
The heteroalkynes $RC\equiv E$ ($E = P, As, Sb$ see p. 164) are related to the heteroalkenes $R_2C=E$ ($E = S, Se, Te$) in that they can also function as π ligands (Nixon, 1981):



This type of coordination results in a considerable lengthening of the C–P bond from 154 pm (free) to 167 pm (η^2 -bonded), a consequence of Pt π ligand backbonding. The well-known alkyne bridging mode is also displayed by phosphalkynes:



This side-on coordination of the phosphalkyne is in contrast to the usual terminal coordination of nitriles (azaalkynes), for which side-on coordination is exceptional (Wilkinson, 1986). Recently, however, an example has been reported in which a phosphalkyne coordinates via the terminal phosphorus atom (Nixon, 1987):



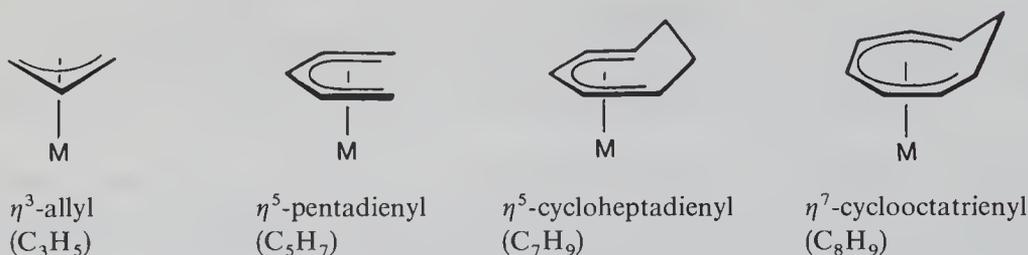
As expected, the $\text{P}\equiv\text{C}$ triple bond is affected only marginally by this bonding mode.

15.3 Allyl and Enyl Complexes

Unsaturated hydrocarbons C_nH_{n+2} with odd numbers of carbon atoms can be regarded as neutral ligands with an odd number of π electrons or as anionic or cationic ligands possessing an even number of valence electrons:



The neutral radicals are highly reactive, whereas the anions in the form of Li-, K-, or Mg salts are stable and characterizable, although very air- and moisture-sensitive (see p. 23). In their transition-metal complexes, allyl- and enyl units are remarkably inert, as evident from thermal robustness and stability towards hydrolysis.



Only the binary allyl complexes are rather labile; they tend to release the metal via dimerization of the organic ligand and thus become important intermediates for homogeneously catalyzed cycles (Chapter 17). As far as bonding and reactivity are concerned, no basic differences exist between enyl- and oligoolefin complexes. As a matter of fact, their mutual interconversion is one of the most important features of their synthesis and reactivity.

15.3.1 Allyl Complexes

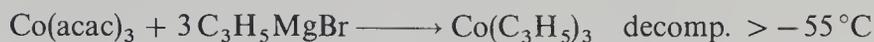
The first synthesis and accurate description of an η^3 -allyl metal complex was reported by Smidt and Hafner (1959), who prepared $[(C_3H_5)PdCl]_2$ from the reaction of palladium chloride with allyl alcohol. Since then, the structural element $(\eta^3\text{-allyl})M$ has become widespread among transition-metal complexes, sometimes appearing as part of larger ligands. The routes to η^3 -allyl metal complexes therefore are manifold.

PREPARATION

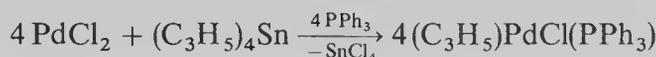
The following synopsis of preparative methods can be divided into the reaction types:

- Replacement of X^- by allyl $^-$ (metathesis reaction) 1
- Rearrangement σ -allyl (η^1) \rightarrow π -allyl (η^3) 2, 3
- Conversion π -olefin (η^2 or η^4) \rightarrow π -allyl (η^3) 4–7

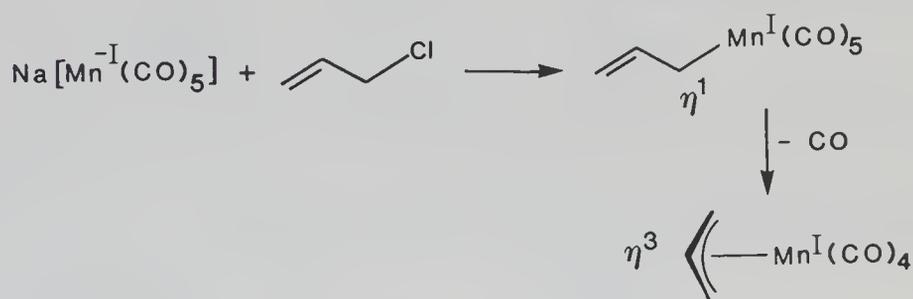
1. Metal Salt + Main-group Organometallic (Metathesis)



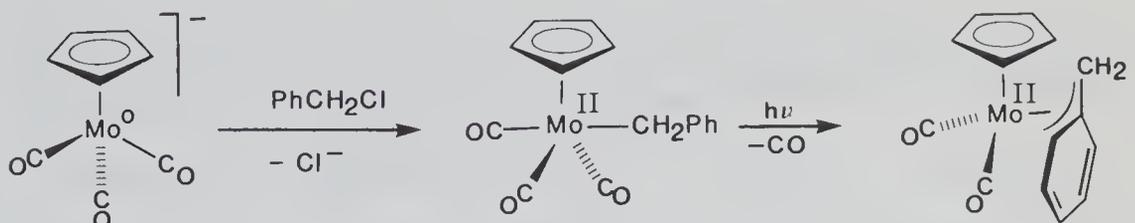
This is a general route to the binary allyl complexes. Synthesis and isolation must be performed at low temperatures, as complexes of this type are very thermolabile (Wilke, 1966 R)



2. Carbonyl Metallate + Allyl Halide



The σ/π rearrangement with attendant loss of CO can be initiated thermally (80°C) or photochemically.

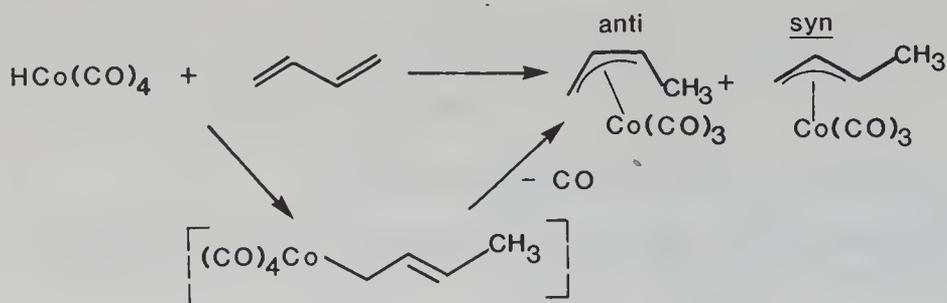


(allyl π -complex of the benzyl anion)

Metal Carbonyl + Allyl Halide

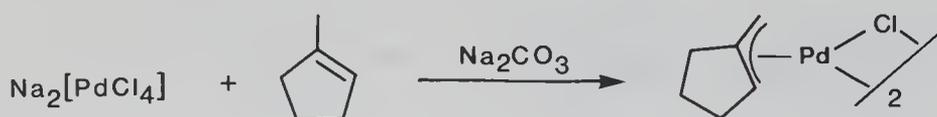


3. Metal Hydride + Diolefin

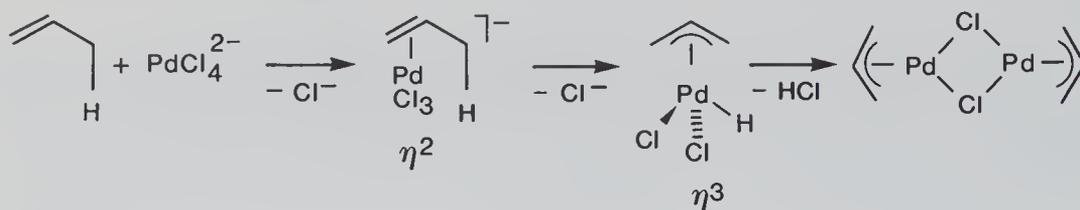


This reaction is initiated by a 1,4-hydrocobaltation of butadiene. The syn-complex is the more stable isomer.

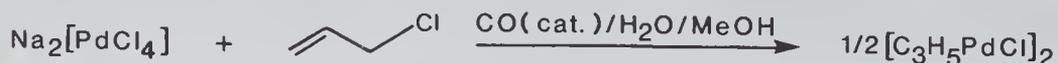
4. Metal Salt + Olefin + Base



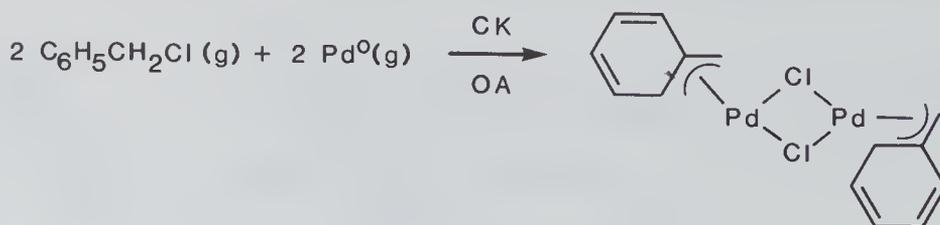
A mechanism for this reaction was proposed by Trost (1978):

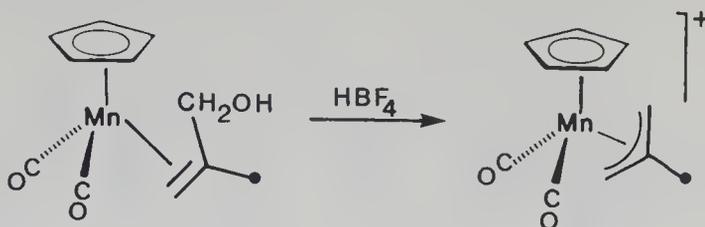


5. Metal Salt + Allyl Halide

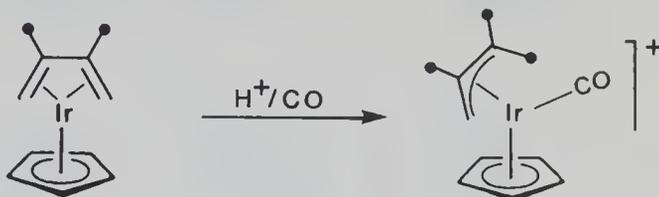


The formation of an η^3 -allyl complex from allyl chloride formally is a disproportionation which yields organic keto products in addition to the coordinated allyl anion (Jira, 1971). The reaction can be accelerated by introducing other reducing agents (e.g. CO, SnCl_2). This measure becomes unnecessary, however, when one starts from Pd^0 (Klabunde, 1977):

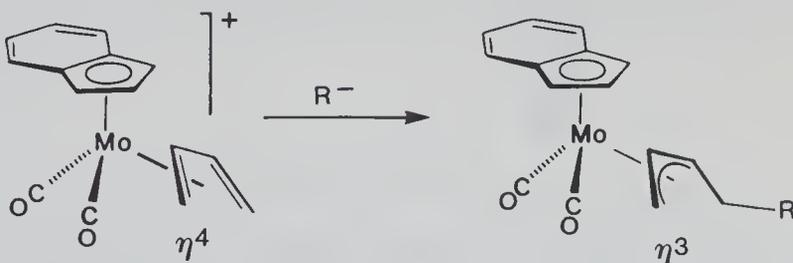


6. Conversion η^2 -Allyl Alcohol \rightarrow η^3 -Allyl:

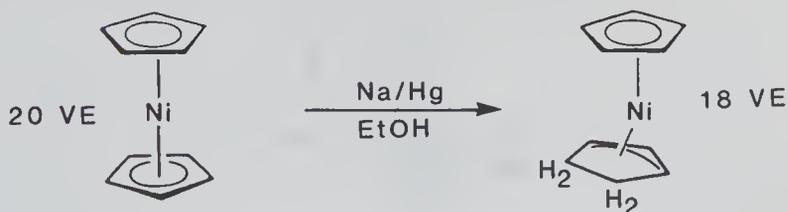
7. Electrophilic or Nucleophilic Addition to Olefin Complexes



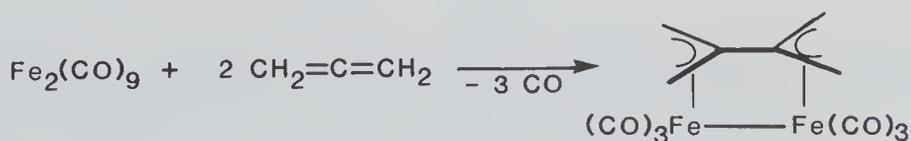
The coordinatively unsaturated 16 electron complex generated by protonation accepts a Lewis base.



8. Hydrogenation of a Complex with Excess Electrons

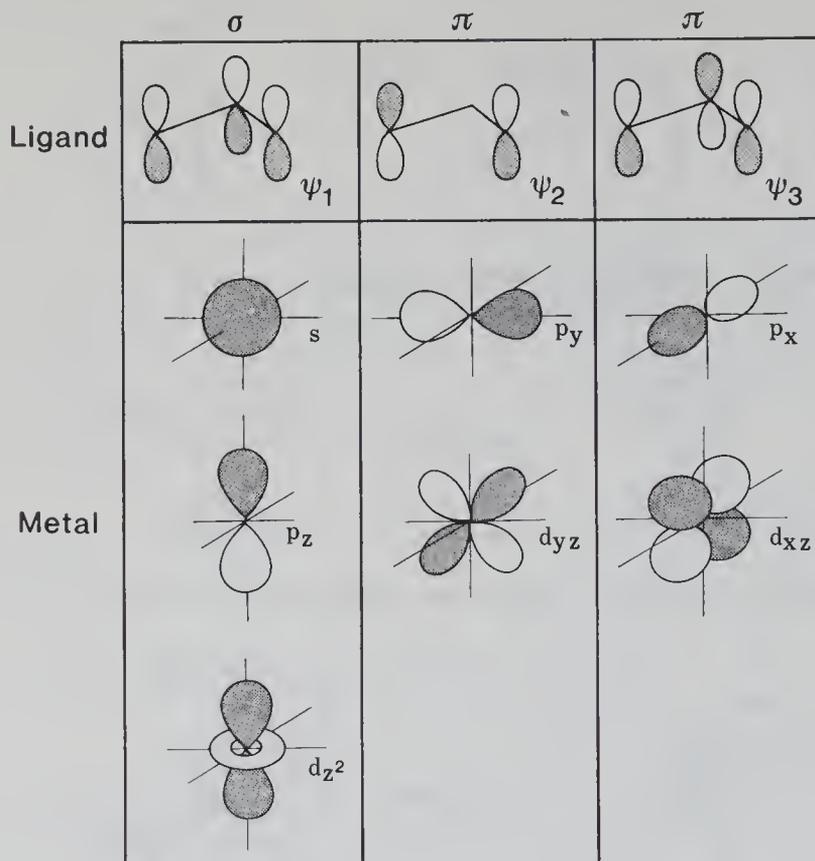


9. Dimerization of an Allene

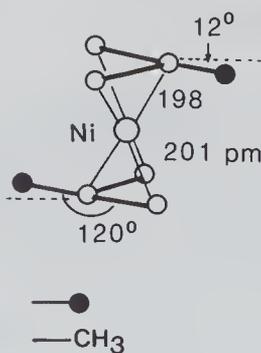


STRUCTURE AND BONDING

Metal-ligand interactions in allyl complexes:

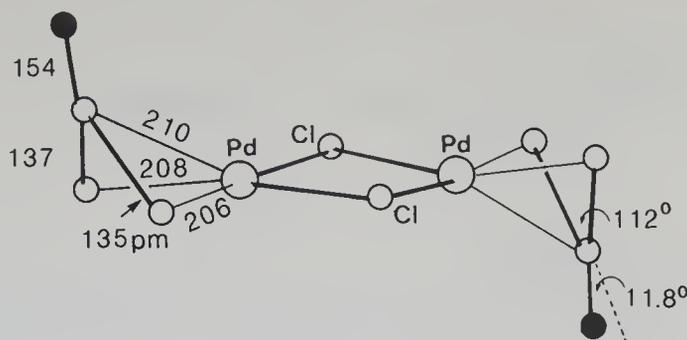


In the ligand $C_3H_5^-$ ψ_1 and ψ_2 are doubly occupied. The metal-ligand bond can be described by the components $\psi_1 \xrightarrow{\sigma} M$, $\psi_2 \xrightarrow{\pi} M$ and $\psi_3 \xleftarrow{\pi} M$. These overlap characteristics induce an electronic rotational barrier within the $(\eta^3\text{-allyl})M$ unit (see p. 287).

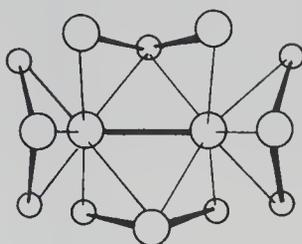


The structure of the prototypical *bis(2-methylallyl)nickel* in the solid state is characterized by a parallel disposition of the two allyl ligands and slight bending of the C-CH₃ bond towards the metal (Dietrich, 1963).

Bis(η^3 -allyl)nickel (Wilke, 1961) was the first binary allyl metal complex to be isolated.



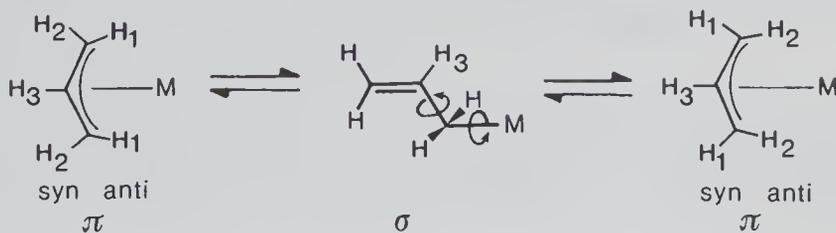
Structure of $[\text{C}_4\text{H}_7\text{PdCl}]_2$. The Pd- and Cl atoms lie in one plane which intersects the plane of the three allyl carbon atoms at an angle of 111.5° .



Structure of the binuclear complex $(\text{C}_3\text{H}_5)_4\text{Mo}_2$. Two allyl groups function as bridging ligands. This complex is fluxional in solution, whereby the bridging and the terminal allyl groups experience ligand scrambling (Cotton, 1971).

$d(\text{Mo}-\text{Mo}) = 218 \text{ pm}$

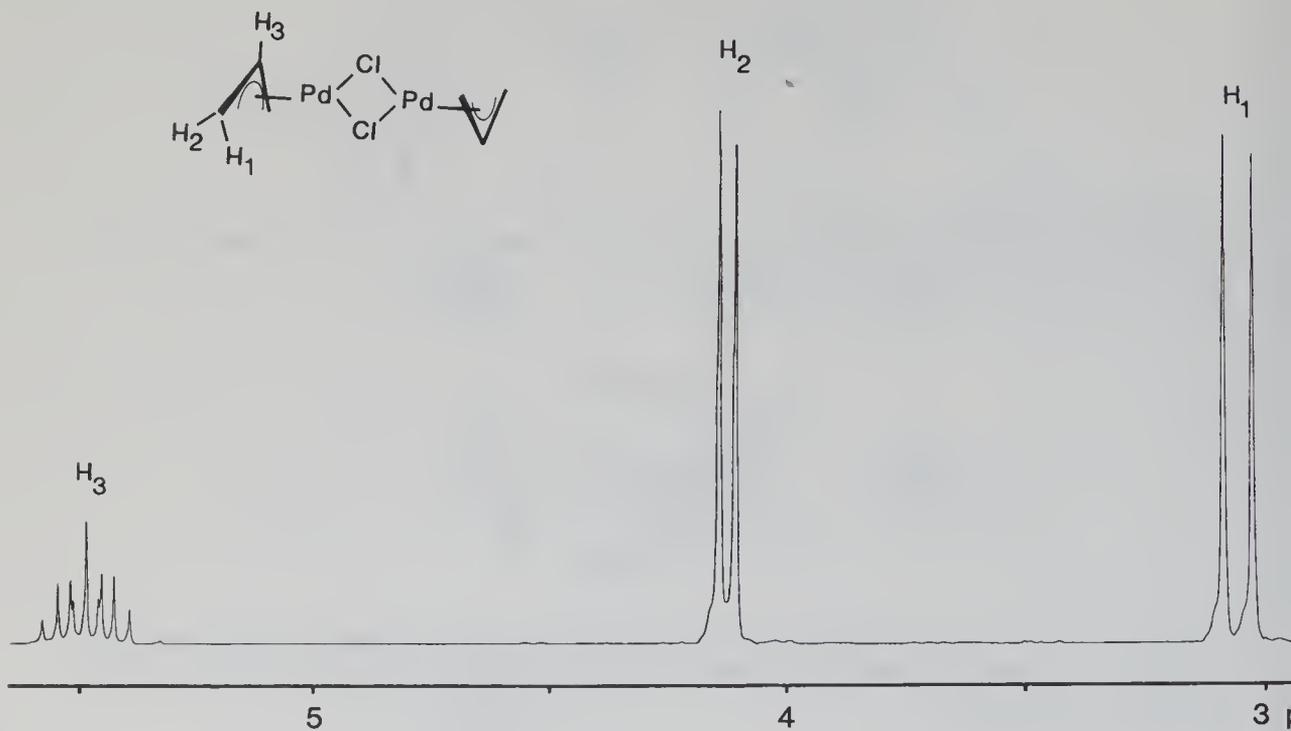
In the $^1\text{H-NMR}$ spectra of allyl complexes, *syn*- and *anti*-protons of the terminal CH_2 groups are generally nonequivalent. Frequently, however, dynamic behavior is observed in solution which renders the terminal protons equivalent on the NMR time scale. The most likely mechanism to explain this phenomenon is a rapid $\pi-\sigma-\pi$ conversion, which at the σ -stage allows free rotation around the $\text{C}-\text{C}$ - and the $\text{M}-\text{C}$ bonds. In this manner, *syn*- and *anti*-protons can exchange their positions:



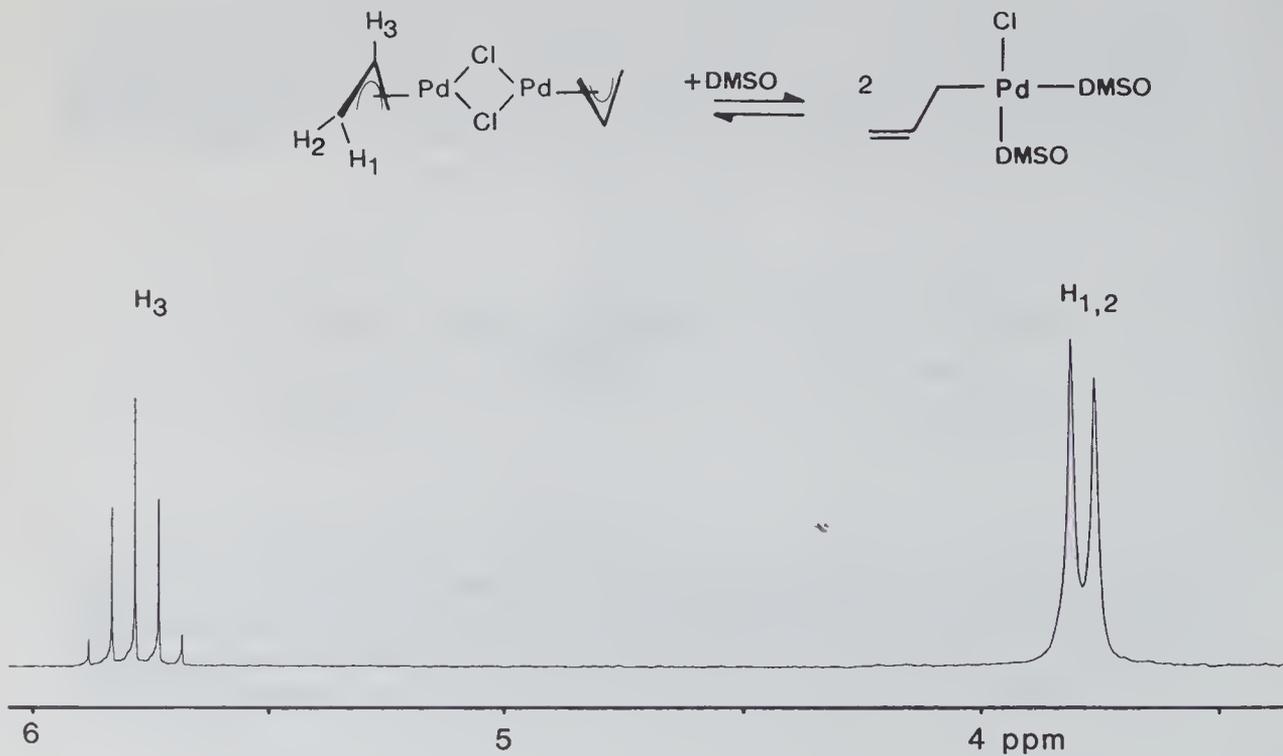
Often, the presence of a Lewis base (e.g. a nucleophilic solvent) is sufficient to trigger this dynamic behavior. This will be illustrated by the $^1\text{H-NMR}$ spectra of $[\text{C}_3\text{H}_5\text{PdCl}]_2$. In CDCl_3 (upper trace), the spectrum of the π -allyl ligand is that of an $\text{A}_2\text{M}_2\text{X}$ system, while in the solvent d^6 -DMSO at 140°C (lower trace) an A_4X pattern with seemingly equivalent terminal hydrogen atoms is observed. Presumably, upon attack of solvent molecules,

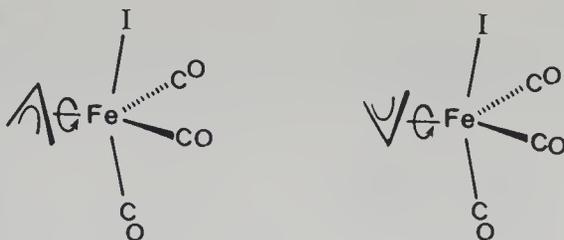
the dimeric structure of the complex is reversibly cleaved with accompanying $\pi - \sigma - \pi$ conversions (Chien, 1961).

$^1\text{H-NMR}$ spectrum of $[\text{C}_3\text{H}_5\text{PdCl}]_2$ (CDCl_3 , 25°C , 200 MHz):



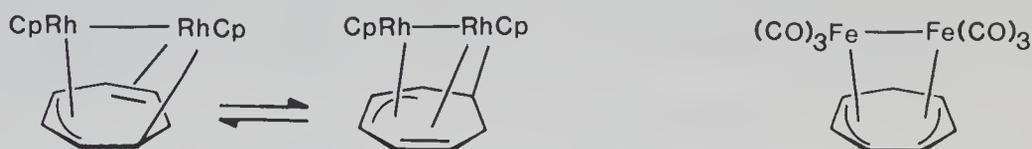
$^1\text{H-NMR}$ spectrum of $[\text{C}_3\text{H}_5\text{PdCl}]_2$ ($d^6\text{-DMSO}$, 140°C , 200 MHz):





During the rotation of the allyl ligand around the $(\eta^3\text{-C}_3\text{H}_5)\text{-M}$ axis *without* $\pi\text{-}\sigma\text{-}\pi$ conversion the terminal syn- and anti-protons necessarily remain nonequivalent; they experience changes in the shielding, however. As this rotation at room temperature is slow on the NMR time scale, both isomers are observable.

Structural fluxionality of a different type is found in binuclear complexes in which two organometallic moieties are synfacially bonded to the bridging ligand cycloheptatriene. For the compound $(\mu\text{-C}_7\text{H}_8)[\text{C}_5\text{H}_5\text{Rh}]_2$, low-temperature NMR results suggest the simultaneous presence of the bonding modes η^3 -allyl and η^1 -alkyl + η^2 -alkene. On raising the temperature, the two enantiomers interconvert, coalescence of the respective NMR signals eventually being reached.

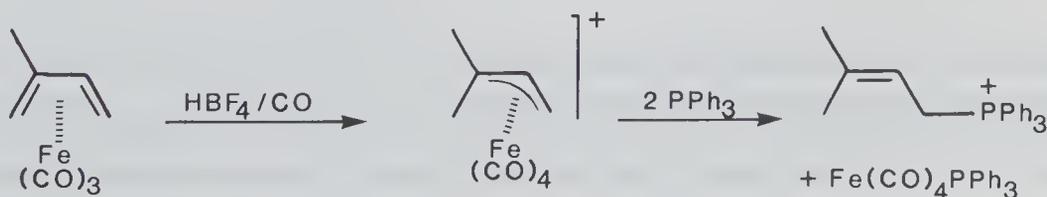


The isoelectronic complex $(\mu\text{-C}_7\text{H}_8)[\text{Fe}(\text{CO})_3]_2$ even at low temperature exhibits the bis(η^3 -allyl) structure.

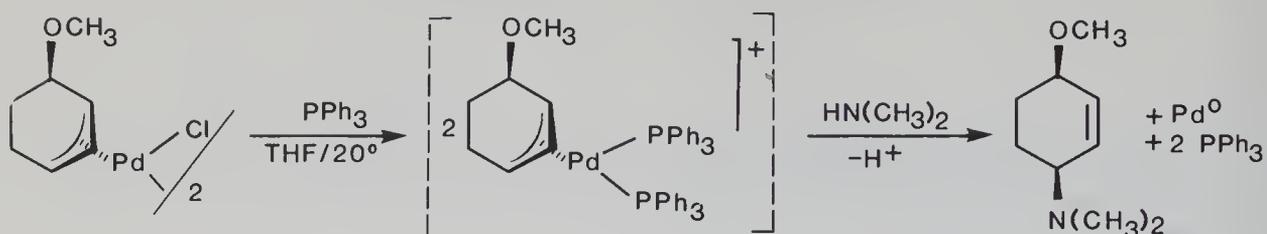
REACTIONS OF ALLYL COMPLEXES

Besides the significance of allyl complexes as intermediates in homogeneous catalysis (e.g. oligomerization reactions, p. 422), they have become increasingly important as **selective electrophilic substrates** in organic synthesis.

Thus, the cations $[(\text{allyl})\text{Fe}(\text{CO})_4]^+$, readily obtained by protonation of $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ complexes in the presence of CO, are highly electrophilic. They are attacked at the terminal carbon atom by a variety of nucleophiles to generate unstable $(\eta^2\text{-olefin})\text{Fe}(\text{CO})_4$ species which easily decompose releasing the respective olefin (Whitesides, 1973):

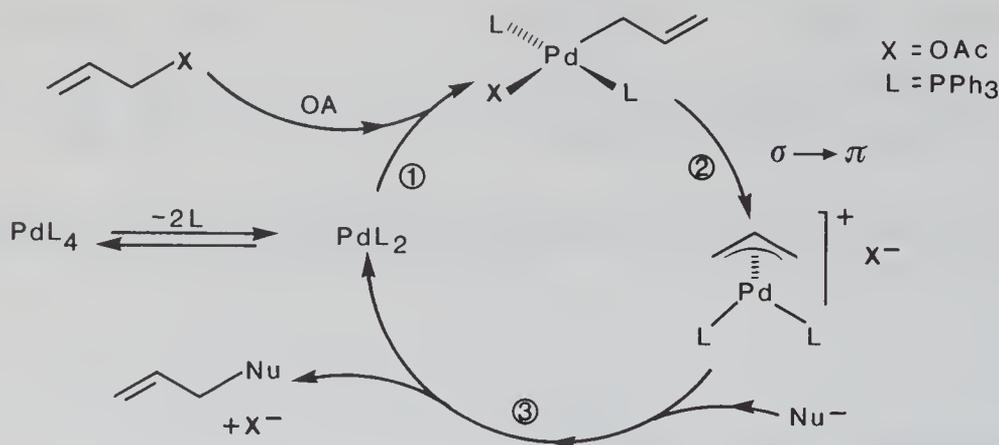


In the case of the dimeric complex $[(\text{allyl})\text{PdCl}]_2$, the reaction usually requires the presence of a phosphine or a nucleophilic solvent, because only the cationic allyl complex formed as an intermediate is sufficiently electrophilic to react with other nucleophiles:

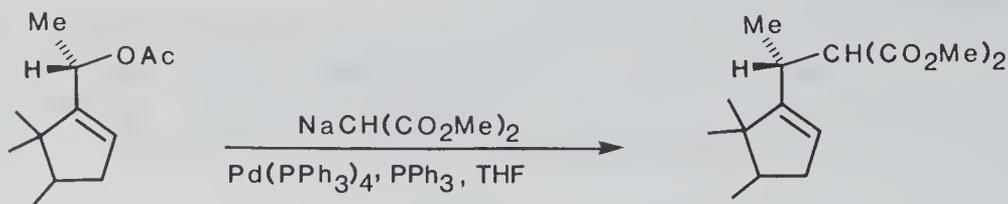


Nucleophilic attack always occurs from an **antifacial** direction, i.e. at the non-complexed side of the ligand.

For economical reasons, palladium complexes are rarely used in stoichiometric amounts. Instead, Pd^0 -catalysed reactions are generally preferred, η^3 -allyl complexes playing an essential role as intermediates (Tsuji, 1986 R). Nucleophilic substitution at allyl acetates may serve as an example:



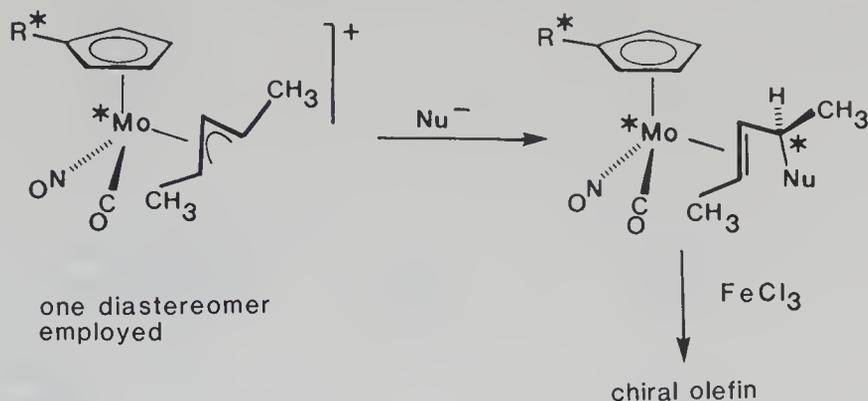
Pd^0 -catalyzed allylic substitutions proceed stereospecifically with retention of configuration at the α -allyl carbon atom (Trost, 1977 R):



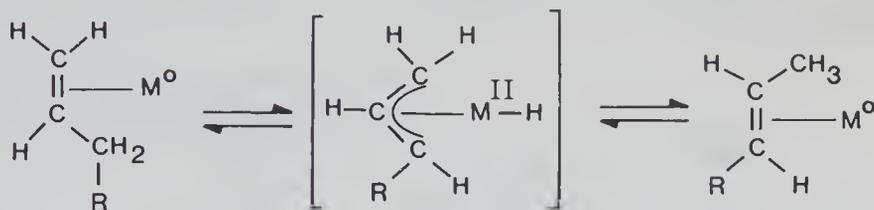
This is due to the fact that the acetate group leaves *trans* to palladium and the new nucleophile again enters from the *trans*-direction.

In **chiral allyl complexes**, even the terminal carbon atoms of symmetrical allyl ligands are nonequivalent. Selective attack by a nucleophile at one of these centers and subsequent

oxidative decomplexation can generate chiral olefins in high enantiomeric purity (Faller, 1983):



Olefin isomerization, catalyzed by transition metals, presumably also proceeds *via* allyl complex intermediates. By metal insertion into a CH_2 group adjacent to a coordinated olefin, an allyl hydride complex is formed, which can then rearrange to give the isomeric olefin complex:

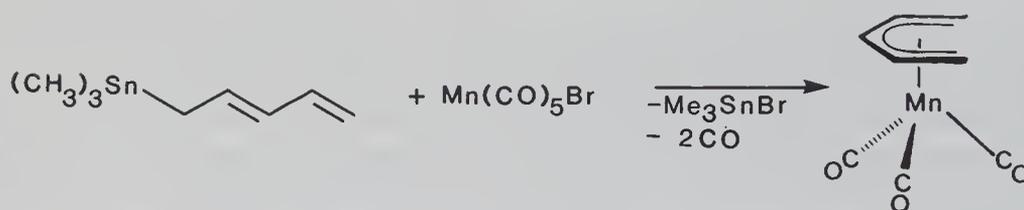
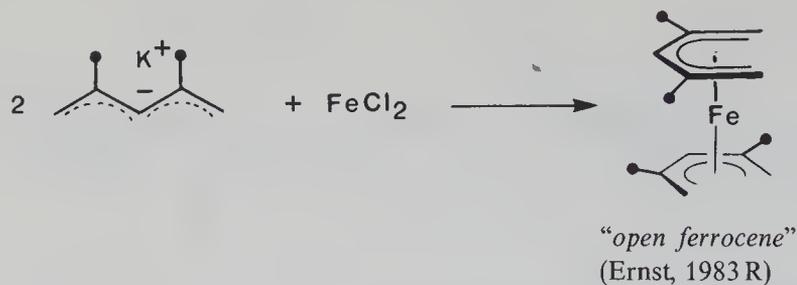
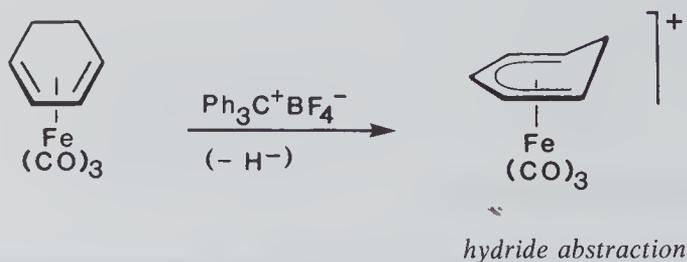
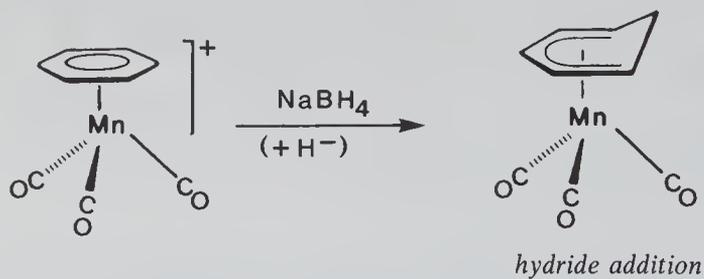


15.3.2 Dienyl and Trienyl Complexes

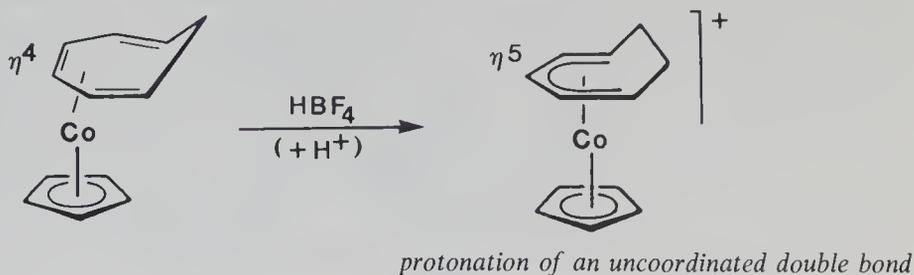
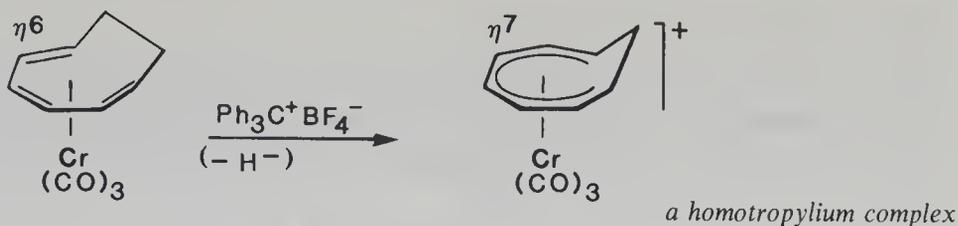
η^5 -Dienyl and η^7 -trienyl complexes can be regarded as **vinyllogues of allyl complexes**. The stabilization of enyl ligands by complex formation facilitates their use as carbocation or carbanion analogues in subsequent reactions. The preparation of dienyl and trienyl complexes in many ways parallels the synthesis of allyl complexes.

PREPARATION

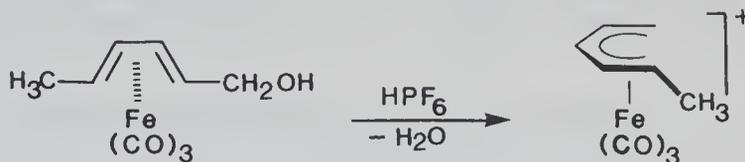
1. Metal Halide + Main-Group Organometallic (Metathesis)

2. Transfer of H⁺ or H⁻

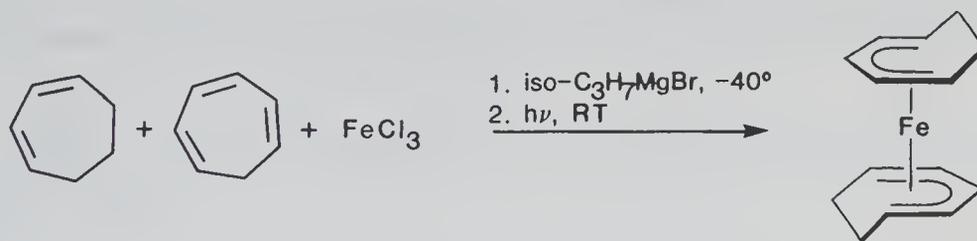
$\text{Ph}_3\text{C}^+\text{BF}_4^-$ is the classical reagent for hydride abstraction. It is usually applied to cyclic systems.



Alternatively, protonation can occur at an α -OH or α -OCH₃ group of an (η^4 -1,3-diene)M unit, water or methanol then being released to yield the dienyl complex:

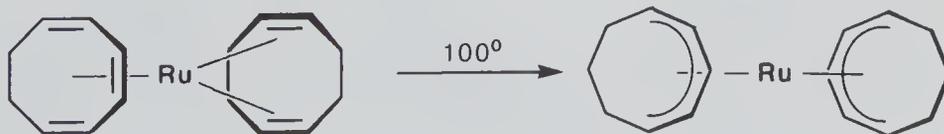


3. Metal Salt + Olefin + Reducing Agent



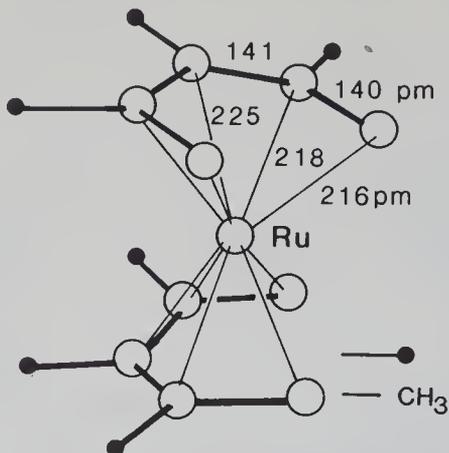
This Fischer-Müller reaction (p. 250) has considerable synthetic scope. Depending on the metal and the olefins involved, either olefin- or enyl complexes are obtained.

In the case of ruthenium and cyclooctadiene, a mixed cycloolefin complex is initially formed which, on heating, undergoes a rearrangement to give the symmetrical bis(cyclooctadienyl) isomer (**metal-induced H-shift**, Vitulli, 1980):



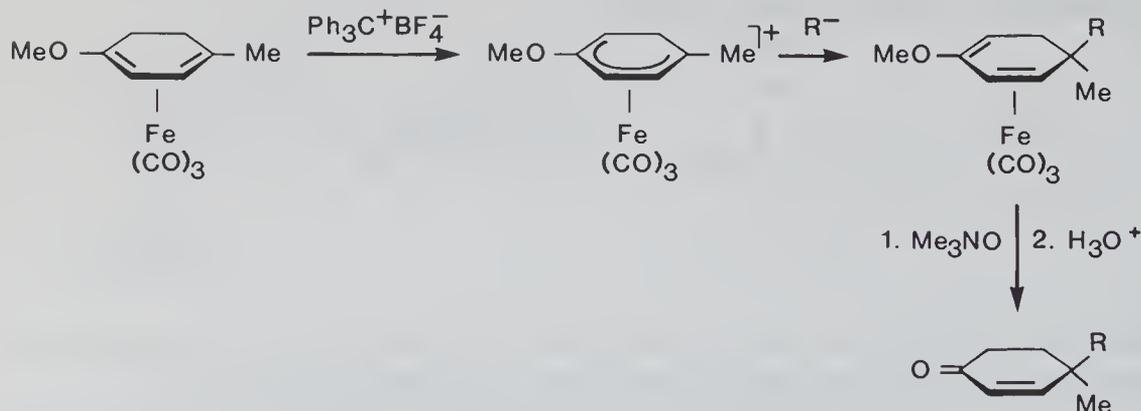
STRUCTURE AND PROPERTIES

The bonding in these complexes, involving synergetic bonding and backbonding contributions, is analogous to that of other π ligands. Structural studies have established planarity and uniform bond orders within the metal-coordinated enyl moiety.

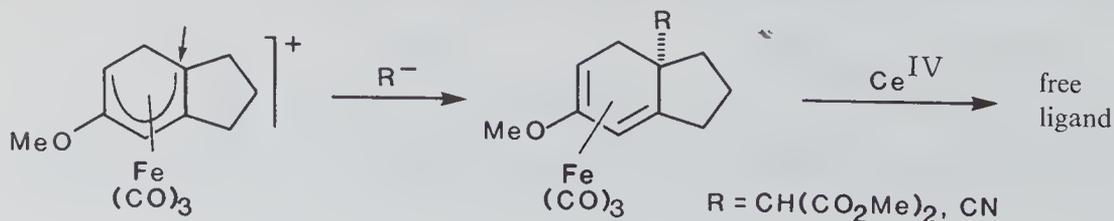


Structure of *bis(2,3,4-trimethylpentadienyl)ruthenium*. The M–C bond lengths differ from each other only slightly and they are very similar to those in the corresponding cyclopentadienyl complex, justifying the designation “*open metallocene*”. The angle of twist in the eclipsed conformation shown above is 52.5° (Ernst, 1983).

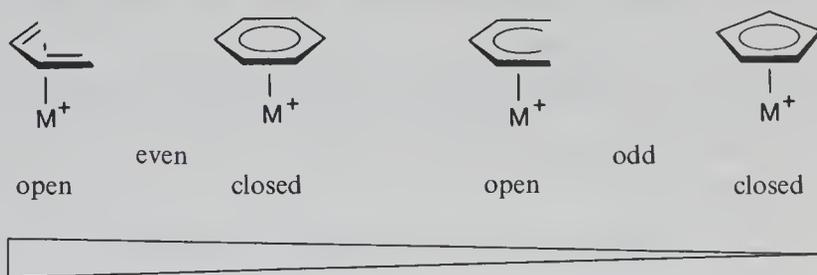
Enyl complexes have gained some importance through their application in **organic synthesis**. This is particularly true for $[(\text{dienyl})\text{Fe}(\text{CO})_3]^+$ cations, to which nucleophiles add regioselectively (at the terminal carbon) and stereospecifically (antifacial to iron) (A. Pearson, 1980 R). The $\text{Fe}(\text{CO})_3$ group can be subsequently removed by oxidation:



In the following example, the ortho-deactivating effect of the methoxy group results in nucleophilic attack at the ipso-C atom (A. Pearson, 1977):



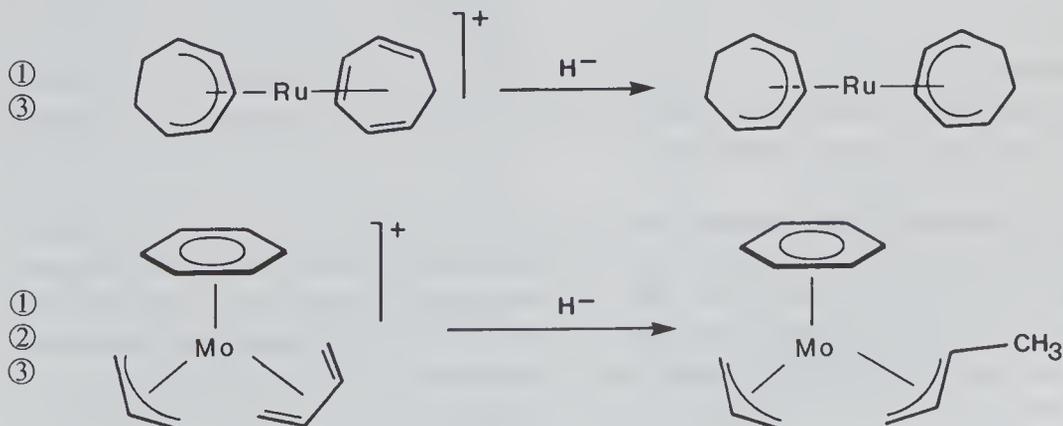
Nucleophilic addition to cationic π -complexes is one of the most important methods for the conversion of η^n -bonded ligands into the corresponding η^{n-1} ligands. Allyl and enyl ligands as well as unsaturated hydrocarbons like ethylene (p. 267), butadiene (p. 283) or benzene (p. 351f), which do not normally undergo nucleophilic addition reactions, are readily attacked by nucleophiles like H^- , CN^- or MeO^- when coordinated to a transition-metal cation. This enhanced reactivity of coordinated polyenes is a consequence of metal-ligand bonding, which results in a transfer of electron density from the hydrocarbon to the positively charged metal atom. Based on perturbation-theoretical considerations, Davies, Green and Mingos (1978) have proposed three general rules which allow predictions of the **direction of kinetically controlled nucleophilic attack** at 18 VE cationic complexes containing unsaturated hydrocarbon ligands. Applications of these rules require the ligands to be classified as **even** (η^2 , η^4 , η^6) or **odd** (η^3 , η^5). Furthermore, a distinction between **closed** (cyclic conjugated) and **open** ligands is necessary. The propensity for kinetically controlled nucleophilic addition to 18 VE cationic complexes decreases in the following order:

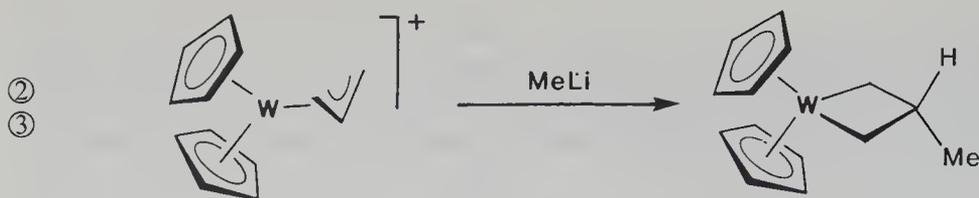


- ① Nucleophilic attack occurs preferentially at **even** coordinated polyenes.
- ② Nucleophilic addition to **open** coordinated polyenes is preferred to addition to closed polyene ligands.
- ③ In the case of even open polyenes, nucleophilic attack always occurs at the **terminal carbon atom**; for odd open polyenyls, attack at the terminal carbon occurs only if L_nM^+ is a strongly electron-withdrawing fragment.

The **Davies-Green-Mingos (DGM) rules** have to be applied in the sequence ① ② ③. Examples:

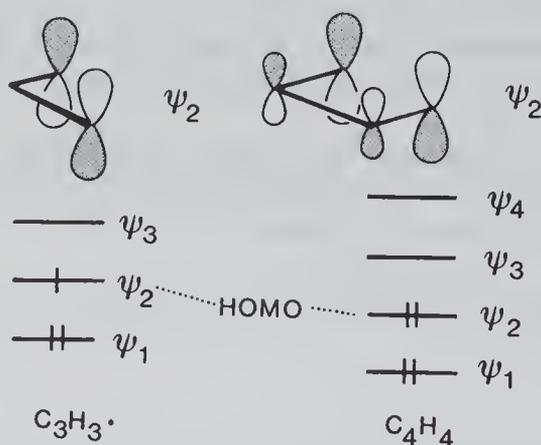
Rule





Understanding the DGM Rules

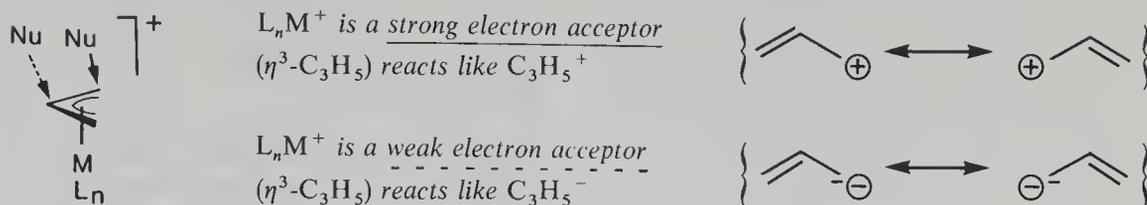
Let us start from the premise that the readiness of a ligand carbon atom to accept a nucleophile is governed by its partial positive charge. Chemo- and regioselectivity of nucleophilic attack then reflects unequal charges at the ligand carbon atoms. These charge differences must be a result of metal coordination, since for free alternating polyenes C_nH_{n+2} as well as for cyclic π -perimeters C_nH_n the charge distribution along the C_n chain is uniform. The occurrence of charge differentiation in the complex cations may be explained using the prototypes $C_3H_3^+$ (allyl) and C_4H_6 (butadiene) as examples. Herein the complex cations are mentally constructed from the respective neutral ligand and the fragment L_nM^+ , realizing that – because of the positive charge on L_nM^+ – the metal-ligand bond should be dominated by the donor contribution $L_nM^+ \leftarrow L$ (HOMO). The removal of electron density from the ligand with concomitant generation of partial charges will then be proportional to the squares of the HOMO coefficients at the individual carbon atoms, depicted qualitatively by the sizes of the orbital lobes.



As suggested by the diagram, removal of charge dominates at the **terminal** carbon atoms, which consequently attain higher partial charges δ^+ and which therefore are the preferred sites for nucleophilic attack (Rule ③).

The limitation to rule ③ is apparent as well. In the case of *even* polyenes, the ligand HOMO is occupied by two electrons which in the complex populate a bonding MO. Thus, irrespective of the acceptor strength of L_nM^+ , MO formation will always generate partial positive charges ($0 < q < +2$) on the polyene. Odd polyenes, on the other hand, contribute with a singly occupied ligand HOMO to metal-ligand bonding with the effect that, depending on the acceptor strength of L_nM^+ , negative or positive partial charges ($-1 < q < +1$) can accrue

on the ligand. In the prototypical example η^3 -allyl, C_3H_5^- - or C_3H_5^+ -like behavior can therefore arise:



Since charge transfer is more extensive for even polyenes ($0 < q < +2$) relative to odd polyenes ($-1 < q < +1$), higher reactivity of the complexes is expected for the former, as compared to the latter (Rule ①).

The preferred nucleophilic attack at complexes of open polyenes probably results from the fact that in open polyene ligands, charge distribution is less balanced than in the cyclic polyene counterparts (Rule ②). Refined discussion must, of course, include substituents effects and possible competing reactions like nucleophilic attack at CO ligands.

Excursion

^{13}C - and ^1H -NMR Spectroscopy of Organometallics

^{13}C -NMR

Despite the low natural abundance (1.1 %) and the relatively low receptivity of the ^{13}C nucleus (p. 25), ^{13}C -NMR has become an indispensable tool in the study of organometallic compounds. Essential features of ^{13}C -NMR as applied to organometallics are the following:

1. Proton decoupled $^{13}\text{C}\{^1\text{H}\}$ spectra, in the absence of other magnetic nuclei, display sharp singlets. Since signal dispersion is far superior in ^{13}C -NMR as compared to ^1H -NMR, ^{13}C spectra lend themselves to the analysis of elaborate molecules, of mixtures of isomers as well as to the recognition of fine structural details.

If the central atom possesses a magnetic moment, high isotopic abundance and relaxation times T_1 and T_2 which are not too short (e.g. ^{103}Rh , ^{195}Pt), scalar cou-

plings $J(\text{M}, ^{13}\text{C})$ are observed. The latter provide insight into the nature of the metal-ligand bond.

2. The analysis of coupled ^{13}C -NMR spectra furnishes the coupling constants $J(^{13}\text{C}, ^1\text{H})$. Together with the values $J(^1\text{H}, ^1\text{H})$ from ^1H -NMR, they reflect ligand structure and the hybridization states of the carbon atoms. Particularly revealing are geminal and vicinal coupling constants which offer hints to coordination induced changes in the intra-ligand π -bond order.

3. Special techniques allow isotopomeric species to be studied (even at natural abundance) which contain two neighboring ^{13}C nuclei so that coupling constants $^1J(^{13}\text{C}, ^{13}\text{C})$ also become available. This parameter again reveals the hybridization states of the respective carbon atoms as well as C, C bond orders in the ligand.

Furthermore, for complexes of a certain metal, linear correlation usually exists between the coupling constants $^1J(^{13}\text{C}, ^{13}\text{C})$ and the bond lengths $d(\text{C}-\text{C})$.

4. ^{13}C -NMR is particularly well-suited for the study of exchange processes. Dispersion of the chemical shifts in ^{13}C -NMR spectra being about five times as large as in ^1H -NMR, considerably faster processes may be studied by ^{13}C -NMR over the total dynamic range. Thus, ligand reorientation in (cyclooctatetraene)- $\text{Fe}(\text{CO})_3$ (p. 366) by means of ^1H -NMR is amenable to study in the fast exchange region only, whereas using ^{13}C -NMR, the total range from slow to fast exchange can be investigated. Additionally, in ^{13}C -NMR spectra simpler splitting patterns are often encountered, rendering line-shape analyses less cumbersome than for the respective ^1H -NMR spectra.

I. Chemical Shifts for ^{13}C Nuclei in Diamagnetic Organometallics

In attempts at a quantitative interpretation, the shielding terminology (σ) introduced by Ramsey is usually employed instead of the chemical shift (δ). Therein, the chemical shifts are governed by diamagnetic and paramagnetic shielding terms, Eq. (1). Note that, by convention, the shift and the shielding possess opposite signs.

$$\sigma_i = \sigma_i^{\text{dia}} + \sigma_i^{\text{para}} + \sigma_{ij} \quad (1)$$

The **diamagnetic shielding term** σ_i^{dia} accounts for the unperturbed spherical motion of the electrons; it dominates in ^1H -NMR.

The **paramagnetic shielding term** σ_i^{para} , which corrects for eventual perturbations of electronic motion and for non-spherical charge distribution, is opposed to σ_i^{dia} . According to Karplus and Pople, σ_i^{para} may be evaluated if a mean electronic

excitation energy ΔE is adopted:

$$\sigma_i^{\text{para}} = -\frac{\mu_0 \mu_B}{2\pi} \langle r^{-3} \rangle_{np} [Q_i + \sum_{i \neq j} Q_j] / \Delta E$$

$$\begin{aligned} \mu_0 &= \text{permeability (vacuum)} \\ \mu_B &= \text{Bohr magneton} \end{aligned} \quad (2)$$

Besides the mean radius r of the $2p$ orbitals of the respective carbon atom, Eq. (2) contains the parameters Q_i (electron density at atom i) and Q_j (bond orders between atoms i and j). Like the mean excitation energy ΔE , which is difficult to infer from experiment, Q_i and Q_j are often derived from MO calculations. ΔE is usually approximated by the energy gap between the HOMO and the LUMO. The third, **nonlocal term** σ_{ij} describes the influence of the remote electrons (e.g. ring current effects); for the ^{13}C nucleus in rudimentary discussions, this term is generally neglected. Apart from hydrogen, for all other magnetic nuclei the paramagnetic shielding term σ_i^{para} dominates. In a number of cases Eq. (2) provides a link between the chemical shift $\delta^{13}\text{C}$ and the electronic structure of the respective molecule. As for other nuclei, however, a quantitative interpretation of $\delta^{13}\text{C}$ is not yet feasible, mainly because various factors which in addition to ΔE influence the paramagnetic term, cannot be assessed precisely. Coordination of an organic ligand to a metal fragment affects the resonance frequencies of the ligand nuclei in a characteristic way. This **coordination shift** $\Delta\delta$ is defined as the chemical shift difference between the metal-bonded and the free ligand:

$$\Delta\delta = \delta^{(\text{complex})} - \delta^{(\text{ligand})} \quad (3)$$

In Figure 15-1 representative examples for various classes of organometallic compounds are depicted, together with values $\delta^{13}\text{C}$ for the metal-coordinated carbon atoms.

1. CHEMICAL SHIFTS FOR σ -BONDED LIGANDS

a) σ -Alkyl Metal Complexes

The $\delta^{13}\text{C}$ values of α -carbon atoms which are directly bonded to the metal, strongly depend on the nature of the metal and the ancillary ligands. Positive as well as negative coordination shifts are observed. Positive values $\Delta\delta^{13}\text{C}$ (shifts to lower field) are primarily found for Zr, Hf, Nb and Ta. Note, however, that the coordination sphere of the metal fragment, which is σ -bonded to an alkyl group, has a dramatic effect on $\delta^{13}\text{C}$ (compare: $\text{W}(\text{CH}_3)_6$, H_3CCH_3 , $\text{Cp}(\text{CO})_3\text{WCH}_3$, p. 297). For the β -carbon atoms, small positive values $\Delta\delta^{13}\text{C}$ are usually encountered whereas for γ -carbon atoms, very small negative values $\Delta\delta^{13}\text{C}$ arise.

b) Carbene- and Carbyne Metal Complexes

$\delta^{13}\text{C}$ values for carbene- and carbyne complexes lie in the range $400 > \delta^{13}\text{C} > 200$ ppm. Deshielding of a similar magnitude is also encountered for carbenium ions. Therefore, it is reasonable to conclude that the carbene- and carbyne carbon atoms in their respective metal complexes bear a partial positive charge. Similarly to carbenium ions, π -donor substituents like OR or NR_2 at the carbene carbon atom cause pronounced high-field shifts of the ^{13}C signals (cf. p. 214).

c) Carbonyl Metal Complexes

Let it be stated at the outset that metal carbonyl carbon atoms can be difficult to detect. This is because the absence of directly bonded hydrogen atoms for ^{13}CO may result in long relaxation times T_1

(p. 24). Furthermore, in double-resonance experiments like $^{13}\text{C}\{^1\text{H}\}$, due to the large carbon-hydrogen distance, nuclear Overhauser enhancement (NOE) is small. Techniques have been developed, however, to cope with this situation.

$\delta^{13}\text{C}$ values for **metal carbonyls** lie in the ranges 150–220 ppm for terminal carbonyl groups and 230–280 ppm for bridging carbonyls. Within a group of metals, shielding of the carbonyl carbon nucleus increases with increasing atomic number [example: $\text{Cr}(\text{CO})_6$ 212, $\text{Mo}(\text{CO})_6$ 202, $\text{W}(\text{CO})_6$ 192 ppm]. For structurally related complexes of the same central metal, correlations between the chemical shift $\delta^{13}\text{CO}$ and the force constant $k(\text{CO})$ of the stretching vibration have been established: increasing force constants are paralleled by increased shielding (I. S. Butler, 1979 R).

2. CHEMICAL SHIFTS FOR π -BONDED LIGANDS

In **olefin metal complexes** for protons and for ^{13}C nuclei large negative coordination shifts $\Delta\delta$ (shifts to high field or low frequency) are observed. Various authors have attempted to rationalize $\Delta\delta^1\text{H}$ as well as $\Delta\delta^{13}\text{C}$ values on the basis of **one** dominant contribution. Possible sources of the coordination shifts include:

- *Changes in charge density on the ligand atoms*
- *Changes in the intra-ligand π -bond orders*
- *Changes in the hybridization states of metal-bonded carbon atoms*
- *Various anisotropy effects*

Since these effects are in part mutually dependent, controversial statements as to the nature of the dominating influence are not surprising (Trahanovsky, 1974; Norton, 1974).

Characteristic ^{13}C -NMR spectra are also displayed by η^3 -allyl- and η^4 -diolefin complexes. In allyl complexes, the terminal carbon nuclei generally are shielded more strongly ($80 > \delta^{13}\text{C} > 40$ ppm) as compared to the central carbons ($110 > \delta^{13}\text{C} > 70$ ppm). For allyl complexes of the d^{10} metals, shielding of terminal as well as of central carbon nuclei usually increases in the order $\text{Pd} < \text{Ni} < \text{Pt}$.

For olefin complexes as well, $\Delta\delta^{13}\text{C}$ values for the terminal carbon atoms C_1 exceed those of the central carbons C_2 up to three-fold. The ratio $\Delta\delta(\text{C}_1)/\Delta\delta(\text{C}_2)$ within a group of metals increases with increasing atomic number.

Example:

$(\eta^4\text{-butadiene})\text{M}(\text{CO})_3$	M = Fe	Ru	Os
$\Delta\delta(\text{C}_1)/\Delta\delta(\text{C}_2)$	1.47	1.65	1.68

A possible rationale for this trend is the more extensive rehybridization $sp^2 \rightarrow sp^3$ of the terminal carbon atoms in complexes of the heavier metals. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of $(\eta^4\text{-cycloheptatriene})\text{Fe}(\text{CO})_3$ may serve to illustrate the shielding difference between coordinated and non-coordinated olefinic carbon atoms as well as between terminal and central carbon atoms in the η^4 -butadiene segment of a coordinated oligoolefin (Figure 15-2).

Free C_7H_8 : $\delta^{13}\text{C} = 120(\text{C}_1)$, $127(\text{C}_2)$, $131(\text{C}_3)$, $28(\text{C}_7)$. Note the low intensity of the signal for the CO groups relative to C_7 (p. 298).

II. Coupling Constants $J(^{13}\text{C}, \text{X})$

In fluid solution, by virtue of thermal molecular motion, through-space dipolar

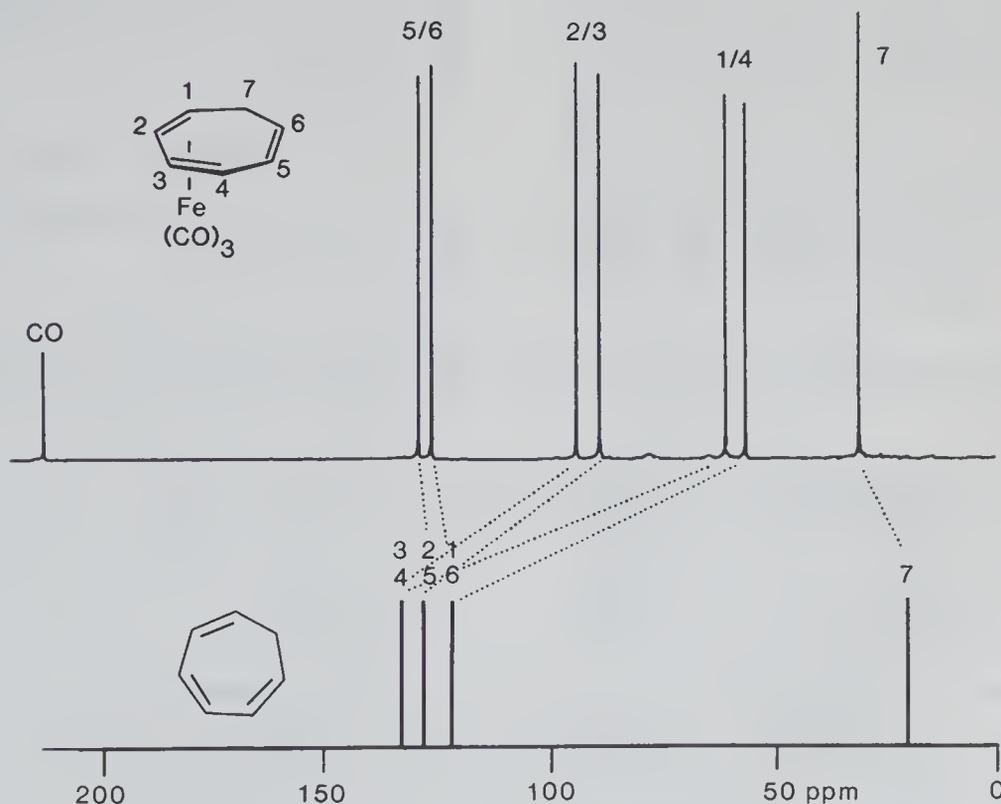


Figure 15-2: $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of $(\eta^4\text{-cycloheptatriene})\text{Fe}(\text{CO})_3$ and of free cycloheptatriene.

interactions are averaged to zero and only the scalar spin-spin interactions, which are transmitted by the electrons, are observed.

Scalar coupling ${}^nJ(A, X)$ is independent of the external magnetic field; it is usually expressed in frequency units (Hz), n designating the number of bonds between the atoms A and X.

If scalar couplings between different kinds of nuclei are to be compared, rather than using the coupling constants ${}^nJ(A, X)$ themselves, it is more convenient to employ the reduced coupling constants ${}^nK(A, X)$. The latter reflect the influence of the electronic environment in a more direct way, being independent of the magnitudes and signs of the magnetogyric ratios γ . Reduced coupling constants are defined according to:

$${}^nJ(A, X) = h \frac{\gamma_A}{2\pi} \frac{\gamma_X}{2\pi} {}^nK(A, X) \quad (4)$$

They are usually represented as the sum of the contributions orbital term K^{OD} , dipole term K^{DD} and Fermi contact term K^{FC} :

$${}^nK(A, X) = K^{\text{OD}} + K^{\text{DD}} + K^{\text{FC}} \quad (5)$$

For the lighter elements void of lone pairs of electrons (e.g. ${}^1\text{H}$, ${}^{13}\text{C}$) coupling

across **one** bond is dominated by the Fermi contact term K^{FC} and the following grossly simplified relation has been proposed (Pople, 1964):

$${}^nK(A, X) \approx K^{\text{FC}} = \frac{16\pi}{9} \mu_0 \mu_B^2 ({}^3\Delta E)^{-1} \cdot [S_A^2(0) S_X^2(0) P^2 s_A s_X] \quad (6)$$

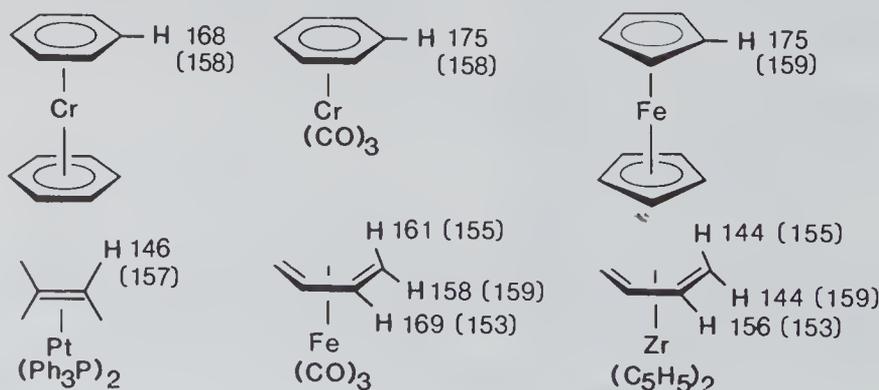
${}^3\Delta E$ is the mean triplet excitation energy, $S_A^2(0)$ and $S_X^2(0)$ represent the electron densities in valence s orbitals at the nuclei A and X, respectively, and $P^2 s_A s_X$ is the s bond order between A and X. In discussions of spin-spin coupling across several bonds and for atoms bearing lone pairs (e.g. ${}^{19}\text{F}$) the terms K^{OD} and K^{DD} must also be considered.

Hence, the **coupling constants** ${}^1J({}^{13}\text{C}, {}^1\text{H})$ in principle provide hints as to the hybridization state of a certain carbon atom. Typical values of ${}^1J({}^{13}\text{C}, {}^1\text{H})$ in free hydrocarbons are 125, 157, and 250 Hz for sp^3 -, sp^2 -, and sp hybridization. Therefore, the following rule of thumb applies:

$${}^1J({}^{13}\text{C}, {}^1\text{H}) \approx 500 s \quad (\text{Hz})$$

s denoting the fraction of s character in the C–H bond orbital.

Coupling constants ${}^1J({}^{13}\text{C}, {}^1\text{H})$ for selected π -complexes and the respective free ligands (in brackets):

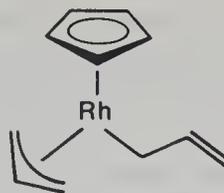


Obviously, π -coordination may increase the coupling constant $^1J(^{13}\text{C}, ^1\text{H})$, leave it unaffected or decrease it. Whereas a simple explanation for the increase of $^1J(^{13}\text{C}, ^1\text{H})$, encountered for η^6 -arene- and η^5 -cyclopentadienyl complexes, is not available at present (Günther, 1980), the coupling constants for olefin complexes may be discussed with reference to structural data. Thus, the decrease of $^1J(^{13}\text{C}, ^1\text{H})$ upon complexation for ethylene in $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$ can be rationalized by a partial rehybridization from sp^2 to sp^3 which is in line with structural data (p. 259). Similarly, the decrease of $^1J(^{13}\text{C}, ^1\text{H})$ for the terminal carbon atoms in $(\text{C}_5\text{H}_5)_2\text{Zr}(\eta^4\text{-C}_4\text{H}_6)$ (p. 263) is a result of rehybridization which diminishes the s orbital contribution to the $\text{C}-\text{H}$ bond. The central carbon atoms apparently remain sp^2 -hybridized. Note that butadiene complexes of the early transition metals – as judged from structural data – are better described as metallacyclopentenes (p. 263). For complexes of the type $(\text{CO})_3\text{Fe}(\eta^4\text{-diene})$ the discussion is more involved since here, in addition to rehybridization, twisting along the terminal $\text{C}-\text{C}$ bond arises (v. Philipsborn, 1976).

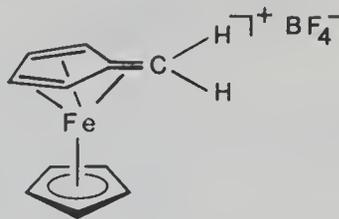
While it is often possible to find *ex post facto* explanations for an observed trend in the coupling constants $^1J(^{13}\text{C}, ^1\text{H})$, this parameter may not yet be regarded as an unambiguous diagnostic tool.

The coupling constants $^1J(\text{M}, ^{13}\text{C})$ contain information concerning the nature of the metal-carbon bond: for $\text{M}^\sigma\text{-C}$ bonds, considerably higher values $^1J(\text{M}, ^{13}\text{C})$ are observed as compared to $\text{M}^\pi\text{-C}$ bonds. Again, the higher s character in the former bond type is responsible.

As a consequence of pronounced differences in the magnetogyric ratios γ_{M} , the parameters $^1J(\text{M}, ^{13}\text{C})$ are spread over a wide range. Thus, in contrast to the small



In the complex $(\text{Cp})\text{Rh}(\sigma\text{-allyl})(\pi\text{-allyl})$, the $\text{Rh}^\sigma\text{-C}$ bond is characterized by a value $^1J(^{103}\text{Rh}, ^{13}\text{C})$ of 26 Hz whereas for the π -bonded allyl ligand $^1J(^{103}\text{Rh}, ^{13}\text{C})$ amounts to 14–16 Hz.



The α -ferrocenylcarbenium ion, enriched in ^{57}Fe , features the coupling constant $^1J(^{57}\text{Fe}, ^{13}\text{C}) = 1.5$ Hz at the exocyclic carbon atom. Therefore, this carbon atom is probably not σ -bonded to the central metal since for $\text{Fe}^\sigma\text{-C}$ bonds, coupling constants of about 9 Hz are typical, whereas for $\text{Fe}^\pi\text{-C}$ bonds, values of 1.5–4.5 Hz are observed (Koridze, 1983).

values $^1J(^{103}\text{Rh}, ^{13}\text{C})$ and $^1J(^{57}\text{Fe}, ^{13}\text{C})$ mentioned above, considerably larger coupling constants are encountered for other metals. Examples:

$$^1J(^{183}\text{W}, ^{13}\text{C}) = 43 \text{ Hz in } \text{WMe}_6;$$

$$^1J(^{183}\text{W}, ^{13}\text{C}) = 126 \text{ Hz in } \text{W}(\text{CO})_6;$$

$$^1J(^{195}\text{Pt}, ^{13}\text{C}_{\text{Me}}) = 568 \text{ Hz,}$$

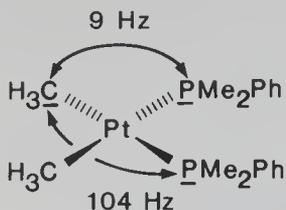
$$^1J(^{195}\text{Pt}, ^{13}\text{C}_{\text{CO}}) = 2013 \text{ Hz}$$

in $\text{cis}[\text{Cl}_2\text{Pt}(\text{CO})\text{Me}]^-$.

Even in the case of high isotopic abundance, a coupling pattern due to $^1J(\text{M}, \text{C})$ is only observable if the relaxation times T_1 of both nuclei engaged in spin-spin coupling are long relative to $1/2\pi J$ ($T_1 > 10 \cdot 1/2\pi J$). This condition is usually fulfilled for interactions between $I = 1/2$ nuclei. If, on the other hand, T_1 for one of the coupling nuclei is very short ($T_1 \ll 1/2\pi J$), a sharp singlet appears instead of the multiplet. This sit-

uation typically arises if nuclei with a quadrupole moment are coupled to ^{13}C . T_1 - and $1/2\pi J$ values of comparable magnitude lead to severely broadened multiplet components.

Geminal coupling constants $^2J(\text{X}, ^{13}\text{C})$ provide stereochemical information:



For complexes of heavy transition metals like Ru, Os, Rh, Ir and Pt, *cis-* and *trans* coupling constants $^2J(\text{X}, ^{13}\text{C})$ strongly differ in magnitude. Example: in *cis*-Pt(Me)₂(PMe₂Ph)₂ the coupling $^2J_{\text{trans}}(^{31}\text{P}, ^{13}\text{C})$ amounts to 104 Hz, the value $^2J_{\text{cis}}(^{31}\text{P}, ^{13}\text{C})$ only to 9 Hz.

Like the coupling constants $^3J(^1\text{H}, ^1\text{H})$ in transition-metal complexes, **vicinal coupling $^3J(\text{M}, ^{13}\text{C})$ and $^3J(^{13}\text{C}, ^1\text{H})$** is governed by the length of the central single- or double bond, the torsional angle φ and the electronegativity of substituents. The dependence on the torsional angle is cast in form of an equation of the Karplus type (see textbooks on NMR spectroscopy):

$$^3J(\text{X}, \text{C}) = A \cos^2 \varphi + B \cos \varphi + C$$

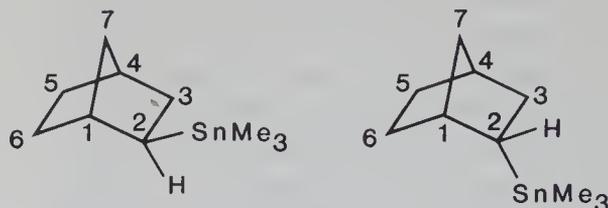
A , B , and C are empirical parameters.



Thus ^{13}C -NMR studies of platinacycles and of *exo-* and *endo-*norbornyl trimethylstannanes have demonstrated that the coupling constants $^3J(\text{M}, \text{C})$ in the $\text{M}-\text{C}-\text{C}-\text{C}$ segments adhere to a Karplus equation.

Example:

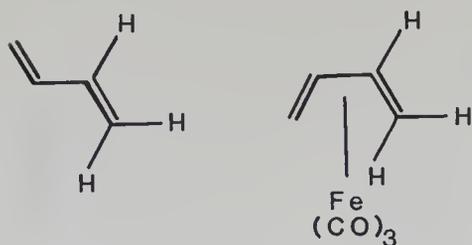
Coupling constants $^3J(^{119}\text{Sn}, ^{13}\text{C})$ in Hz



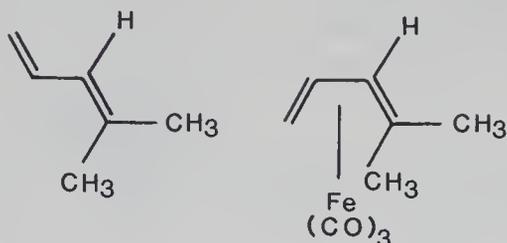
Sn-C(4) = 23.0	Sn-C(4) = 22.0	A = 25.2
Sn-C(6) = 69.0	Sn-C(6) = 34-38	B = -7.6
Sn-C(7) = 0.0	Sn-C(7) = 59.0	C = 30.4

The parameters A , B and C , derived from experimental data, provide a **Karplus relation** for $^3J(^{119}\text{Sn}, ^{13}\text{C})$ which can be applied in the study of structure and conformation of organotin compounds (Kuivila, 1974).

In (η^4 -1,3-diene)metal complexes, where the ligand is π - rather than σ -bonded, vicinal couplings $^3J(\text{X}, \text{H})$, $\text{X} = \text{C}$ or H , furnish information concerning ligand geometry. Upon coordination to a metal fragment ML_n , the vicinal *cis-* and *trans* couplings $^3J(^{13}\text{C}, ^1\text{H})$ and $^3J(^1\text{H}, ^1\text{H})$ are reduced to different extents. This effect may be explained by a twisting of the terminal $\text{C}-\text{C}$ bond such that the *endo* substituent moves away from the metal and the *exo* substituent towards the metal (cf. p. 264). In the case of (4-methyl-1,3-pentadiene)Fe(CO)₃ the vicinal coupling $^3J_{\text{trans}}(^{13}\text{C}_{\text{Me}}, ^1\text{H})$ is reduced to such a degree that it becomes smaller than the coupling $^3J_{\text{cis}}(^{13}\text{C}_{\text{Me}}, ^1\text{H})$ - a situation never encountered for free olefins (v. Philipsborn, 1988).



$J_{\text{trans}}(\text{H}, \text{H}) = 10.17$	$^3J_{\text{cis}}(\text{H}, \text{H}) = 6.93 \text{ Hz}$	Reduction
$J_{\text{trans}}(\text{H}, \text{H}) = 17.05$	$^3J_{\text{trans}}(\text{H}, \text{H}) = 9.33 \text{ Hz}$	32%
		45%



$J_{\text{trans}}(\text{C}, \text{H}) = 7.0$	$^3J_{\text{cis}}(\text{C}, \text{H}) = 5.0 \text{ Hz}$	Reduction
$J_{\text{trans}}(\text{C}, \text{H}) = 8.2$	$^3J_{\text{trans}}(\text{C}, \text{H}) = 3.5 \text{ Hz}$	28%
		57%

III. Influence of Dynamic Processes

^{13}C -NMR is not limited to the analysis of static molecular structures; it is well-suited for the study of reversible intra- and intermolecular processes and the determination of the respective activation energies, since the line-shapes of the resonance signals in these cases show temperature dependence. For dynamic processes in which an observed nucleus is transferred from the magnetic environment A to the environment B with a rate constant k , the following cases may be distinguished:

- limit of slow exchange ($k \ll \Delta\omega$)
- coalescence region ($k \approx \Delta\omega$)
- limit of fast exchange ($k \gg \Delta\omega$)

wherein $\Delta\omega$ is the difference in the resonance frequencies of the observed nucleus in the two magnetic environments. The quantitative interpretation of these spectra is possible without computer simulation only for the simplest case which in-

volves a periodic change between two magnetic environments ("two-site exchange"). For this type of exchange process, which frequently occurs in practice, temperature-dependent rate constants are readily calculated with the aid of approximate formulae. Assuming equal populations of the sites A and B, the following expressions apply:

slow-exchange region

$$k = \pi(W_{1/2} - W_{0_{1/2}})$$

coalescence

$$k = \pi \Delta\omega / \sqrt{2} = 2.22 \Delta\omega$$

fast-exchange region

$$k = (\pi \Delta\omega^2) / 2(W_{1/2} - W_{0_{1/2}})$$

$W_{0_{1/2}}$ represents the half-width in the absence of exchange (e.g. width of the solvent signal in Hz), and $W_{1/2}$ the half-width of the signal broadened by exchange. If the spectrum is recorded at different temperatures, the free enthalpy of activation ΔG^\ddagger as well as ΔH^\ddagger and ΔS^\ddagger can be calculated by means of the Eyring formula. The activation enthalpy ΔH^\ddagger is a measure of the height of the energy barrier, the activation entropy ΔS^\ddagger reflects the change in geometry upon approaching the transition state.

In many exchange processes, several magnetically active nuclei (e.g. ^1H , ^{31}C , ^{31}P) are affected simultaneously. The appropriate choice of the nucleus to be observed by NMR then simplifies the analysis of the process considerably. Alternatively, in order to check for internal consistency, an investigation of the exchange process using all NMR active nuclei is advisable.

Example: The cation $[(\text{C}_5\text{Me}_5)\text{Rh}(2,3\text{-dimethylbutenyl})]^+$ undergoes an interconversion between the enantiomeric forms A

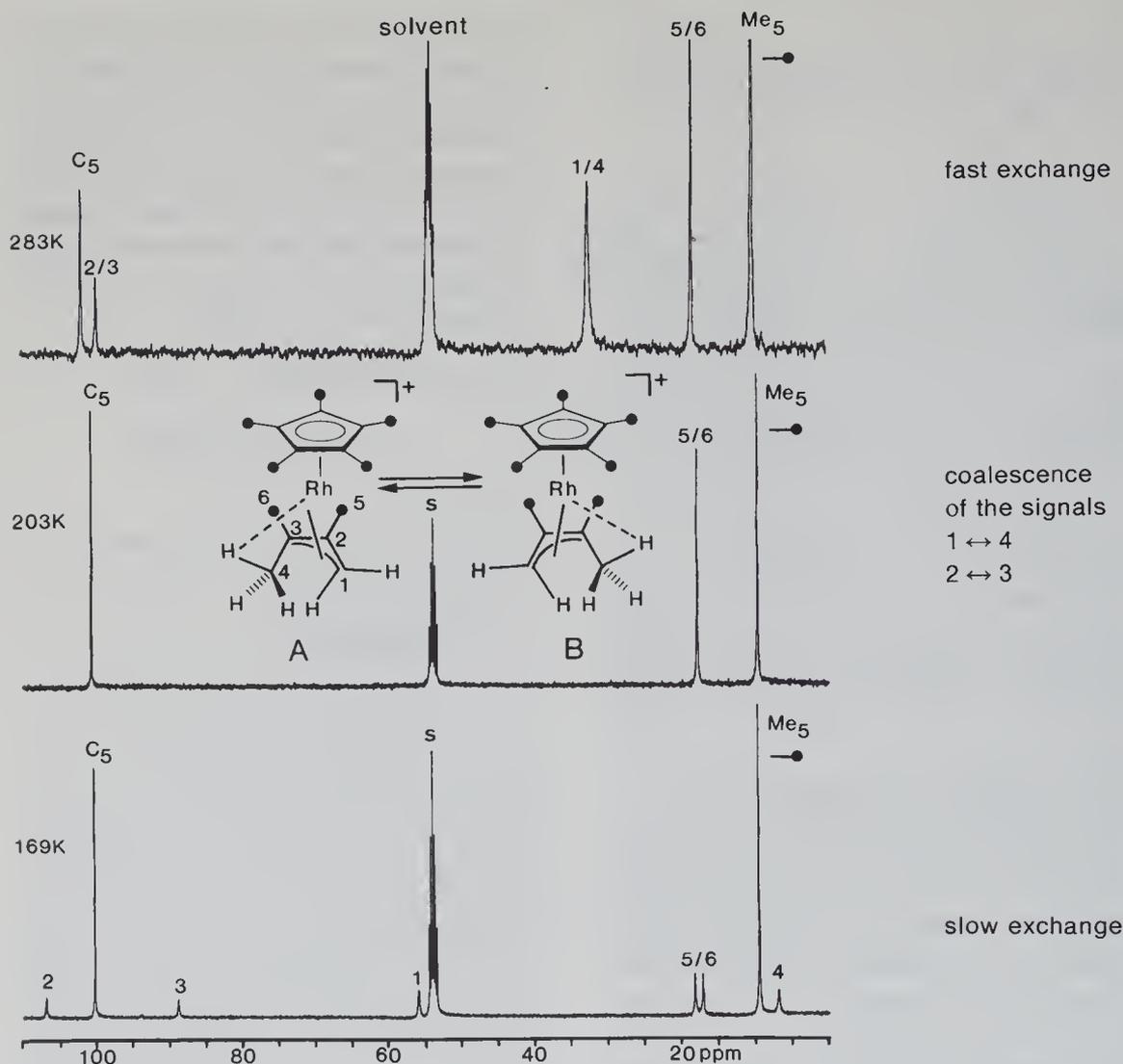


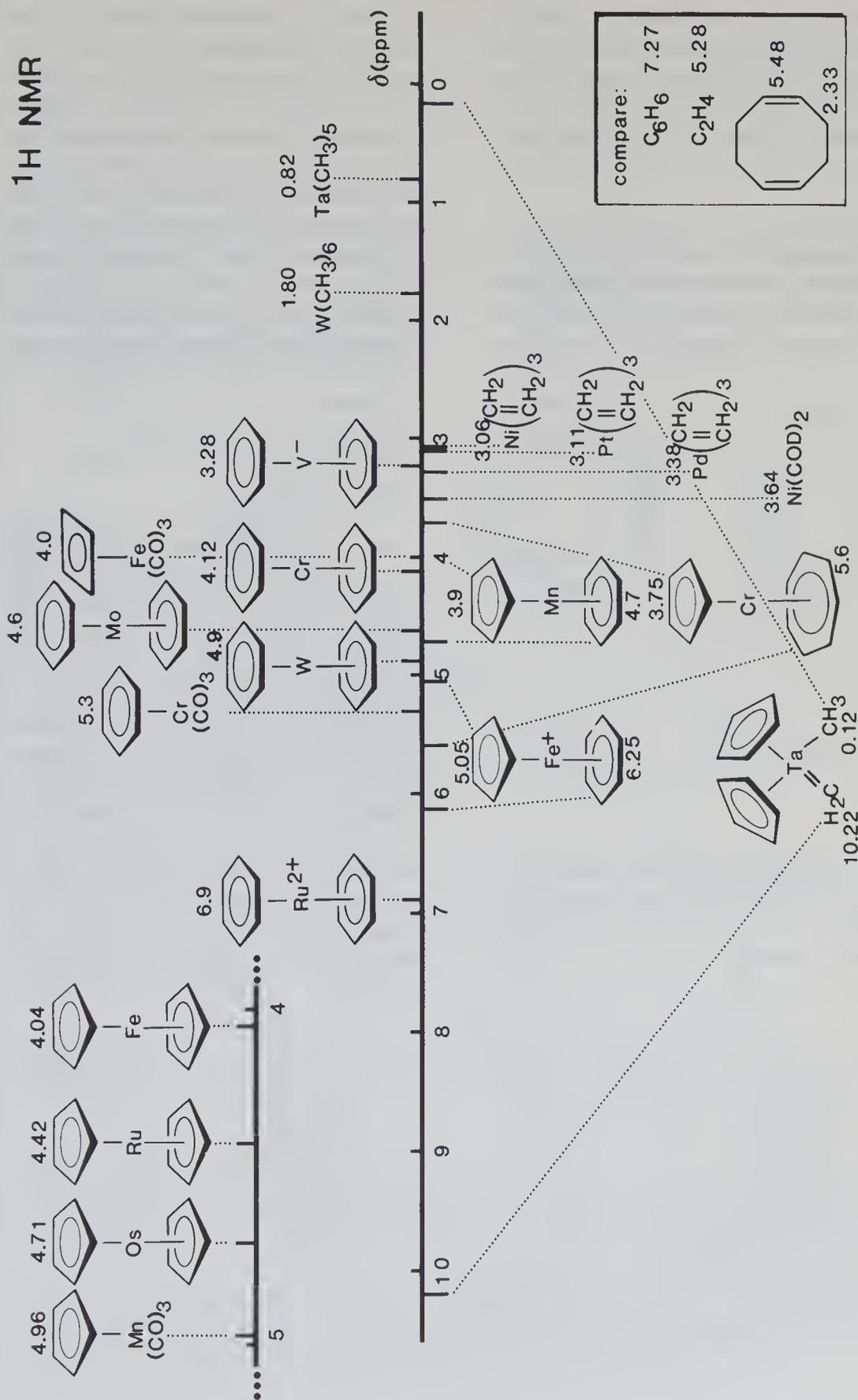
Figure 15-3: $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of $[(\text{C}_5\text{Me}_5)\text{Rh}(2,3\text{-dimethylbutenyl})]\text{BF}_4$ in CD_2Cl_2 at 100.8 MHz.

and B (p. 264). In ^1H -NMR this fluxionality represents a "five-site exchange" because the rotation of the terminal methyl group, which is fixed to the metal by means of an agostic interaction $\text{C}-\text{H}\rightarrow\text{M}$, must be taken into account. In ^{13}C -NMR, on the other hand, the simpler "two-site exchange" case applies ($1\leftrightarrow 4$, $2\leftrightarrow 3$, $5\leftrightarrow 6$) (Figure 15-3). For the exchange $\text{A}\leftrightarrow\text{B}$ the following parameters were derived: $\Delta G_{300\text{K}}^\ddagger = 38.9\text{ kJ/mol}$, $\Delta H^\ddagger \approx 29\text{ kJ/mol}$, and ΔS^\ddagger

$\approx -35\text{ J/mol K}$ (Salzer, v. Philipsborn, 1987).

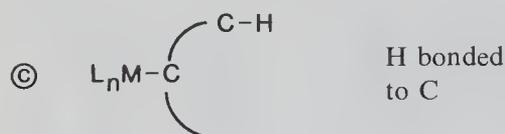
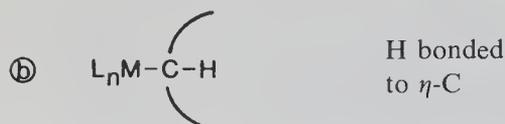
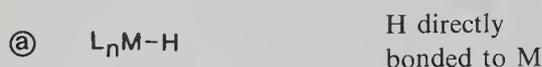
^1H -NMR

Proton magnetic resonance for diamagnetic organotransition metal compounds is observed in the chemical shift range $25 > \delta^1\text{H} > -40\text{ ppm}$. Paramagnetic organometallics may give rise to chemical shifts of several hundred ppm [Example: $(\text{C}_6\text{H}_6)_2\text{V}^\cdot$, $\delta^1\text{H} = 290\text{ ppm}$]. In the

Figure 15-4: δ ^1H values for diamagnetic organotransition-metal compounds.

latter case, detection depends on certain restrictions imposed by the electron spin relaxation time, further details being beyond the scope of this text (cf. La Mar, Horrocks, Holm, *NMR of Paramagnetic Molecules*, New York, 1973).

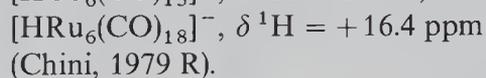
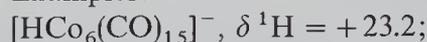
In discussions of the ^1H -NMR properties of **diamagnetic organotransition-metal complexes** it is convenient to differentiate the following three cases of increasing metal-proton distance:



Ⓐ **Metal-bonded protons** which in organometallic chemistry are regarded as hydridic (p. 234), experience particularly strong shielding:

For related compounds, across a row with increasing atomic number shielding tends to increase; smooth group trends are not discernible, however. A bridging hydride ($\mu\text{-H}$) absorbs at higher field than a terminal hydride. Positive charge causes resonance to appear at low field, negative charge shifts the signal to high field. Hydridometal clusters in which the hydrogen atom is buried in the cavity of M_n -polyhedron (p. 406), display totally different ^1H -NMR behavior, in that resonance occurs at extremely low field.

Examples:



In attempts to rationalize the ^1H -NMR data of transition-metal hydrides, it must be borne in mind that the proton – as opposed to heavier nuclei – is exposed to intra (σ_i)- and inter (σ_{ij}) atomic shielding contributions of similar magnitude.

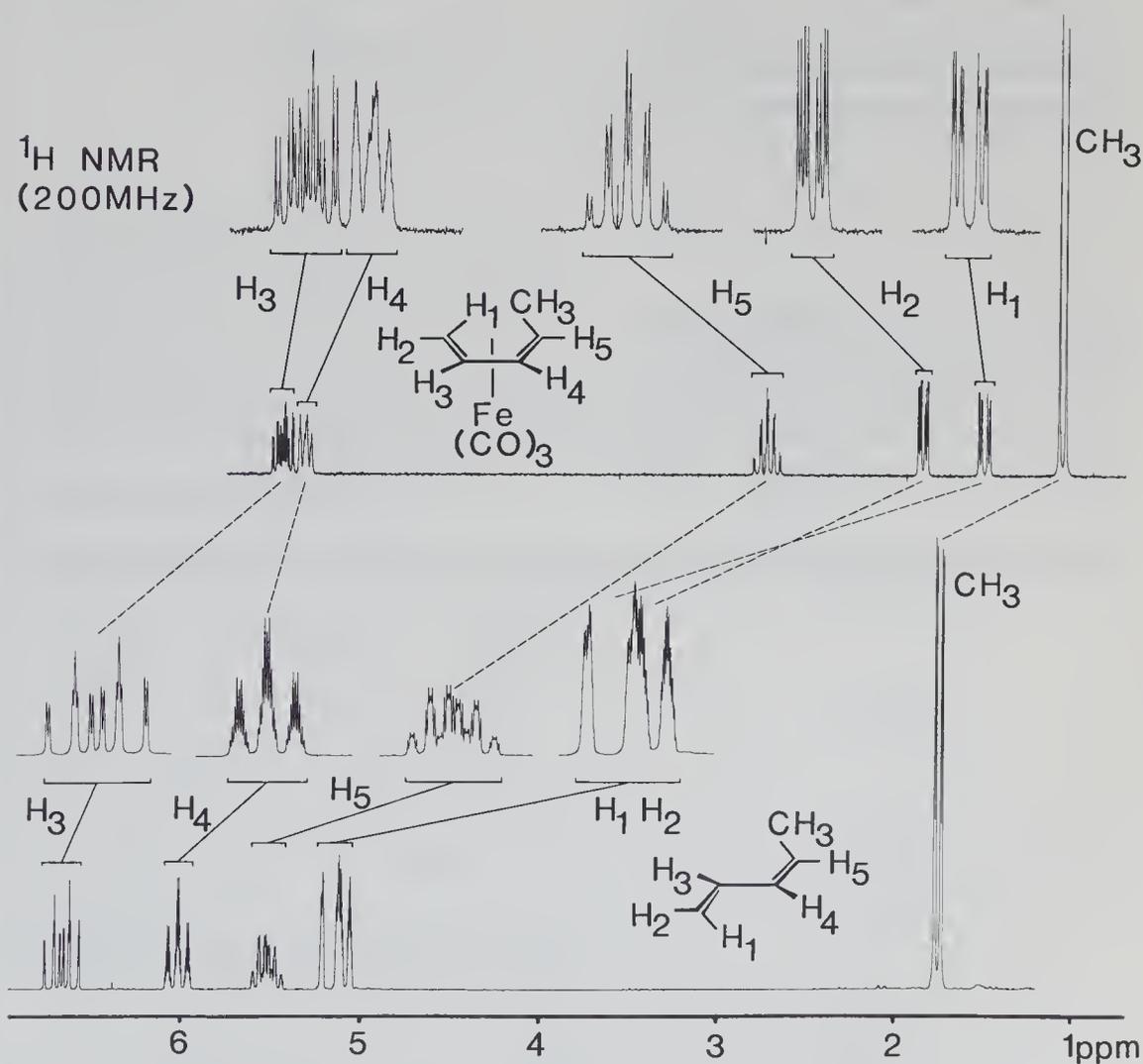
If the range of $\delta \text{ } ^1\text{H}$ values for transition-metal hydrides is compared to the chemical shift of a typical main-group element hydride ($[\text{AlH}_4]^-$, $\delta \text{ } ^1\text{H} = 0.00$ ppm), one immediately recognizes that the transition metal, as a bond partner to hydrogen, plays a special role. Hence, the strongly negative $\delta \text{ } ^1\text{H}$ values have been attributed to the paramagnetic shielding

	$\delta(^1\text{H})/\text{ppm}$		$\delta(^1\text{H})/\text{ppm}$
$(\text{CO})_5\text{MnH}$	-7.5	Cp_2MoH_2	-8.8
$(\text{CO})_5\text{ReH}$	-5.7	$\text{Cp}_2\text{MoH}_3^+$	-6.1
$(\text{CO})_4\text{FeH}_2$	-11.1	$\text{Cp}(\text{CO})_3\text{CrH}$	-5.5
$(\text{CO})_4\text{RuH}_2$	-7.6	$\text{Cp}(\text{CO})_3\text{MoH}$	-5.5
$(\text{CO})_4\text{OsH}_2$	-8.7	$\text{Cp}(\text{CO})_3\text{WH}$	-7.3
$(\text{CO})_4\text{CoH}$	-10.7	Cp_2FeH^+	-2.1
<i>trans</i> -(Et_3P) $_2\text{ClPtH}$	-16.8	Cp_2RuH^+	-7.2
$\mu\text{-H}$ { $(\text{CO})_{10}\text{Cr}_2\text{H}^-$	-19.5 (p. 235)		
{ $(\text{CO})_{11}\text{Fe}_3\text{H}^-$	-15.0 (p. 234)		
{ $(\text{CO})_{24}\text{Rh}_{13}\text{H}_3^{2-}$	-29.3 (p. 410)		

term σ_i^{para} of the neighboring transition metal (Buckingham, 1964). A characteristic feature of transition-metal complexes is the existence of low-lying, electronically excited states which are admixed to the ground state under the influence of the external magnetic field. In this way, the field induces a magnetic moment at the metal which exerts a deshielding effect at the central atom and – due to the distance relationship – a shielding effect at the hydride ligand (σ_{ij} , non-local effect).

(b) Protons which are fixed to metal-bonded carbon atoms display a much smaller span of chemical shifts. The coordination shifts usually lie in the range $1 < \Delta\delta^1\text{H} < 3$ ppm; they are always negative.

The gradation of the coordination shifts for a ligand of low symmetry can be read off the ^1H -NMR spectrum of (η^4 -cis-1,3-pentadiene) $\text{Fe}(\text{CO})_3$:

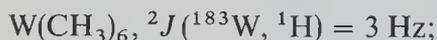


^1H -NMR spectra of (η^4 -cis-1,3-pentadiene) $\text{Fe}(\text{CO})_3$ and of free 1,3-pentadiene in CDCl_3 at 200 MHz.

$\Delta\delta^1\text{H}$ decreases in the order terminal, endo (H_1) > terminal, exo ($\text{H}_{2,5}$) > central ($\text{H}_{3,4}$)

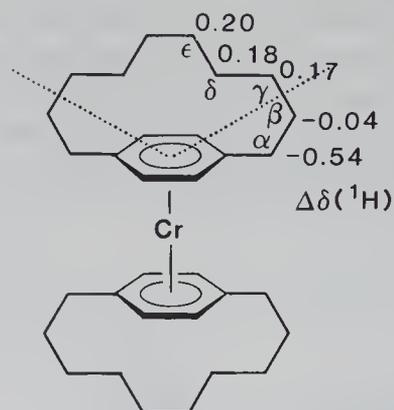
The coordination shifts $\Delta\delta(^1\text{H})$ of η -CH units are ruled by local effects (partial charge, rehybridization) and by non-local effects (neighboring group anisotropy of the metal, coordination-induced perturbation of diamagnetic ring currents). A quantitative assessment of these contributions is not yet possible. Notwithstanding, the coordination shift $\Delta\delta(^1\text{H})$ is of considerable heuristic value.

The **coupling constants** $J(^1\text{H}, ^1\text{H})$ – like the values $J(^{13}\text{C}, ^1\text{H})$ – yield information with regard to intra-ligand bond orders, hybridization states of the carbon atoms and therefore ligand geometry. Occasionally, **coupling constants** $^2J(\text{M}, ^1\text{H})$ are also resolved; they characterize the type of metal-ligand bonding. Examples:



© **Protons at non-coordinated carbon atoms**, not surprisingly, show very small coordination shifts $\Delta\delta(^1\text{H})$. In contrast to their influence on the shielding of carbon nuclei, non-local effects make a signifi-

cant contribution to the shielding of protons. Specifically, non-local contributions to $\Delta\delta(^1\text{H})$ are expected in cases where metal coordination affects the diamagnetic ring current which governs the shielding in the periphery of arenes.

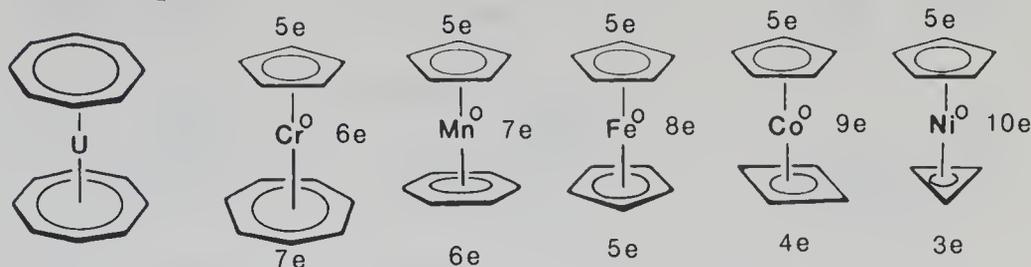


Bis(1,4-decamethylene- η^6 -benzene)chromium may serve as an example. The area in space, where $\Delta\delta(^1\text{H})$ changes sign corresponds to the conical surface which, for free arenes, separates shielding and deshielding regions. The conclusion that metal coordination partially quenches the diamagnetic ring current therefore suggests itself (Elschenbroich, 1984).

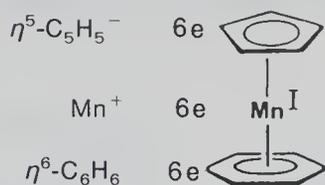
15.4 Complexes of the Cyclic π -Perimeters C_nH_n

Cyclic conjugated ligands $C_nH_n^{+,0,-}$ are known to occur in five different classes of compounds:

I Sandwich complexes

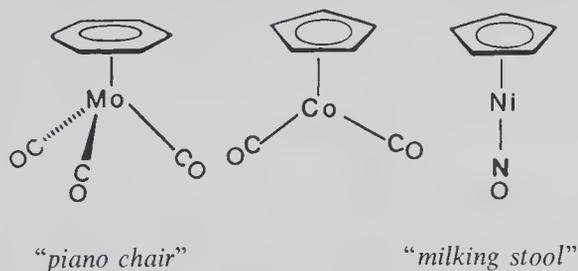


If an oxidation state of zero is assigned to the central metal atom, the rings in this series become 7- to 3-electron ligands. The combinations shown above result in 18 VE complexes. They have all been synthesized. The 18 VE rule cannot, however, be applied to lanthanoid and actinoid sandwich complexes (cf. p. 364).

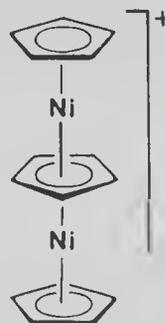


An alternative approach is to assign the complexed ligand the same charge as in its most stable uncoordinated form. The formal oxidation state of the metal is then derived by balancing the charge.

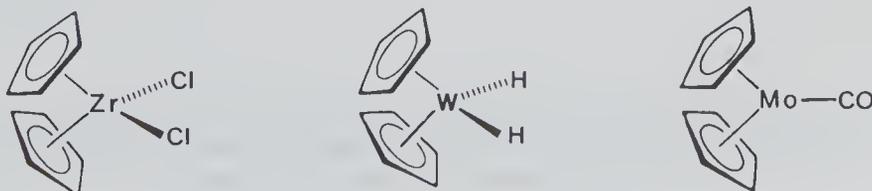
II Half-sandwich complexes

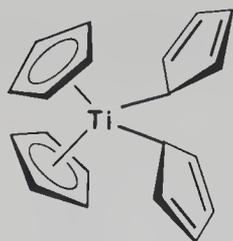


III Multidecker sandwich complexes

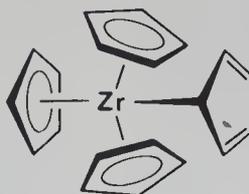


IV Complexes with tilted sandwich structure



V Complexes with more than two C_nH_n ligands

Cp₄Ti
 $r(\text{Ti}^{4+}) = 74 \text{ pm}$
 $(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})_2\text{Ti}$



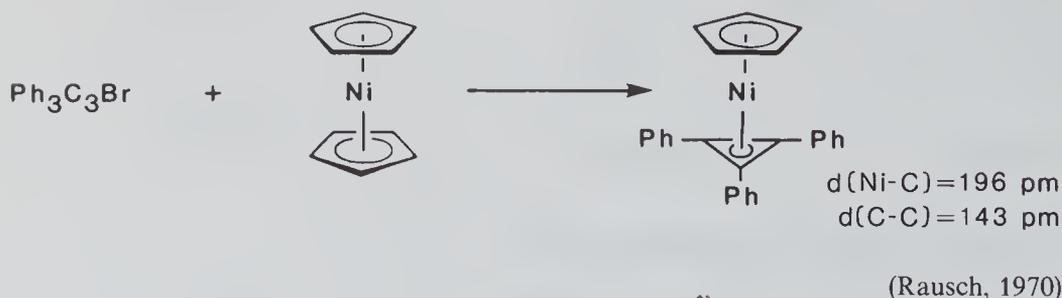
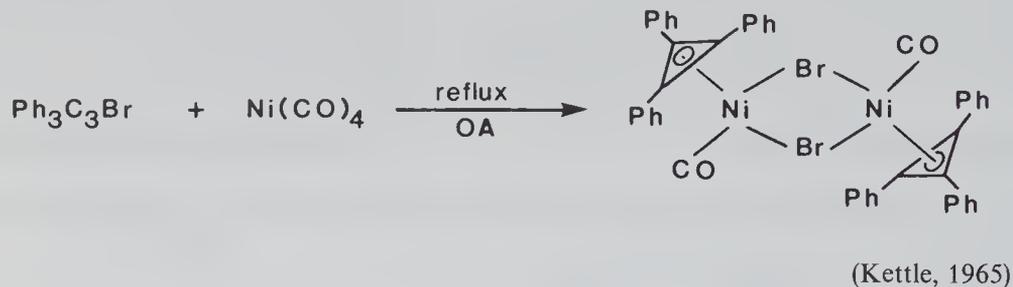
Cp₄Zr
 $r(\text{Zr}^{4+}) = 91 \text{ pm}$
 $(\eta^5\text{-Cp})_3(\eta^1\text{-Cp})\text{Zr}$



Cp₄U
 $r(\text{U}^{4+}) = 117 \text{ pm}$
 $(\eta^5\text{-Cp})_4\text{U}$

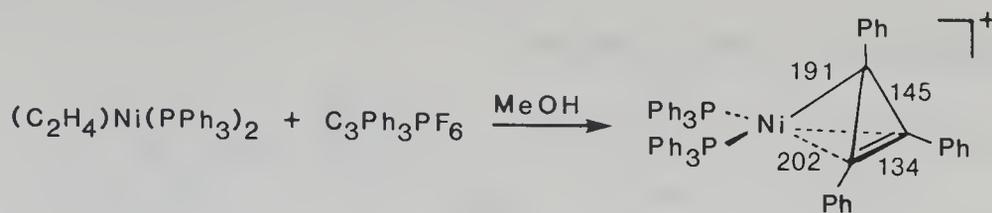
15.4.1 $C_3R_3^+$ as a Ligand

A cyclopropenyl cation Ph_3C_3^+ , the most simple aromatic system obeying the Hückel rule $[(4n + 2) \pi\text{-electrons}, n = 0]$, was first synthesized by Breslow in 1957, the parent ion C_3H_3^+ appearing in 1967. The number of η^3 -cyclopropenyl complexes known to date is still relatively small.

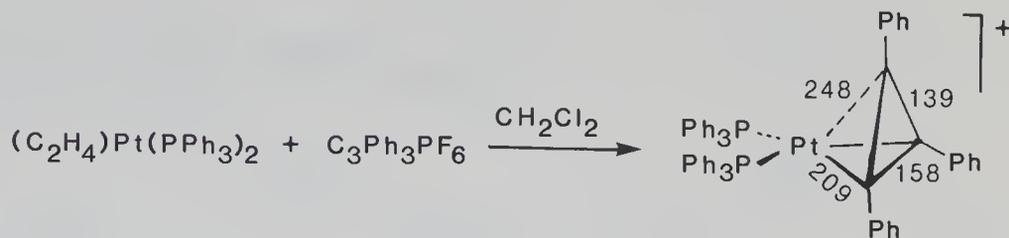


An interesting aspect of cyclopropenyl transition-metal complexes is the variety of coordination modes for the C_3 moiety. In addition to axial symmetry found in the $\text{Ni}-\text{C}_3\text{Ph}_3$ complex, unsymmetrical bonding modes are also encountered.

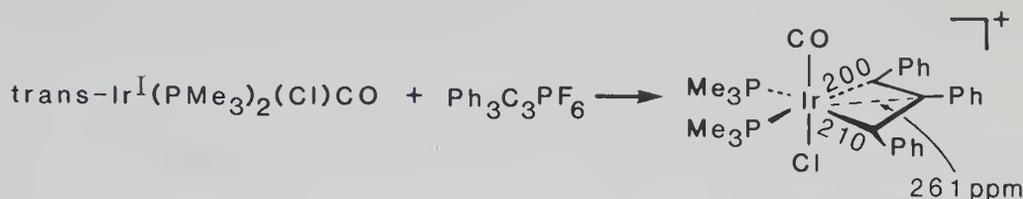
One short, two long M–C bonds (Sacconi, 1980):



One long, two short M–C bonds (Weaver, 1973):



The difference in bond lengths, established for $(\text{Me}_3\text{P})_2\text{Cl}(\text{CO})\text{Ir}(\text{Ph}_3\text{C}_3)$, may be regarded as a continuation of the trend discernible for the Ni- and Pt complexes above:



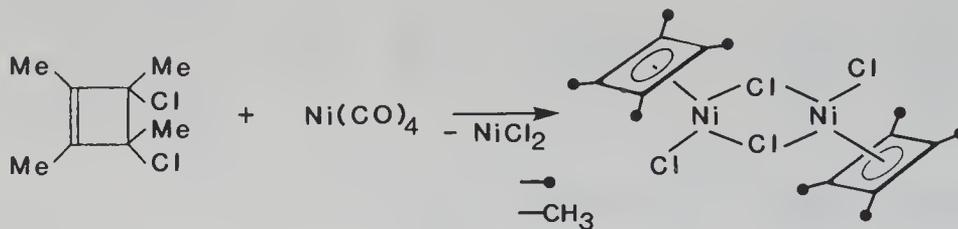
This structural gradation from the $(\eta^3\text{-cyclopropenyl})\text{Ni}$ complex to the iridacyclobutane structure is interesting since it mimics the various stages of strained three-membered ring opening (cf. Chapter 17.2).

15.4.2 C₄H₄ as a Ligand

The preparation of free cyclobutadiene by photolytic methods in low-temperature matrices (8–20 K) is a relatively recent accomplishment. The stabilization of C₄H₄ by coordination to a transition metal had, however, been predicted on theoretical grounds by Longuet-Higgins and Orgel in 1956, the first synthesis of a cyclobutadiene transition-metal complex being carried out by Criegee in 1959.

PREPARATION

1. Dehalogenation of Cyclobutene Dihalides

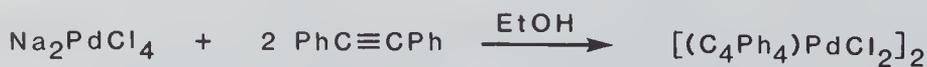
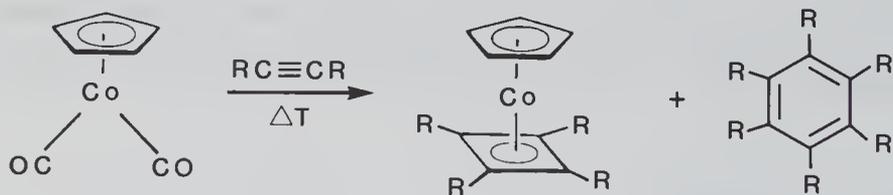


$d(\text{Ni}-\text{C}) = 199-205 \text{ pm}$, $d(\text{C}-\text{C}) = 140-145 \text{ pm}$
 air-stable, red-violet crystals (Criegee, 1959)



planar C_4 ring, $d(\text{C}-\text{C}) = 146 \text{ pm}$, diamagnetic,
 mp 26°C (Pettit, 1965)

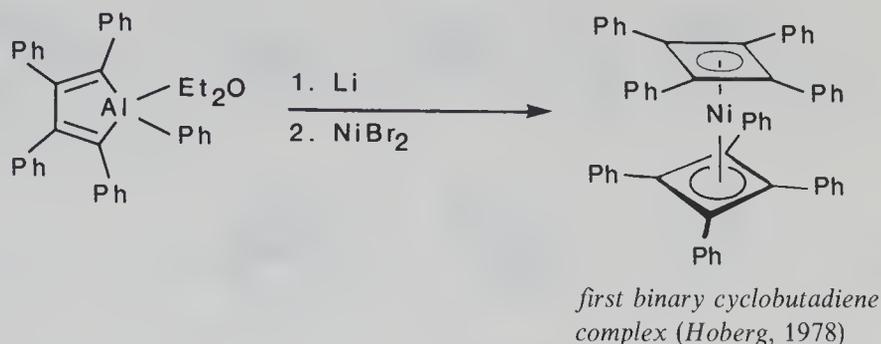
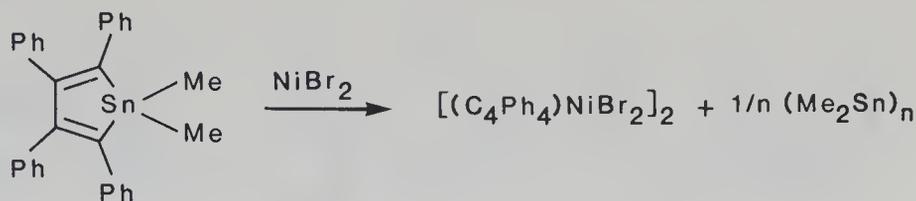
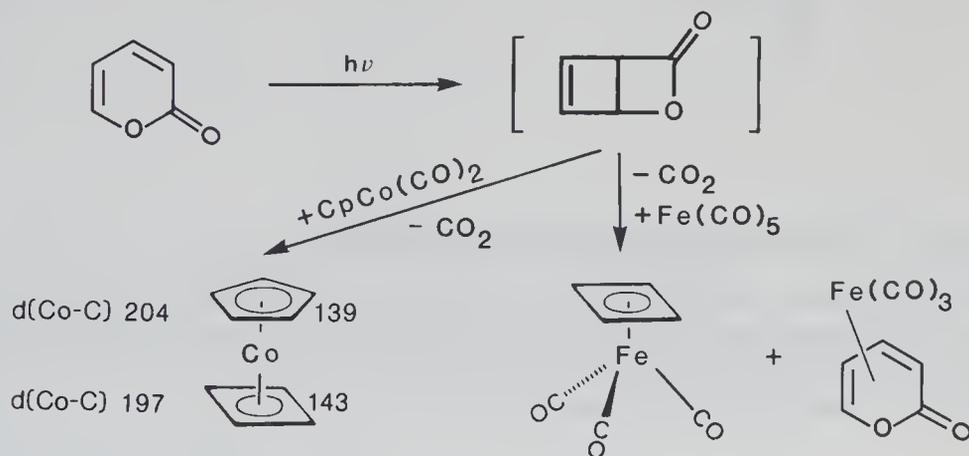
2. Dimerization of Acetylenes



3. Ligand Transfer



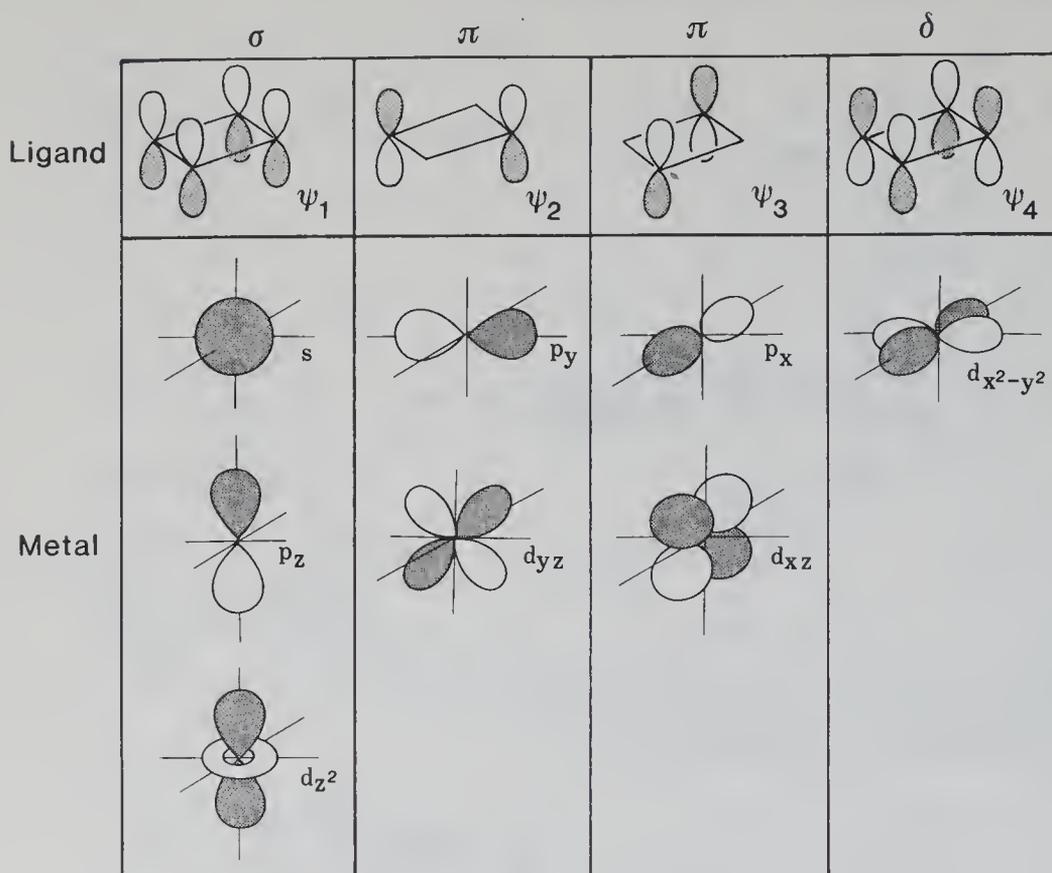
4. Ring Contraction of Metallacyclopentadienes

5. Decarboxylation of photo- α -Pyrone

STRUCTURE AND BONDING

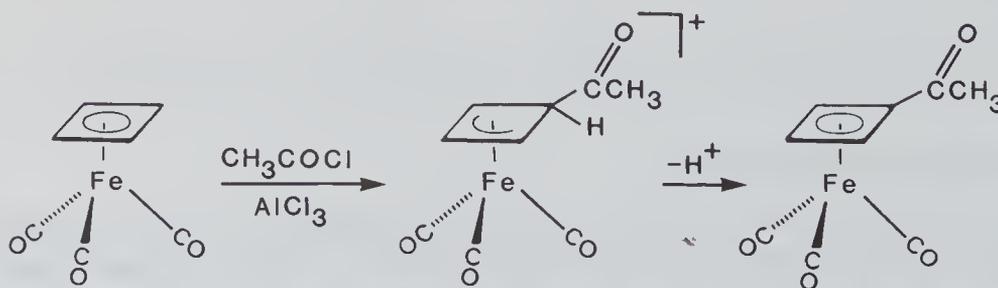
While free cyclobutadiene, according to spectroscopic evidence, is rectangular (Schweig, 1986 R), η^4 -cyclobutadiene in transition-metal complexes clearly adopts a square structure. Square cyclobutadiene should possess two unpaired electrons (single occupancy of the two degenerate MO's ψ_2 and ψ_3). The diamagnetism of η^4 -C₄H₄ complexes is explained by the interaction of these singly-occupied π MO's with singly-occupied metal orbitals of matching symmetry (formation of two covalent bonds).

Metal-ligand interactions in cyclobutadiene complexes:



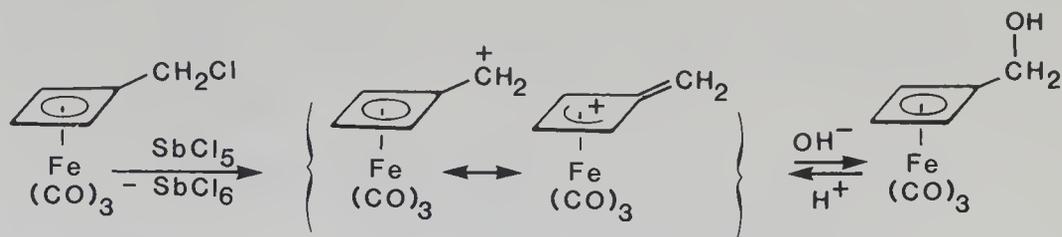
REACTIVITY OF CYCLOBUTADIENE COMPLEXES

The most important feature of $(\eta^4\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ is its similarity to aromatic compounds; this is exemplified by the ease with which it undergoes electrophilic substitution at the ring to form $\text{C}_4\text{H}_3\text{RFe}(\text{CO})_3$ ($\text{R} = \text{COMe}, \text{COPh}, \text{CHO}, \text{CH}_2\text{Cl}$ etc). The following mechanism has been proposed for this reaction:

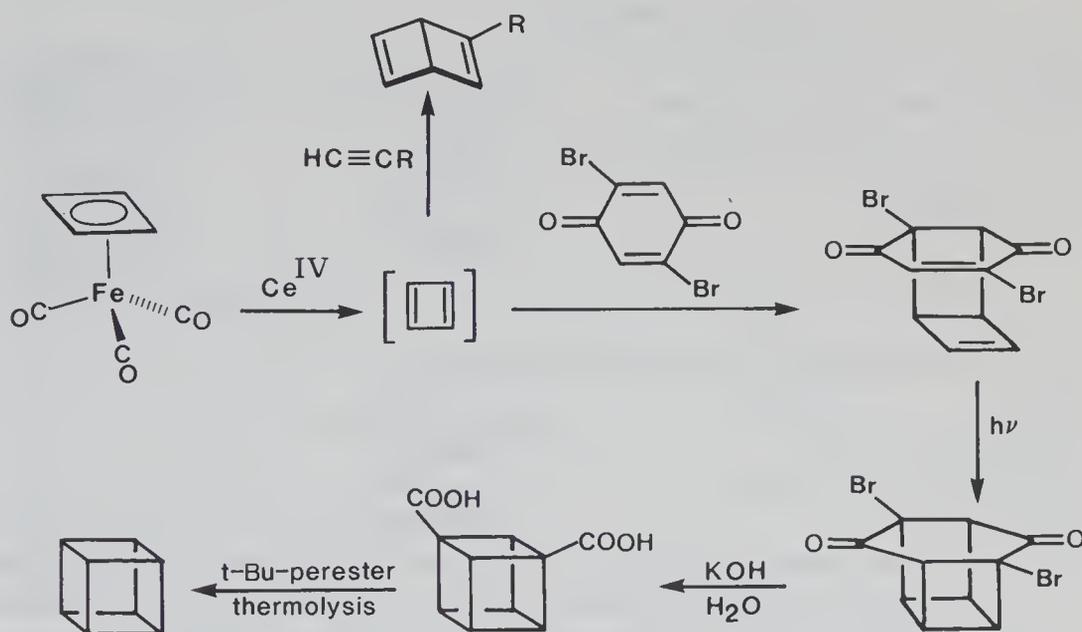


α - CH_2X -groups attached to $\text{C}_4\text{H}_4\text{Fe}(\text{CO})_3$ are easily solvolyzed. Apparently, coordination to iron results in a **stabilization of the α -carbenium ion**; this effect is also attributed

to the ferrocenyl group (Watts, 1979 R). The intermediate cation may be isolated as a PF₆⁻ salt:



In organic synthesis, C₄H₄Fe(CO)₃ serves as a source of free cyclobutadiene. After low-temperature oxidation, the liberated C₄H₄ reacts with alkynes to give Dewar-benzene derivatives, while its treatment with *p*-quinones opens up an elegant route for the synthesis of cubane (Pettit, 1966):



15.4.3 C₅H₅⁻ as a Ligand

HISTORICAL BACKGROUND

1901 Thiele: Synthesis of KC₅H₅ from potassium and C₅H₆ in benzene.

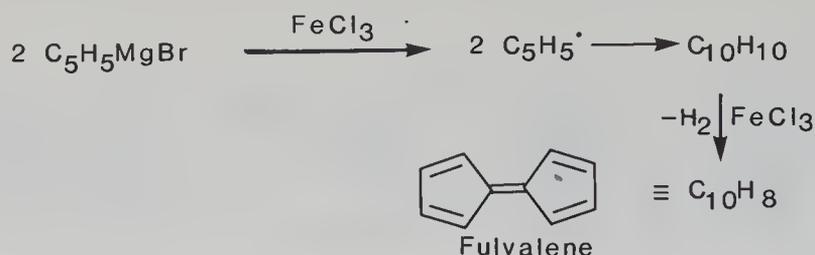
1951 Miller, Tebboth, Tremaine: Formation of Fe(C₅H₅)₂ in the reaction of C₅H₆ vapor with freshly reduced iron at 300 °C.



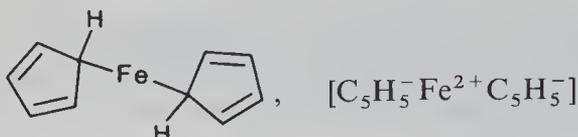
1951 Kealy, Pauson:



Their actual goal was the synthesis of fulvalene:



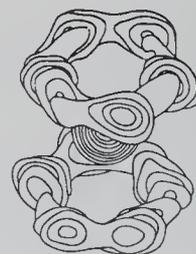
Structures which were originally proposed:



1952 E. O. Fischer: “Double-cone structure”

based on:

- X-ray structural analysis (compare the electron density contour lines)
- diamagnetism
- chemical behavior



1952 G. Wilkinson, R. B. Woodward: “Sandwich structure”

based on:

- IR spectroscopy
- diamagnetism
- dipole moment = 0



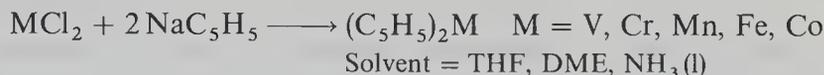
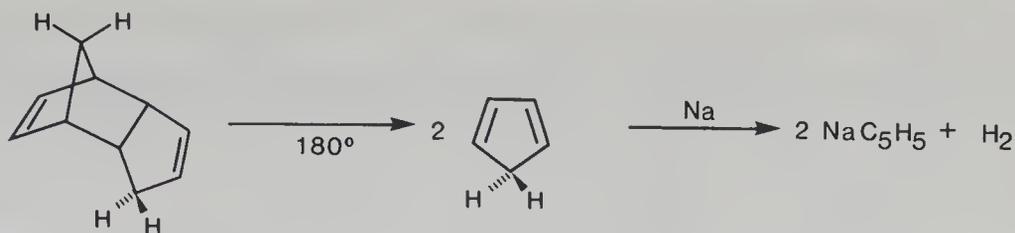
Woodward: The cyclopentadienyl rings of $\text{Fe}(\text{C}_5\text{H}_5)_2$ are amenable to electrophilic substitutions. This similarity to the aromatic behavior of benzene led to the trivial name **ferrocene**, later being extended to the designation **metallocenes** for compounds $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2$ in general.

15.4.3.1 Binary Cyclopentadienyl Transition-Metal Complexes

PREPARATION

1. Metal Salt + Cyclopentadienyl Reagent

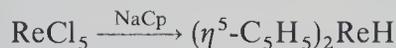
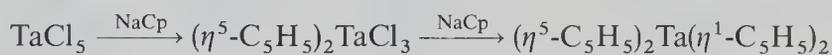
Dicyclopentadiene has first to be “cracked” in a retro-Diels-Alder reaction to give monomeric C_5H_6 . Cyclopentadiene is a weak acid, $\text{p}K_a \approx 15$; it can be deprotonated by strong bases or by alkali metals. Cyclopentadienylsodium (NaCp) is the most common reagent for the introduction of cyclopentadienyl ligands.



Apart from being a ligand source, NaC₅H₅ can also act as a reducing agent:



In many cases, treatment of NaC₅H₅ with metal (4*d*, 5*d*) salts does not give MCp₂ complexes, but Cp-metal hydrides or complexes containing σ-bonded cyclopentadienyl rings:

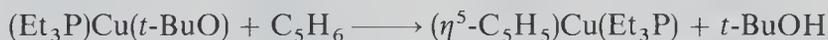


2. Metal + Cyclopentadiene



The less electropositive metals react only at elevated temperatures or as metal atoms in the cocondensation method (cf. p. 255).

3. Metal Salt + Cyclopentadiene



In this process, an auxiliary base is required if the basicity of the salt anion is insufficient to deprotonate cyclopentadiene:



In other cases, a reducing agent is needed:

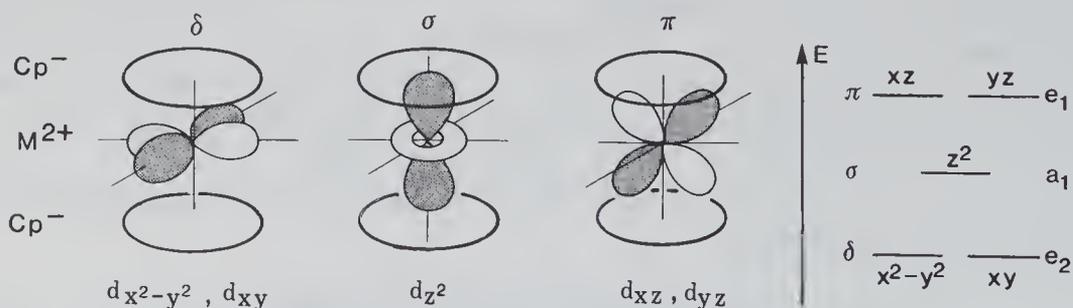


ELECTRONIC STRUCTURE AND BONDING IN THE COMPLEXES $(C_5H_5)_nM$

The properties and bonding types of (cyclopentadienyl)metal compounds can vary over a wide range. In the following table, main-group compounds are also included.

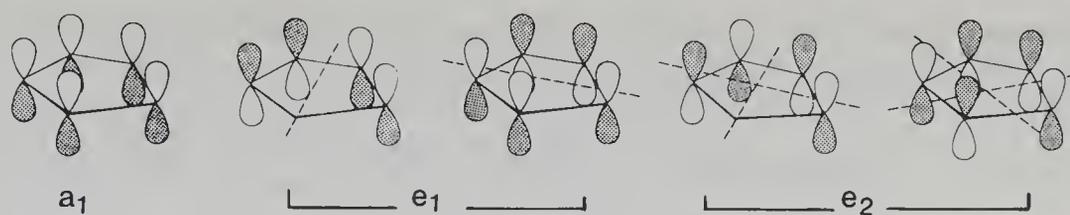
Character	Bonding	Properties	Examples
Ionic	Ionic lattice $M^{n+}[C_5H_5^-]_n$ similar to the halides MX_n	Highly reactive towards air, water and other com- pounds with active hy- drogen, not sublimable	$n = 1$: alkali metals $n = 2$: heavy alkaline earth metals $n = 2, 3$: lanthanoids
Intermediate		Partially sensitive to hydrolysis (exception: TlCp), sublimable	$n = 1$: In, Tl $n = 2$: Be, Mg, Sn, Pb, Mn, Zn, Cd, Hg
Covalent	molecular lattice π -MO(C_5H_5) \downarrow M (s, p, d) and π^* -MO(C_5H_5) \uparrow M (d)	Only partially air-sensi- tive, in general stable to hydrolysis, sublimable	$n = 2$: (Ti), V, Cr, (Re), Fe, Co, Ni, Ru, Os, (Rh), (Ir) $n = 3$: Ti $n = 4$: Ti, Zr, Nb, Ta, Mo, U, Th

The sequence of the chemically relevant **frontier orbitals** which follows from MO-calculations on metallocenes with axial symmetry is already apparent from a simple electrostatic model. This is based on the presence of a crystal field, generated by two negatively charged rings, which splits the energy levels of the metal d orbitals as a result of disparate electrostatic "repulsions" between the metal d electrons and the charge loops, intended to represent the ligands.

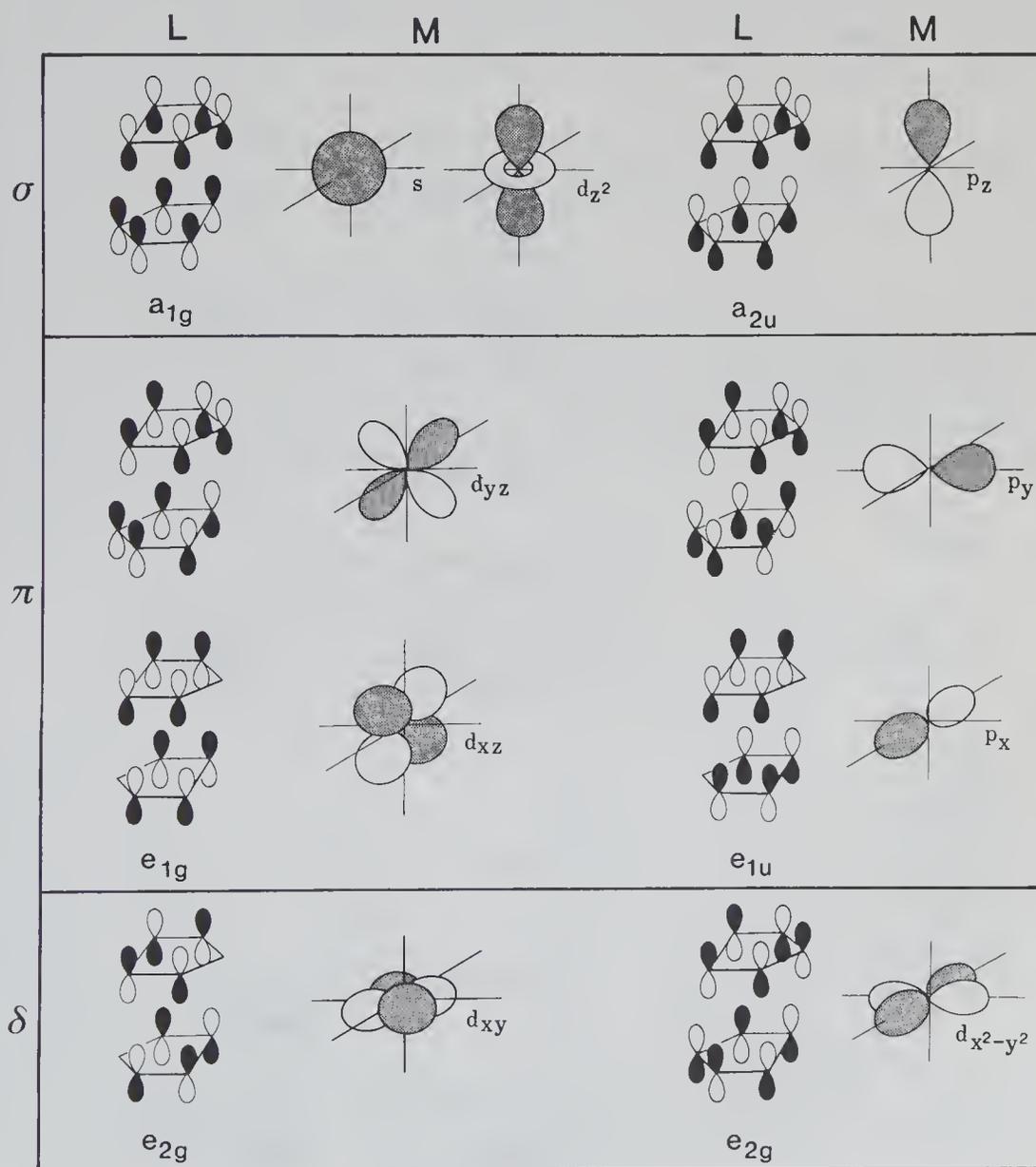


For ferrocene (Fe^{II} , d^6), the (correct) electronic configuration $\dots(e_2)^4(a_1)^2(e_1)^0$ in the frontier region is thus obtained. This crystal-field picture does not, however, do justice to the nature of chemical bonding in metallocenes which, in the case of transition metals, is essentially covalent.

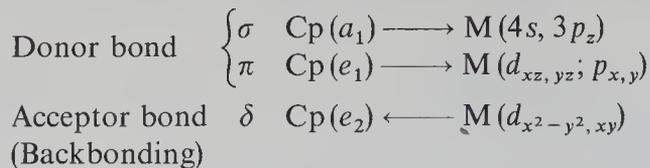
The MO treatment of the cyclopentadienyl-transition-metal bond is based on the principle outlined for olefin complexes (Chapter 15.1). The π MO's of C_5H_5 may be classified in order of increasing energy as follows:



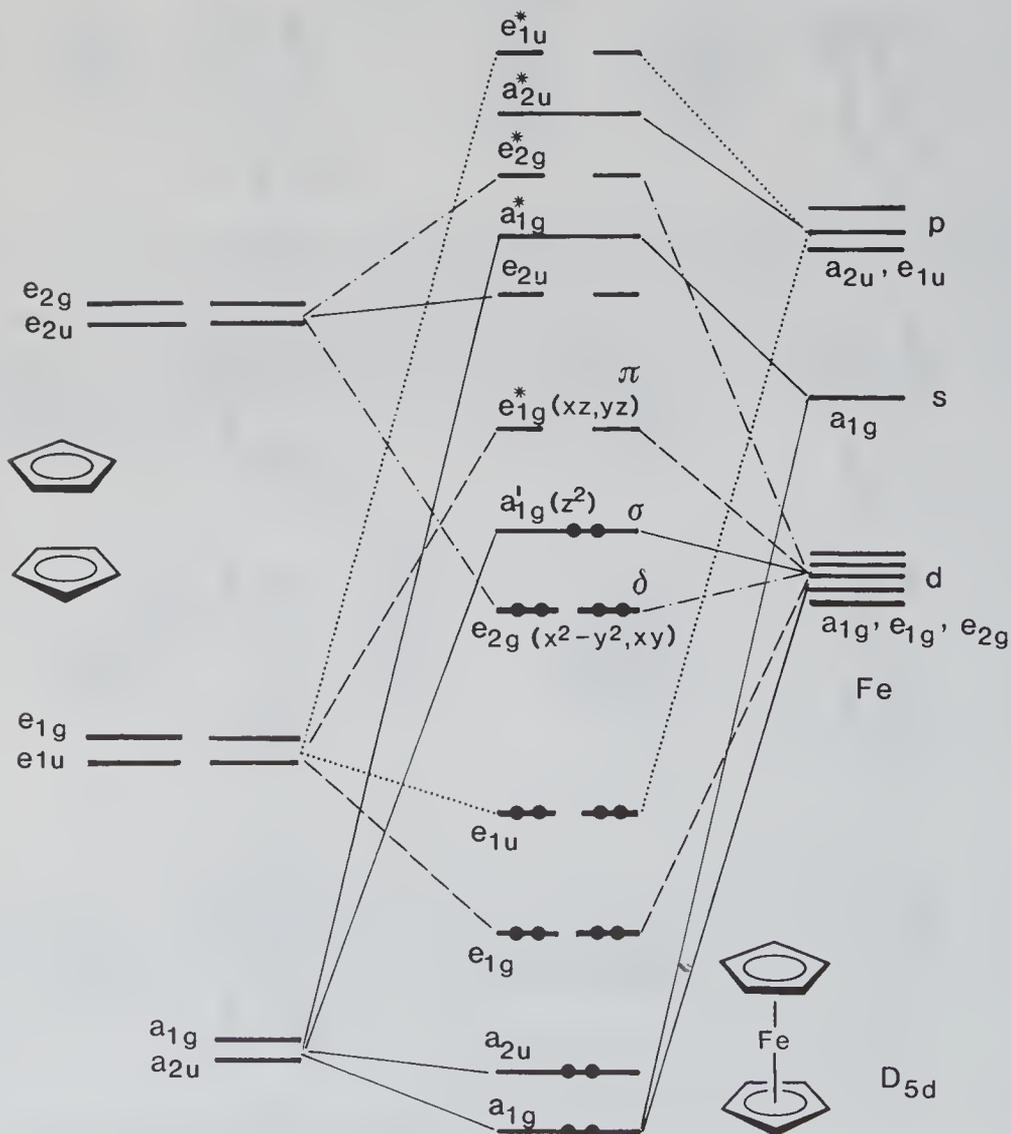
These ligand π orbitals are united pairwise, using plus and minus signs, to form symmetry-adapted linear combinations (SALC) which then overlap with metal orbitals of appropriate symmetry. For a metallocene in its staggered conformation (D_{5d}) the following interactions result:



If the metallocenes Cp_2M are visualized as being comprised of the components M^{2+} and 2Cp^- , the concept of synergism (p. 185) may be applied:



A generally accepted qualitative MO diagram for ferrocene in its staggered conformation (D_{5d}) has the following appearance (intra-ligand σ orbitals are not included):



Analogous metal-ligand interactions, albeit of different group-theoretical designation, pertain to eclipsed ferrocene (D_{5h}) or to any other rotamer (D₅), the bond energy being nearly invariant to rotation. The preference for one or the other conformation in specific cases is governed by packing forces or by repulsive effects of peripheral substituents. A theoretical interpretation for the preference “eclipsed” over “staggered” is given by Murrell (1980).

Details in the MO diagram such as the energetic separation or even the sequence of the molecular orbitals can vary depending on the quantum-chemical method used. Furthermore, upon ionization, the sequence of certain MO's may invert, which means that the MO scheme should not be regarded as “frozen”, but subject to modification with changing complex charge. Koopmans' theorem (Ionization energy = - orbital energy) therefore occasionally fails in organometallic chemistry, the most prominent example being the apparent inconsistency in the electron configurations of Cp₂Fe and Cp₂Fe⁺ (Veillard, 1972). This “failure” is, of course, a result of the oversimplification inherent in equating electron configurations with electronic states whereby electron correlation effects are neglected.

In the chemically relevant frontier-orbital region, the order $e_2 < a_1 < e_1$, already deduced from the crystal-field model, reappears. Judging from their energy relative to the basis orbitals, the frontier orbitals must be regarded as bonding (e_2), nonbonding (a_1) and antibonding (e_1^*).

For some metallocenes, electron configurations can be inferred from the general MO scheme (p. 320) which correctly predicts magnetic properties. In other cases, an *a priori* decision between a high-spin or low-spin form cannot be made (example: Cp₂V), and a more refined approach is called for. Thus, the magnetic moment of the Cp₂Fe⁺ cation, which considerably exceeds the ‘spin-only’ value, is not directly deduced from a rigid MO scheme, which would suggest a ground state ²A_{1g} at variance with the experimentally found ground state ²E_{1g}.

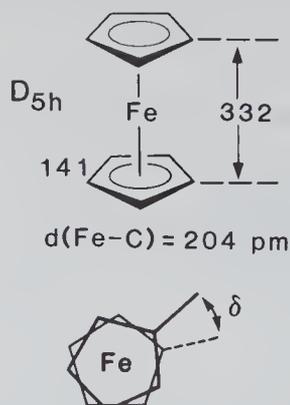
Electron Configurations and Magnetism of Metallocenes

	Electron configuration $\left\{ \begin{array}{l} (a_{1g})^2 (a_{2u})^2 \\ (e_{1g})^4 (e_{1u})^4 \end{array} \right\}$ +	Number of unpaired electrons n	Spin only value $\sqrt{n(n+2)}$	Magnetic moment (in Bohr magnetons)	
				expected	found
Cp ₂ Ti ⁺	$(e_{2g})^1$	1	1.73	>1.73	2.29 ± 0.05
Cp ₂ V ²⁺	$(e_{2g})^1$	1	1.73	>1.73	1.90 ± 0.05
Cp ₂ V ⁺	$(e_{2g})^2$	2	2.83	2.83	2.86 ± 0.06
Cp ₂ V	$(e_{2g})^2 (a'_{1g})^1$	3	3.87	3.87	3.84 ± 0.04
Cp ₂ Cr ⁺	$(e_{2g})^2 (a'_{1g})^1$	3	3.87	3.87	3.73 ± 0.08
Cp ₂ Cr	$(e_{2g})^3 (a'_{1g})^1$	2	2.83	>2.83	3.20 ± 0.16
Cp ₂ Fe ⁺	$(e_{2g})^3 (a'_{1g})^2$	1	1.73	>1.73	2.34 ± 0.12
Cp ₂ Fe	$(e_{2g})^4 (a'_{1g})^2$	0	0	0	0
Cp ₂ Mn	$(e_{2g})^2 (a'_{1g})^1 (e_{1g}^*)^2$	5	5.92	5.92	5.81
Cp ₂ Co ⁺	$(e_{2g})^4 (a'_{1g})^2$	0	0	0	0
Cp ₂ Co	$(e_{2g})^4 (a'_{1g})^2 (e_{1g}^*)^1$	1	1.73	>1.73	1.76 ± 0.07
Cp ₂ Ni ⁺	$(e_{2g})^4 (a'_{1g})^2 (e_{1g}^*)^1$	1	1.73	>1.73	1.82 ± 0.09
Cp ₂ Ni	$(e_{2g})^4 (a'_{1g})^2 (e_{1g}^*)^2$	2	2.83	2.83	2.86 ± 0.11

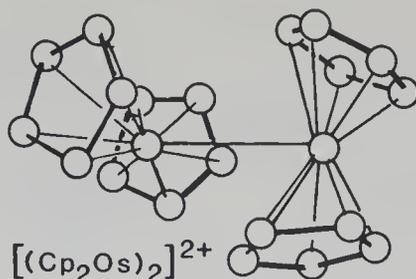
Some Further Properties of Metallocenes

Complex	Color	Melting point °C	Miscellaneous
"(C ₅ H ₅) ₂ Ti"	green	200 (decomp.)	Dimeric with two μ -H bridges and a fulvalene bridging ligand
(C ₅ H ₅) ₂ V	purple	167	very air-sensitive
"(C ₅ H ₅) ₂ Nb"	yellow		Dimeric with $\eta^1:\eta^5$ -C ₅ H ₄ bridges and terminal hydride ligands
(C ₅ H ₅) ₂ Cr	scarlet	173	very air-sensitive
"(C ₅ H ₅) ₂ Mo"	black		several dinuclear isomers with
"(C ₅ H ₅) ₂ W"	yellow green		fulvalene or $\eta^1 - \eta^5$ bridges and terminal hydride ligands, diamagnetic
(C ₅ H ₅) ₂ Mn	brown	173	air-sensitive and readily hydrolyzed; at 158 °C converted into a pink form
(C ₅ H ₅) ₂ Fe	orange	173	air-stable, can be oxidized to blue-green (C ₅ H ₅) ₂ Fe ⁺
(C ₅ H ₅) ₂ Co	purple-black	174	air-sensitive, oxidation gives the air-stable, yellow cation (C ₅ H ₅) ₂ Co ⁺
(C ₅ H ₅) ₂ Ni	green	173	slow oxidation by air to the labile, orange cation (C ₅ H ₅) ₂ Ni ⁺

SPECIAL STRUCTURAL FEATURES

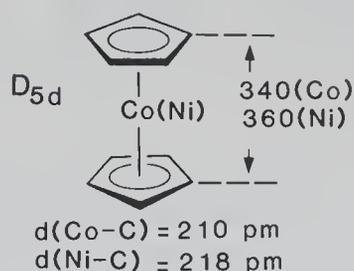


Ferrocene at room temperature crystallizes in a monoclinic, at $T < 164 \text{ K}$ in a triclinic, and at $T < 110 \text{ K}$ in an orthorhombic modification. In the monoclinic form, disorder phenomena feign a staggered conformation (D_{5d}) of individual sandwich molecules. In the triclinic form, the molecules deviate from the eclipsed conformation (D_{5d}) by $\delta = 9^\circ$, while in the orthorhombic form, the rings are fully eclipsed (D_{5h}) (Dunitz, 1982). In the gas phase, ferrocene also adopts an eclipsed conformation, the rotational barrier being small ($\approx 4 \text{ kJ/mol}$, Haaland, 1968). Decamethylferrocene (Cp^*)₂Fe, however, has been shown to exist in a staggered conformation (D_{5d}) in both the solid state (Raymond, 1979) as well as in the gas phase (Haaland, 1979).

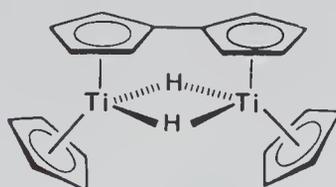


The neutral complexes *ruthenocene* and *osmocene* in the solid state exhibit the eclipsed conformation of orthorhombic ferrocene, with $d(Ru-C) = 221$ pm, $d(Os-C) = 222$ pm. The *osmocinium cation* $[Cp_2Os]^+$ forms a dimer with a long metal-metal bond, $d(Os-Os) = 304$ pm (Taube, 1987).

The permethylated cation $[Cp_2^*Os]^+$, however, possesses a monomeric sandwich structure, the ligands assuming a staggered conformation (D_{5d}) (J. S. Miller, 1988).

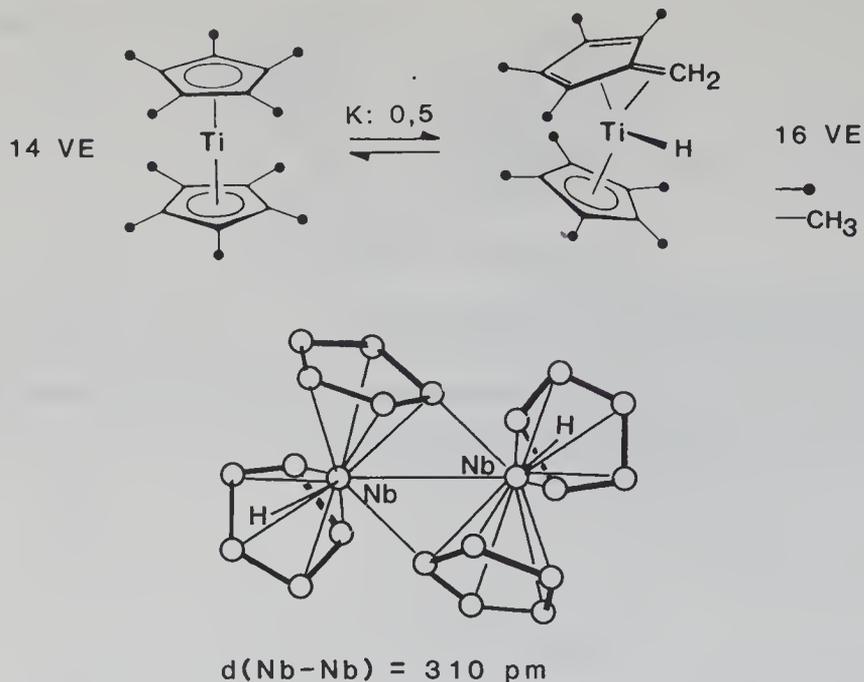


Structure of *cobaltocene* and *nickelocene*: The five-membered rings are reported to be staggered (E. Weiss, 1975). A comparison of $M-C$ distances in various metallocenes shows a distinct minimum for ferrocene, in accordance with the occupation of all bonding orbitals in this molecule. Placing one or two electrons, respectively, into the antibonding orbitals of $CoCp_2$ and $NiCp_2$ weakens the metal-ring bond, thereby increasing $d(M-C)$.



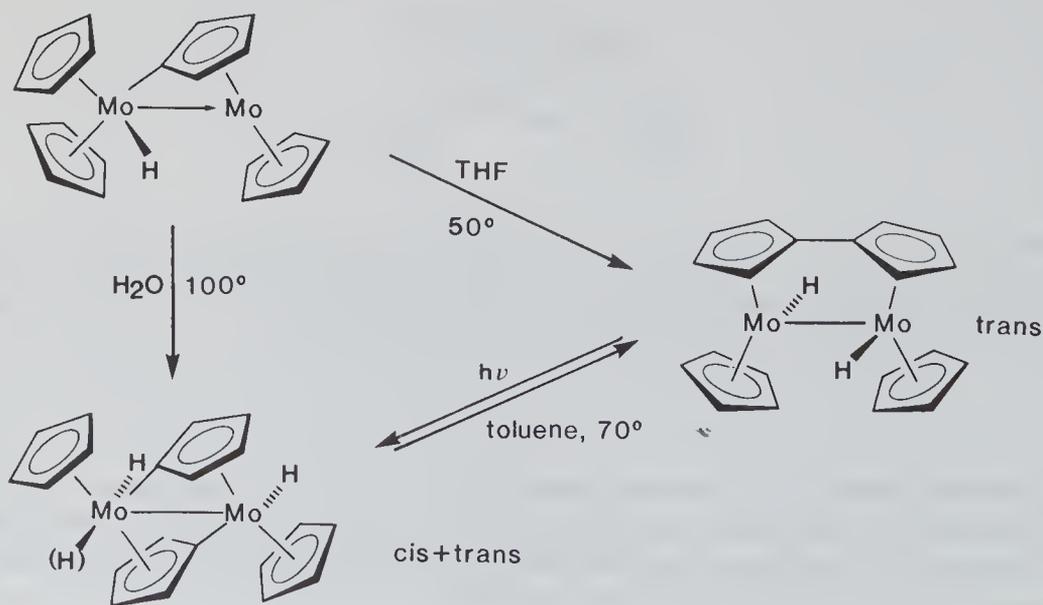
“*Titanocene*”. At least two isomers exist, possibly more, depending on the method used for their synthesis. Reduction of Cp_2TiCl_2 or treatment of $TiCl_2$ with $NaCp$ leads to the formation of a dimer with a fulvalene bridge and two hydride bridges. Under the assumption of $2e\ 3c\ M-H-M$ bridges and a $Ti-Ti$ bond, both titanium atoms acquire a 16 VE configuration.

Decamethyltitanocene at room temperature exists as an equilibrium mixture of two isomers: a yellow paramagnetic 14 VE complex and a green diamagnetic 16 VE compound formed by insertion of titanium into the $C-H$ bond of a methyl group of the pentamethylcyclopentadienyl ligand (Bercaw, 1978):

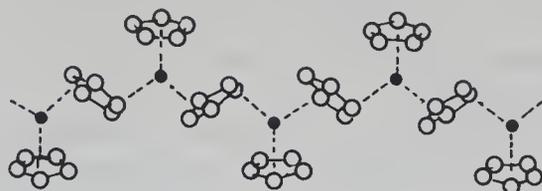


A complex of the stoichiometric composition " $(\text{C}_5\text{H}_5)_2\text{Nb}$ " also represents a dimeric species $[\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{NbH}]_2$. It contains two $\eta^1:\eta^5$ -cyclopentadienyl bridges and two terminal hydride ligands. This complex, in contrast to fictitious "niobocene", has an 18 VE shell.

Monomeric metallocenes which would be analogous to chromocene are unknown for molybdenum and tungsten. So far, four dimeric isomers of composition $[\text{C}_{10}\text{H}_{10}\text{M}]_2$ ($\text{M} = \text{Mo}, \text{W}$) have been characterized, some of which appear to be interconvertible. Like the titanium and niobium dimers, they possess $\eta^1:\eta^5$ -cyclopentadienyl bridges or $\eta^5:\eta^5$ -fulvalene bridges as well as terminal hydride ligands (M. L. H. Green, 1982):



Manganocene Cp₂Mn in the solid state has a chain structure without individual sandwich entities (E. Weiss, 1978):



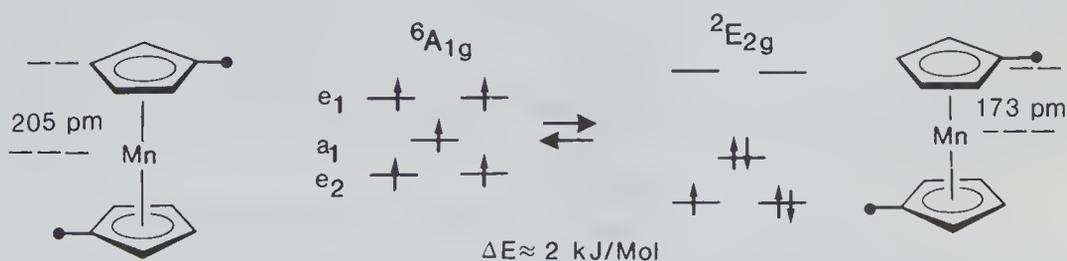
$$d(\text{Mn}-\text{C})_{\text{terminal}} = 242 \text{ pm}$$

$$d(\text{Mn}-\text{C})_{\text{bridge}} = 240-330 \text{ pm}$$

The magnetic moment of (C₅H₅)₂Mn shows an unusual temperature dependence: as a solid at $T > 432 \text{ K}$, in the melt and in solutions at room-temperature, the complex has a magnetic moment of $\mu = 5.9 \text{ B.M.}$ as expected from an electron configuration $(e_{2g})^2(a'_{1g})^1(e^*_{1g})^2$ [ground state ${}^6A_{1g}$]. Between 432 and 67 K, with decreasing temperature increasing antiferromagnetic behavior is observed, corresponding to an increase of cooperative interactions. A dilute solid solution of (C₅H₅)₂Mn (8%) in (C₅H₅)₂Mg has a magnetic moment of $\mu = 5.94 \text{ B.M.}$ over the whole temperature range (Wilkinson, 1956).

Decamethylmanganocene Cp*₂Mn displays a “normal” sandwich structure (Raymond, 1979), and the magnetic moment $\mu = 2.18 \text{ B.M.}$ points to a low-spin Mn(d^5) configuration [ground state ${}^2E_{2g}$]. 1,1'-Dimethylmanganocene, on the other hand, in the gas phase consists of an equilibrium mixture of high-spin (${}^6A_{1g}$) and low-spin (${}^2E_{2g}$) states according to He-photoelectron spectroscopic evidence.

Other derivatives of manganocene also show a puzzling dependence of the magnetic behavior on the molecular environment. Today, it is known that the free molecules (C₅H₅)₂Mn and (CH₃C₅H₄)₂Mn are so close to the **high-spin/low-spin cross-over point**, that the small intermolecular forces existing in frozen solutions or in molecular crystals are sufficient to incite the observed changes of the electronic ground-state (Ammeter, 1974). As expected from ligand-field theory, environments which tolerate a large Mn–Cp distance favor the high-spin state (${}^6A_{1g}$), while matrices enforcing a small Mn–Cp distance promote a low-spin state (${}^2E_{2g}$). The energy difference is only 2 kJ/mol. (In this context, compare the pressure dependence of the electronic spectra of metal complexes.)

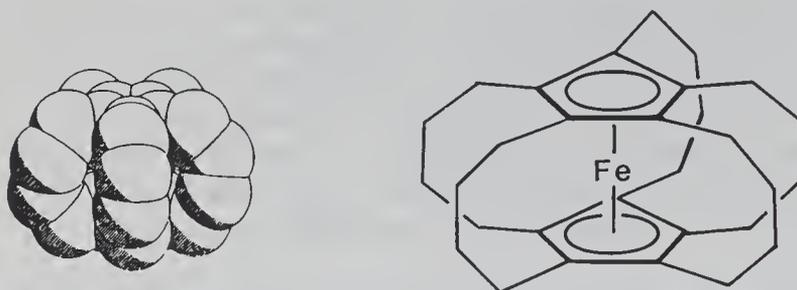


Rhenocene Cp₂Re, isoelectronic with the osmocinium cation, is thought to have a dimeric structure with a metal–metal bond (Pasman, 1984).

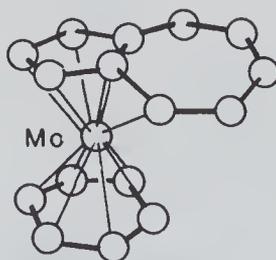
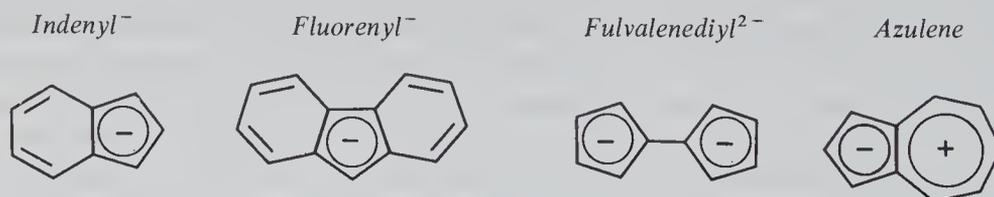
Decamethylrhencene Cp_2^*Re , however, like decamethylmanganocene is monomeric. The magnetic behaviour of decamethylrhencene is as complicated as that of manganocene. The application of an arsenal of spectroscopic and magnetochemical methods has led to the conclusion that Cp_2^*Re , depending on the state of aggregation and the medium, exists as an equilibrium of ${}^2\text{A}_{1g}$ and ${}^2\text{E}_{5/2}$ species (Cloke, 1988).

These examples show that **ring methylation** can have a considerable influence on the structure and properties of metallocenes (cf. p. 47).

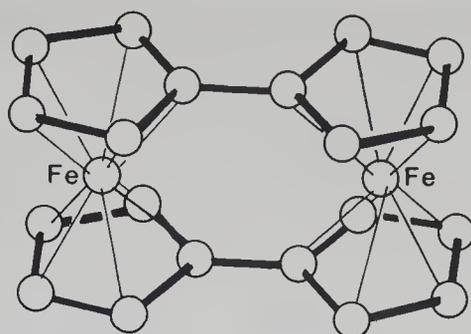
A special type of alkylmetallocene is the recently prepared superferrocenophane (Hisatome, 1986). In this sandwich complex, the shielding of the central atom from its environment is perfect:



Several ring-anellated derivatives of the cyclopentadienyl anion can also form metal π -complexes.

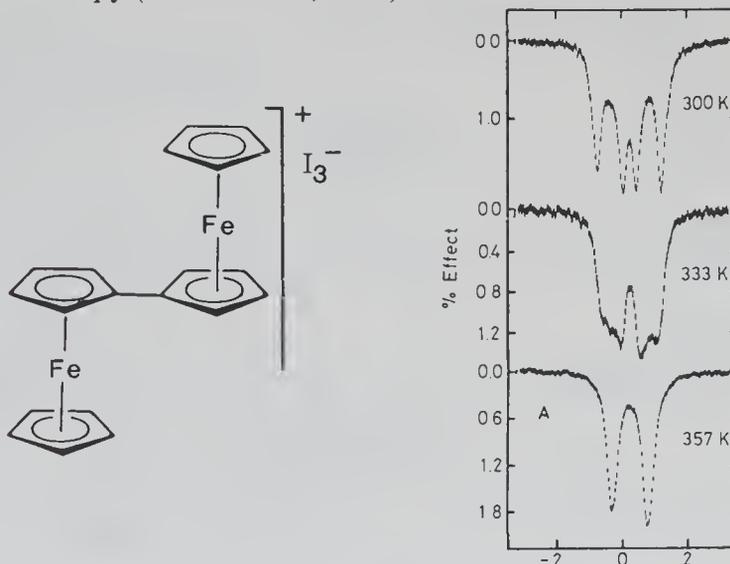


Azulene prefers η^5 -coordination via the 5-membered ring. An interesting variant is revealed in the structure of *azulene(benzene)Mo*: the azulene ring coordinates in an η^6 -fashion via a fulvene-like unit (Behrens, 1987). The deviation from ligand planarity is reminiscent of the structure of ferrocenyl carbenium ions (p. 329).



Bis- μ (fulvalenediyl)diiron (Biferrocenylene) interestingly forms a dication (Fe^{3+} , Fe^{3+}) which is diamagnetic. It has been suggested that despite the large Fe–Fe distance of 398 pm, direct exchange interaction (p. 388) between the two central metal ions M (d^5) accounts for spin pairing here (Hendrickson, 1975).

Intersandwich compounds with fulvalenediyl bridges have been extensively studied as model compounds in the context of intramolecular electron transfer and the mixed-valence phenomenon. The following example also illustrates an application of ^{57}Fe -Mössbauer spectroscopy (Hendrickson, 1985):



The observation of *two* doublets at room temperature points to the presence of both Fe^{2+} and Fe^{3+} ; it demonstrates that intramolecular electron transfer is slow on the time scale ($\approx 10^{-8}$ s) of the Mössbauer experiment, *mixed valence* case.

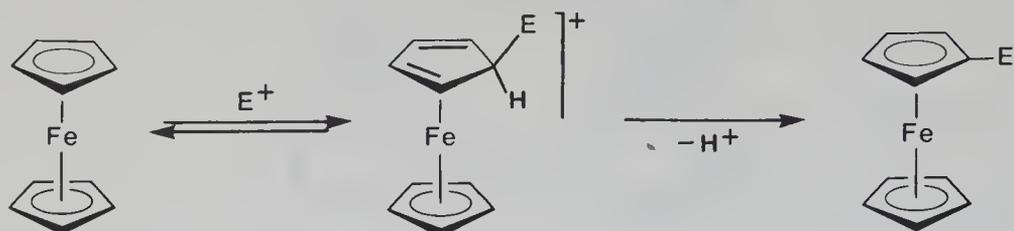
The merging into *one* doublet at temperatures > 350 K indicates but one type of iron to which an oxidation state of $Fe^{2.5+}$ must be assigned; electron transfer is fast at this temperature, *intermediate valence* case.

SELECTED REACTIONS OF METALLOCENES

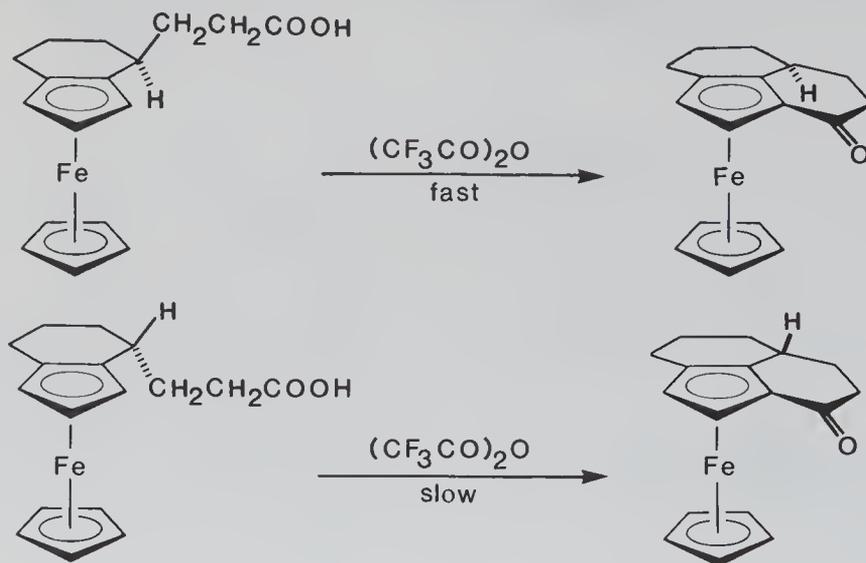
The cyclopentadienyl ring in ferrocene carries a partial negative charge. This is reflected in the following properties:

$C_5H_5FeC_5H_4NH_2$	is a stronger base than aniline	} The ferrocenyl group therefore acts as an electron donor
$C_5H_5FeC_5H_4COOH$	is a weaker acid than benzoic acid	

Ferrocene, ruthenocene and osmocene are susceptible to **electrophilic substitution**. Compared to benzene, ferrocene reacts 3×10^6 times faster.

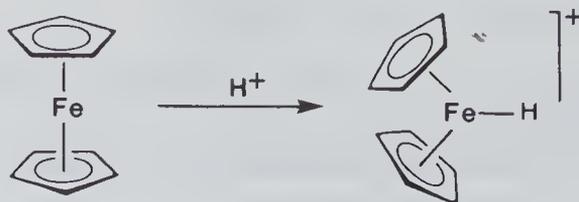


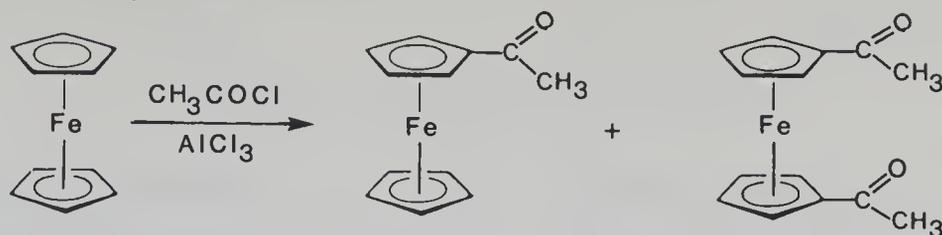
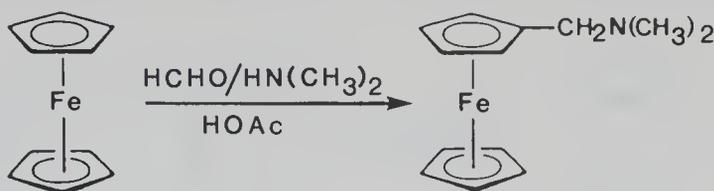
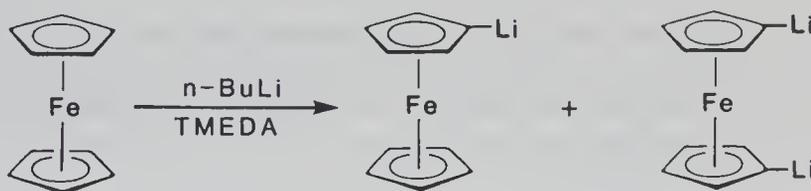
The electrophile should not be an oxidizing agent, as substitution would then be suppressed by oxidation to the ferricinium ion $[\text{FeCp}_2]^+$ which is inert to attack by electrophiles. That electrophilic substitution of ferrocene does not involve direct participation of the metal has been established by the intramolecular acylation of two isomeric ferrocene carboxylic acids. It was found that the *exo*-isomer, in which the acylium ion cannot directly interact with the metal, cyclizes faster than the *endo*-isomer (Rosenblum, 1966):



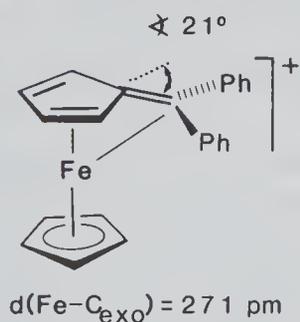
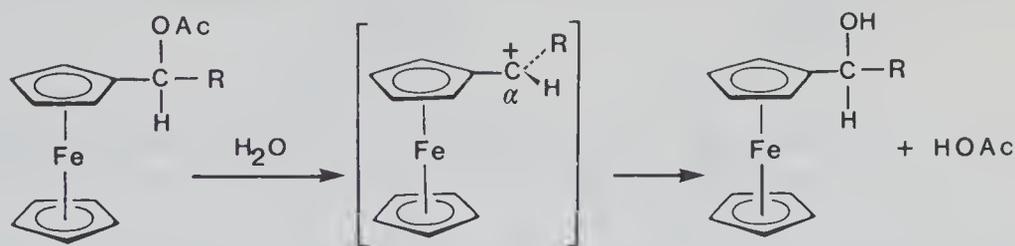
This result suggests that electrophilic attack occurs from the *exo*-direction.

Using strong acids, ferrocene can, however, be protonated at the metal; the cation $[(\text{C}_5\text{H}_5)_2\text{FeH}]^+$ is detectable by $^1\text{H-NMR}$ spectroscopy, ($\delta = -2.1$ ppm):



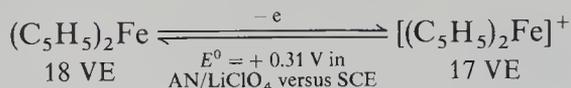
Friedel-Crafts acylation:**Mannich reaction (Aminomethylation):****Metallation:**

Ferrocene exhibits an extensive organic chemistry. α -Ferrocenyl carbenium ions are particularly stable and even isolable as salts with BF₄⁻, PF₆⁻ as counterions (Watts, 1979 R):

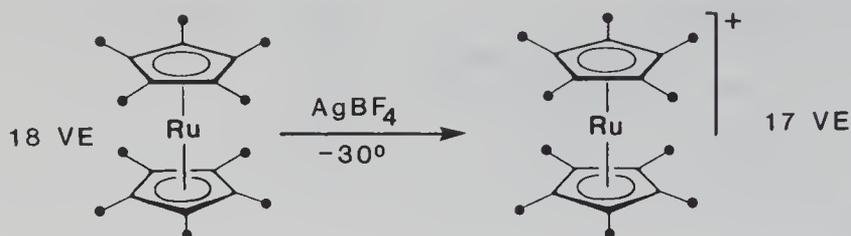


These species may also be regarded as *pentafulvene complexes*. X-ray structural data reveal that the α -carbon atom is involved in bonding to the metal, since the iron atom is displaced from its position below the center of the substituted ring towards the substituent (Behrens, 1979). As to the nature of the Fe-C _{α} bond, compare p. 301.

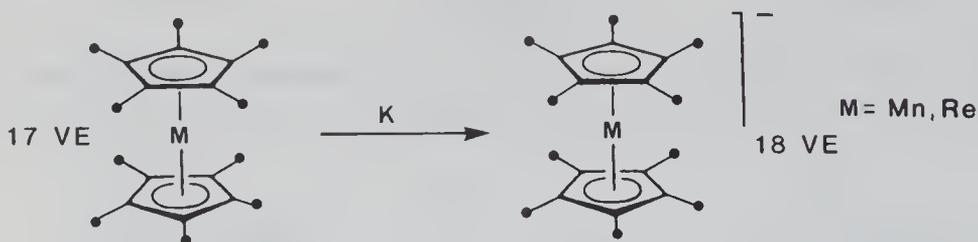
Ferrocene can be oxidized both electrochemically and by many chemical oxidizing agents, *e.g.* HNO_3 :



Ruthenocene and osmocene can also be oxidized, but the corresponding metallocinium ions are not stable as monomers. Dimerization occurs instead (see p. 323) or disproportionation to give MCp_2 and $[\text{MCp}_2]^{2+}$. In contrast, the permethylated complex $(\text{C}_5\text{Me}_5)_2\text{Ru}$ forms a cation $[(\text{C}_5\text{Me}_5)_2\text{Ru}]^+$, which is stable at -30°C (Kölle, 1983):

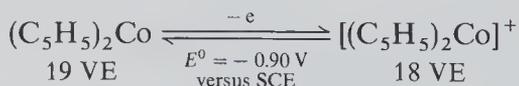


The influence methyl substitution exerts on the stability of metallocenes is also manifested in the properties of manganocenes and rhenocenes. While MnCp_2 cannot be reduced and monomeric ReCp_2 has only been detected in low-temperature matrices, both **decamethylmanganocene** and **decamethylrhenocene** form stable 18 VE anions (Smart, 1979; Cloke, 1985):

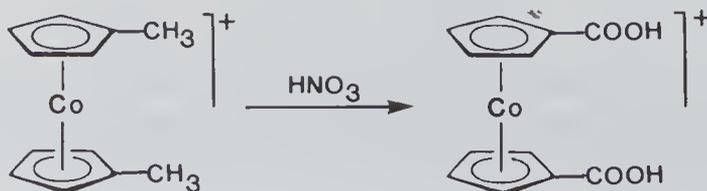


$[(\text{C}_5\text{Me}_5)_2\text{Ru}]^+$, $[(\text{C}_5\text{Me}_5)_2\text{Os}]^+$ and $(\text{C}_5\text{Me}_5)_2\text{Re}$ are therefore the only documented examples of metallocenes of the 4*d*- and 5*d* series that do not follow the 18 VE rule but can nevertheless be isolated in quantity.

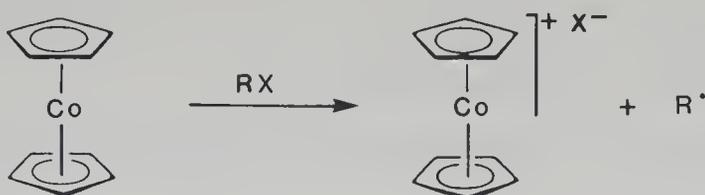
The chemistry of the metallocenes of cobalt and nickel and their homologues is influenced by their tendency to attain an 18 VE configuration:



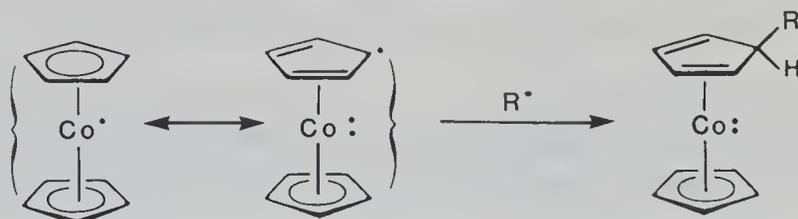
Cobalticinium salts are remarkably stable to further oxidation; with strong oxidizing agents, the dimethylcobalticinium cation gives the dicarboxylic acid without rupture of the $\text{Co}-\text{Cp}$ bonds:



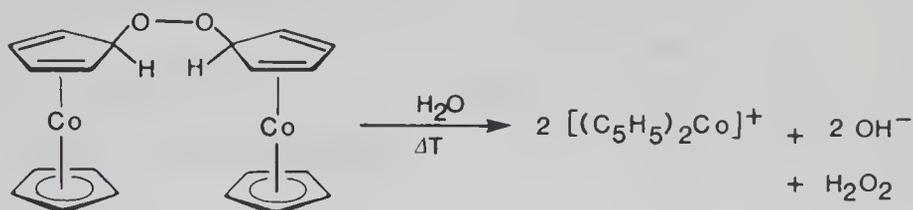
Towards alkyl halides, cobaltocene acts as a reducing agent:



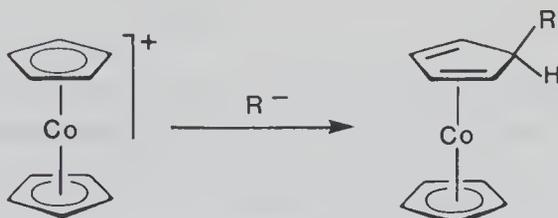
Organic radicals add to cobaltocene. The η^5 -cyclopentadienyl ligand is thereby converted to η^4 -cyclopentadiene with attendant change from a 19 VE- to an 18 VE configuration:



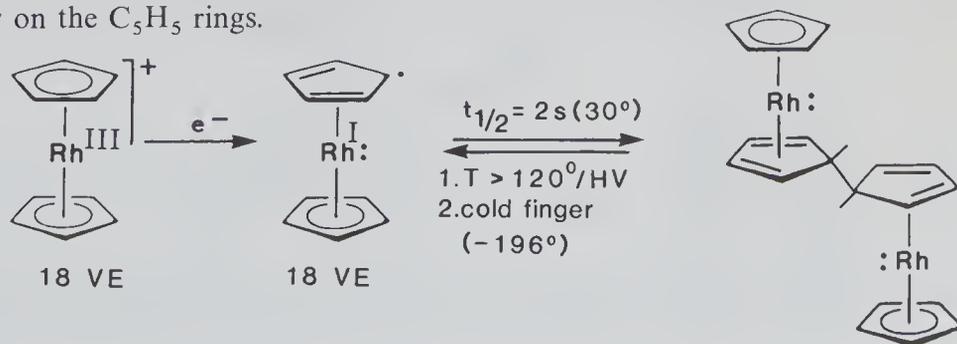
The biradical O₂ as well adds to cobaltocene; the resulting bis(cobaltocenyl)peroxide may only be isolated at low temperatures:



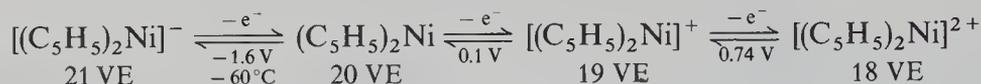
Nucleophilic addition to cobaltocenium ions occurs from an *exo*-direction:



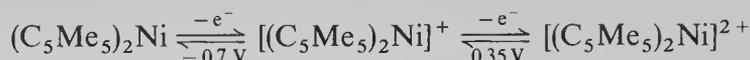
The 18 VE ions [RhCp₂]⁺ and [IrCp₂]⁺, like [CoCp₂]⁺, are very stable, as opposed to the neutral monomers RhCp₂ and IrCp₂ which as yet have only been observed in matrix isolation. At room temperature, they immediately dimerize. ESR measurements and EH-MO calculations suggest that the unpaired electron in these complexes is located mainly on the C₅H₅ rings.



Nickelocene is the only metallocene with 20 valence electrons. It is paramagnetic and easily oxidized to the nickelicinium ion (19 VE), which is of low stability. At low temperatures and in extremely pure solvents, further oxidation to a dication has been observed as well as reduction to a monoanion (Geiger, 1984 R):

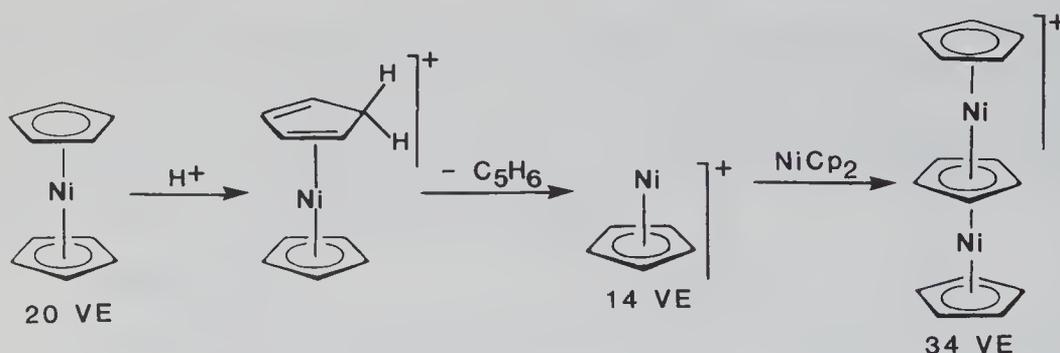


Decamethylnickelocene is also oxidizable in two steps:

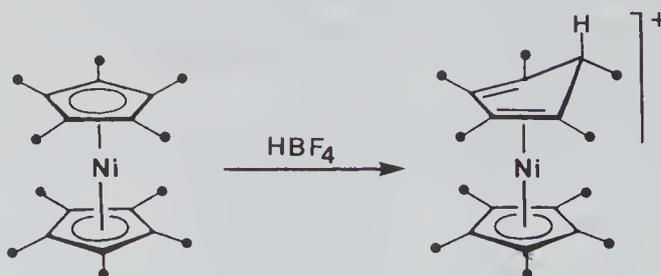


Both cations can be isolated as salts.

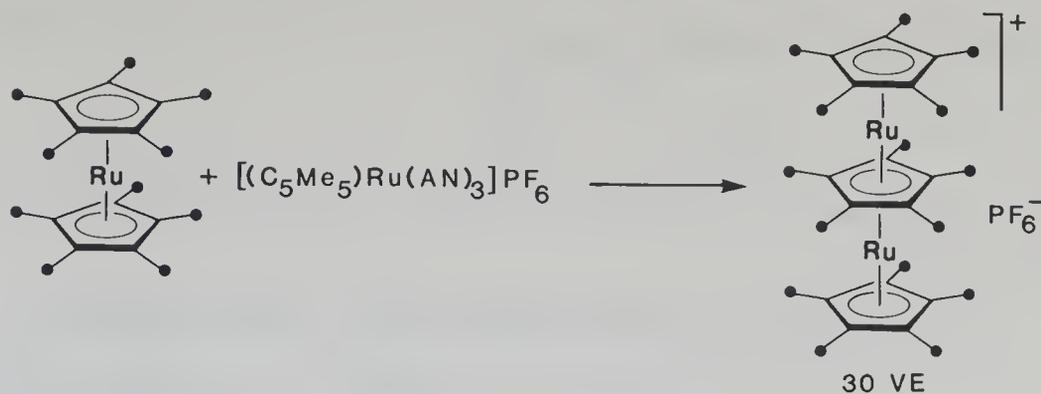
Quite unexpectedly, upon treating nickelocene with HBF_4 in propionic anhydride, the prototype of the **multidecker-sandwich complexes** is formed (Werner, 1972):



While numerous multidecker-sandwich complexes containing larger rings or heterocycles have been synthesized since, the cation $[(C_5H_5)_3Ni_2]^+$ (**tripledecker sandwich**) remains the only complex of its type which features unsubstituted cyclopentadienyl rings exclusively. Intermediates can only be detected under special conditions. On protonating **decamethylnickelocene**, the reaction stops at the first stage:



Tripledecker complexes with the ligand $C_5Me_5^-$ have recently been prepared with group 8 metals (Rybinskaya, 1987):

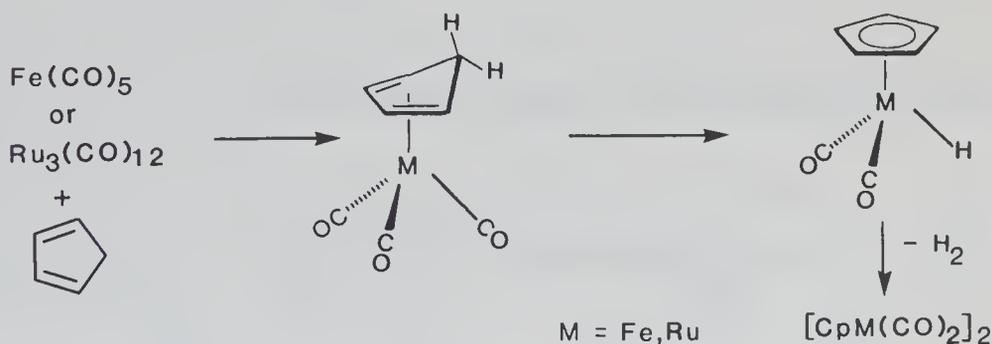


These two tripledecker complexes are representative for the two series containing **34** and **30 valence electrons**, which according to MO calculations should display exceptional stability (R. Hoffmann, 1976). Tripledecker species with 31–33 valence electrons have, however, also been prepared (p. 383), as have examples in which the number of valence electrons falls considerably short of the “magic number” of 30 (p. 357).

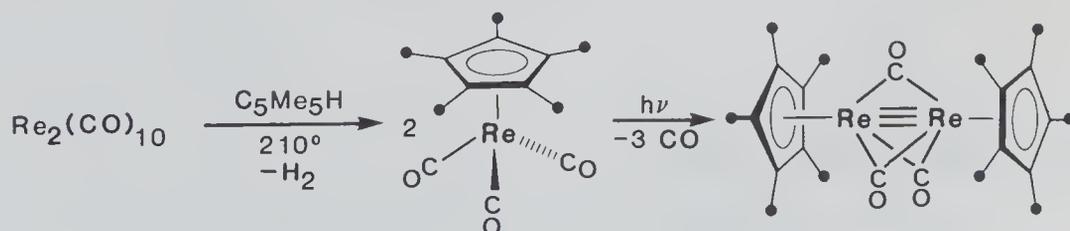
15.4.3.2 Cyclopentadienyl Metal Carbonyls

PREPARATION

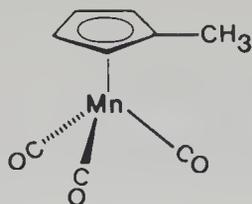
1. Metal Carbonyl + Cyclopentadiene



The cyclopentadiene- and cyclopentadienyl hydride complexes which appear as intermediates here can both be independently synthesized under mild conditions. They are sensitive to heat and sunlight, readily dimerizing under elimination of H_2 .

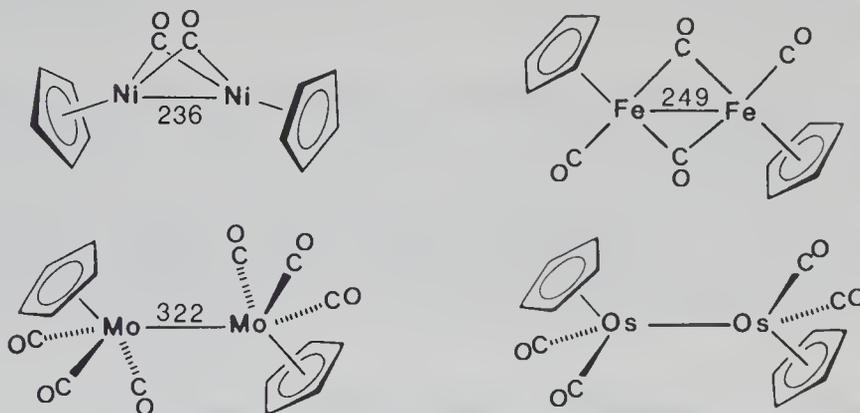


STRUCTURES



The monomeric complexes $CpM(CO)_n$ are called half-sandwich complexes.

The previously mentioned capability of the carbonyl group to act as a terminal or as a bridging ligand is also exhibited by the dinuclear (cyclopentadienyl)metal carbonyls:

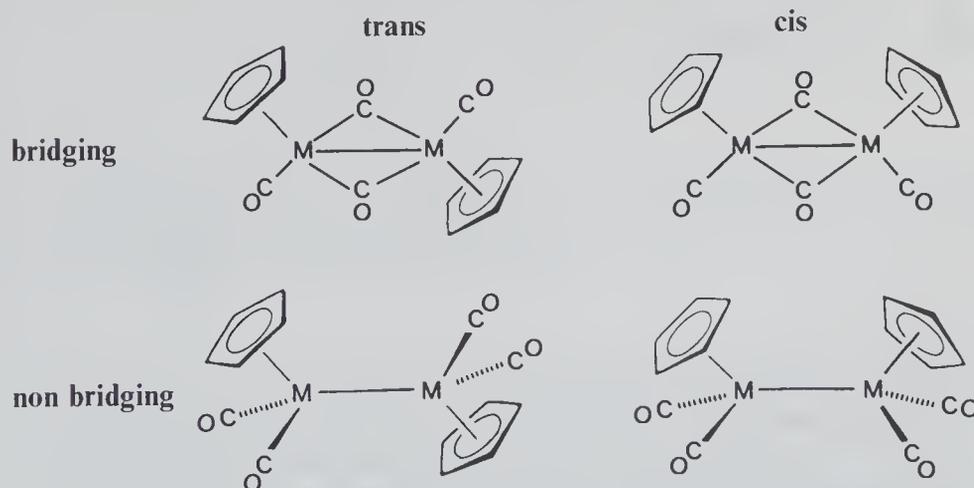


Note that carbonyl bridging is avoided by the heavier metals.

$[CpFe(CO)_2]_2$ is a **fluxional molecule**. In solution, the following processes occur:

- *cis/trans* isomerization
- “scrambling” (redistribution of terminal and bridging CO ligands).

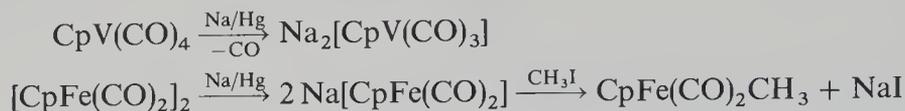
By IR and NMR spectroscopy, four different species can be detected:



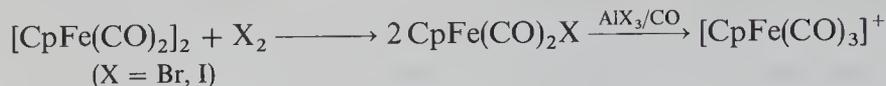
The structural dynamics have been unravelled by Cotton (1973).

REACTIONS OF CYCLOPENTADIENYL METAL CARBONYLS

(a) Reduction



(b) Reaction with Halogens

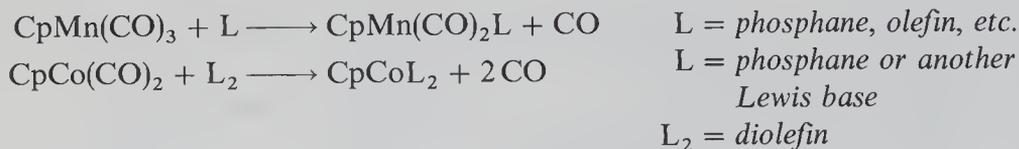


Under photochemical conditions, CCl_4 or PhCH_2Cl serve as the halide source.

(c) Ring Substitution

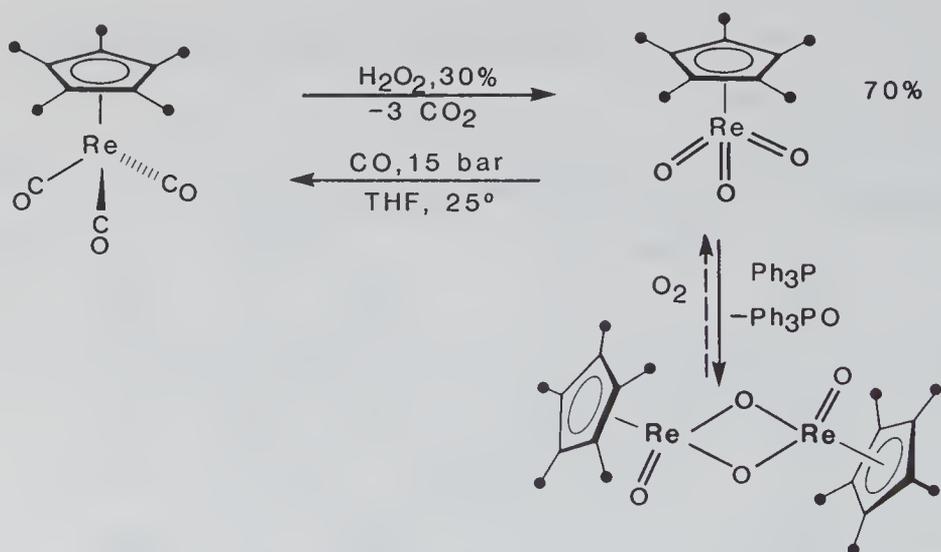
CpV(CO)_4 , CpMn(CO)_3 and CpRe(CO)_3 readily undergo electrophilic substitution, similar to ferrocene.

(d) Substitution of CO



Thermal as well as photochemical reaction conditions are suitable.

(e) Oxidative Decarbonylation



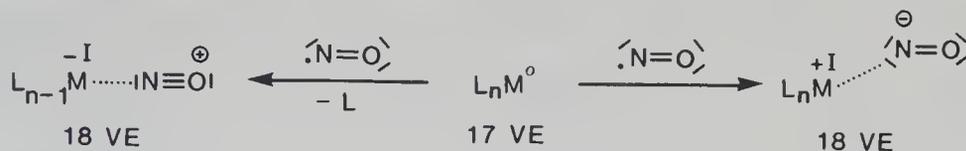
Apart from the vigorous conditions, a surprising aspect of this reaction is the fact that $(\eta^5\text{-C}_5\text{R}_5)\text{-M}$ bonding apparently is not restricted to metals in low oxidation states. The distance $d(\text{Re}-\text{O}) = 170 \text{ pm}$ points to a high degree of double bond character and shows that the oxo ligand acts as a strong π -donor. Partial deoxygenation leads to organometallic oxides with terminal as well as bridging oxygen atoms (Herrmann, 1987 R).

15.4.3.3 Cyclopentadienyl Metal Nitrosyls

Nitric oxide is a very versatile ligand; it can function in two ways:

as a coordinated NO⁺ ion
(isoelectronic with CO)

as a coordinated NO⁻ ion
(isoelectronic with O₂)

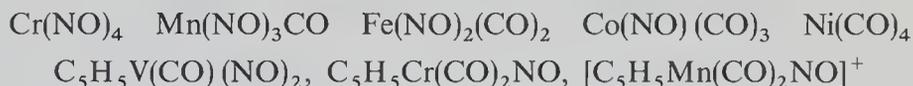


NO as 3e ligand
linear structure MNO

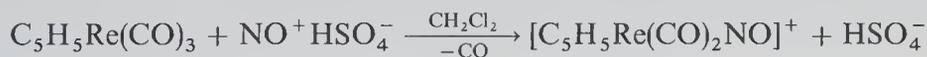
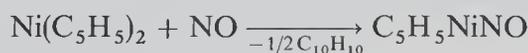
NO as 1e ligand
bent structure MNO

The conversion MNO(linear) to MNO(bent) is triggered by intramolecular transfer of two electrons from the metal to the ligand; during this process, a free coordination site is generated and associative mechanisms of substitution become possible (cf. p. 232).

In organometallic chemistry, NO is generally regarded as a 3e ligand; isoelectronic complexes are obtained by substituting three CO groups for two NO ligands, or by compensating the substitution of one CO for one NO by the introduction of a positive charge. Examples:



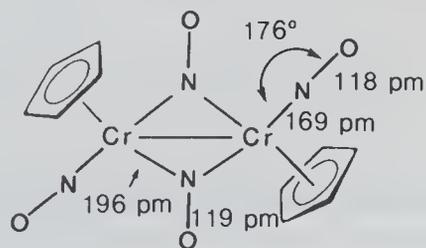
PREPARATION

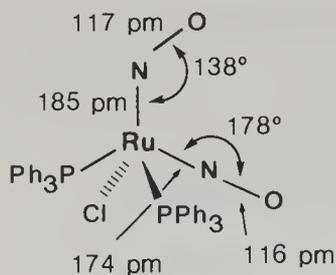


STRUCTURE AND PROPERTIES

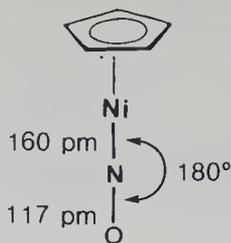
Like CO, NO can serve as a terminal as well as a bridging ligand; an additional variable is the MNO angle of terminal nitrosyls. In certain cases both linear and bent NO configurations coexist in the same molecule:

$\nu(\text{NO})$ [cm⁻¹]
 $\nu(\text{NO})_{\text{linear}} = 1677$
 $\nu(\text{NO})_{\text{bridge}} = 1518$
 (Fontana, 1974)

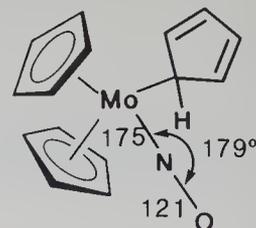




$$\begin{aligned} \nu(\text{NO})_{\text{linear}} &= 1845 \\ \nu(\text{NO})_{\text{bent}} &= 1687 \\ (\text{Eisenberg, 1975 R}) \end{aligned}$$



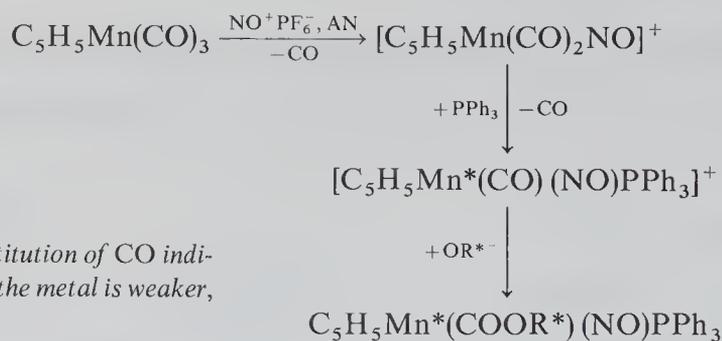
$$\begin{aligned} \nu(\text{NO})_{\text{linear}} &= 1830 \\ (\text{Cox, 1970}) \end{aligned}$$



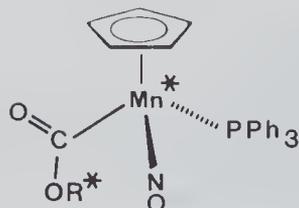
$$\begin{aligned} \nu(\text{NO})_{\text{linear}} &= 1610 \\ \text{fluxional at room} \\ \text{temperature} \\ (\text{Cotton, 1970}) \end{aligned}$$

$$\text{Compare: } \nu(\text{NO})_{\text{free}} = 1876 \text{ cm}^{-1}, \nu(\text{NO}^+)_{\text{free}} = 2250 \text{ cm}^{-1}$$

The ν_{CO} frequency is not a reliable criterion to distinguish between linear or bent MNO units, because the two absorption ranges overlap (Ibers, 1975). Bridging NO groups, however, exhibit considerably lower ν_{NO} frequencies and therefore are easily identified. Starting from $\text{CpMn}(\text{CO})_3$, optically active compounds have been synthesized with **manganese as a centre of chirality**:



The preferential substitution of CO indicates that its bond to the metal is weaker, as compared to NO.



For $\text{OR}^- = \text{OC}_{10}\text{H}_{19}^-$ (L-mentholate), **diastereomers** can be separated based on their different solubilities. In the solid state, the diastereomers are configurationally stable.

The significance of these chiral complexes derives from their use in the study of organometallic reaction mechanisms, the observation of retention or inversion serving as an experimental probe (Brunner, 1971 R).

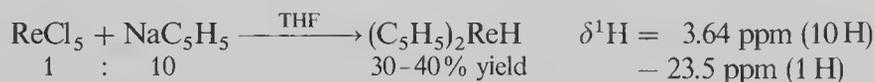
15.4.3.4 Cyclopentadienyl Metal Hydrides

This type of complex is mainly encountered with 4*d*- and 5*d* metals:

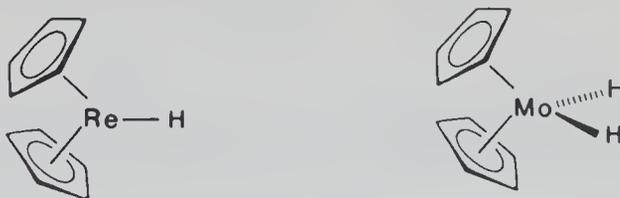


Corresponding complexes of the 3*d* metals tend to dimerize with attendant loss of dihydrogen.

PREPARATION

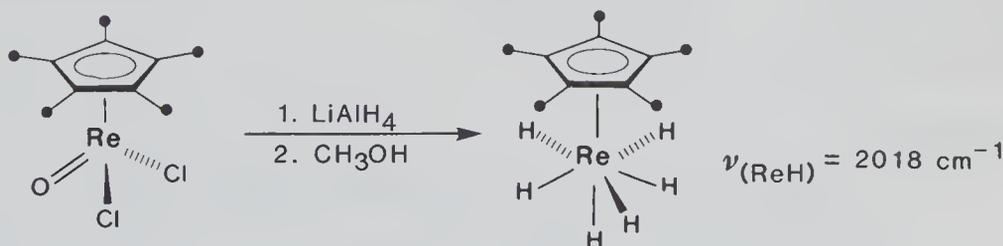


Cp₂ReH (Wilkinson, 1955) in contrast to the expected product Cp₂Re (cf. p. 325) is air-stable and diamagnetic. The investigation of Cp₂ReH was one of the first applications of ¹H-NMR spectroscopy in organometallic chemistry.



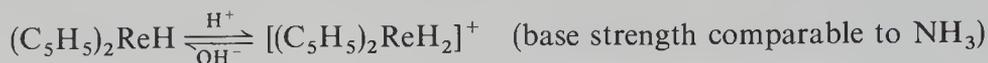
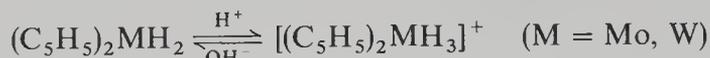
Structure: In all complexes of composition (C₅H₅)_mMH_n known to date, the planes of the C₅H₅ rings are tilted in a fashion similar to Sn(C₅H₅)₂ (see p. 134).

The ability of Re^{VII} to accommodate a large number of hydride ligands in its coordination shell [cf. (R₃P)₂ReH₇, K₂(ReH₉)] also manifests itself in the (cyclopentadienyl)metal hydrides (Herrmann, 1986):

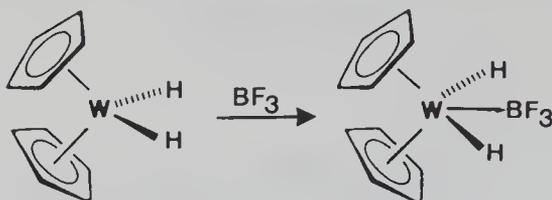


At -90°C , the ¹H-NMR spectrum shows separate signals for the axial and the equatorial hydride ligands, which at 60°C coalesce due to rapid exchange between the two positions. Proton chemical shifts of transition-metal hydrides are listed on p. 306.

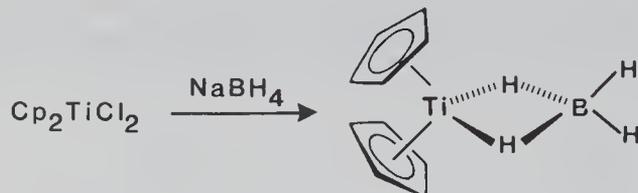
The **reactivity** of cyclopentadienyl metal hydrides is largely governed by the **Lewis-basicity of the central metal**. These complexes are readily protonated:



Other Lewis acids like BF_3 can also add to cyclopentadienyl metal hydrides:



Adduct formation of a different type is realized in titanocenyl boranate where the moieties Cp_2TiH and BH_3 – unknown in free form – associate through $2e\ 3c$ hydride bridges:



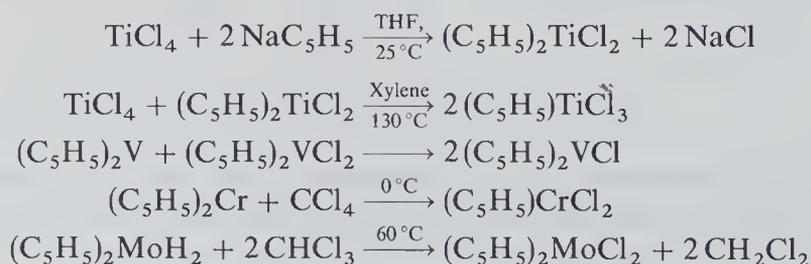
The formation of Cp_2MH structural units, which then dimerize in a variety of ways, is a characteristic feature of the electron-poor metallocenes, $\Sigma \text{VE} < 16$ (cf. p. 323).

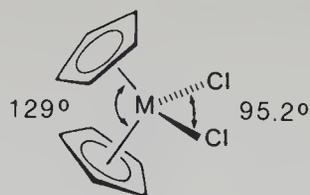
15.4.3.5 Cyclopentadienyl Metal Halides

Halide ions and hydride ions share the property of both being anionic $2e$ ligands. The variety of Cp-metal halides considerably outweighs that of the Cp-metal hydrides.

CpMCl_2 (Ti, V, Cr)	Cp_2MCl_2 (Ti, Zr, Hf, V, Mo, W)	Cp_3MCl (Th, U)
CpMCl_3 (Ti, Zr, V)	Cp_2MBr_2 (Nb, Ta)	
CpMCl_4 (Nb, Ta, Mo)	Cp_2MCl (Ti, V)	

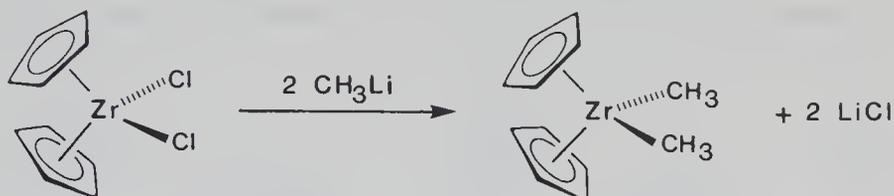
PREPARATION



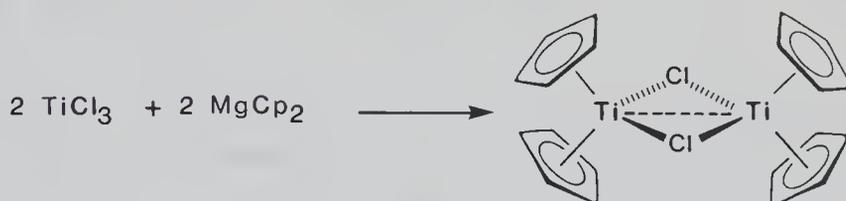


Complexes of the type Cp_2MCl_2 ($M = Ti, Zr, Hf$) have a "pseudotetrahedral" structure. They are air-stable and sublimable. The bond parameters quoted here refer to the titanium derivative.

Cp-metal halides are starting materials for the synthesis of Cp-metal alkyls and Cp-metal aryls:

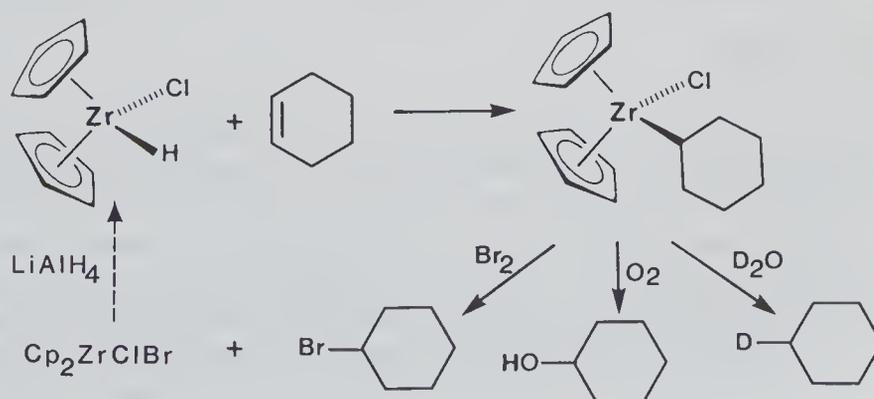


The Cp_2 -metal chloride of Ti(III) is dimeric:

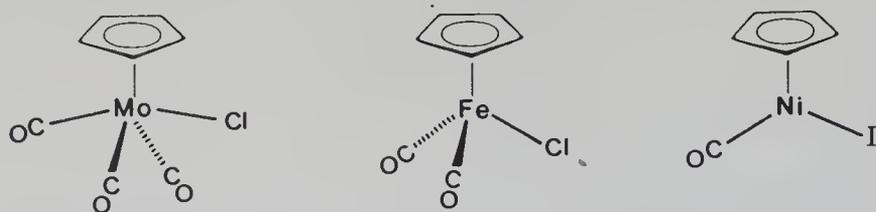


Measurements of the magnetic susceptibility of $[Cp_2TiCl]_2$ show that the singlet and triplet states coexist in thermal equilibrium thereby signaling a weak intramolecular Ti–Ti interaction (R. L. Martin, 1965).

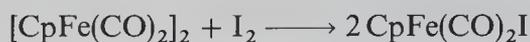
The mixed Cp-metal chloride hydride $Cp_2ZrCl(H)$, presumably of polymeric structure, was introduced into organic synthesis as **Schwartz's reagent**: By **hydrozirconation** and subsequent oxidative decomplexation alkenes are converted into substituted alkanes (Schwartz, 1976 R).



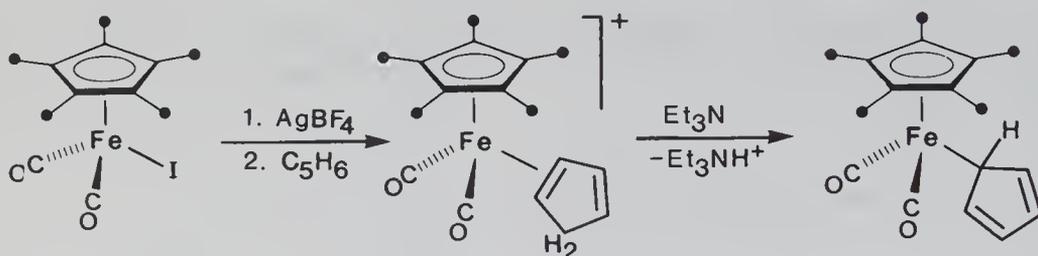
Mixed Cp-metal carbonyl halides are important reagents in organometallic synthesis:



These compounds are prepared through the oxidative cleavage of dinuclear precursors by dihalogens:

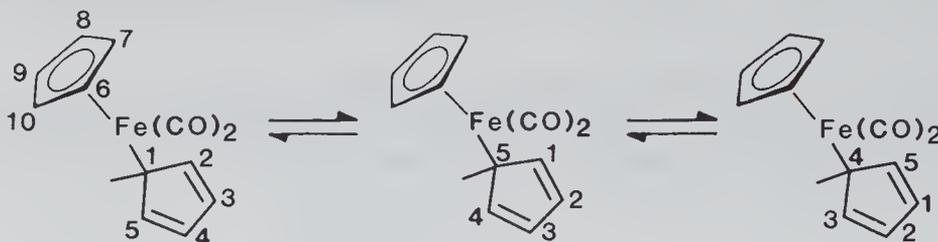


They serve as starting materials in the formation of new transition-metal carbon bonds:



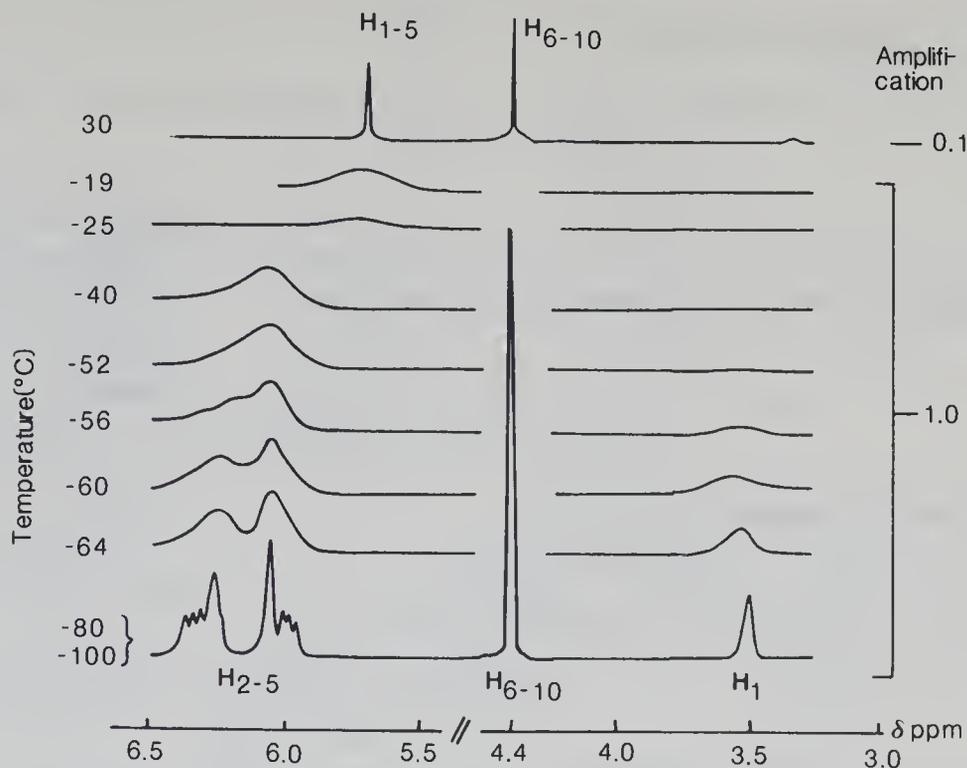
(Glass, 1985)

(η^1 -Cp)(η^5 -Cp)Fe(CO)₂ was the first transition-metal complex for which the phenomenon of fluxionality (non-rigidity) was studied (Wilkinson, 1956; Cotton, 1966). The two Cp-rings display the different bonding modes π (η^5 -) and σ (η^1 -) respectively, the latter being subject to haptotropic shifts, which cause the position 1–5 to become equivalent at room temperature: (¹H-NMR, p. 343):



15.4.4 C₆H₆ as a Ligand

The coordination of neutral arenes to metals has been previously discussed in the context of main-group organometallics (p. 90). However, whereas for main-group elements metal-arene coordination must be regarded as a weak interaction, more or less confined to the solid state, the transition elements form the basis of a large variety of molecules containing (η^6 -arene)metal segments. As early as 1919, F. Hein isolated “phenylchromium compounds” by treating CrCl₃ with PhMgBr in diethylether. Although unrecognized at that time, these materials were bis(η^6 -arene)chromium(I) cations. The first rational synthesis of bis(arene)metal complexes was developed by E. O. Fischer and W. Hafner in 1955.

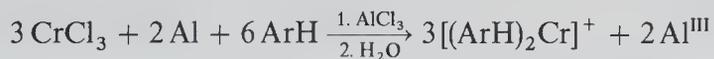


¹H-NMR spectrum of (η¹-Cp)(η⁵-Cp)Fe(CO)₂ (60 MHz)

15.4.4.1 Bis(arene)metal Complexes

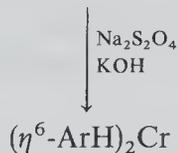
PREPARATION

1. Fischer-Hafner Synthesis



Scope:

V	Cr	—	Fe	Co	Ni
—	Mo	Tc	Ru	Rh	—
—	W	Re	Os	Ir	—

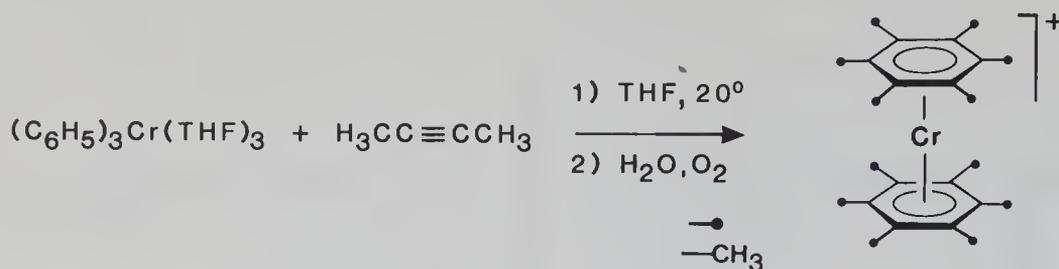


Limitations:

The arene must be inert towards AlCl₃. Alkylated arenes are isomerized by AlCl₃. Aromatic ligands with substituents having lone pairs like halobenzenes, dimethylaniline or phenols cannot be used since they form Lewis adducts with AlCl₃.

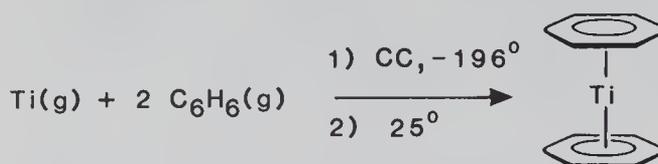
2. Cyclotrimerization of Alkynes

This route to bis(arene)metal complexes is of minor preparative importance (cf. p. 277).

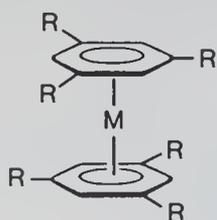


3. Peripheral Substitution (see Reactions)

4. Metal-Atom Ligand-Vapor Cocondensation (CC) (cf. p. 255)

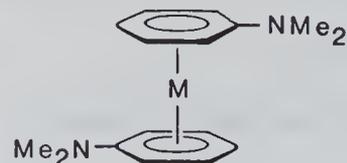
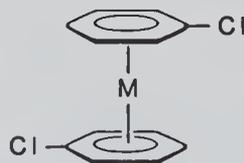


The following simple bis(η^6 -arene)metal complexes as yet can only be prepared by means of cocondensation techniques:

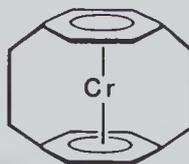


R = H, M = Ti, Nb (Green, 1974)

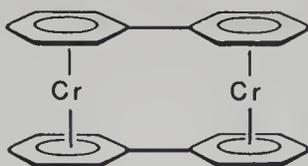
R = t-Bu, M = Ti, Zr, Hf, Y, Gd (Cloke, 1987)



M = Cr, Mo (Skell, 1971)

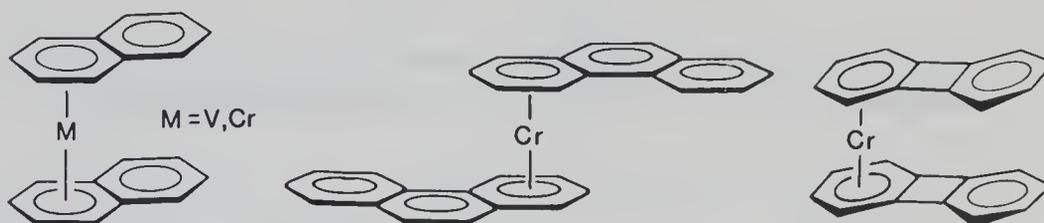


(η^{12} -[2.2]Paracyclophane)chromium(0) is a compressed sandwich complex; the average distance between the two rings (ca. 290 pm) falls considerably short of the corresponding distance in (η^6 -C₆H₆)₂Cr (322 pm) (Elschenbroich, 1978).

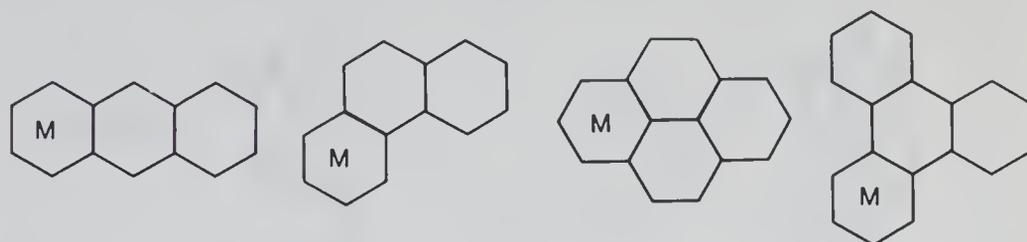


Bis[μ -(η^6 : η^6 -biphenyl)]dichromium. In solution, the monocation []⁺ represents the *intermediate valence* case Cr^{+1/2}, Cr^{+1/2}. The paramagnetic dication []²⁺ is an organometallic triplet species (Elschenbroich, 1979). In contrast, the structurally related cation [bis- μ -(η^5 : η^5 -fulvalenediyl)]diiron]²⁺ is diamagnetic (p. 327).

Neutral sandwich complexes of anellated arenes are also accessible by the CC method only (Elschenbroich, Kündig, Timms, 1977f). Examples:



In the case of higher anellated arenes like phenanthrene, triphenylene and coronene, the metal atom preferentially coordinates to the ring with the highest index of local aromaticity (ILA), i.e. the ring which among the canonical forms most frequently appears with a Kekulé structure. This invariably is the terminal, least anellated ring:

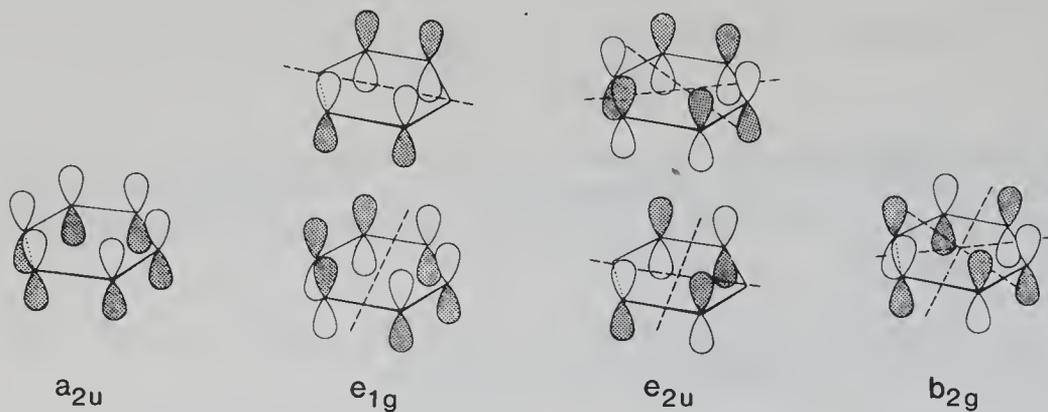


ELECTRONIC STRUCTURE AND BONDING IN BIS(ARENE)METAL COMPLEXES

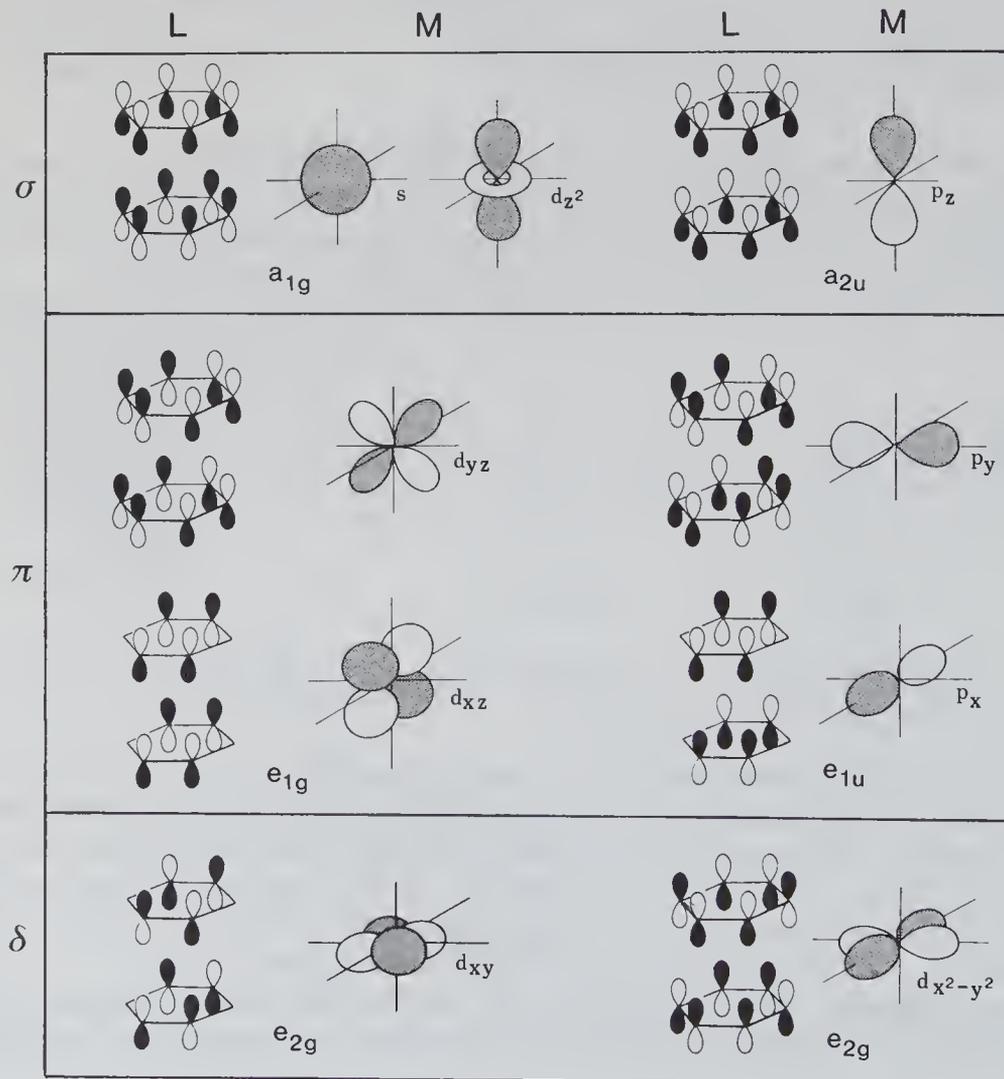
The situation largely resembles that of the metallocenes. Shifts of the energy levels in the MO diagram of bis(benzene)chromium, as compared to ferrocene, result from differences in the energies of the respective basis orbitals. These are lower for C₆H₆ than for C₅H₅⁻ and higher for Cr⁰ than for Fe²⁺. As suggested by the X-ray photoelectron spectrum (ESCA), the central metal atom in bis(benzene)chromium(0) bears a partial positive charge (ca. + 0.7) and the ligands partial negative charges (ca. - 0.35).

The **bond energy per ring** $E(\text{Cr}-\text{C}_6\text{H}_6)$, as determined by thermochemical measurements, amounts to about **170 kJ/mol**; it is lower than the corresponding value (**220 kJ/mol**) found for **ferrocene**.

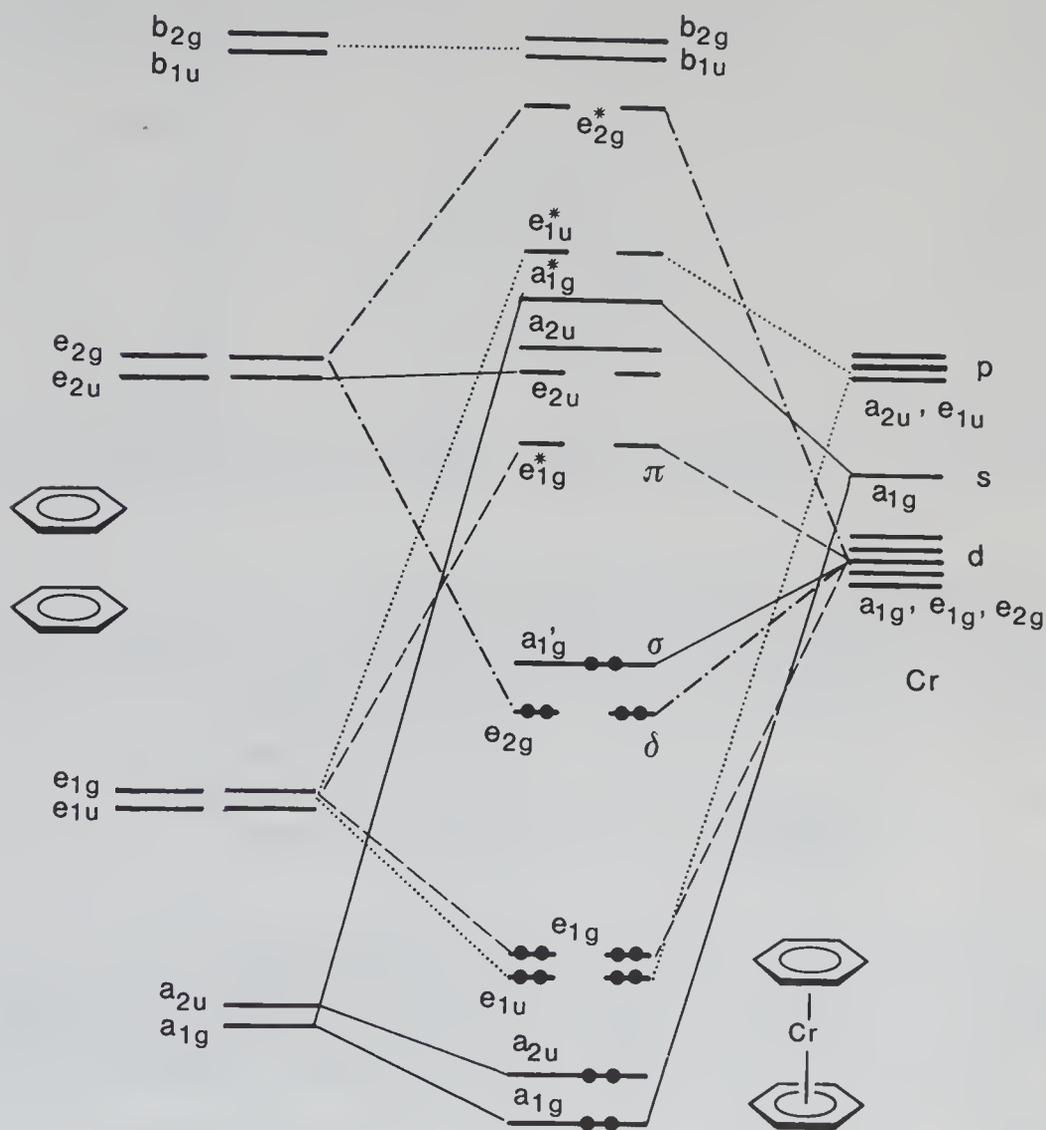
As usual, the MO treatment starts from a consideration of the ligand π MO's:



Interactions of symmetry-adapted linear combinations of the π MO's of two C_6H_6 ligands with appropriate metal orbitals in bis(benzene)chromium (D_{6h}):



A qualitative MO diagram for bis(benzene)chromium (D_{6h} , intra-ligand σ orbitals are not included) is shown below:



This MO diagram for $(C_6H_6)_2Cr$ is similar to that of $(C_5H_5)_2Fe$. As the basis orbitals of symmetry e_{2g} are closer in energy for the combination Cr^0/C_6H_6 than for $Fe^{2+}/C_5H_5^-$, the δ bond (backbonding, $C_6H_6 \leftarrow M$) contributes more significantly in bis(benzene)chromium as compared to ferrocene.

Magnetic Properties of Bis(arene)metal Complexes

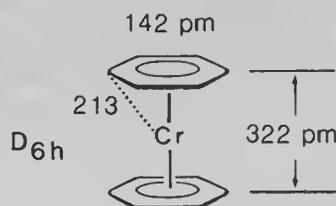
	Number of unpaired electrons	ΣVE^+	Magnetic moment	
			Spin-only value in B.M.	Experimental value in B.M.
$(C_6H_6)_2Ti$	0	16	0	0
$(C_6H_6)_2V$	1	17	1.73	1.68 ± 0.08
$[(C_6H_6)_2V]^-$	0	18	0	0
$[(C_6Me_3H_3)_2V]^+$	2	16	2.83	2.80 ± 0.07
$(C_6H_6)_2Cr$	0	18	0	0
$(C_6H_6)_2Mo$	0	18	0	0
$[(C_6H_6)_2Cr]^+$	1	17	1.73	1.77
$[(C_6Me_6)_2Fe]^{2+}$	0	18	0	0
$[(C_6Me_6)_2Fe]^+$	1	19	1.73	1.89
$(C_6Me_6)_2Fe$	2	20	2.83	3.08
$[(C_6Me_6)_2Co]^{2+}$	1	19	1.73	1.73 ± 0.05
$[(C_6Me_6)_2Co]^+$	2	20	2.83	2.95 ± 0.08
$(C_6Me_6)_2Co$	1	21	1.73	1.86
$[(C_6Me_6)_2Ni]^{2+}$	2	20	2.83	3.00 ± 0.09

Some Further Properties of Bis(arene)metal Complexes

Complex	Color	mp/ $^{\circ}C$	Miscellaneous
$(C_6H_6)_2Ti$	red	—	air-sensitive, autocatalytic decomposition in aromatic solvents
$(C_6H_6)_2V$	solid: black solution: red	227	very air-sensitive, paramagnetic, reducible to $[(C_6H_6)_2V]^-$
$(C_6H_5F)_2V$	red	—	air-sensitive
$(C_6H_6)_2Nb$	purple		very air-sensitive, paramagnetic, decomposes at ca. $90^{\circ}C$
$(C_6H_6)_2Cr$	brown	284	air-sensitive, the cation $[(C_6H_6)_2Cr]^+$ is air-stable, $E^{\circ} = -0.69 V$ in DME against SCE
$(C_6H_6)_2Mo$	green	115	very air-sensitive
$(C_6H_6)_2W$	yellow-green	160	less air-sensitive than $(C_6H_6)_2Mo$
$[(C_6Me_6)_2Mn]^+$	pale pink	—	diamagnetic
$[(C_6Me_6)_2Fe]^{2+}$	orange	—	reducible to $[(C_6Me_6)_2Fe]^+$, violet, and to $(C_6Me_6)_2Fe^0$, black, paramagnetic, extremely air-sensitive
$[(C_6Me_6)_2Ru]^{2+}$	colorless	—	air-stable, diamagnetic, reducible to $(C_6Me_6)_2Ru$, orange, diamagnetic
$[(C_6Me_6)_2Co]^+$	yellow		paramagnetic, reducible to $(C_6Me_6)_2Co^0$, very air-sensitive

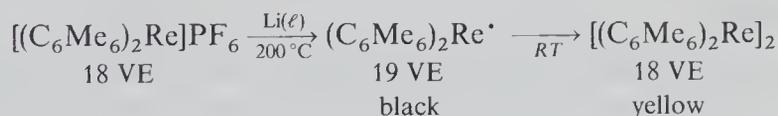
STRUCTURAL FEATURES

In the years immediately following the synthesis of **bis(benzene)chromium**, the structure and symmetry of this complex (D_{3d} or D_{6h} ?) was the subject of considerable debate. While IR spectra and neutron-diffraction studies spoke for “localized” electron pairs and alternating C–C bond lengths as in a fictitious cyclohexatriene, electron diffraction and low-temperature X-ray diffraction studies confirmed a geometry with equal bond lengths (symmetry D_{6h}). This is the structure generally accepted today.

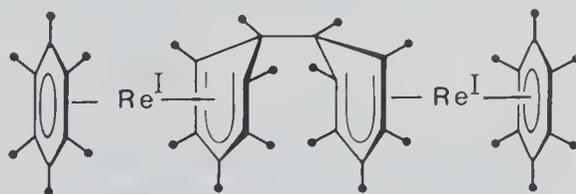


The ring-ring distance is approximately equal to the van der Waals separation of two π -systems; compared to free benzene, $d(\text{C}-\text{C})$ is somewhat elongated in the complex.

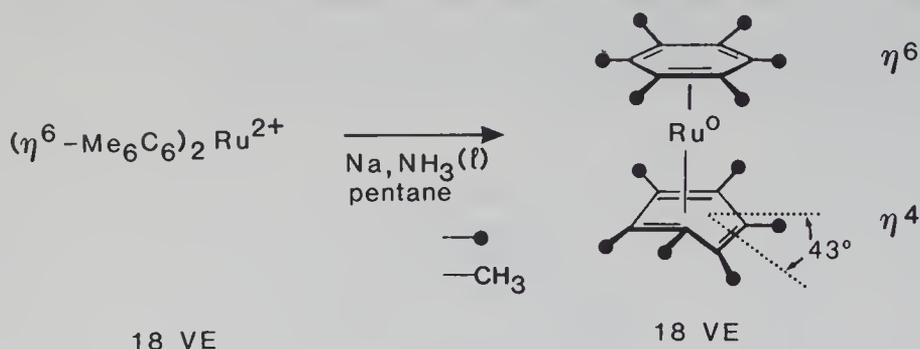
Paramagnetic **bis(hexamethylbenzene)rhenium** is unstable as a monomer at room temperature. The monomeric form can only be detected by means of ESR spectroscopy at -196°C . At room temperature, the dimer is irreversibly formed (E. O. Fischer, 1966):



This process can be formally ascribed to a transition $\text{Re}(0) \rightarrow \text{Re}(\text{I})$ and the formation of a cyclohexadienyl ligand bearing an unpaired electron which is then used in inter-ligand bonding. The transition metal thus retains its 18 VE configuration. (Compare the analogous dimerization of rhodocene!) The most likely structure of the dimer is:



Bis(hexamethylbenzene)ruthenium(0) as an axially symmetrical sandwich complex would be a 20 VE system. However, since one of the rings is only η^4 -coordinated, an 18 VE configuration is attained. The complex is **fluxional** in solution (E.O. Fischer, 1970):



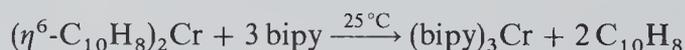
REACTIONS

(a) Oxidation

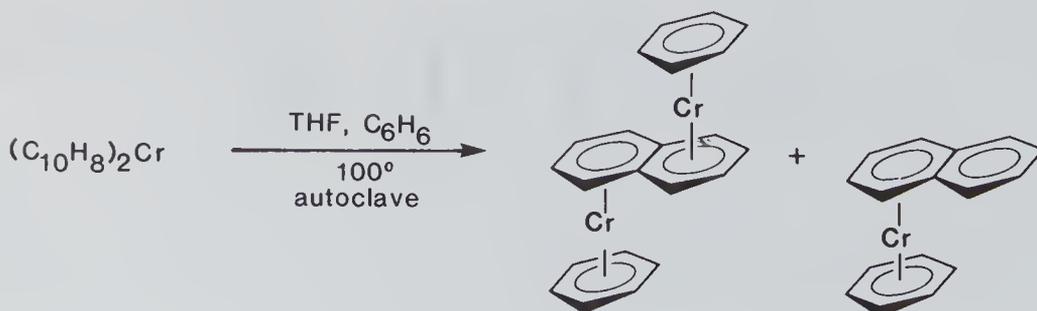
All neutral bis(arene)metal complexes with hydrocarbon ligands are **air-sensitive**. This sensitivity to oxidation is diminished on replacement of the ring hydrogen atoms by electron-withdrawing groups. Example: $(\eta^6\text{-C}_6\text{H}_5\text{Cl})_2\text{Cr}$ is air-stable.

(b) Ligand Exchange

Bis(benzene)chromium(0) is **kinetically inert**. Ring exchange occurs only in the presence of a Lewis acid like AlCl_3 . This reaction is, however, unsuitable for the synthesis of other derivatives (compare the limitations to the Fischer-Hafner synthesis, p. 343). In contrast, binary complexes of condensed arenes are **labile**. Example:



This lability of $(\text{C}_{10}\text{H}_8)_2\text{Cr}$ renders possible the synthesis of a mixed benzene-naphthalene dinuclear complex (Lagowski, 1987):

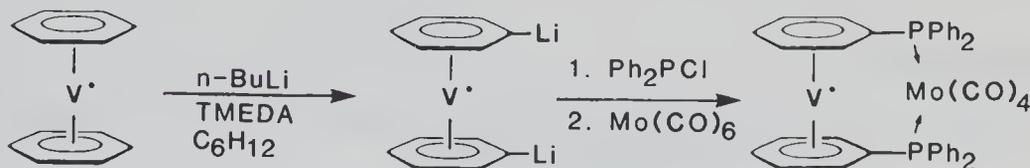
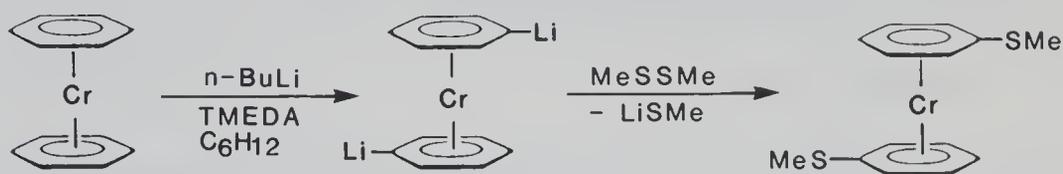


(c) Electrophilic Aromatic Substitution

In contrast to ferrocene, this reaction is not applicable to bis(benzene)chromium, since the attacking electrophile oxidizes Cr(0) to Cr(I), yielding the cation $[(C_6H_6)_2Cr]^+$ which does not undergo peripheral electrophilic substitution.

(d) Metallation

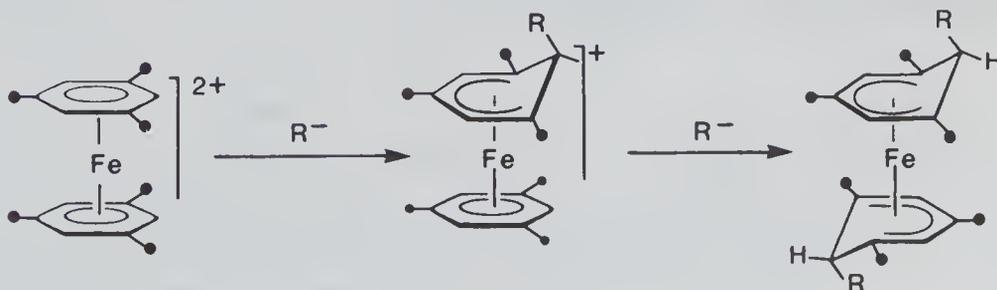
H/metal exchange is effected by means of *iso*-amylsodium or, better, by *n*-butyllithium in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). π -Bonded benzene is metallated more readily than free benzene, i.e. the kinetic acidity of benzene is increased upon coordination to chromium. A mixture of lithiation products is obtained, however. This reaction paves the way for the preparation of substituted bis(arene)metal complexes. Examples:



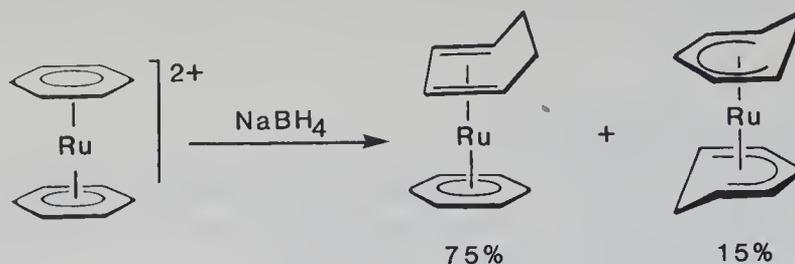
The vanadium complex with π -bonded PPh₃ may function as a paramagnetic bidentate ligand.

(e) Addition of nucleophiles

Cationic bis(arene)metal complexes readily react with nucleophiles by ring addition:

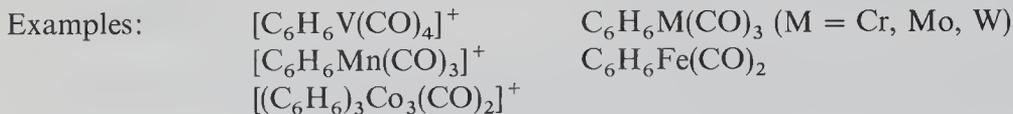


The second addition of R^- to the iron complex is in accordance with the DGM rule ① (p. 293). The analogous ruthenium complex, on the other hand, also undergoes homoannular secondary addition, two products being obtained:



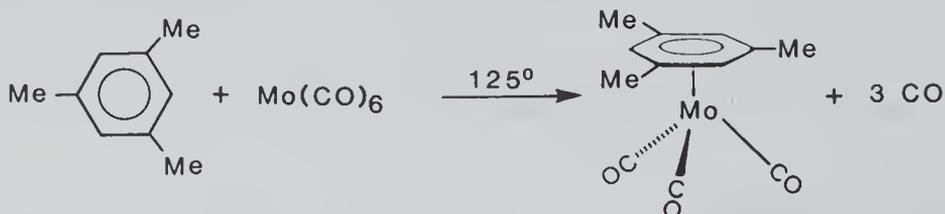
This difference could be an outcome of thermodynamic control, in that the more noble metal ruthenium prefers the oxidation state M^0 . (Note that the DGM-rules only apply to kinetically controlled reactions).

15.4.4.2 Arene Metal Carbonyls



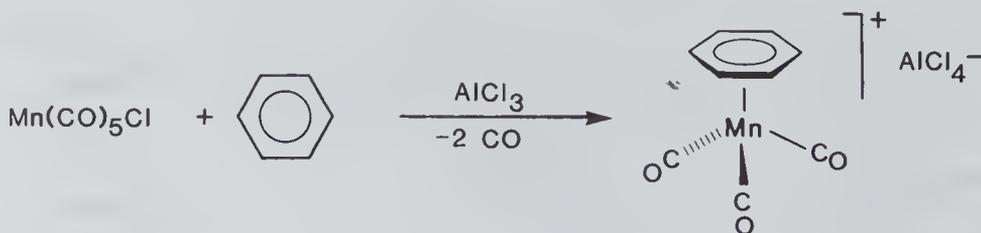
PREPARATION

1. Metal Carbonyl + Arene (Carbonyl Substitution)

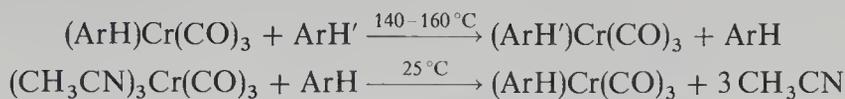


This CO substitution does not proceed beyond the stage $(ArH)M(CO)_3$.

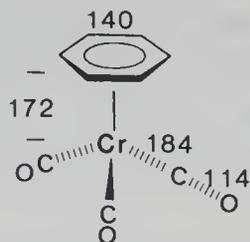
2. Metal-Carbonyl Halide + Arene + $AlCl_3$



3. Ligand Exchange (Arene Substitution)



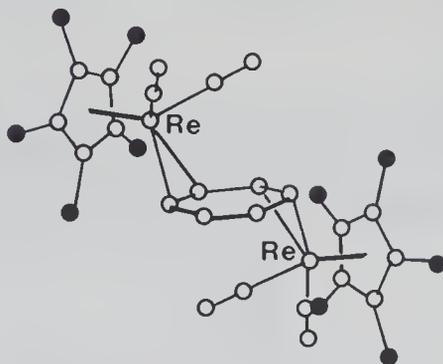
STRUCTURAL FEATURES



The prototype “piano-chair” complex, η^6 -benzene(tricarbonyl)chromium, does not present any structural surprises. The $\text{M}(\text{CO})_3$ unit and the arene are staggered and the six-fold symmetry of η^6 -benzene is maintained (Dahl, 1965).

Compare $d(\text{C}\equiv\text{O})_{\text{free}} = 113 \text{ pm}$.

(Carbonyl)metal units also furnish examples for bonding modes of benzene which diverge from the usual η^6 -type:



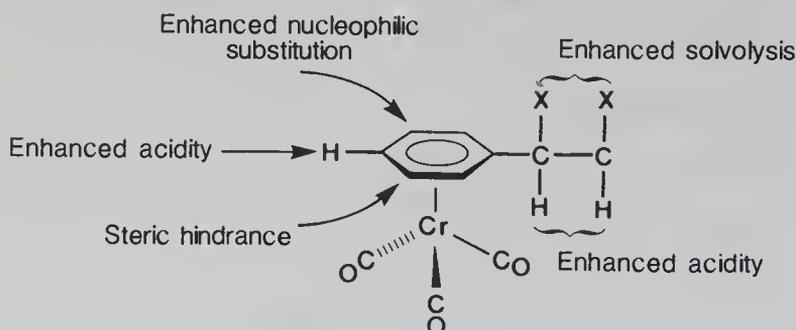
μ_2 - $(\eta^2:\eta^2\text{-C}_6\text{H}_6)$ $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2]_2$. This complex forms on irradiation of $(\text{C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ in benzene solution (Orpen, 1985). The benzene ring shows pronounced C–C bond length alternation.



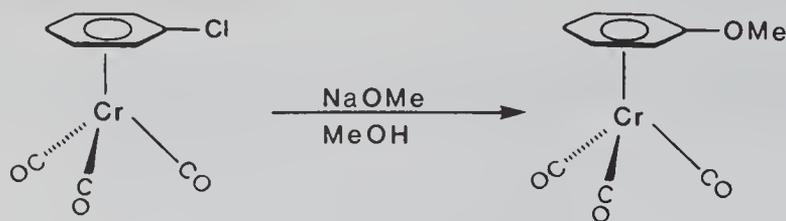
μ_3 - $(\eta^2:\eta^2:\eta^2\text{-C}_6\text{H}_6)$ $\text{Os}_3(\text{CO})_9$. Benzene displays the novel “face-capping” ligation here (B. F. G. Johnson, J. Lewis, 1985); the C–C bonds attached to the osmium atoms are shorter than the unattached C–C bonds. This coordination mode mimics the interaction of arenes with metal surfaces.

REACTIONS OF ARENE METAL CARBONYLS

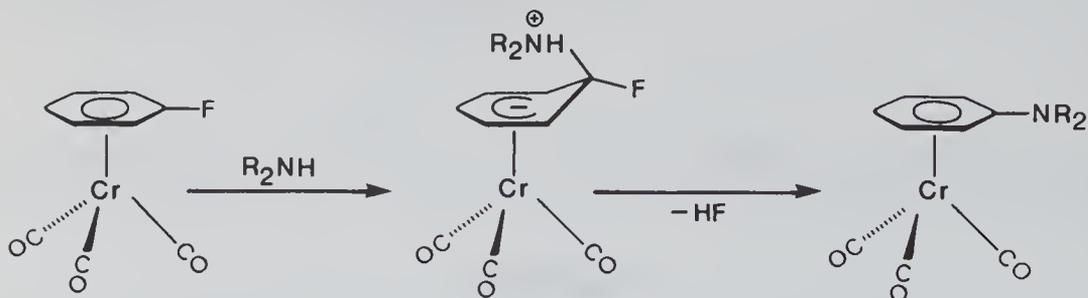
Complexation of an arene to the $\text{Cr}(\text{CO})_3$ fragment alters its reactivity in several ways, as summarized below (adapted from Semmelhack, 1976):



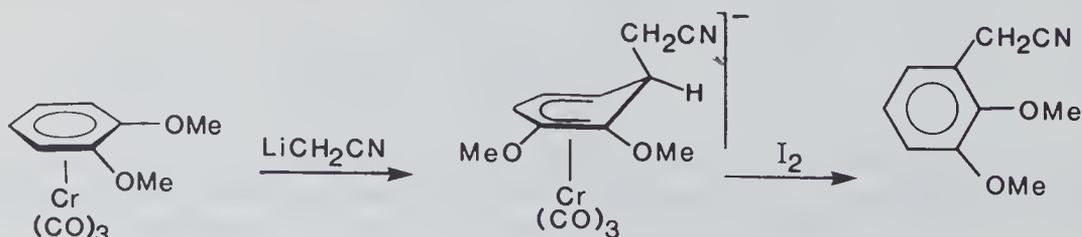
The $\text{Cr}(\text{CO})_3$ unit exerts an electron-withdrawing effect. Compared to the free arene, the complexed arene is thus deactivated toward **electrophilic substitution**, but particularly susceptible to **nucleophilic substitution**:



The reaction rate of $(\text{C}_6\text{H}_5\text{Cl})\text{Cr}(\text{CO})_3$ resembles that of *p*-nitrochlorobenzene. According to kinetic measurements, the reaction proceeds via an intermediate with an η^5 -bonded cyclohexadienyl ring, the rate-determining step being the *endo*-loss of the halide ion.



Of greater preparative importance is the reaction between substituted arene chromium tricarbonyls and carbanions:

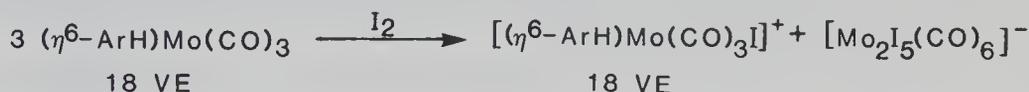


Nucleophilic attack occurs at the uncomplexed face of the arene ligand (*exo*). The intermediary anionic cyclohexadienyl complex has been isolated in some cases (Semmelhack, 1981 R).

Attack of σ -donor/ π -acceptor ligands can cause a **displacement of the η^6 -arene ligand**:

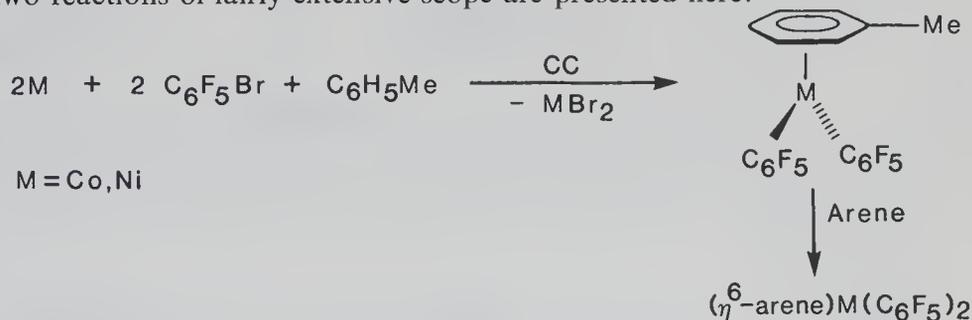


Oxidation of 18 VE (arene)metal carbonyls in contrast to bis(arene)metal complexes does not lead to stable 17 VE radical cations. On oxidation of (arene)molybdenum tricarbonyl with iodine, molybdenum is oxidized to Mo^{II} and an unusual counterion is formed (Calderazzo, 1986):



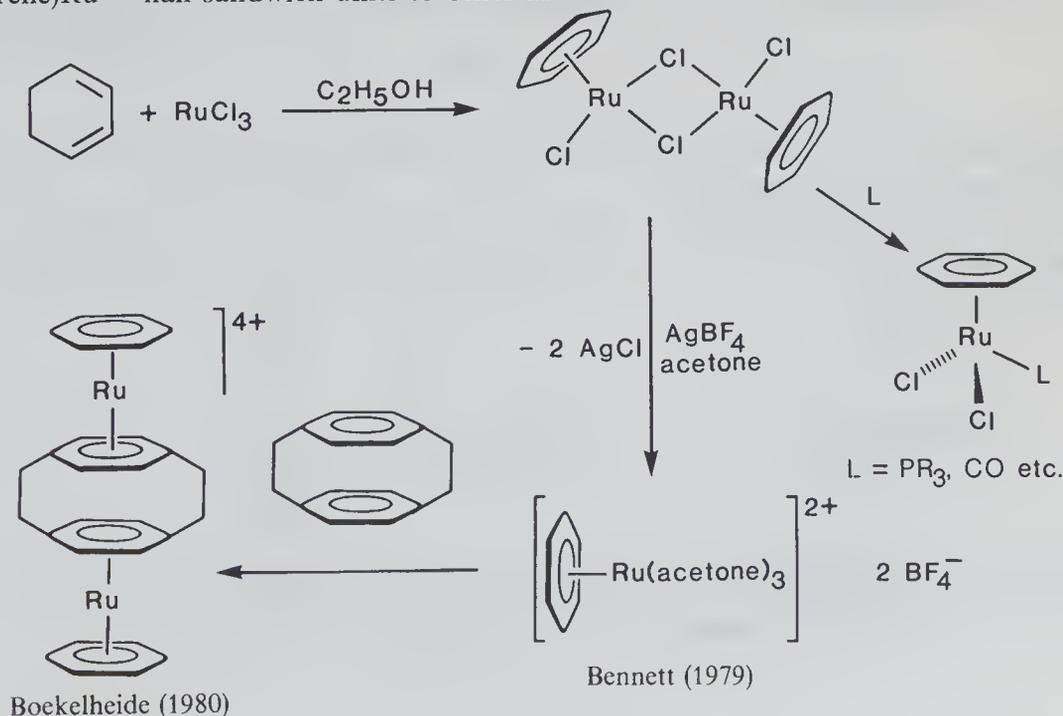
Other Complexes of the General Type ($\eta^6\text{-ArH}$)ML_n

Only two reactions of fairly extensive scope are presented here:



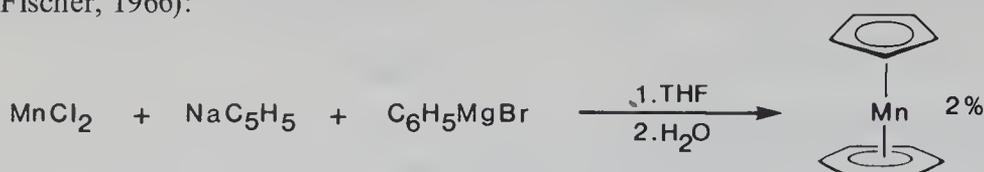
In this way, (C₆F₅)₂M fragments can be transferred to a large number of arenes (Klabunde, 1978).

Cationic complexes of the type [(η^6 -arene)Ru(sol_v)₃]²⁺ are useful reagents for transferring (arene)Ru²⁺ half-sandwich units to other arenes:



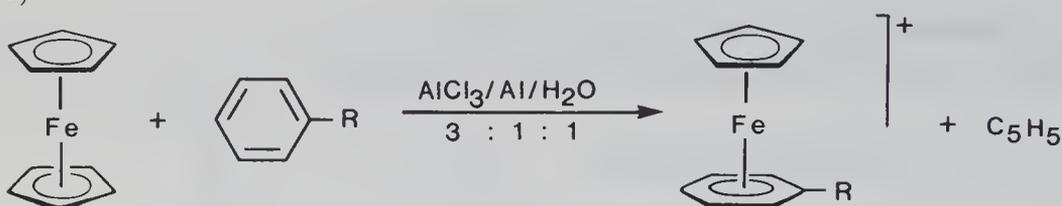
15.4.4.3 Benzene Cyclopentadienyl Metal Complexes

Complexes containing both six- and five-membered rings are accessible by several routes (E.O. Fischer, 1966):

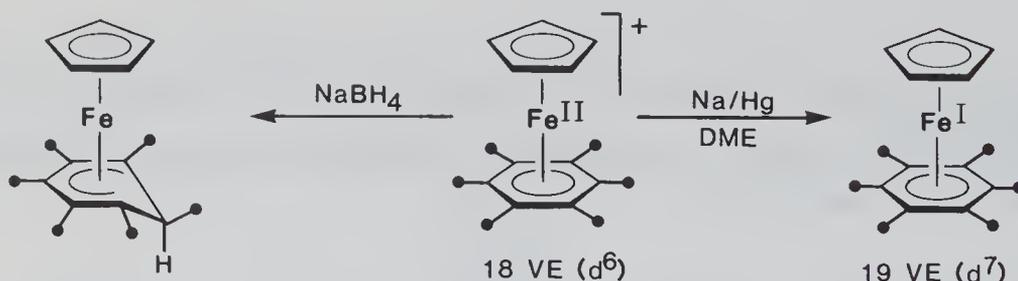


(Biphenyl) MnC_5H_5 is formed as the main product; a further byproduct is the dinuclear complex μ -($\eta^6:\eta^6$ -biphenyl)bis[(cyclopentadienyl)manganese]. $(\text{C}_6\text{H}_6)\text{CrC}_5\text{H}_5$ (17 VE) can be prepared in an analogous manner.

One cyclopentadienyl ring of ferrocene can be exchanged for an arene (Nesmeyanow, 1963):

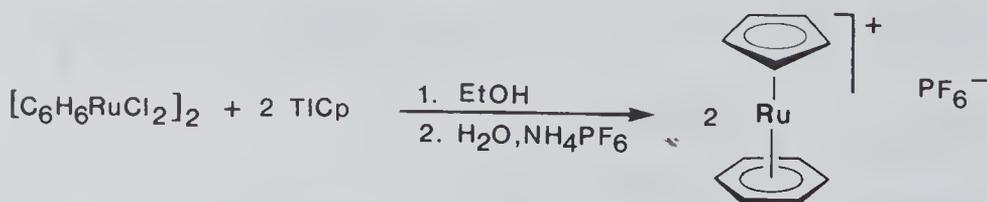


Reduction of these 18 VE (arene)(cyclopentadienyl)iron cations affords stable 19 VE radicals (Astruc, 1983 R):

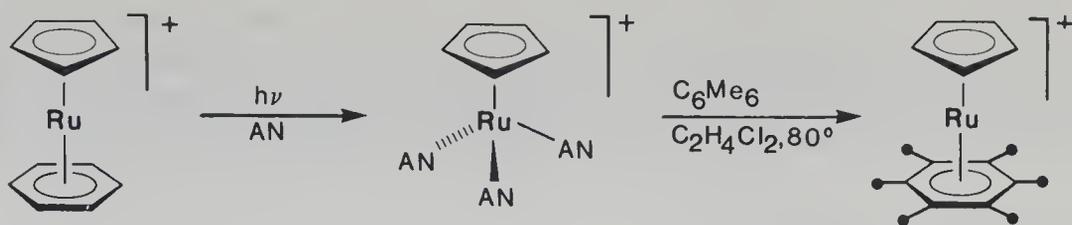


Nucleophilic addition occurs exclusively at the six-membered ring with the formation of neutral cyclohexadienyl complexes.

(Arene)(cyclopentadienyl)ruthenium cations are only obtained in low yields from ruthenocene; a better synthetic route proceeds from dimeric (benzene)ruthenium dichloride (Baird, 1972):

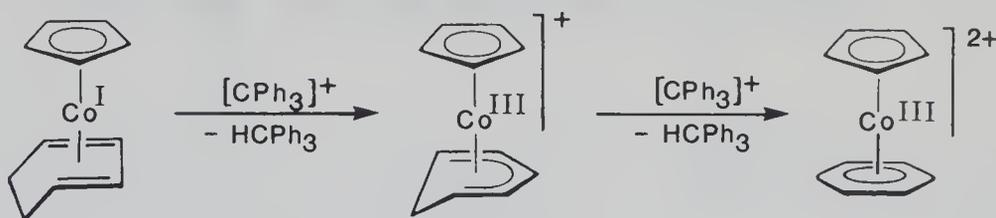


The cation $[(\text{C}_5\text{H}_5)\text{Ru}(\text{C}_6\text{H}_6)]^+$ is photolabile, forming solvates $[(\text{C}_5\text{H}_5)\text{Ru}(\text{sol})_3]^+$ which transfer $(\text{C}_5\text{H}_5)\text{Ru}^+$ fragments to other arenes (cf. p. 333, 368):

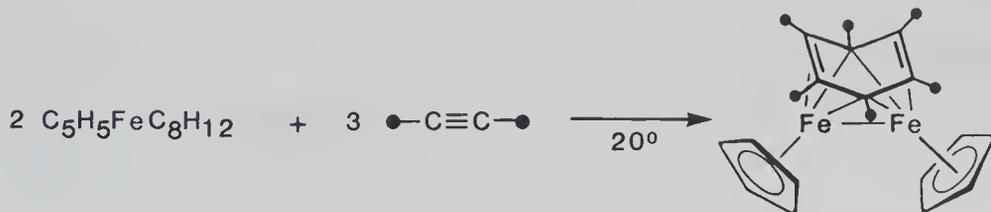


(K. R. Mann, 1982)

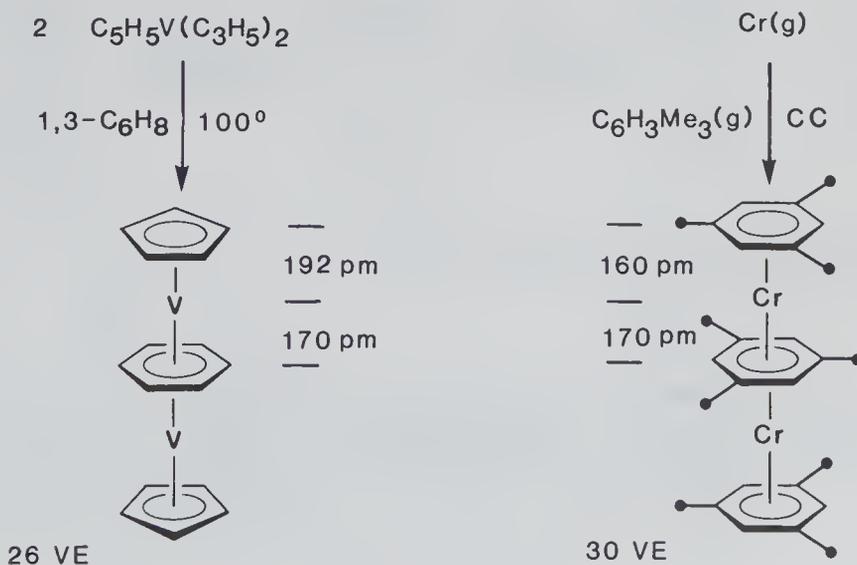
Successive elimination of two H⁻ ions from a cyclohexadiene complex can also lead to the formation of an ($\eta^5\text{-C}_5\text{H}_5$)M($\eta^6\text{-C}_6\text{H}_6$) species:



The class of mixed ligand complexes features examples in which arenes act as bridging ligands, displaying *syn*- as well as *anti*-coordination. In the following *syn*-complex of iron, the bridging ligand is generated by trimerization of acetylenes (Jones, 1983):



Noteworthy is also the first **tripledecker complex** with a bridging benzene ligand [$\text{C}_5\text{H}_5\text{V}$]₂C₆H₆ (Jonas, 1983):

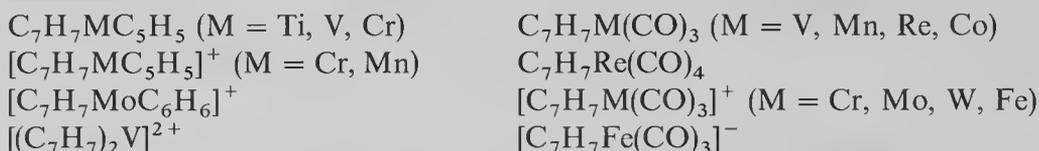


A tripledecker complex containing arene ligands only has been obtained from metal-ligand cocondensation (Lamanna, 1987). With an increased number of decks and further development beyond the current state of laboratory curiosities, such complexes, when partially oxidized or reduced, could show interesting conductivity properties (cf. p. 383).

15.4.5 $C_7H_7^+$ as a Ligand

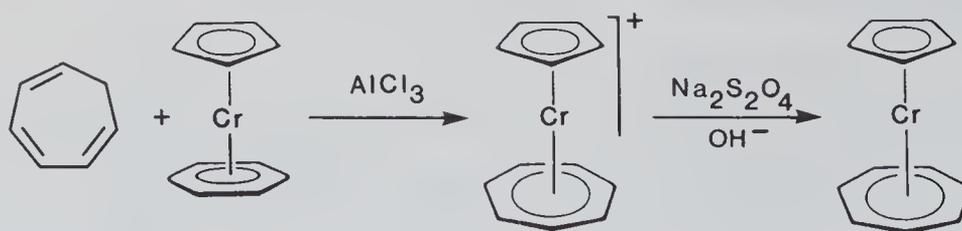
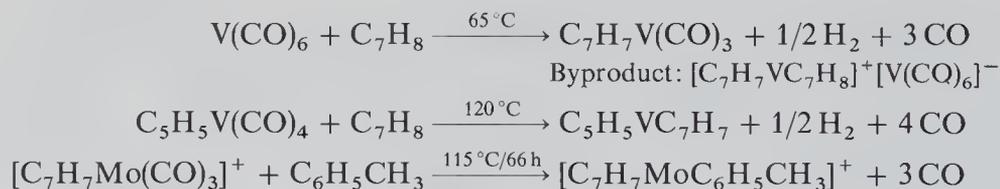
η^7 - C_7H_7 metal complexes are almost exclusively of the mixed-ligand or half-sandwich type, other ligands being present in addition to the cycloheptatrienyl ring. The ligand C_7H_7 is generally regarded as a coordinated aromatic tropylium ion η^7 - $C_7H_7^+$ and is thus classified as a **6e ligand**. C_7H_7 occasionally also acts as an η^3 - or η^5 -ligand.

Examples:

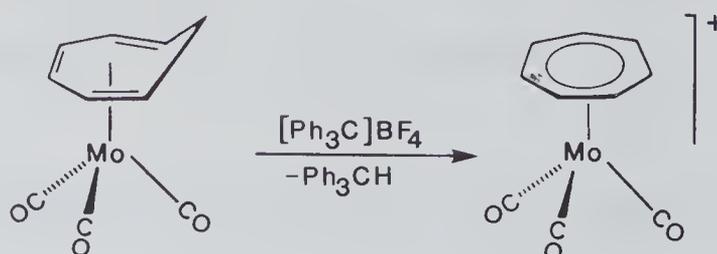


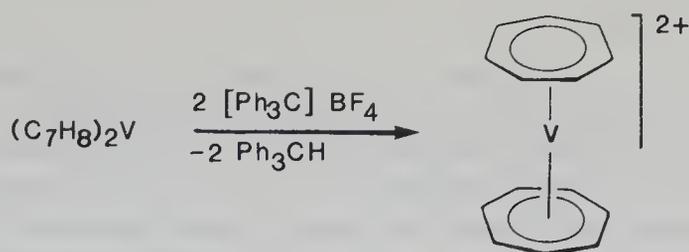
PREPARATION

1. Substitution Reactions

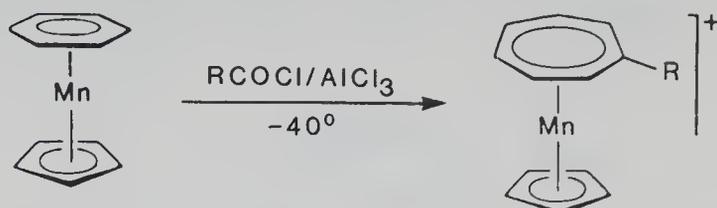


2. Hydride Elimination from η^6 - C_7H_8



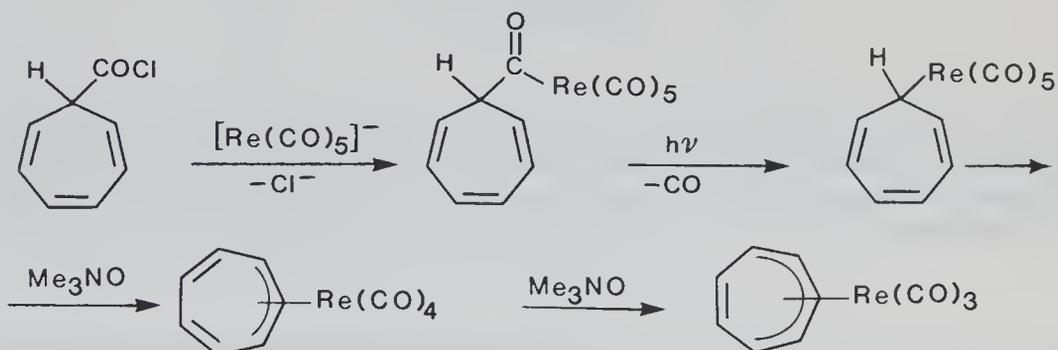


3. Ring Expansion



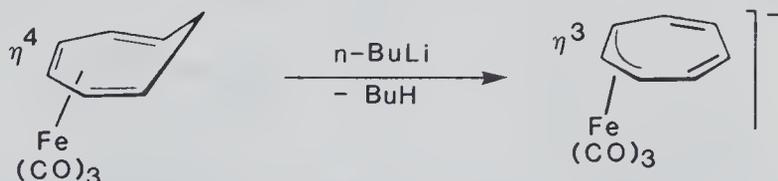
Formally, this reaction is an insertion of RC⁺ into the six-membered ring. This remarkable transformation is only feasible for the combination ($\eta^5\text{-C}_5\text{H}_5$)/($\eta^6\text{-C}_6\text{H}_6$); it is also observed for C₅H₅CrC₆H₆, but not for C₆H₆Cr(CO)₃ or for free C₆H₆.

4. Photochemically or Chemically Induced σ/π -Rearrangement



The analogous irradiation of C₇H₇COMn(CO)₅ at -68 °C yields $\eta^5\text{-C}_7\text{H}_7\text{Mn}(\text{CO})_3$ directly, intermediates being too short-lived for isolation.

5. Deprotonation

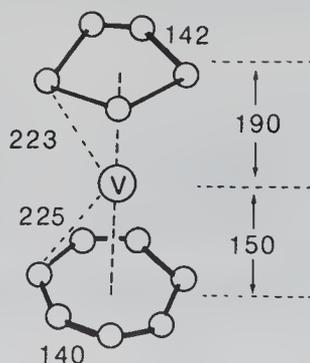


In the case of larger cyclic ligands, application of the 18 VE rule does not generally allow unequivocal structural prediction because increasingly, only partial coordination of the π -perimeters is encountered. Partially coordinated seven-membered rings often show **fluxional behavior**.

STRUCTURE AND BONDING

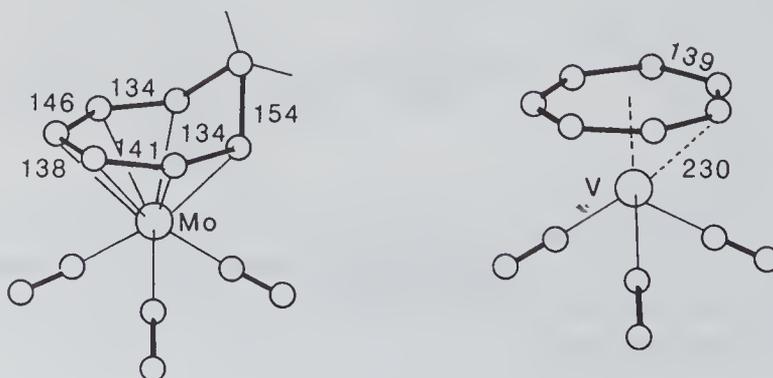
The description of the η^7 - C_7H_7 -metal bond is analogous to that for η^5 - C_5H_5 and η^6 - C_6H_6 . A common feature of all three carbocycles is the existence of π orbitals with symmetries a , e_1 and e_2 which, by interaction with the appropriate metal orbitals, generate bonds of σ -, π - and δ symmetry.

The different energies of the ligand orbitals of 5- and 7-membered rings induce an unsymmetrical charge distribution in mixed-ligand sandwich molecules. $C_5H_5CrC_7H_7$ therefore has a dipole moment, the negative end being located on the C_5H_5 ring ($\mu = 0.73$ Debye = 2.44×10^{-30} C · m). For the vanadium analog, planarity of the C_7H_7 ring and the centrosymmetric bond to the transition metal was confirmed by X-ray studies.



The crystal structure of $C_5H_5VC_7H_7$ reveals that the V—C distances to both rings are almost identical. Accordingly, the distances from the metal to the ring centers differ in that larger rings are approached more closely by the metal. This situation leads to relatively poor metal-ligand orbital overlap, so that centrosymmetric bonding of a first row transition metal to a large ring is less favorable than to a smaller ring (Rundle, 1963).

Comparison of the structures of $C_7H_8Mo(CO)_3$ (left) and $C_7H_7V(CO)_3$ (right): The triolefin complex shows considerable exo-bending of the non-coordinated CH_2 group as well as alternating C—C bond lengths; the tropylium complex, on the other hand, exhibits planar coordination of the C_7H_7 ring and equal C—C distances (Dunitz, 1960; Allegra, 1961).



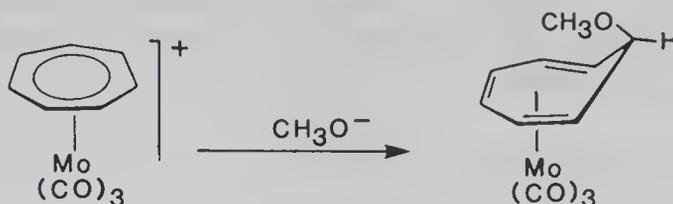
REACTIONS

(a) Redox Reactions

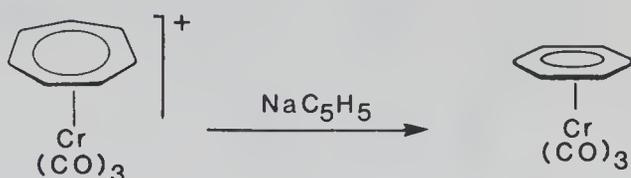


The redox potential for the couple $\text{C}_5\text{H}_5\text{CrC}_7\text{H}_7^{0/+}$ (-0.55 V in DME versus SCE) is shifted anodically compared to the symmetrical isomer $\text{C}_6\text{H}_6\text{CrC}_6\text{H}_6$ (-0.69 V).

(b) Addition of Nucleophiles

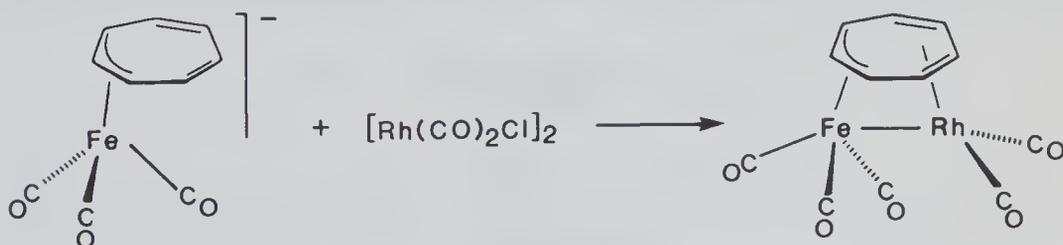


(c) Ring Contraction



Labeling experiments prove that the six-membered ring is formed from the tropylium ring rather than from the cyclopentadienyl ring, since reaction with $\text{NaC}_5\text{H}_4\text{CH}_3$ also gives (benzene) $\text{Cr}(\text{CO})_3$ whereas treatment of $[\text{C}_7\text{H}_6\text{CH}_3\text{Cr}(\text{CO})_3]^+$ with NaC_5H_5 generates (toluene) $\text{Cr}(\text{CO})_3$ (Pauson, 1961).

(d) Formation of Dinuclear Complexes



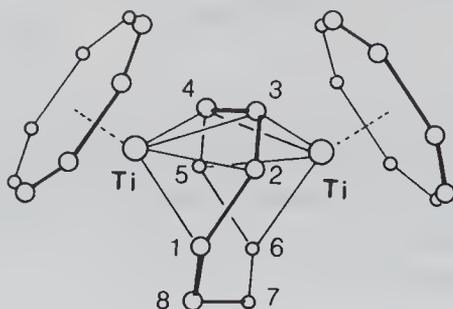
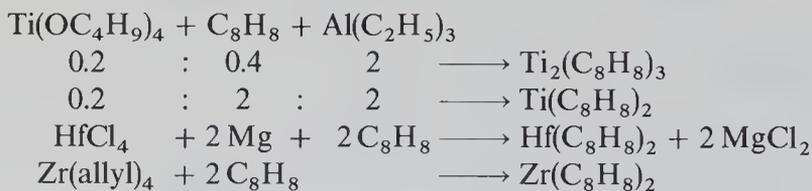
Partially coordinated seven-membered rings can form additional bonds to a second transition metal. This quite often results in the formation of a metal-metal bond as well as fluxional behavior of the bridging ligand (Takats, 1976).

15.4.6 C_8H_8 as a Ligand

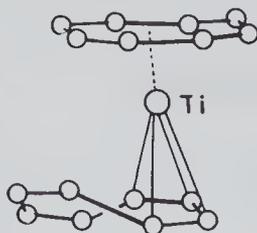
In its versatility as a ligand, C_8H_8 (COT) resembles the acetylenes. The variety of COT complex chemistry is due to the following facts:

- C_8H_8 can coordinate as a tub-shaped tetraolefin or as a planar aromatic anion $C_8H_8^{2-}$
- Potential coordination modes are η^2 , η^4 , η^6 and η^8 (in binuclear complexes also η^3 and η^5).
- C_8H_8 can function as a bridging ligand, supporting either syn- or anti-coordination.
- As an $8e(C_8H_8)$ or a $10e(C_8H_8^{2-})$ ligand cyclooctatetraene forms complexes with metals from the actinoid- and lanthanoid series, in which, in varying degrees, metal f orbitals contribute to bonding.

COMPLEXES WITH PLANAR C_8H_8 RINGS



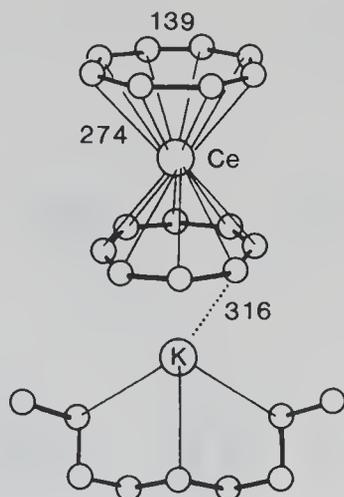
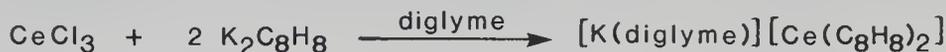
μ -[1-4 η :3-6 η - C_8H_8] [(η^8 - C_8H_8)Ti] $_2$: yellow crystals, very air-sensitive, paramagnetic. One double bond of the bridging ligand remains uncoordinated; two carbon atoms are coordinated to **both** titanium atoms (Dietrich, 1966).



(η^8 - C_8H_8) (η^4 - C_8H_8)Ti: Violet crystals, very air-sensitive. One COT ring is planar (all $d(C-C) = 141$ pm), while the other is puckered and bonded in a butadiene-like fashion. In solution, *fluxional behavior* is observed (Wilke, 1966).

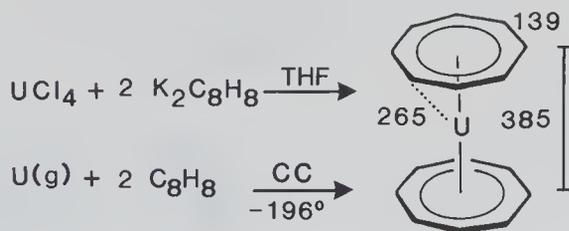
The cyclooctatetraene complexes of the lanthanoids and actinoids are of particular interest. A comparison of the two series reveals a marked difference in the extent to which

f orbitals participate in metal-ligand bonding. The 4*f* orbitals of the lanthanoids have no radial nodes and are deeply buried in the atomic core, so that their overlap with ligand orbitals is negligible. Therefore, the metal-ligand bond in lanthanoid-C₈H₈ complexes is predominantly ionic. In actinoid-C₈H₈ complexes, on the other hand, a considerable contribution from covalent interactions may be assumed since the 5*f* orbitals are subject to less shielding than 4*f* orbitals and therefore overlap more extensively with the ligand orbitals. Examples:



[K(diglyme)] [Ce(C₈H₈)₂]: Pale-green crystals, paramagnetic, air- and moisture-sensitive. Both COT rings are planar and oriented in *staggered* conformation, symmetry *D*_{8d}. The solvated K⁺ ion in this contaction- pair is attached centrosymmetrically to one of the COT rings. This type of structure is realized by a number of *lanthanoidocenes* (Raymond, 1972).

“**Uranocene**” (Streitwieser, Müller-Westerhoff, 1968):



U(C₈H₈)₂: Green crystals, paramagnetic, pyrophoric, but *stable to hydrolysis*.

Structure: uniform, planar COT rings which are oriented in an *eclipsed* conformation, symmetry *D*_{8h}, *d*(C–C) = 139 pm (Raymond, 1972).

ELECTRONIC STRUCTURE AND BONDING

(η^8 -C₈H₈)₂U is a 22 VE complex (8 + 8 + 6 or 10 + 10 + 2). Whereas for sandwich complexes of the d metals, this electron configuration would lead to the occupation of antibonding MO's (cf. the MO scheme of ferrocene p. 320), in the case of *f* metals further bonding MO's, capable of accepting additional electrons, can be formed through interac-

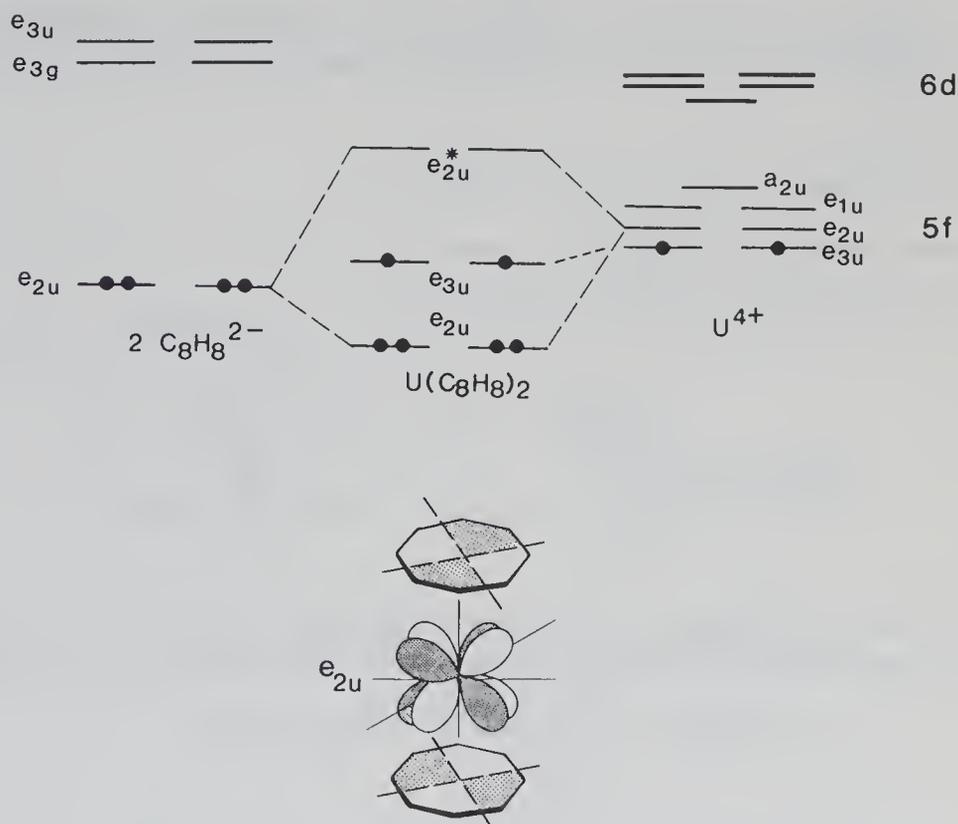
tions of symmetries e_2 and e_3 . In the following survey symmetry-adapted linear combinations (SALC) of the π MO's of two parallel $C_8H_8^{2-}$ ligands are matched with the appropriate metal orbitals:

$C_8H_8^{2-}$		$C_8H_8^{2-}$	Metal-AO			
Occupation	Symmetry*	SALC	Metal AO's with the same symmetry as the SALC		Metal- C_8H_8 Bond type	
—	b_{2u}		—			
==	e_{3g}		e_{3u}		5f	φ
=••	e_{2u}		e_{2u}		5f	δ
			e_{2g}		6d	δ
=••	e_{1g}		e_{1u}		7p	π
			e_{1g}		6d	π
•••	a_{2u}		a_{2u}		7p	σ
			a_{1g}		6d	

* For the sake of clarity, ligand MO's are shown from above. Their phases invert in the plane of the paper (= nodal plane).

The energetic sequence in the MO scheme for uranocene up to the level e_{2g} qualitatively resembles that for ferrocene (p. 320). However, instead of the essentially nonbonding level a_{1g} (Fe, $3d_{z^2}$) which follows in ferrocene, uranocene possesses molecular orbitals which are derived from C₈H₈ – U($5f$) interactions, namely the frontier orbitals e_{2u} and e_{3u} . Thus, for the 22 VE complex uranocene, a triplet ground state ensues.

Frontier orbitals for uranocene and related complexes (adapted from Streitwieser, 1973):



Interactions of symmetry e_{2u} cannot occur in sandwich complexes of the d metals. In the case of f metals, they allow the covalent bonding of large, electron-rich π perimeters.

Apart from uranocene, other **actinoidocenes** have also been prepared. The magnetic moments of these complexes can be rationalized on the basis of the above MO scheme.

Th(C ₈ H ₈) ₂	= 20 VE diamagnetic
Pa(C ₈ H ₈) ₂	= 21 VE paramagnetic
U(C ₈ H ₈) ₂	= 22 VE paramagnetic
Np(C ₈ H ₈) ₂	= 23 VE paramagnetic
Pu(C ₈ H ₈) ₂	= 24 VE diamagnetic

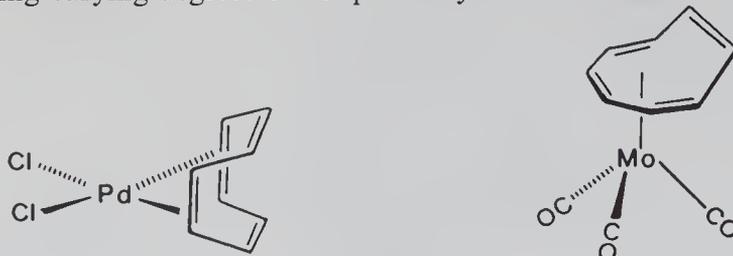
C_8H_8 also occurs in sandwich complexes of mixed ring size:



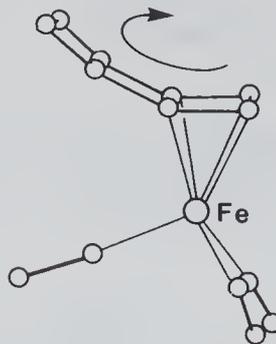
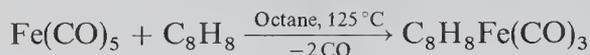
$C_5H_5TiC_8H_8$, prepared from $CpTiCl_2$ and $C_8H_8^{2-}$ in THF, is obtained as green paramagnetic crystals with one unpaired electron. Structure: centrosymmetrically bonded five- and eight-membered rings (Kroon, 1970).

COMPLEXES WITH NON-PLANAR C_8H_8 RINGS

In numerous cases, C_8H_8 ligates like a mono-, di- or triolefin to a transition metal, thereby exhibiting varying degrees of nonplanarity:

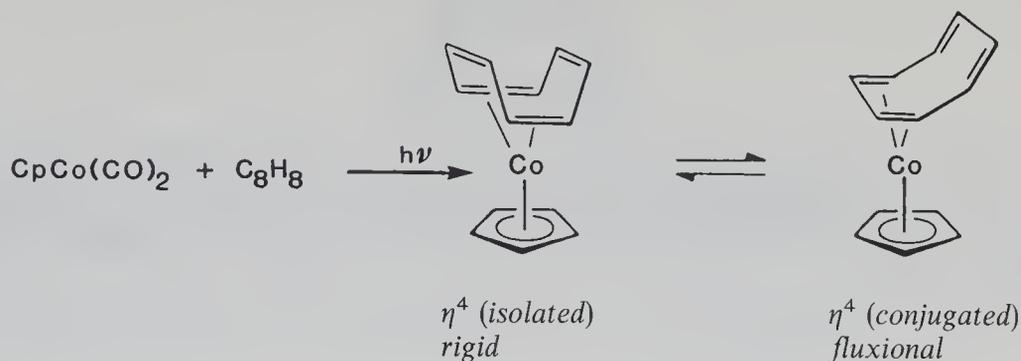


The coordination of conjugated double bonds in the C_8H_8 molecule to a metal frequently results in fluxionality. $(\eta^4-C_8H_8)Fe(CO)_3$ was a subject of long-standing controversy:

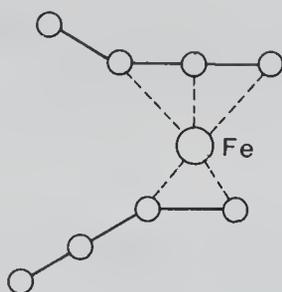
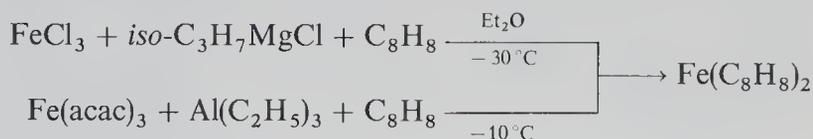


This complex cannot be catalytically hydrogenated although it appears to contain two free $C=C$ double bonds. In the 1H -NMR spectrum, a single line is observed, even at low temperatures, the slow-exchange limit (cf. p. 303) not being reached even at -150°C . The ^{13}C -NMR spectrum, on the other hand, at $T < -110^\circ\text{C}$ displays four signals for the $\eta^4-C_8H_8$ ring which merge into a single line at -60°C , $E_a = 34 \text{ kJ/mol}$ (Cotton, 1976). The ring rotation apparently involves simultaneous ring distortion, so that the geometry of the complex is retained despite successive 1,2 shifts. There are indications that fluxionality continues even in the solid state (Fyfe, 1972).

In cases where there is only partial coordination of a C_nH_n perimeter to a transition metal, isomerism can arise. CpCoC₈H₈ is an inseparable mixture of (1,2η : 5,6η-C₈H₈)CoCp and (1-4η-C₈H₈)CoCp, which slowly interconvert. The 1-4η complex, like (η⁴-C₈H₈)Fe(CO)₃, is fluxional in solution (Geiger, 1979):

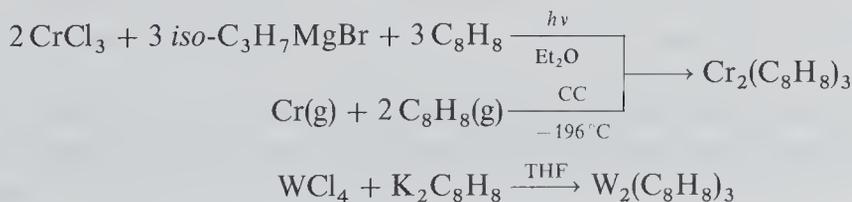


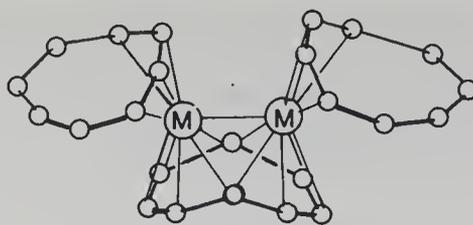
Two different bonding modes of cyclooctatetraene to the same central metal are present in Fe(C₈H₈)₂:



Black crystals, very air-sensitive, active as an oligomerization catalyst. Crystal structure of Fe(C₈H₈)₂: One COT ring coordinates with 3 double bonds (η⁶), the other COT ring with 2 double bonds (η⁴). The complex is fluxional in solution.

In a number of binuclear complexes, cyclooctatetraene acts as a **bridging ligand**, e.g. in the binary complexes M₂(C₈H₈)₃ (M = Cr, Mo, W):



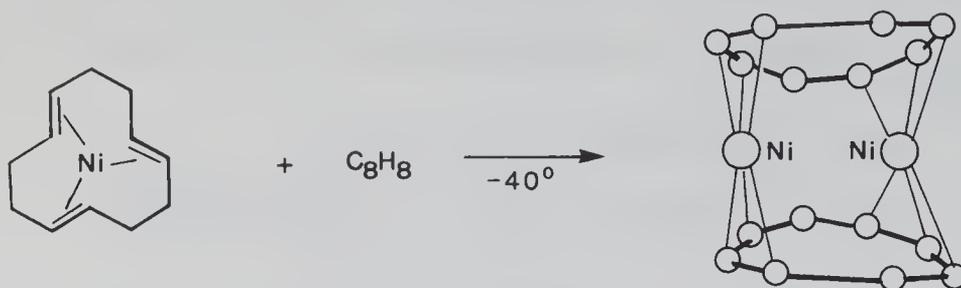


$$d(\text{Cr-Cr}) = 221 \text{ pm}$$

$$d(\text{W-W}) = 237 \text{ pm}$$

In both the $\text{M}_2(\text{C}_8\text{H}_8)_3$ complexes, the terminal rings are only η^4 -coordinated (Krüger, 1976). Under the assumption of a metal-metal triple bond, the metals attain an 18 VE shell. Both complexes are fluxional in solution, $^1\text{H-NMR}$: singlet, δ 5.26 ppm. Obviously, all three COT rings participate in the structural dynamics.

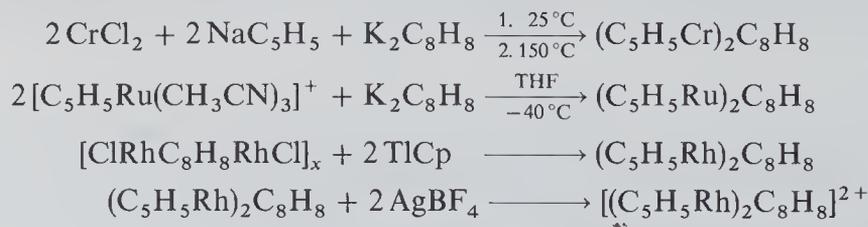
The C_8H_8 ligands in $\text{Ni}_2(\text{C}_8\text{H}_8)_2$ are exclusively bridging:



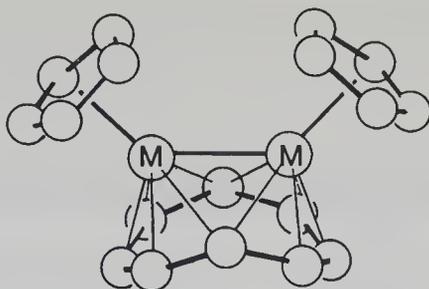
Both nickel atoms are coordinated in an η^3 -allyl fashion; due to disorder problems, the Ni–Ni distance could only be approximated (272–295 pm) (Krüger, 1976).

An interesting aspect of **cyclooctatetraene bridging** is the occurrence of **syn- and anti-variants**. The most thoroughly studied complexes in this respect are those of the composition $(\text{C}_5\text{H}_5\text{M})_2\text{C}_8\text{H}_8$ ($\text{M} = \text{V}, \text{Cr}, \text{Fe}, \text{Ru}, \text{Co}, \text{Rh}$).

Preparative examples:

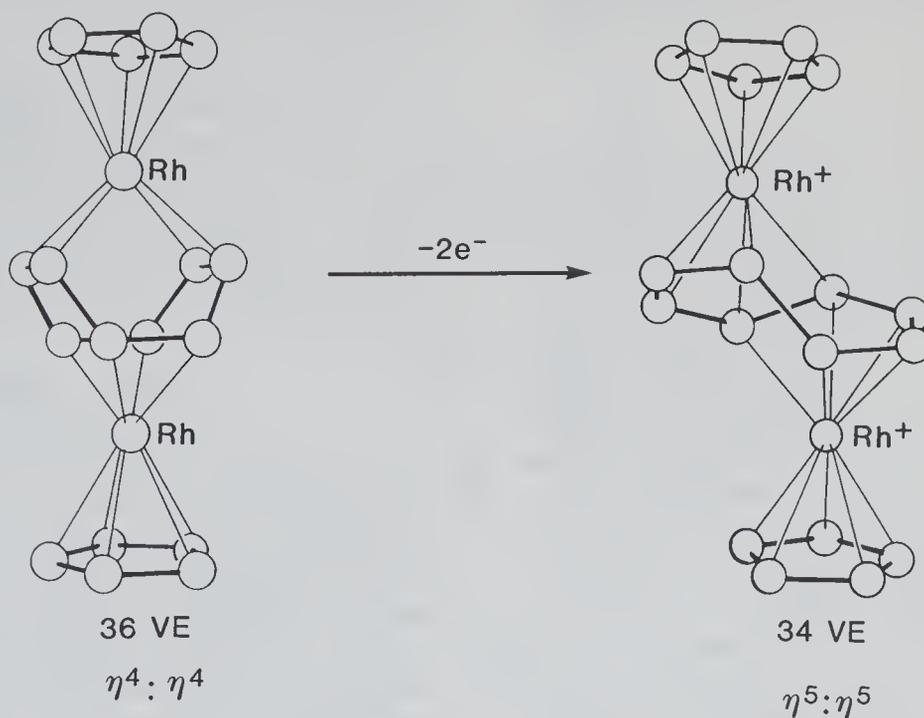


In $(\text{C}_5\text{H}_5\text{Co})_2\text{C}_8\text{H}_8$ and $(\text{C}_5\text{H}_5\text{Rh})_2\text{C}_8\text{H}_8$ (36 VE), where both metal atoms are *anti*-coordinated, each metal is bonded to a separate pair of non-conjugated double bonds of the tub-shaped C_8H_8 ring, ($\eta^4 : \eta^4$). On oxidation, the rhodium complex forms a stable



The complexes $(C_5H_5V)_2C_8H_8$ and $(C_5H_5Cr)_2C_8H_8$ possess almost identical structures: in the chromium complex (30 VE), the bridging C_8H_8 ring consists of two virtually planar C_5 moieties which are inclined at a dihedral angle of 134° , and which have two carbon atoms in common. The Cr–Cr bond (239 pm) is formulated as a double bond. The vanadium complex (28 VE, $d(V-V) = 244$ pm) should contain a V–V triple bond if 18 VE shells are to be attained by the vanadium atoms. $(C_5H_5)_2VC_8H_8$ shows slight temperature-dependent paramagnetism, however, thereby implying that the “third V–V bond” is weak (J. Heck, 1983).

dication (34 VE), in which two carbon atoms of the C_8H_8 ring are coordinated to **both** metal atoms, ($\eta^5 : \eta^5$) (Geiger, Rheingold, 1984). This “slipped-tripledecker” structure is also found for the isoelectronic complex $(C_5H_5Ru)_2C_8H_8$ (Salzer, 1986).



By way of summary it can be stated that for complexes of the type $(C_5H_5M)_2C_8H_8$ **decreasing number of valence electrons** leads to more **closed structures**. This trend is already noticeable from the structural change which accompanies the oxidation of $(C_5H_5Rh)_2C_8H_8$ (36 VE \rightarrow 34 VE, see above) and leads to dramatic results once 30 VE- and 28 VE configurations are reached in that a change from *anti*- to *syn*-coordination and concurrent formation of metal-metal bonds occurs.

Excursion:

Transition Metal NMR in Organometallic Chemistry

As in the chemistry of main-group organo-metallics (cf. p. 24, 73, 122) for the transition elements as well, NMR spectroscopy of metal nuclei increasingly gains in importance. In the sequel a few characteristics and applications will be outlined, using two representative examples, namely ^{57}Fe (2.2%, $I = 1/2$) and ^{59}Co (100%, $I = 7/2$). To underline the significance of transition metal NMR, it should be remembered that it was the detection of the magnetic resonance of ^{59}Co nuclei which led to the discovery of the chemical shift phenomenon (Proctor, Yu, 1951).

^{57}Fe -NMR

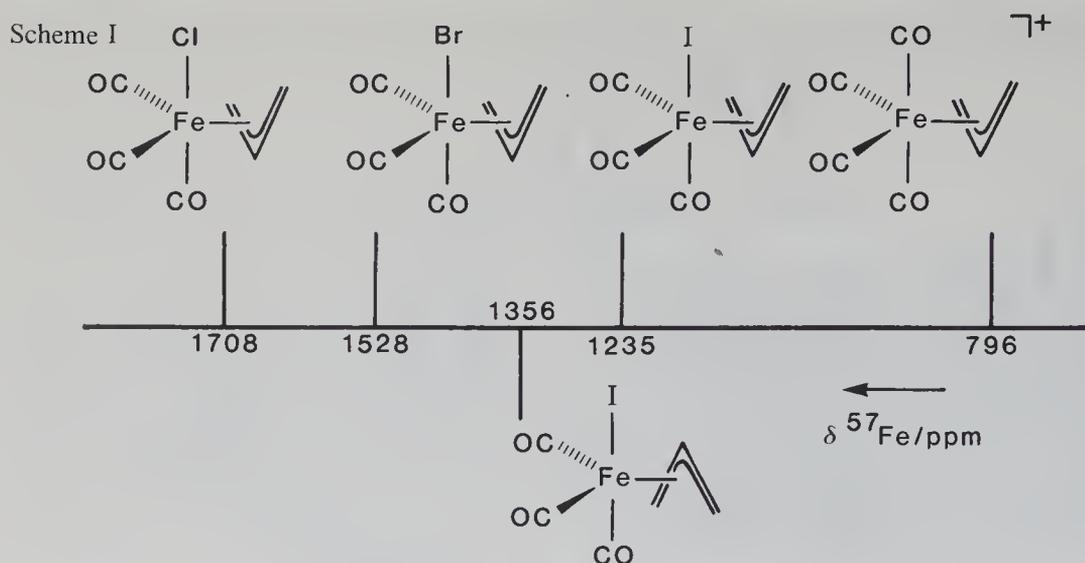
The relative receptivity of ^{57}Fe amounts to only 0.4% of that of ^{13}C and the nuclear spin $I = 1/2$ of ^{57}Fe , because of the absence of quadrupolar relaxation, may lead to saturation problems with concomitant low signal intensity. Nevertheless, the availability of high-field spectrometers equipped with superconducting magnets, special pulse techniques like the steady-state method, and polarization transfer experiments have rendered NMR studies on $I = 1/2$ nuclei with small magnetic moments like ^{57}Fe , ^{103}Rh or $^{107,109}\text{Ag}$ feasible. The pronounced increase in sensitivity achieved at high magnetic fields is a result of the more favorable Boltzmann distribution and the more efficient T_1 relaxation. For $I = 1/2$ nuclei in strong magnetic fields B_0 , the relaxation rate is dominated by the anisotropy of the chemical shift, $1/T_1$ being proportional to B_0^2 . In the case of

Rh- and Fe diolefin complexes in a magnetic field of strength $B_0 = 9.4\text{ T}$, nuclear spin lattice relaxation times T_1 are usually shorter than 20 s (for Fe^{II} porphyrins, T_1 may even be as low as 0.02 s). Transition metal NMR can then be detected even with conventional Fourier transform (FT) techniques (Benn, 1986 R).

The **chemical shifts** $\delta^{57}\text{Fe}$ for diamagnetic compounds of iron encompass a range of about 12000 ppm. As an external standard, $\text{Fe}(\text{CO})_5$ is usually employed. $\text{Fe}(\text{CO})_5$ absorbs at the upper end of the field scale. In the survey (p. 371) a few inorganic coordination compounds of iron have been included for comparison. Since the paramagnetic shielding term σ_i^{para} dominates, the chemical shifts $\delta^{57}\text{Fe}$ of many iron complexes may be interpreted by means of Eq. (2) (p. 296) under the assumption of a mean excitation energy ΔE :

$$\delta_i \sim -\sigma_i^{\text{para}} \sim \langle r^{-3} \rangle_{nd} (Q_i + \sum_{i \neq j} Q_j) / \Delta E$$

Accordingly, the chemical shift $\delta^{57}\text{Fe}$ depends on the electron density at the nucleus (Q_i), the bond orders ($\sum Q_j$), the mean electronic excitation energy ΔE and the mean distance of the valence d electrons from the nucleus (for transition metals with partially filled d shells, the contribution from p electrons can be neglected). Therefore, **deshielding**, which is 1500 ppm stronger in ferrocene, as compared to $(\text{butadiene})\text{Fe}(\text{CO})_3$, may be rationalized by the **smaller HOMO-LUMO gap** ($\delta \Delta E = 0.2\text{ eV}$) in the former as compared to the latter. An additional



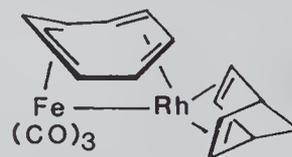
contribution to the deshielding is the smaller charge density on the central metal in ferrocene, formally an Fe^{II} compound.

The dependence of the chemical shift on the **oxidation state of the metal** is a general trend, resonances of Fe^{II} compounds occurring at low fields and those of Fe^0 compounds at intermediate and higher fields. If electronegative atoms are directly bonded to the metal, particularly large deshielding is observed [examples: $(\eta^4\text{-phenylbutene-3-one})\text{Fe}(\text{CO})_3$, Fe^{II} (porphyrine) complexes]. In the series $(\text{allyl})\text{Fe}(\text{CO})_3\text{X}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$, the chemical shifts $\delta^{57}\text{Fe}$ correlate with the electronegativity of the halogen (Scheme I).

The influence, **charge density on the central metal** exerts on its magnetic shielding also manifests itself in the fact that the chemical shift range for neutral olefin- or diolefin iron carbonyl complexes

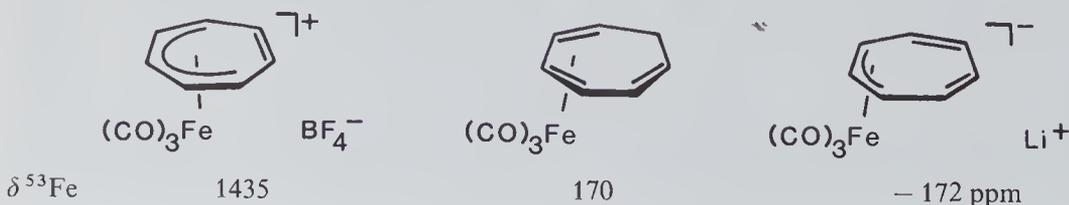
($550 > \delta^{57}\text{Fe} > -600$ ppm) clearly differs from the range for the complexes $[(\text{allyl})\text{Fe}(\text{CO})_4]^+$ and $[(\text{dienyl})\text{Fe}(\text{CO})_3]^+$ ($1500 > \delta^{57}\text{Fe} > 600$ ppm). This charge dependence is convincingly demonstrated by the $\delta^{57}\text{Fe}$ values for a series of structurally related but differently charged species (Scheme II).

As an application of ^{57}Fe -NMR, consider the binuclear complex $(\text{CO})_3\text{Fe}(\mu\text{-C}_7\text{H}_7)\text{Rh}(\text{C}_7\text{H}_8)$ which results from the reaction between $[(\text{C}_7\text{H}_7)\text{Fe}(\text{CO})_3]\text{Li}$ and $[(\text{norbornadiene})\text{RhCl}]_2$.



A comparison of the $\delta^{57}\text{Fe}$ values for $[(\text{C}_7\text{H}_7)\text{Fe}(\text{CO})_3]^-$ and the binuclear product suggests that in the latter, no charge equilibration between the electron rich Fe^0 atom (18 VE) and Rh^{I} (16 VE) takes place (Salzer, v. Philipsborn, 1982).

Scheme II



Contrary to expectation, the iron nucleus in protonated ferrocene and in ferrocenylcarbenium ions (p. 329) is strongly shielded as compared to ferrocene. This contradicts simple arguments which take only inductive effects into consideration; in fact, rehybridization of non-bonding Fe(3d) orbitals is generally deemed responsible for this unusual shielding (Koridze, 1983).

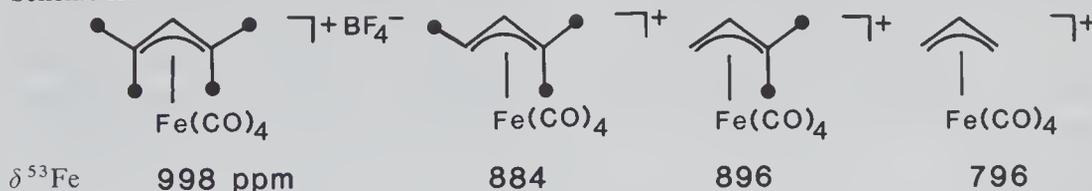
These examples clearly show that in order to rationalize chemical shifts of metal nuclei, all contributions to the paramagnetic shielding term must be assessed.

An interesting **stereoelectronic effect** is the dependence of the shifts $\delta^{57}\text{Fe}$ on olefin geometry and on the presence of alkyl substituents (v. Philipsborn, 1986 R):

$\delta^{57}\text{Fe}$ Values for (diene)Fe(CO)₃ Complexes

Diene	$\delta^{57}\text{Fe}$	Diene	$\delta^{57}\text{Fe}$
Cyclobutadiene	-583	Buta-1,3-diene	0
Cyclohexa-1,3-diene	-72	Isoprene	+54
Cyclohepta-1,3-diene	+86	<i>trans</i> -Penta-1,3-diene	+31
Cycloocta-1,3-diene	+169	<i>cis</i> -Penta-1,3-diene	+119
Cyclopentadiene	+185	2-Methylpenta-2,4-diene	+179
Norborna-1,4-diene	+382	Hexa-2,4-dienal	+378
Cycloocta-1,5-diene	+380	Hexa-1,3-dien-5-on	+335

Scheme III



For the iron carbonyl complexes of cyclic diolefins, with increasing ring size, i.e. with increasing CCC bond angle in the *s-cis*-diene segments, deshielding of the ^{57}Fe nucleus increases. For 1,3-dienes, this effect is usually more pronounced than for 1,4- or 1,5-dienes. (Cyclopentadiene)Fe(CO)₃, whose ligand may be regarded either as a 1,3- or a 1,4-diene, assumes an intermediate value for $\delta^{57}\text{Fe}$.

Methylsubstitution at (butadiene)-Fe(CO)₃ causes deshielding of the ^{57}Fe resonance, a finding which cannot be explained by inductive effects. Instead, a correlation of $\delta^{57}\text{Fe}$ with changes in ligand geometry applies. Thus, strongest deshielding of the ^{57}Fe nuclei is displayed by those complexes which possess diene ligands with carbon atoms most extensively rehybridized towards a higher *p* orbital content (cf. 302). Similar deshielding effects are also encountered with methyl substituted [(allyl)Fe(CO)₄]⁺ species (Scheme III).

These deshielding stereoelectronic effects are most likely caused by modifications of metal-ligand (*d_π* - *p_π*) overlap.

A correlation of a different kind is that between thermal and ^{57}Fe -NMR spec-

troscopic behavior: for (diene)Fe(CO)₃ - as well as for [(allyl)Fe(CO)₄]⁺ higher thermal stability is paralleled by increased ^{57}Fe shielding.

^{59}Co -NMR

In contrast to most transition metals, ^{59}Co nuclei boast a very high receptivity which is comparable to that of the pro-

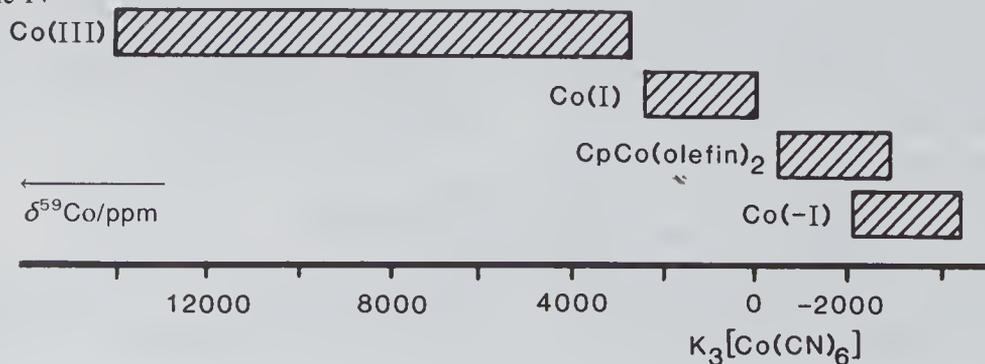
ton. ^{59}Co ($I = 7/2$) also carries a high quadrupole moment, however (p. 24). Consequently, for organocobalt compounds of low symmetry and/or of large molecular dimension, due to the large field gradient and/or slow tumbling rates in solution, very large line widths may arise (5–30 kHz), rendering the detection of ^{59}Co resonances difficult. Furthermore, chemical shifts $\delta^{59}\text{Co}$ and the line widths $W_{1/2}$ in particular are temperature- and solvent dependent. Interpretations of these NMR parameters therefore call for identical conditions of measurement.

The influence that molecular symmetry exerts on the line widths $W_{1/2}$ is exemplified by the cobalamins (p. 201):

	Conc. in mol L^{-1}	T in K	Solvent (pH)	$\delta^{59}\text{Co}$ in ppm	$W_{1/2}$ in kHz	Symmetry
K[Dicyanocobalamin]	0.06	313	D_2O (7)	4040	14.0	axial
Cyanocobalamin	0.01	313	D_2O (7)	4670	29.5	non-axial

In the axially symmetric dicyanocobalamin anion the nucleus ^{59}Co is shielded more strongly than in neutral cyanocobalamin. Moreover, the axially symmetric anion features smaller line widths (v. Philipsborn, 1986). ^{59}Co -NMR line widths therefore aid in the elucidation of molecular structure, an example being the differentiation between *cis/trans*- and *fac/mer* isomeric cobalt complexes (Yamasaki, 1968).

Scheme IV



The chemical shifts $\delta^{59}\text{Co}$ are spread over a range of 18000 ppm; they are referred to $\text{K}_3[\text{Co}(\text{CN})_6]$ as an external standard. Again, the dependence of the chemical shift on the oxidation state of the central metal is a general trend. However, because of the ambiguities which may be inherent in oxidation state assignments, there is considerable overlap between the different regions and Scheme IV should only be regarded as a crude guide line. There are also irritating exceptions: $[\text{Cp}_2\text{Co}^{\text{III}}]\text{Cl}$ absorbs at $\delta^{59}\text{Co} = -2400$ ppm, a spectral region typical for Co^{-1} complexes, and resonance for the standard $\text{K}_3[\text{Co}(\text{CN})_6]$, a Co^{III} complex, occurs at 0 ppm.

The significance of the $1/\Delta E$ factor in the paramagnetic shielding term σ_i^{para} emerges from a comparison of $\delta^{59}\text{Co}$ values for compounds of the type CpCoL_2 . Contrary to expectations based on ligand electron affinities, ^{59}Co is shielded more strongly in $\text{CpCo}(\text{CO})_2$ relative to $\text{CpCo}(\text{C}_2\text{H}_4)_2$. Apparently, the different magnitudes of the mean excitation energy ΔE dominate here. This conjecture is

supported by the results of Extended Hückel calculations according to which the HOMO-LUMO gap in $\text{CpCo}(\text{C}_2\text{H}_4)_2$ is smaller by 0.3 eV as compared to $\text{CpCo}(\text{CO})_2$ (Benn, 1985). The magnitude of the energy difference between the frontier orbitals HOMO and LUMO plays the dual role of influencing the magnetic shielding of ^{59}Co nuclei via the $1/\Delta E$ dependence, and of reflecting the strength of the metal-ligand bond. Therefore, besides correlations between ^{59}Co -NMR data and electronic spectra (Griffith, 1957) relationships between $\delta^{59}\text{Co}$ values and chemical behavior would be expected. Parallels of the latter type have in fact been observed. They can be illustrated with a recent example, the activity of organocobalt complexes in the homogeneously catalyzed synthesis of pyridine derivatives (Scheme V, Bönemann, v. Philipsborn, 1984).

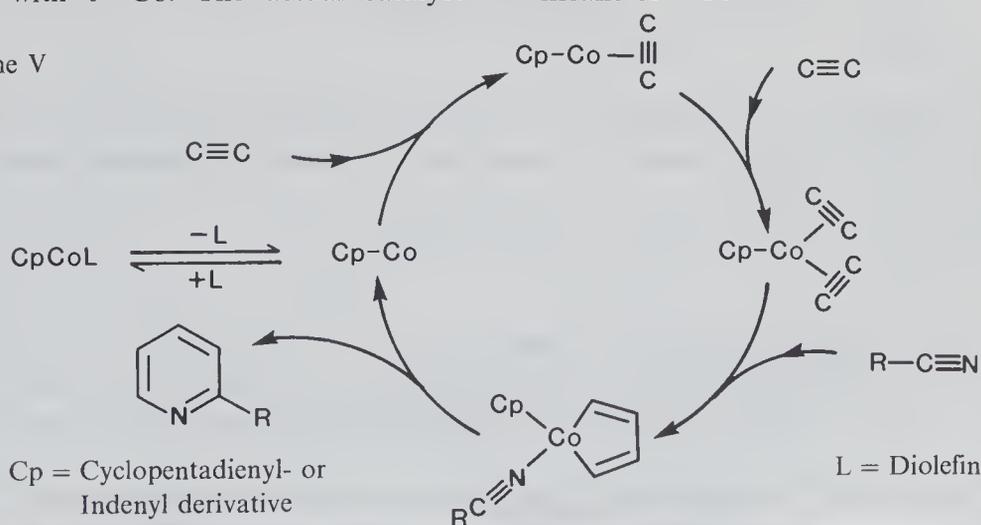
In this process, depending on the catalyst employed, singly and multiply substituted pyridine- as well as benzene derivatives are obtained from alkynes and nitriles (p. 277). For a series of complexes $(\text{R-Cp})\text{CoL}_2$ and $(\text{R-indenyl})\text{CoL}_2$ as catalyst precursors, it has been demonstrated that their activity and selectivity correlates with $\delta^{59}\text{Co}$. The actual catalyst

CpCo (14 VE) is formed via thermal ligand dissociation. **Precatalysts** of high activity, which operate even at low temperature, contain weakly shielded ^{59}Co nuclei [example: $\text{CpCo}(\text{COD})$, $\delta^{59}\text{Co} = -1176$ ppm]. The complex $\text{CpCo}(\text{cyclobutadiene})$, on the other hand, in which the central atom is strongly shielded ($\delta^{59}\text{Co} = -2888$ ppm), is catalytically ineffective. Obviously, cyclobutadiene is strongly bonded to cobalt (ΔE is large) and $\text{CpCo}(\text{C}_4\text{H}_4)$ is not capable of initiating the catalytic cycle by forming the coordinatively unsaturated species $\{\text{CpCo}\}$.

The **chemo- and regioselectivities** of these catalytic cyclizations are governed by the nature of the cyclopentadienyl ligand which remains attached to cobalt. Here as well, a correlation with NMR data was discovered in that the product ratio 1,3,5-trisubstituted-pyridine/1,2,5-trisubstituted-pyridine rises with increasing shielding of the ^{59}Co nucleus.

A quantitative interpretation of these findings is of course extremely difficult; correlations of the type discussed above are of high practical value, however, since they indicate a way to systematically search for catalytically active species by means of ^{59}Co -NMR.

Scheme V



15.5 Metal π -Complexes of Heterocycles

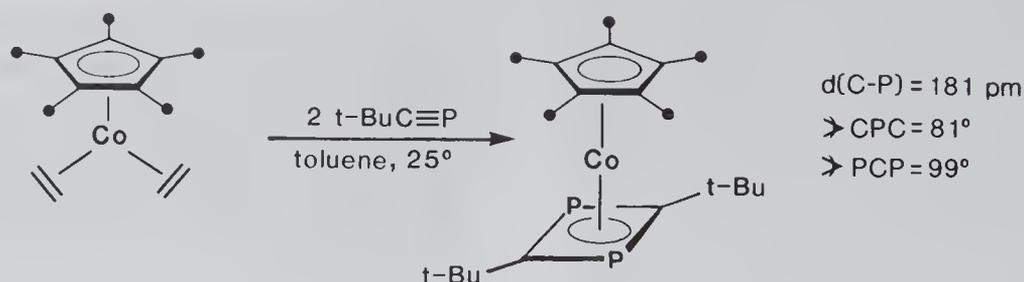
Unsaturated ring systems in which individual (or all) carbon atoms have been exchanged for heteroatoms can form transition-metal π -complexes under certain conditions. In some cases, this can also lead to the stabilization of heterocycles unknown in the free state.

15.5.1 Nitrogen-, Phosphorus- and Sulfur Heterocycles as Ligands

The ability of organic molecules containing heteroatoms like N, P, O or S to bind to transition metals is relevant in classical coordination chemistry as well as for the *in vivo* binding of metals. If the heteroatoms are part of rings such as pyridine, thiophene or the pyrrolyl anion, they usually retain their Lewis basicity and the rings tend to coordinate through their lone pairs rather than via the cyclic conjugated π system. The number of π complexes containing N-, P- and S-heterocyclic ligands is therefore relatively small compared to their carbocyclic counterparts.

FOUR-MEMBERED RING LIGANDS

The heterocycle **1,3-diphosphete** (= 1,3-diphosphacyclobutadiene), unknown in the free state, has been obtained through cyclodimerization of *t*-butylphosphaalkyne (p. 164) in the coordination sphere of cobalt (Nixon, Binger, 1986):



Like coordinated cyclobutadiene (p. 311), this 1,4-diphosphacyclobutadiene displays equal intra-ligand bond distances, although, due to unequal angles, the planar ring assumes a diamond shape.

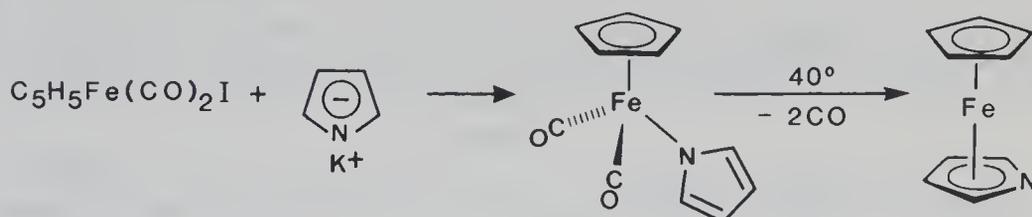
FIVE-MEMBERED RING LIGANDS

C_5H_5^- (cyclopentadienyl), $\text{C}_4\text{H}_4\text{N}^-$ (pyrrolyl), $\text{C}_4\text{H}_4\text{P}^-$ (phospholyl) and $\text{C}_4\text{H}_4\text{As}^-$ (arsolyl) are *iso*- π -electronic. The synthesis of π complexes containing these heterocycles is therefore often analogous to that of corresponding cyclopentadienyl and arene complexes.

Azacyclopentadienyl complexes can be prepared in a redox reaction from pyrrole (Pauson, 1962):

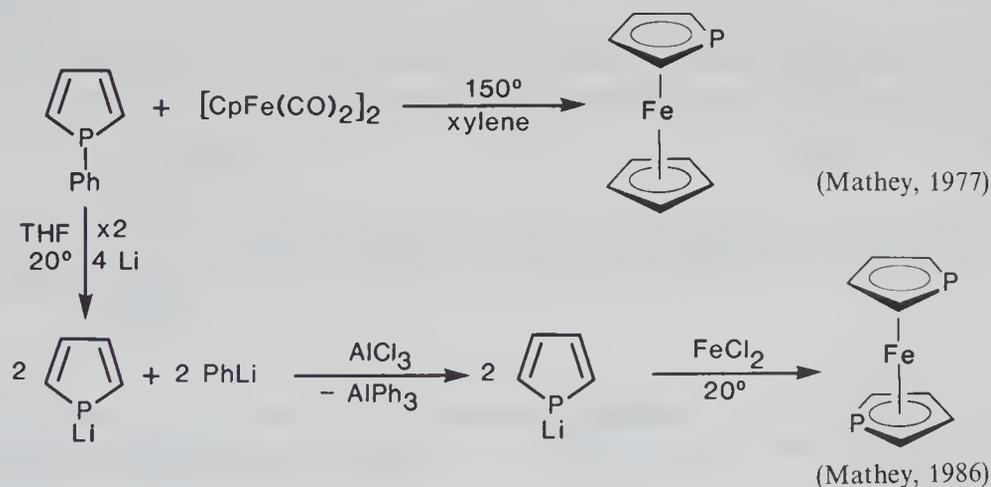


or via a preformed pyrrolyl anion (Pauson, 1964):



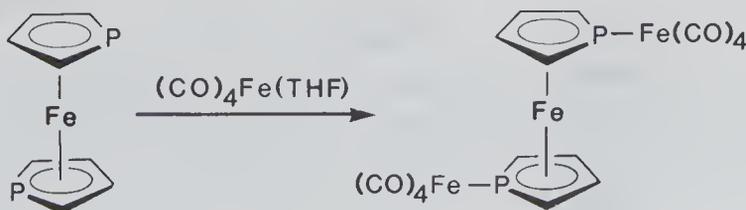
Azaferrocene ($\text{C}_5\text{H}_5\text{FeC}_4\text{H}_4\text{N}$) forms orange-red, diamagnetic, easily sublimable crystals, which are isomorphous to ferrocene. Treatment with acids leads to protonation at the nitrogen atom. Compared to C_5H_5^- , the pyrrolyl anion $\text{C}_4\text{H}_4\text{N}^-$ is a weaker π -donor and/or a stronger π -acceptor. 1,1'-Diazaferrocene is as yet unknown.

For the elements phosphorus and arsenic, however, both single and multiple incorporation of the heteroatom into the ferrocene frame has been achieved:

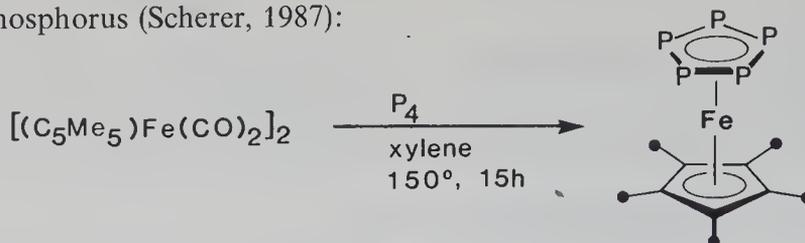


1,1'-Diarsaferrocene is accessible by the same route (Ashe, 1987).

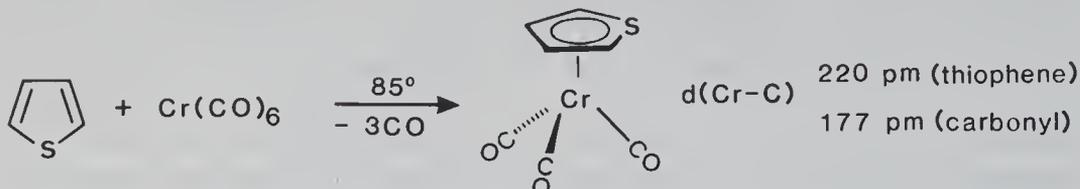
1,1'-diphosphaferrocene via its phosphorus atoms is capable of σ -donor/ π -acceptor interactions. It can act as a diphos-type chelating ligand and can become a building block for oligonuclear complexes. Example:



Pentaphosphaferrocene, is formed in a surprisingly mundane fashion using P_4 as the source of phosphorus (Scherer, 1987):



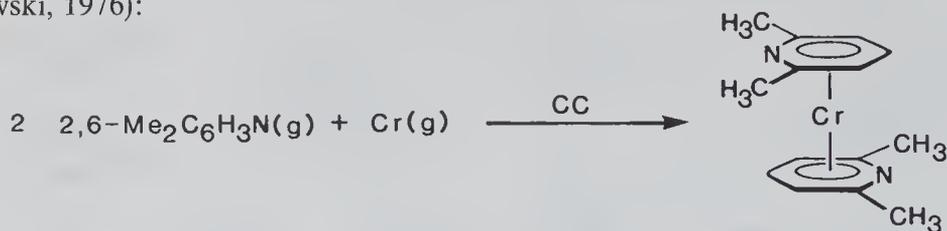
The similarity of **thiophene** to benzene also extends to coordination chemistry. Like benzene, thiophene forms $M(CO)_3$ adducts, albeit of lower stability (Öfele, 1958):



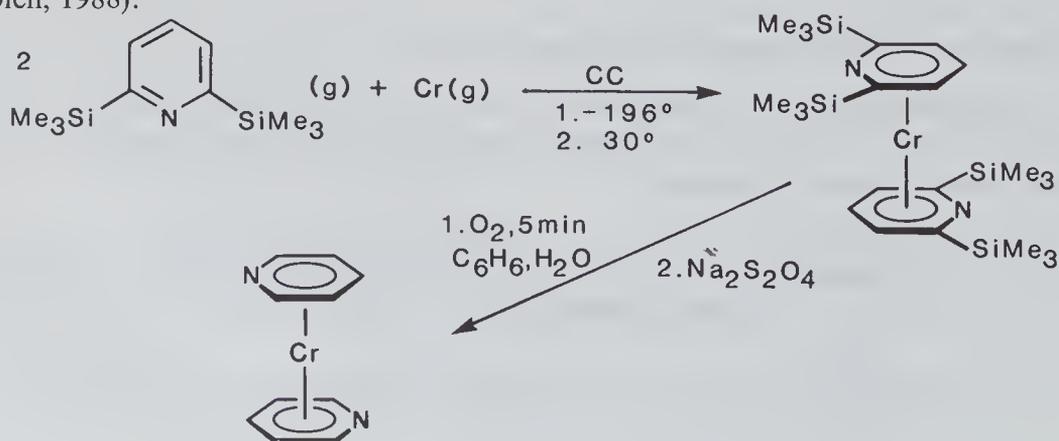
$C_4H_4SCr(CO)_3$ is obtained as orange-colored diamagnetic crystals which are isomorphous with $C_6H_6Cr(CO)_3$. Selenophene and tellurophene complexes are prepared in the same way.

SIX-MEMBERED RING LIGANDS

For **pyridine**, σ coordination via its lone pair is highly preferred over bonding which utilizes the π -electron system. Therefore, the direct synthesis of η^6 -pyridine metal complexes requires the N atom to be blocked by means of substitution in the 2,6-positions (Lagowski, 1976):



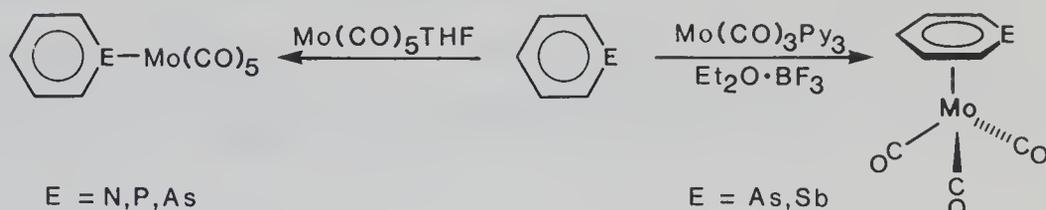
The parent complex **bis(η^6 -pyridine)chromium** can be prepared by occupying the 2,6-positions with protecting groups, which can be removed after complex formation (Elschenbroich, 1988):



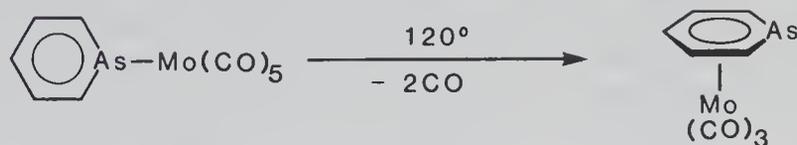
Red bis(η^6 -pyridine)chromium differs from bis(benzene)chromium in its high thermal and solvolytic lability.

Bis(η^6 -arsabenzene)chromium (η^6 -C₅H₅As)₂Cr, which can be directly prepared by metal-atom ligand-vapor cocondensation, is considerably more stable (Elschenbroich, 1986).

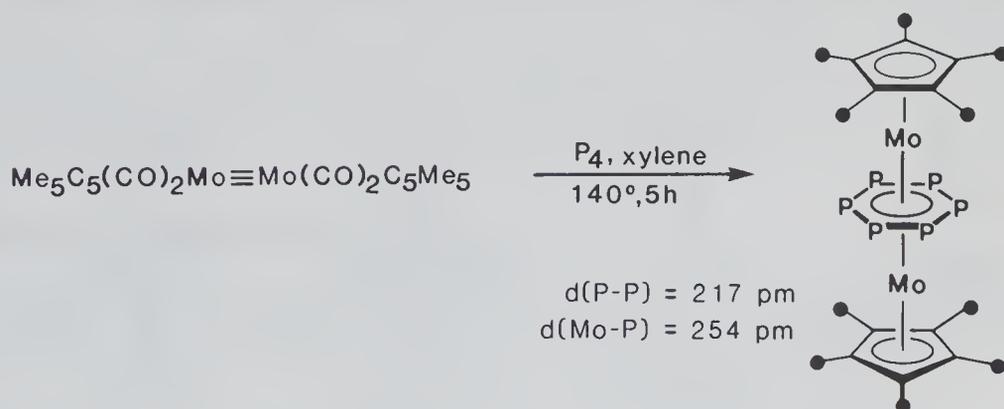
The observation that for arsabenzene, η^1 -coordination (via the As atom) is disfavored as compared to η^6 -coordination (via the π -electron system) concords with the Lewis basicities, which decrease in the order pyridine > phosphabenzene > arsabenzene. The π -donor character of the heteroarene is expected to follow an opposite trend, since the electropositive character increases in the order N < P < As. The disparate behaviour of the heteroarenes towards metal carbonyls conforms with this notion (Ashe, 1977):



Thus, as the atomic number of E increases, π coordination (η^6) dominates over σ coordination (η^1). In the particular case of arsabenzene, a $\sigma \rightarrow \pi$ rearrangement has been established:

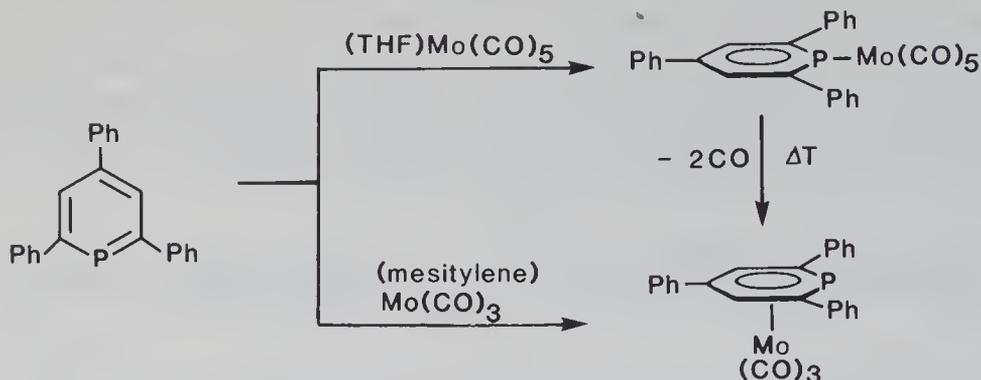


A spectacular result is the formation of **hexaphosphabenzene** P₆ as a bridging ligand in a tripledecker complex (Scherer, 1985):



The formation of the P₆ ring can be regarded as a cyclotrimerization of three |P \equiv P| units in analogy to the alkyne trimerization. The complex μ -(cyclo-P₆) [Mo(C₅Me₅)₂] is obviously related to the cyclopentaarsyne complex μ -(cyclo-As₅) [Mo(C₅H₅)₂] which has already been mentioned (p. 160). For substituted heterocycles (E = N, P, As, Sb), the

respective products formed reflect the interplay of steric and electronic effects. For example, substituted pyridines, in which N-coordination is sterically hindered, react with $\text{Cr}(\text{CO})_6$ to give $(\eta^6\text{-R}_n\text{C}_5\text{H}_{5-n}\text{N})\text{Cr}(\text{CO})_3$, while pyridine itself solely forms N-coordinated complexes $(\text{C}_5\text{H}_5\text{N})_n\text{Cr}(\text{CO})_{6-n}$ ($n = 1-3$). (1,3,5-Triphenyl)phosphabenzene, depending on the metal carbonyl precursor, gives both types of complexes (Nöth, 1973):

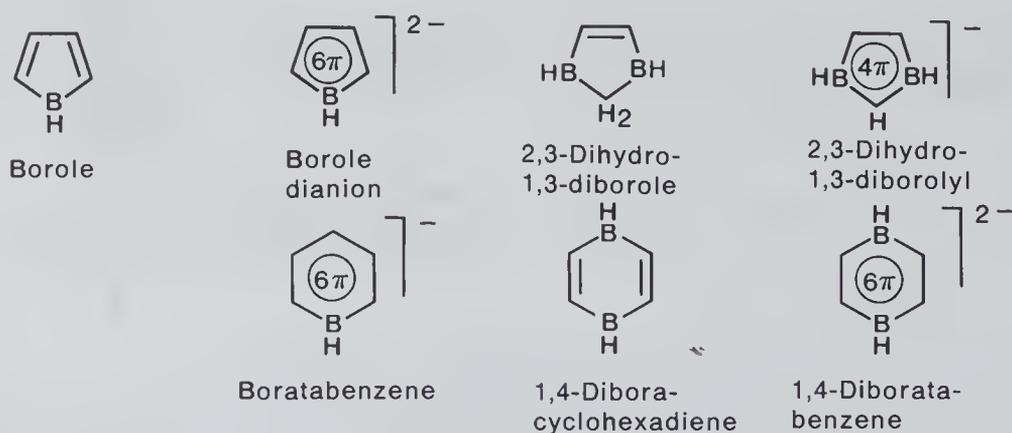


15.5.2 Boron Heterocycles as Ligands

The first transition-metal complexes of boron-containing rings were synthesized as **carbaborane-metal complexes** by Hawthorne from 1967 onwards. While these compounds, consisting of metal cations and carbaboranyl anions, in many cases parallel the corresponding cyclopentadienyl compounds (p. 72), complex fragments built from metal atoms and simple boron heterocycles excel in their ability to form stacks (**multidecker complexes**).

Not all principally conceivable B, C heterocycles have yet been realized; some hitherto have only appeared as ligands in metal complexes.

The most important B, C heterocycles, serving as ligands in organometallic chemistry, are shown below:



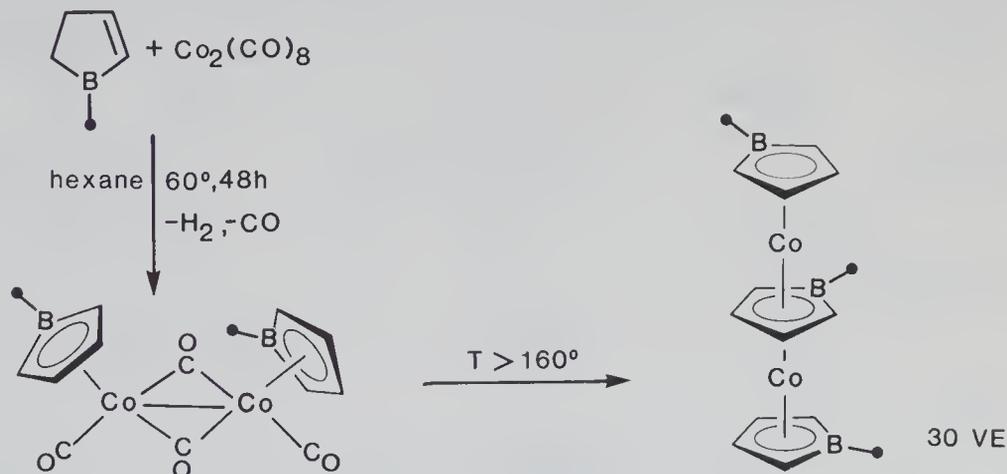
The prefix *bora-* designates the replacement of a CH fragment by B, *borata-* the replacement of CH by BH^- .

Neutral boron-carbon cycles like borole and diboracyclohexadiene have low-lying, unoccupied molecular orbitals. Consequently, these neutral ligands are strong electron acceptors, provided the substituents at boron are void of π -donor properties. The existence of anions such as boratabenzene, 1,4-diboratabenzene and the borol dianion are in keeping with this idea. In their coordination to metals, B, C heterocycles can be regarded as neutral ligands (the number of π -electrons being equal to the number of sp^2 carbon atoms) or as anions with 4 or 6 π electrons. Isoelectronic replacement of BH^- for CH relates the anionic species to carbocyclic aromatic systems (compare $C_4BH_5^{2-}$ and $C_5H_5^-$ or $C_5BH_6^-$ and C_6H_6).

HETEROCYCLES WITH ONE BORON ATOM

Borole Complexes

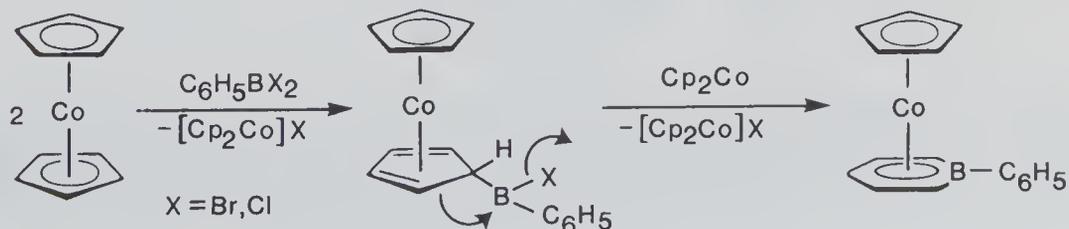
A versatile route to (η^5 -borole)metal complexes is the dehydrogenative complexation of borolenes to metal carbonyls (Herberich, 1987 R):



$[(\eta^5\text{-C}_4\text{H}_4\text{BMe})\text{Co}(\text{CO})_2]_2$ is isostructural with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ which is a consequence of the isoelectronic nature of the building units $\text{C}_4\text{H}_4\text{BMe}(4\pi) + \text{Co}(d^9)$ and $\text{C}_5\text{H}_5(5\pi) + \text{Fe}(d^8)$.

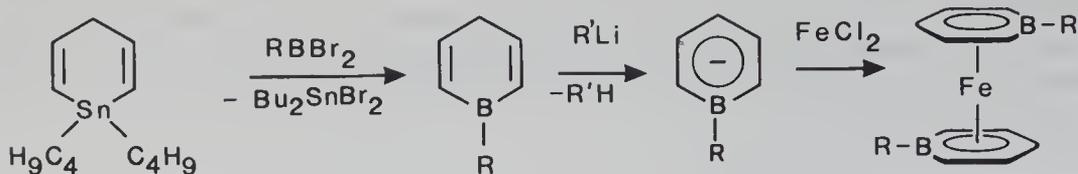
Complexes of Boratabenzene Derivatives

The first synthesis of a boratabenzene complex was accomplished by the treatment of cobaltocene with organoboron dihalides via an unusual ring expansion (Herberich, 1970):

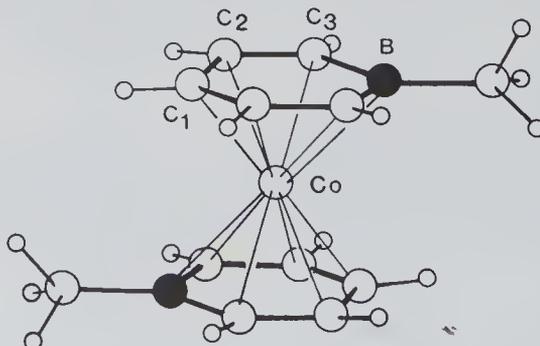
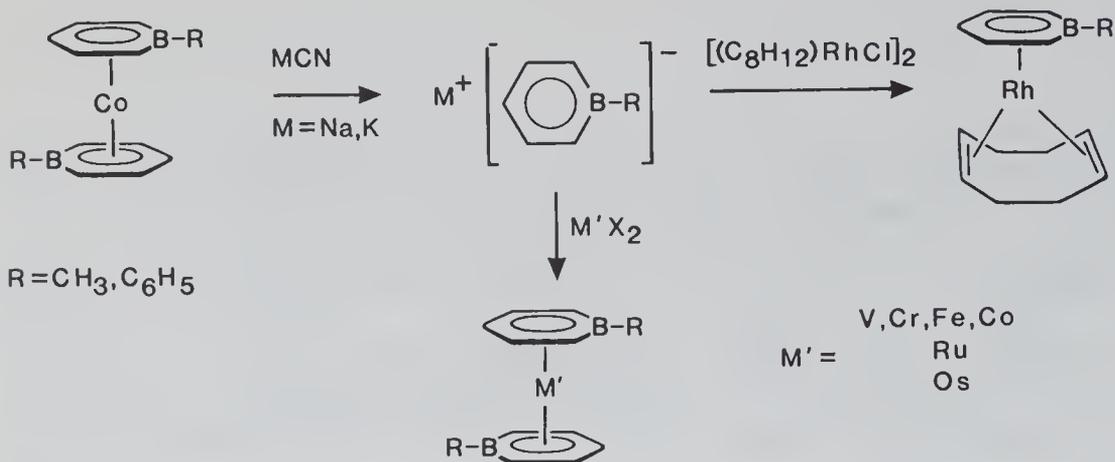


Today, boratabenzene complexes are known in a substantial number. Their preparation follows two general routes:

1. Independent Synthesis of the Boratabenzene Ligand (Ashe, 1975 R):



2. Bis(boratabenzene)cobalt as a Source for Boratabenzene (Herberich, 1976):

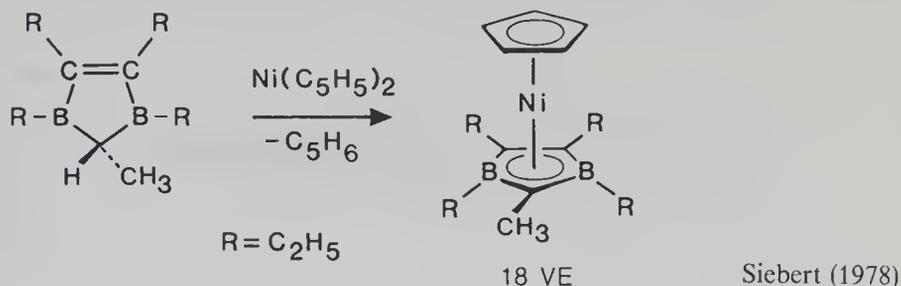


The structure of *bis(B-methyl-boratabenzene)-cobalt* reveals that the metal is not centro-symmetrically bonded, but has slipped away from boron. The differences in the M–C and M–B bond lengths are greater than would be expected from the sum of the covalent radii, $d(\text{Co}-\text{C}_1) = 208$, $d(\text{Co}-\text{C}_2) = 217$, $d(\text{Co}-\text{C}_3) = 222$, $d(\text{Co}-\text{B}) = 228$ pm (Huttner, 1972).

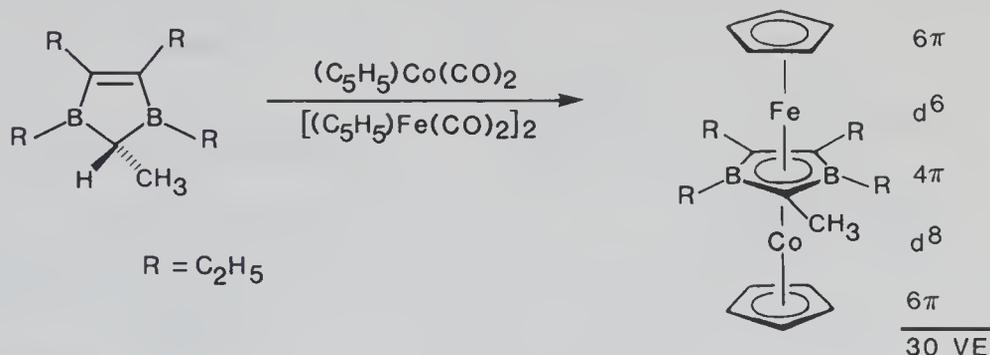
HETEROCYCLES WITH TWO BORON ATOMS

2,3-Dihydro-1,3-diborolyl Complexes

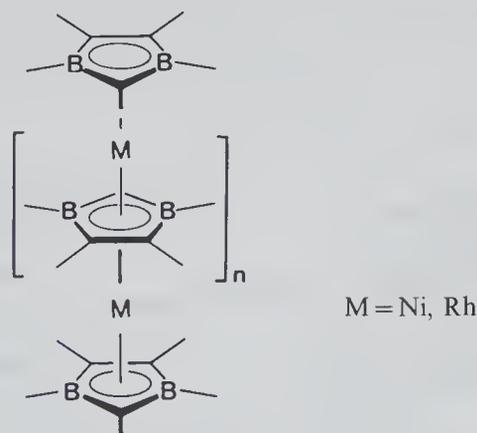
The neutral ligand 2,3-dihydro-1,3-diborole can be regarded as a neutral $3e$ ligand (after elimination of a hydrogen atom) or as an anionic $4e$ ligand (after deprotonation):



The replacement of carbon by boron appears to enhance the ability of planar ring systems to engage in bifacial coordination to metal atoms. While a characteristic of the carboranes is the formation of three-dimensional clusters with incorporation of metal atoms, the five- and six-membered rings with more than one boron atom described here show a pronounced tendency to form **multidecker complexes**. As “stacking reagents”, (cyclopentadienyl)metal carbonyls are of great utility (Siebert, 1977):



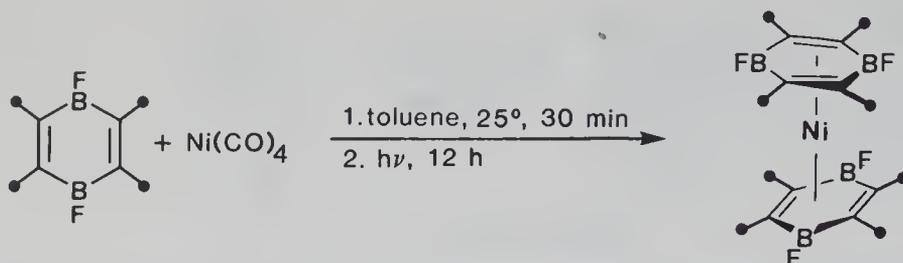
This structural type is not limited to 30 VE complexes, a complete series with 29–34 VE having been realized: FeFe(29 VE), FeCo(30 VE), CoCo(31 VE), CoNi(32 VE), NiNi(33 VE), [NiNi]⁻(34 VE).



In addition to the **tripledecker complexes**, which are now known in a large variety, **tetra-, penta-, and hexadecker complexes**, in which 1,3-diborolyl acts as the bridging ligand, have also been synthesized. The ultimate extension of this series has been reached by the preparation of **polydecker-sandwich complexes**, the nickel complex being a semiconductor and the Rh compound an insulator (Siebert, 1986).

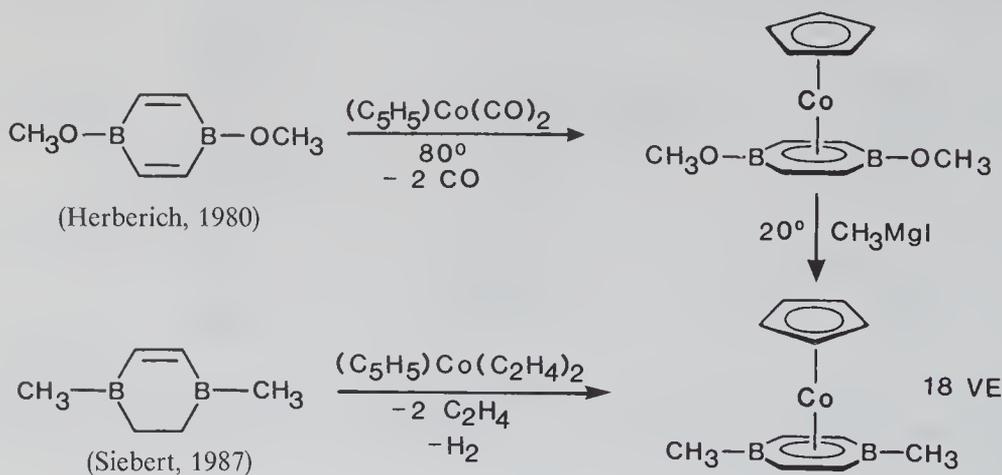
Complexes of 1,4-Diboracyclohexa-2,5-diene Derivatives

The unsubstituted heterocycle $C_4B_2H_6$ is as yet unknown. Its 1,4-difluoro-2,3,5,6-tetramethyl derivative, however, which is prepared from boron monofluoride and 2-butyne (p. 64), reacts with nickel tetracarbonyl to give a sandwich complex (Timms, 1975):

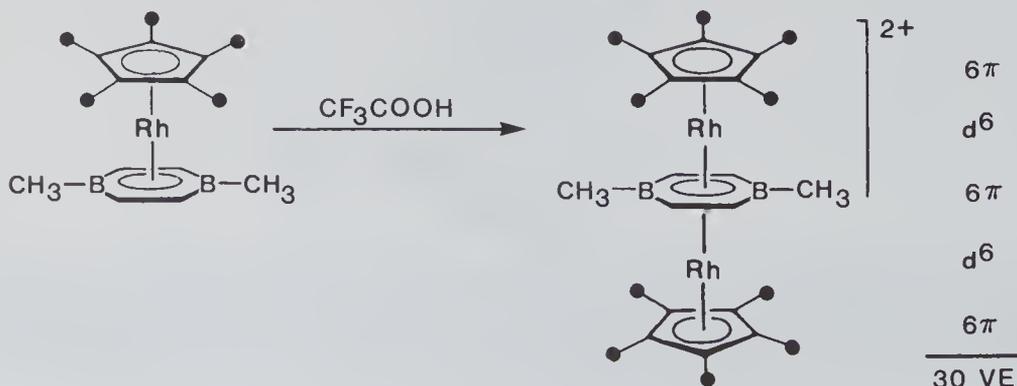


X-ray structural data point to bis- η^6 -coordination. As expected from the isoelectronic nature of $\text{>C}=\overline{\text{O}}$ and $\text{>B}-\overline{\text{F}}$, this complex is isostructural with bis(duroquinone)-nickel (Schrauzer, 1964 R).

The synthesis of a B-alkylated derivative, coordinated to Co, proceeds as follows:

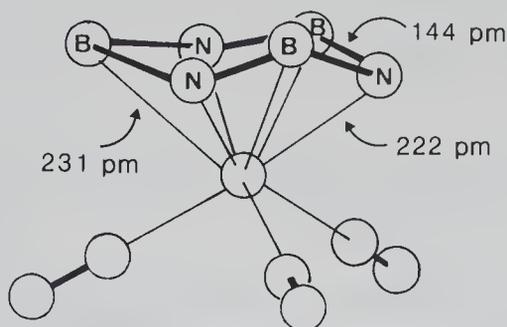
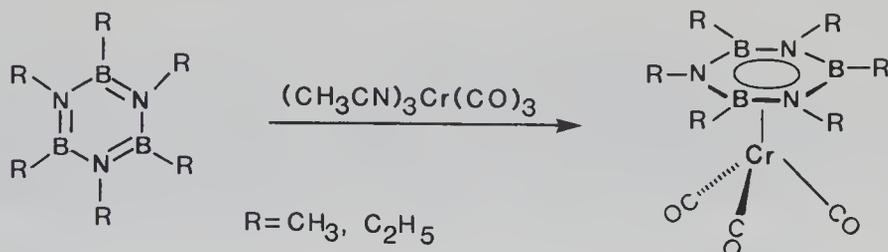


The corresponding rhodium species, upon reaction with protic acids, converts into a tripledecker complex (Herberich, 1981):



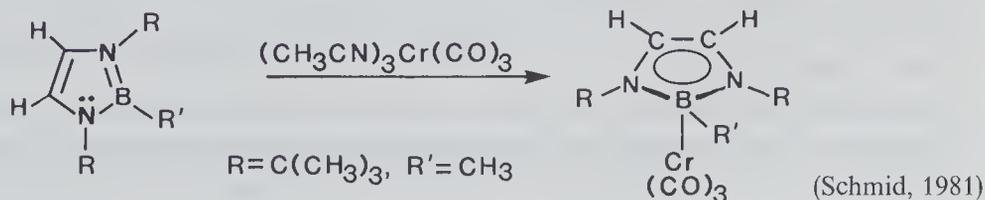
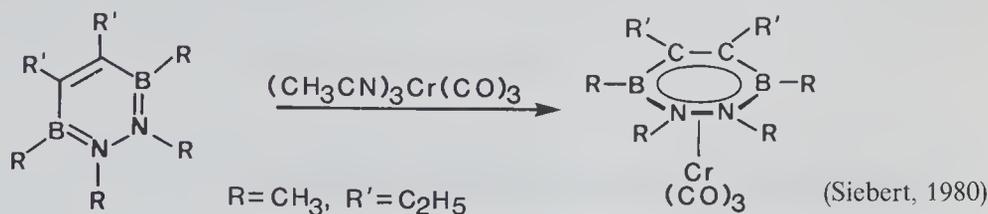
15.5.3 Boron-Nitrogen Heterocycles

Cyclo-trisborazine $B_3N_3H_6$ is occasionally referred to as “inorganic benzene”. Some of its alkyl derivatives actually form half-sandwich π -complexes which are, however, considerably less stable than the corresponding arene counterparts (Werner, 1969):



Structure of (hexaethyl-cyclo-trisborazine)Cr(CO)₃: In contrast to the free ligand, the ring is not exactly planar. The plane defined by the boron atoms deviates from the plane of the nitrogen atoms by 7 pm. The Cr-B and Cr-N distance differ to an extent which is expected from the different covalent radii of B and N. The $Cr(CO)_3$ unit is oriented such that the CO groups and the N atoms are trans-positioned (Huttner, 1971).

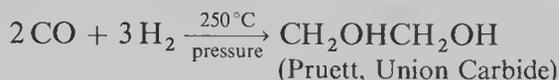
The synthesis of sandwich complexes of cyclo-trisborazine has not yet been successful. Further examples involving boron-nitrogen heterocycles as ligands are the following:



Clusters of the main-group elements (i.e. Pb_9^{4-} , Bi_3^{3+} , Te_4^{2+}) are not treated here since they are void of metal–carbon bonds.

Apart from their fascinating structures, metal atom clusters possess properties which are highly interesting for potential practical applications:

- $[\text{Rh}_{12}(\text{CO})_{34}]^{2-}$ is effective in homogeneous catalysis of the Fischer-Tropsch synthesis:



- Chevrel phases MMo_6S_8 (e.g. PbMo_6S_8) remain superconducting even in very strong magnetic fields. This is essential in the manufacture of electromagnets of extremely high field strength (Sienko, 1983 R).
- Certain clusters with $\text{M}\equiv\text{M}$ quadruple bonds display photochemical properties with possible relevance for the conversion of solar energy (H. B. Gray, 1983).
- Cluster units Fe_4S_4 are encountered in the important redox enzyme ferredoxin (p. 396).

Transition-metal atom clusters may be divided into three groups of which only group ③ will be treated in this text:

- ① **Naked clusters**, i.e. metal atoms in low states of aggregation. They are accessible in inert matrices and at low temperatures only and have to be studied by physical methods.

Example: Ag_6 .

- ② **Metal halides and oxides, the metal being in a low oxidation state.**

Examples: $[\text{Mo}_6\text{Cl}_8]^{4+}$, $[\text{Re}_3\text{Cl}_{12}]^{3-}$.

- ③ **Oligonuclear metal carbonyls, nitrosyls and mixed-ligand complexes containing cyclopentadienyl groups.**

Example: $[\text{CpFe}(\text{CO})]_4$.

Favorable conditions for the occurrence of **M–M bonds** include a **low formal oxidation state** and a **high atomic number** since under these circumstances widely protruding *d* orbitals with good overlap properties are encountered. M–M bonds are likely for elements which possess high enthalpies of atomization. In their cluster compounds these elements tend to maintain structural features of the metallic state.

Analogies between metal atom clusters and bulk metals:

- Color (many closely spaced energy levels)
- Redox activity (relationship to metallic conductivity)
- Malleability (wide range of M–M bond distances)

Diagnostic criteria for the presence of M–M bonds:

- Thermochemical data.** The chemical relevance of M–M bonds should be reflected in the thermochemical bond enthalpy $D(\text{M–M})$. Due to the difficulty in formulating correct equations for the combustion of organometallics (product analysis!), the num-

ber of experimentally determined bond enthalpies for $M \equiv M$ multiple bonds is small.

Approximate value: $D(M \equiv M) \approx 400 - 600 \text{ kJ/mol}$
 compare: $D(N \equiv N) = 946 \text{ kJ/mol}$ (N_2 molecule)
 $D(Mn - Mn) = 160 \text{ kJ/mol}$ [$Mn_2(CO)_{10}$]

- b. **Bond distances $d(M - M)$ from X-ray diffraction.** In the evaluation of a bond distance, the oxidation states of the metals involved as well as the nature of the ligands have to be taken into account. Assigning a bond order from structural data gets more difficult as the bond order increases, since with rising bond order the extent of bond shortening diminishes. Example:

	$d(Mo - Mo)$	$d(Mo = Mo)$	$d(Mo \equiv Mo)$	$d(Mo \equiv Mo)$
Cluster:	272 pm	242 pm	222 pm	210 pm
Mo(s):	278 pm			

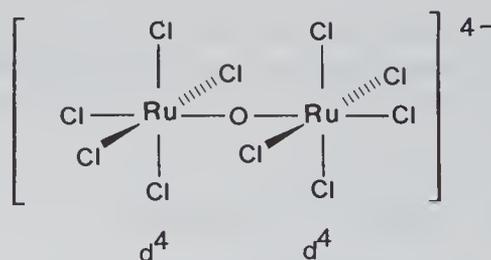
- c. **Spectroscopic data.** A measure of bond strength is also provided by the position of the metal–metal stretching mode in the Raman spectrum. Examples:

$\nu(Cr \equiv Cr)$	$\nu(Mo \equiv Mo)$	$\nu(Re \equiv Re)$
556 cm^{-1}	420 cm^{-1}	285 cm^{-1}

Considering the large masses, these are surprisingly high values.

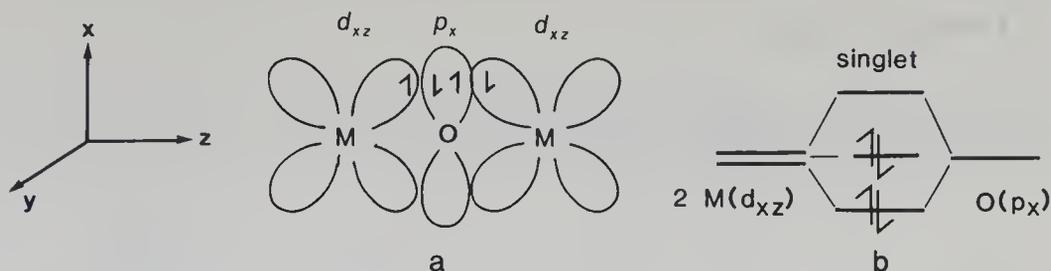
- d. **Magnetic properties.** Spin pairing is not synonymous with chemical bonding! Whereas for $Mn_2(CO)_{10}$ diamagnetism is a consequence of the metal–metal bond between the two paramagnetic units $Mn(CO)_5$ (**direct exchange**), spin pairing can also arise without direct metal–metal interaction, in which case a ligand-mediated mechanism is responsible (**superexchange**).

An example for a superexchange interaction is provided by the magnetic properties of the ion $[Ru_2OCl_{10}]^{4-}$:



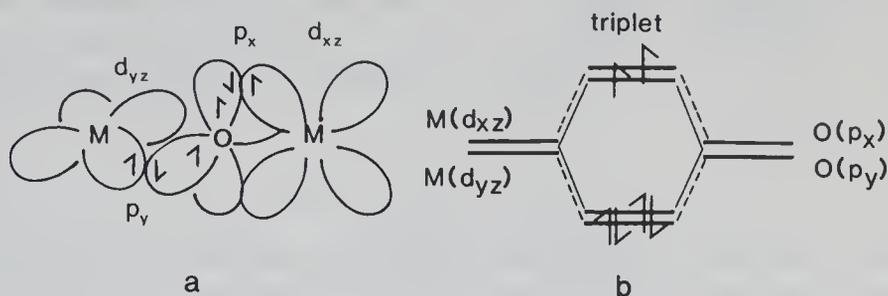
$Ru^{IV} (d^4)$ in an octahedral environment possesses the electronic configuration $(xy)^2 (xz)^1 (yz)^1$. Nevertheless, the dinuclear complex is diamagnetic.

This diamagnetism may be rationalized by the idea that in the regions where the singly occupied metal orbitals overlap with the doubly occupied orbitals of the bridging ligands, antiparallel spin orientation accrues. The result is an antiparallel disposition of the electron spins on the two metal atoms, a (**antiferromagnetic coupling**). An alternative description proceeds in terms of $4e\ 3c$ interactions which lead to a low-spin state for the dinuclear complex, **b**:



The combination $2 M(d_{yz}) + O(p_x)$ is analogous.

If, on the other hand, two **orthogonal** singly occupied **metal orbitals** contribute to the interaction, Hund's rule calls for parallel spin orientation in the vicinity of the bridging atom leading to a preference for parallel spins on the metal atoms, a (**ferromagnetic coupling**). The alternative description (two orthogonal $3e2c$ bonds) demands that in the dinuclear complex a degenerate pair of antibonding molecular orbitals is occupied by two electrons. Consequently, a high-spin state is encountered, **b**:

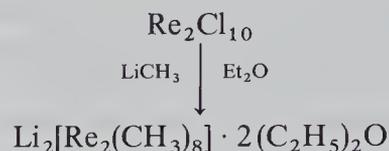
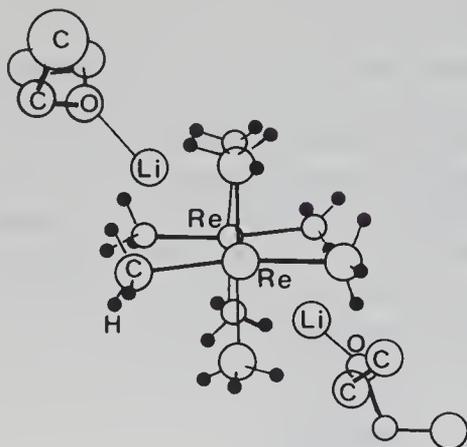


The terms *ferromagnetic* and *antiferromagnetic* originally served to characterize the magnetic behavior of extended solid state structures; increasingly they are used for descriptions on the molecular level as well. In the interpretation of a lowering or quenching of the magnetic moment of an oligonuclear complex which consists of units with unpaired electrons, the possible contribution of three mechanisms (direct, indirect antiferromagnetic and indirect ferromagnetic) must be invoked. Thus, a sizable proportion of work in the field of molecular magnetochemistry deals with the relative weight of these pathways. As a guideline it may be stated that under the provision of sufficient approach of the interacting centers, direct interactions are more effective than indirect interactions and that among the latter type, antiferromagnetic coupling is more effective than ferromagnetic coupling (see Gerloch, 1979 R). Ambiguities may arise in the case of ligand-bridged oligonuclear complexes which possess M–M distances in the range 300–500 pm; here direct and indirect antiferromagnetic contributions can be of comparable magnitude and a decision for the dominance of one of the paths is tantamount to a decision for or against a prevailing chemical bond (example: $[\text{Cp}_2\text{TiCl}]_2$, p. 341 and R. L Martin, 1965). Therefore the study of magnetic properties eventually leads to statements of chemical relevance.

In the following, a few metal atom clusters from the realm of organotransition-metal chemistry will be discussed. Oxo- and halometal clusters are part of inorganic coordination chemistry and will not be treated here. In the designation “ n -nuclear”, n implies the number of metal atoms in the cluster frame.

16.2 Dinuclear Clusters

The organometallic analogue of the well known ion $[\text{Re}_2\text{Cl}_8]^{2-}$ was first described by F. A. Cotton and G. Wilkinson in 1976:



red, sensitive to air and moisture, stable at RT

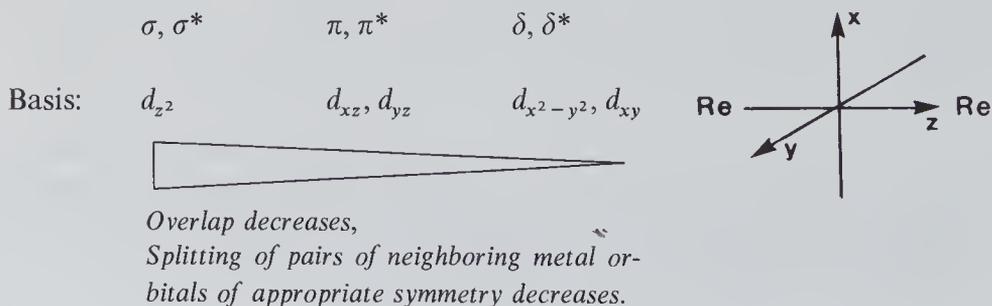
$$d(\text{Re}\equiv\text{Re}) = 218 \text{ pm}$$

compare $d(\text{Re}-\text{Re}) = 274 \text{ pm}$ (Re metal)

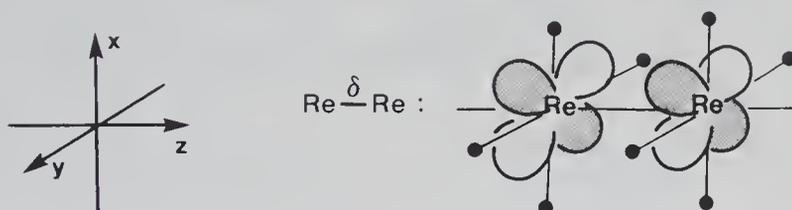
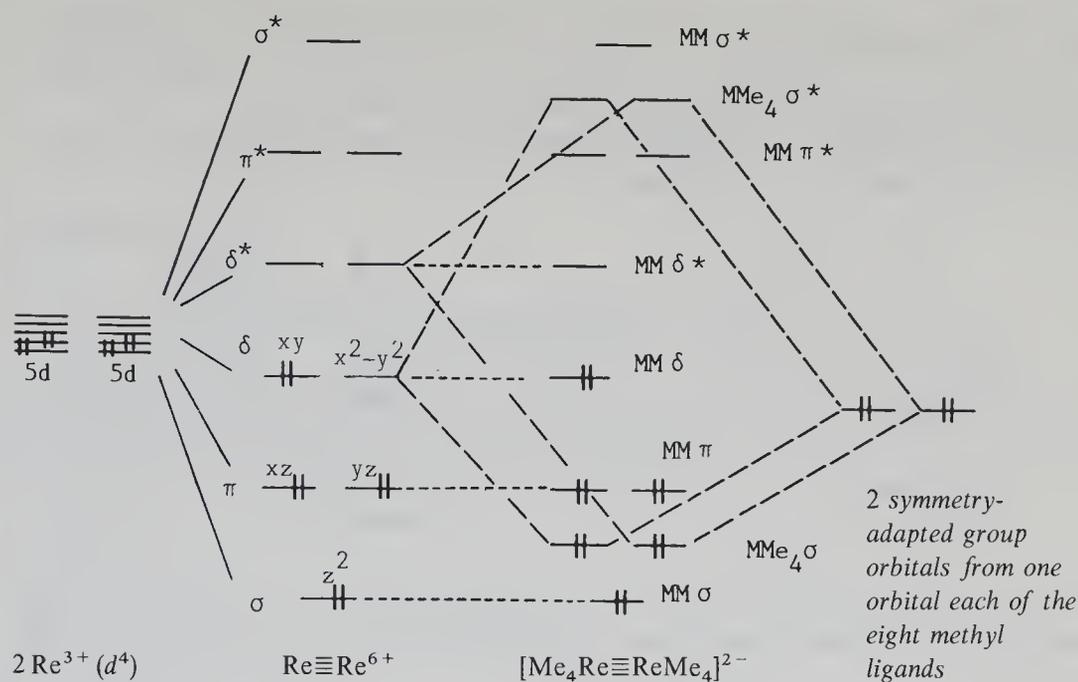
The short Re–Re bond distance and the eclipsed conformation (symmetry D_{4h}) attest to the presence of an $\text{M}\equiv\text{M}$ quadruple bond with a δ -component. The preference for a staggered conformation (D_{4d}) resulting from ligand-ligand repulsions should be even more pronounced for $\text{L} = \text{CH}_3$ as compared to $\text{L} = \text{Cl}$ considering the van der Waals radii of these two ligands. Notwithstanding, the ion $[\text{Re}_2(\text{CH}_3)_8]^{2-}$ also displays D_{4h} symmetry.

A qualitative MO scheme for $[\text{Re}_2(\text{CH}_3)_8]^{2-}$ may be set up in the following way (Cotton, 1978 R):

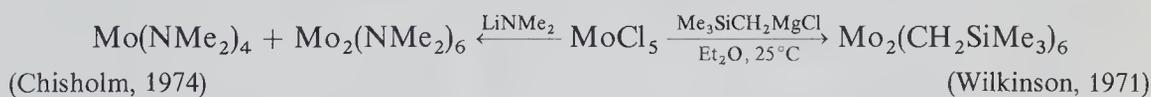
- Only $\text{Re}(5d)$ AO's are considered as a first approximation
- Interactions between two Re atoms split the basis of the d -orbitals into the levels



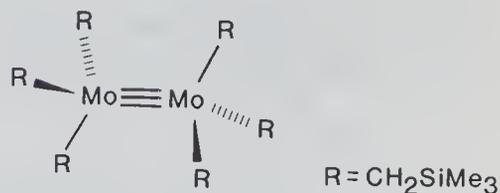
- One component each of the δ, δ^* -pairs interacts with a symmetry-adapted group orbital from eight CH_3 ligands; the other δ, δ^* -component is used for the $\text{Re}\overset{\delta}{-}\text{Re}$ bond.



Additional contributions to $\text{Re}-\text{CH}_3$ bonding are provided by an admixture of $\text{Re}(6s, p_x, p_y)$ AO's. Isoelectronic and isostructural with $[\text{Re}_2(\text{CH}_3)_8]^{2-}$ are the complex ions $[\text{M}_2(\text{CH}_3)_8]^{4-}$ ($\text{M} = \text{Cr}, \text{Mo}$). Occupation of the bonding MO $\text{MM}\delta$ is responsible for the realization of an eclipsed conformation of $[\text{Re}_2(\text{CH}_3)_8]^{2-}$ and its congeners. Twisting about the $\text{Re}-\text{Re}$ bond axis would entail a decrease in overlap of the $\text{Re}(d_{xy})$ orbitals and thus a sacrifice in bond energy. Conversely, the representatives of another important class of dinuclear clusters, M_2R_6 , assume a staggered conformation.



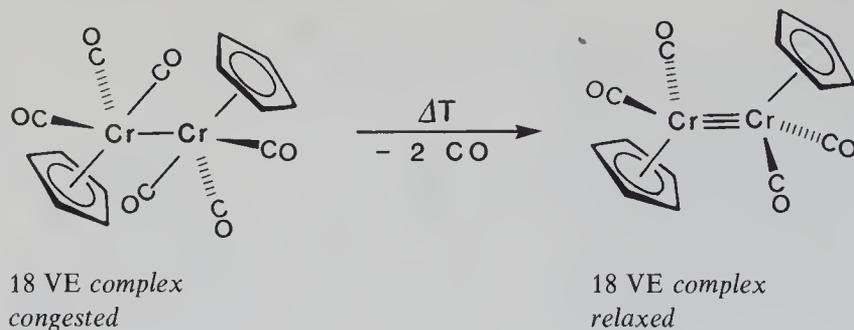
Structure of $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$ in the crystal, symmetry D_{3d} (idealized), $d(\text{Mo} \equiv \text{Mo}) = 217 \text{ pm}$, compare: $d(\text{Mo}-\text{Mo}) = 278 \text{ pm}$ (Mo metal).



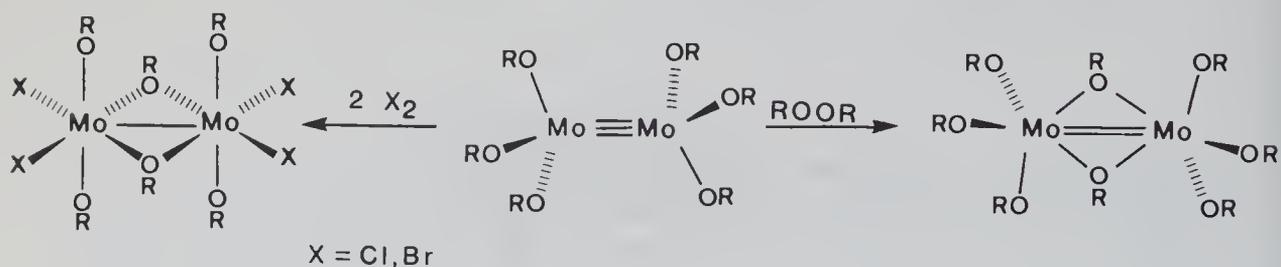
The $\text{Mo} \equiv \text{Mo}$ triple bond linking two ions $\text{Mo}^{3+} (d^3)$ can be described in terms of the electronic configuration $(\sigma_{z^2})^2 (\pi_{xz})^2 (\pi_{yz})^2$. In analogy to $-\text{C} \equiv \text{C}-$, this leads to an

electron distribution which is cylindrically symmetrical along the z axis. As far as the $M \equiv M$ interaction is concerned, the bond energy is rotationally invariant and it is ligand-ligand repulsion that dictates the staggered conformation.

The **generation** of a metal–metal multiple bond from a single bond sometimes occurs spontaneously under ligand dissociation:

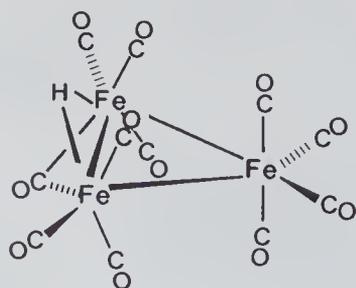


A **reduction** of metal–metal bond order is effected by oxidative addition:

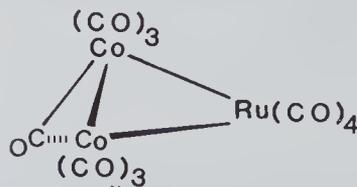


16.3 Trinuclear Clusters

Examples of a **triangular arrangement** M_3 :

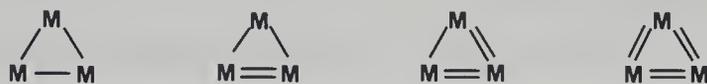


$[\text{HFe}_3(\text{CO})_{11}]^-$
from $\text{Fe}_3(\text{CO})_{12}$ by means of
a Hieber base reaction



$\text{RuCo}_2(\text{CO})_{11}$
from $\text{Ru}_3(\text{CO})_{12}$
and $\text{Co}_2(\text{CO})_8$

For triangular M_3 clusters the 18 VE rule demands the following total number of valence electrons Σ VE:

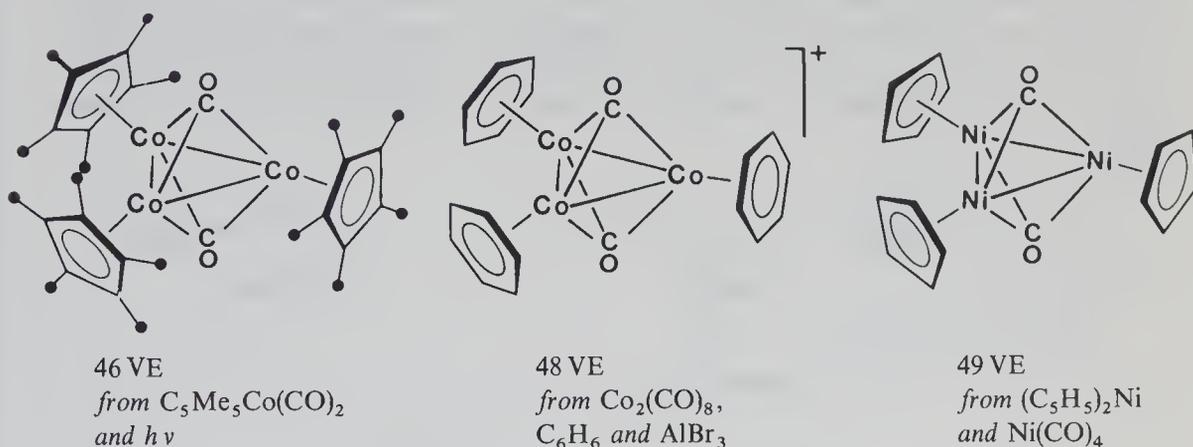


“magic number”

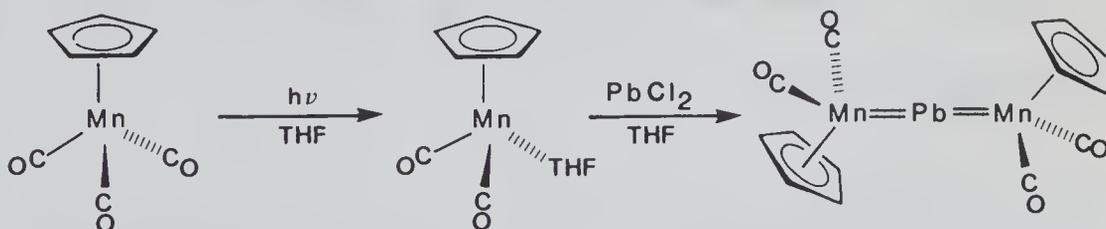
Σ VE: 48 46 44 42

$$\Sigma VE = 3 \cdot 18 - m \cdot 2 \quad (m = \text{number of metal-metal bonds})$$

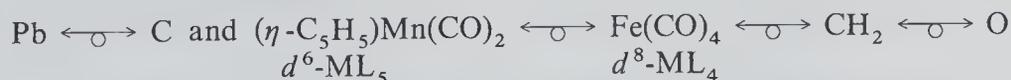
Apparently, depending on the respective metal-metal bond orders, a considerable variety of valence-electron numbers may lead to triangular M_3 clusters, odd VE numbers also being encountered occasionally (L. Dahl, 1986 R):



A compound with a **linear arrangement** M_3 and an anticlinal conformation is formed in the following way (Herrmann, 1985):



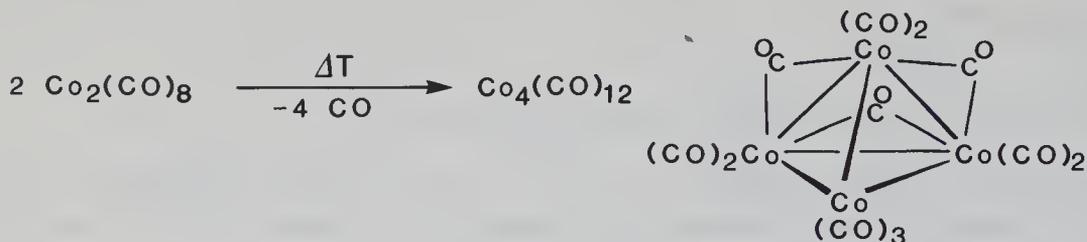
A related species featuring the unit $Mn=Ge=Mn$ was obtained by E. Weiss (1981). The application of isolobal relationships (p. 396) reveals an analogy between $[(\eta-C_5H_5)Mn(CO)_2]_2Pb$ and CO_2 , since



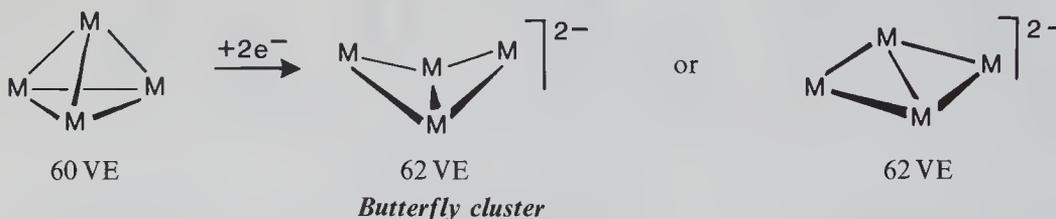
16.4 Tetranuclear Clusters

BINARY METAL CARBONYLS

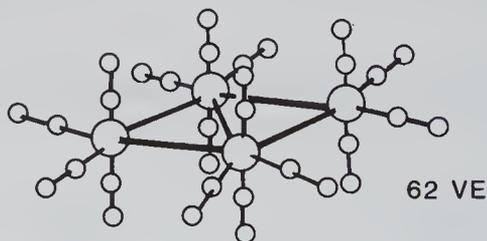
A widespread geometry for M_4 clusters is the **metallatetrahedrane** structure.



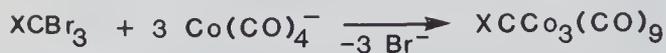
As the “magic number” for the formation of a tetrahedral M_4 cluster one obtains $\Sigma \text{VE} = 4 \cdot 18 - 6 \cdot 2 = 60$. The presence [$\text{Co}_4(\text{CO})_{12}$] or absence [$\text{Rh}_4(\text{CO})_{12}$, $\text{Ir}_4(\text{CO})_{12}$] of CO bridges does not affect the VE book-keeping. Like the generation of metal lattices, cluster formation is an aspect of electron deficiency. An increase of ΣVE above the respective “magic number” partially dispels this shortage and may result in **cluster opening**:



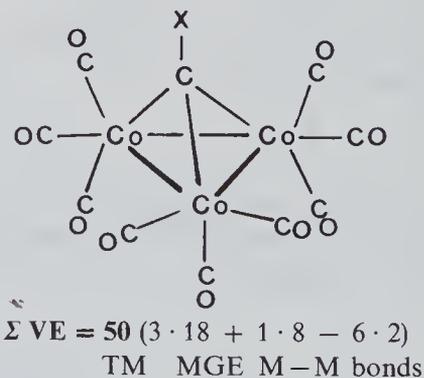
An example is provided by the structure of the anion $[\text{Re}_4(\text{CO})_{16}]^{2-}$ (Churchill, 1967):



ALKYLIDYNE CLUSTERS



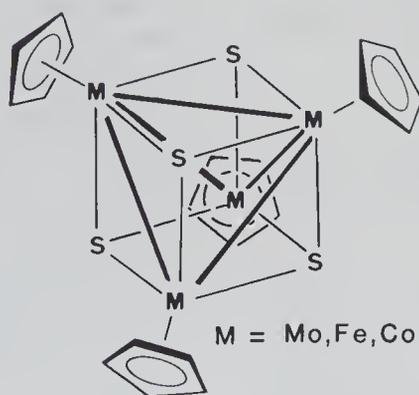
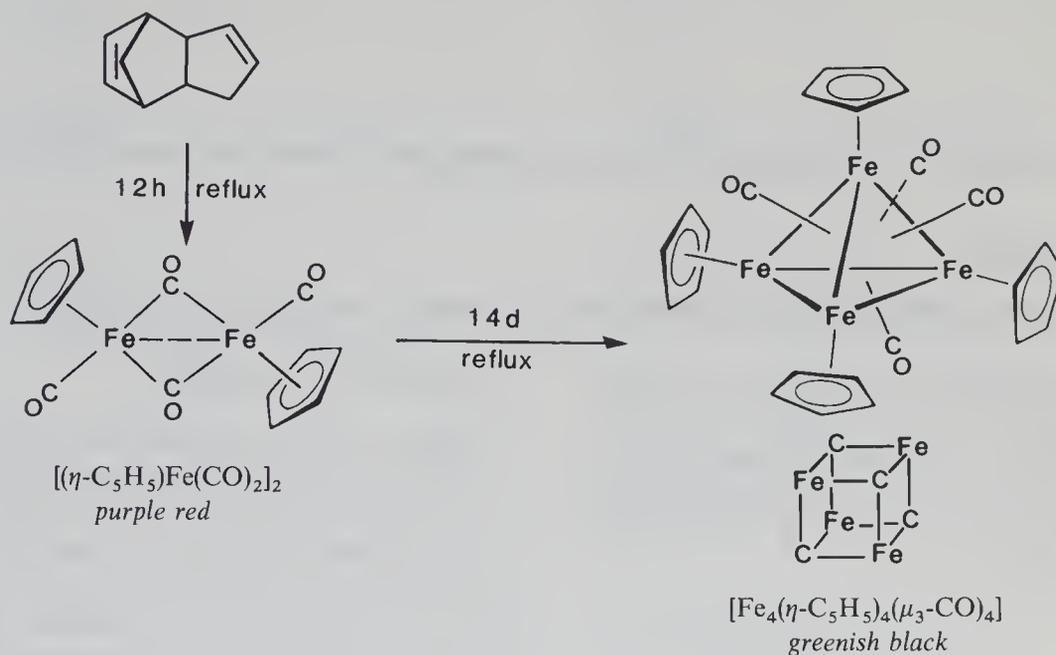
X = halogen or an organic group



Because of the participation of a main-group element which requires eight electrons only for a closed valence shell, the “magic number” for a tetrahedral frame is lower here.

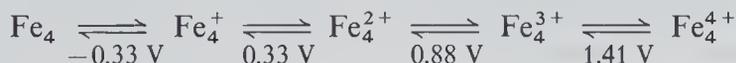
CUBANE CLUSTERS $M_4(\eta\text{-C}_5\text{H}_5)_4(\mu_3\text{-L})_4$

Four μ_3 -ligands which cap the triangular faces of an M_4 tetrahedron generate a **hetero-cubane** structure M_4L_4 . In transition-metal complexes the role of the μ_3 -ligand is often assumed by CO:



Examples with $\mu_3\text{-L} = \text{S}^{2-}$ are the **cubane clusters** $M_4(\eta\text{-C}_5\text{H}_5)_4(\mu_3\text{-S})_4$. They are formed from the respective cyclopentadienylmetal carbonyls and sulfur or cyclohexene sulfide.

By means of **cyclovoltammetry** it has been demonstrated that the iron sulfur cubanes undergo four reversible electron transfer steps whereby the tetrahedral Fe_4 frame is preserved:



The oxidations are accompanied by increasing distortion of the cubane frame (Dahl, 1977). ^{57}Fe -Mössbauer spectra indicate, however, that the four iron atoms remain equivalent. This finding suggests delocalized bonding in the Fe_4 frame. The significance of these M_4S_4 clusters rests in their similarity to the active centers of iron-sulfur redox proteins (ferredoxin, rubredoxin) and possibly nitrogenase.

Excursion:

Structure and Bonding Conditions in Clusters, the Isolobal Analogy

A generalized treatment which embraces all types of clusters and metal–metal bonded species is not possible at present. Therefore, a variety of interpretations has been advanced (see B. F. G. Johnson, 1981 R):

	Cluster size	M_n
● 18 VE Rule (dating back to Sidgwick)	small	$n = 2-4$
● Skeletal Electron Theory (Wade, Mingos)	medium	$n = 5-9$
● Isolobal Relations (R. Hoffmann)		
● Closest Packing (metal lattices)	large	$n \geq 10$

The success in applying these approaches varies with the class of compounds and with cluster size. An evaluation of the power of these models requires comprehensive knowledge of descriptive organometallic chemistry which is out of the scope of the present text. In the following, the course of argumentation will be illustrated with a few selected examples. The 18 VE rule (p. 186f) and Wade's rules (p. 68f) were already introduced.

ISOLOBAL ANALOGIES

Applications of the skeletal electron theory (SET) necessitate an a priori division of the metal orbitals into skeleton-binding and ligand-binding functions; they depend on a preconception of the structure of the molecule to be treated. An alternative approach was devised by R. Hoffmann who calculated the **bonding characteristics of cluster fragments ML_n** in the frontier orbital region by means of the Extended-Hückel-method and compared them with the units CH_1 and BH_m .

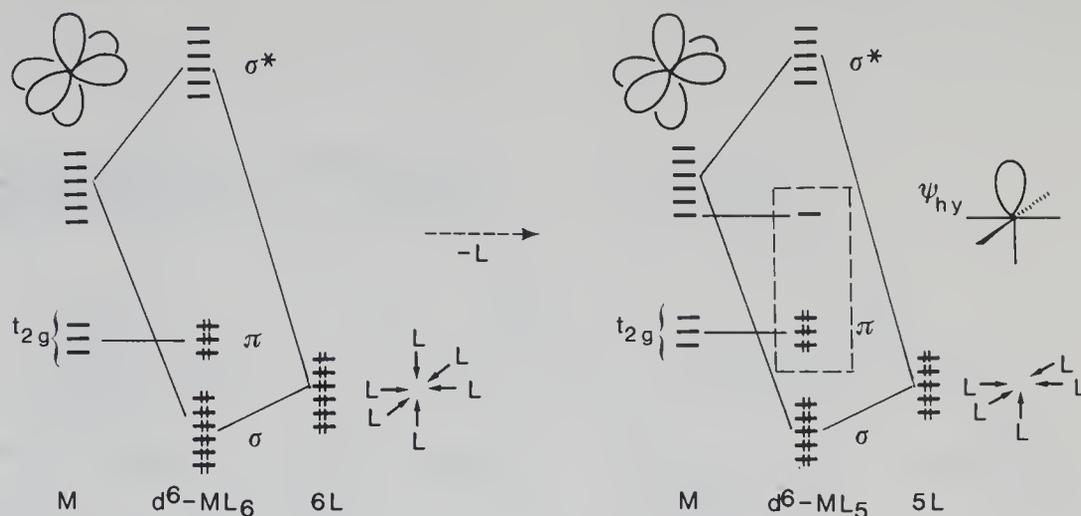
Definition: Two fragments are **isolobal** if the number, symmetry properties, approximate energy and shape of their frontier orbitals as well as the number of electrons occupying them are similar – not identical but similar.

Example:

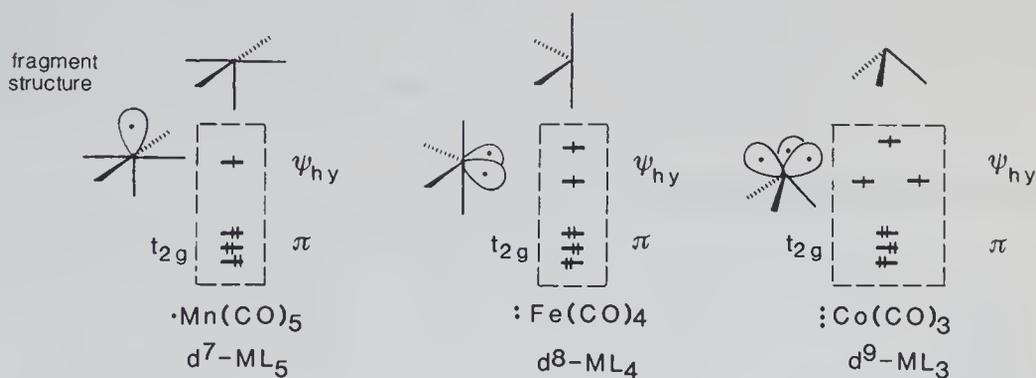


The symbol $\xleftrightarrow[\text{O}]{\text{isolobal}}$ will be used not only for the fragments but also for the molecules they constitute.

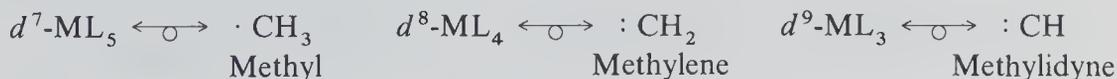
Starting-point for the derivation of the lobal properties of organometallic fragments is the simplified MO scheme of an octahedral complex. The removal of one ligand L converts a bonding σ -MO of the complex ML_6 into a nonbonding frontier orbital ψ_{hy} of the fragment ML_5 :



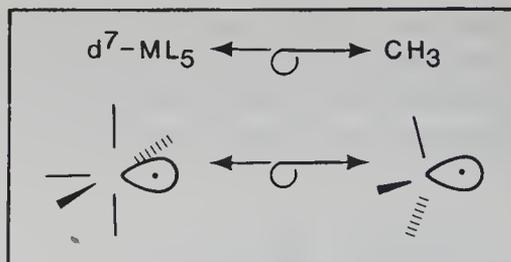
The removal of 2 L creates two, the removal of 3 L three new frontier orbitals ψ_{hy} :



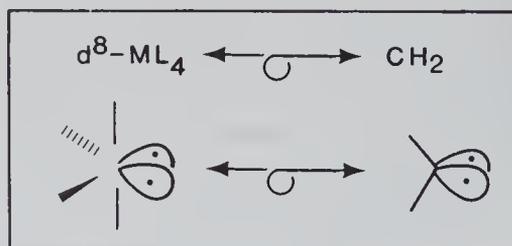
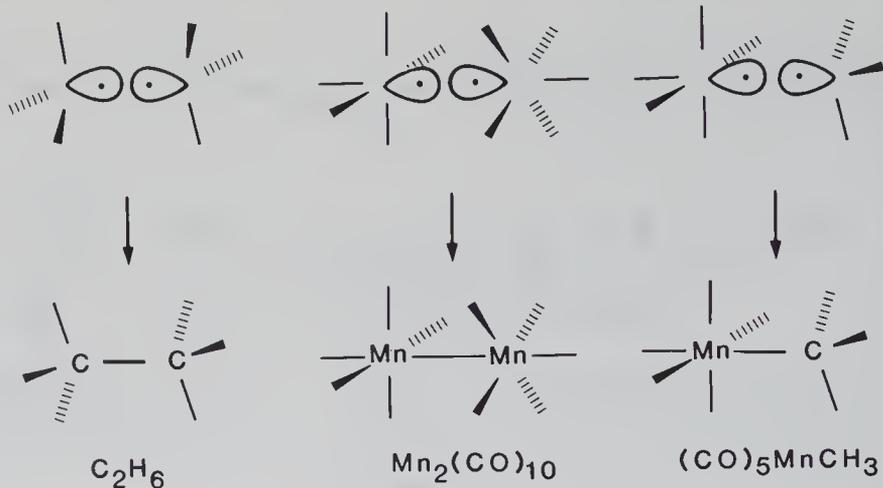
The frontier orbitals t_{2g} and ψ_{hy} are filled by n electrons of the central metal (configuration d^n). This provides $Mn(CO)_5$ with one, $Fe(CO)_4$ with two and $Co(CO)_3$ with three singly occupied orbitals with distinct spatial orientation. These organometallic fragments are complementary to organic analogues:



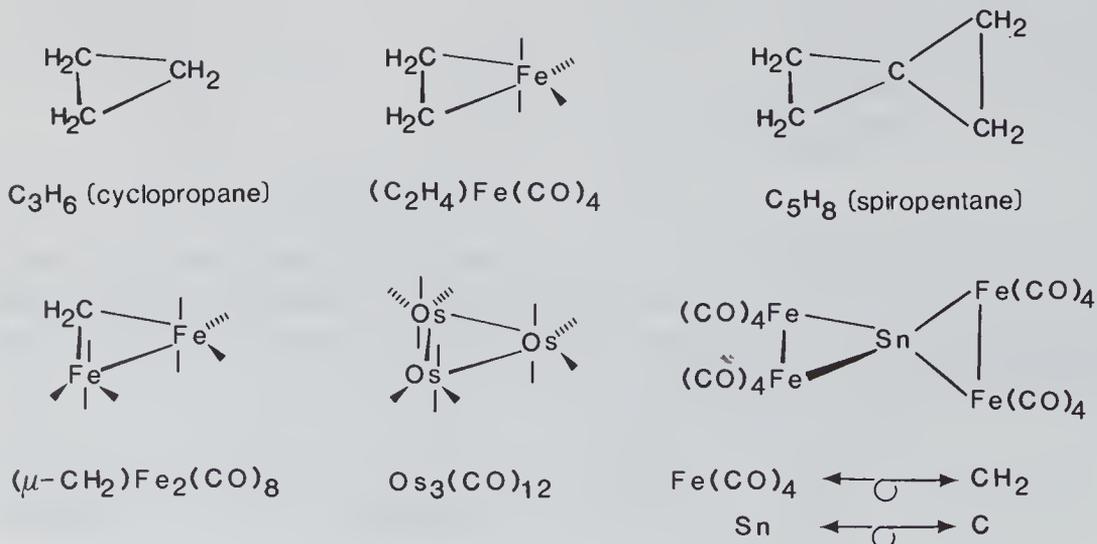
The isolobal connection allows a **joint consideration of inorganic, organic and organometallic structures**, the relationships being based on the isolobal nature of the respective molecular fragments:

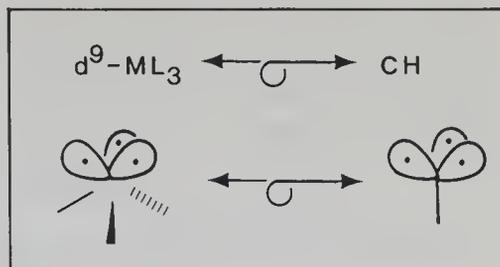


An analogy of the following compounds is implied:

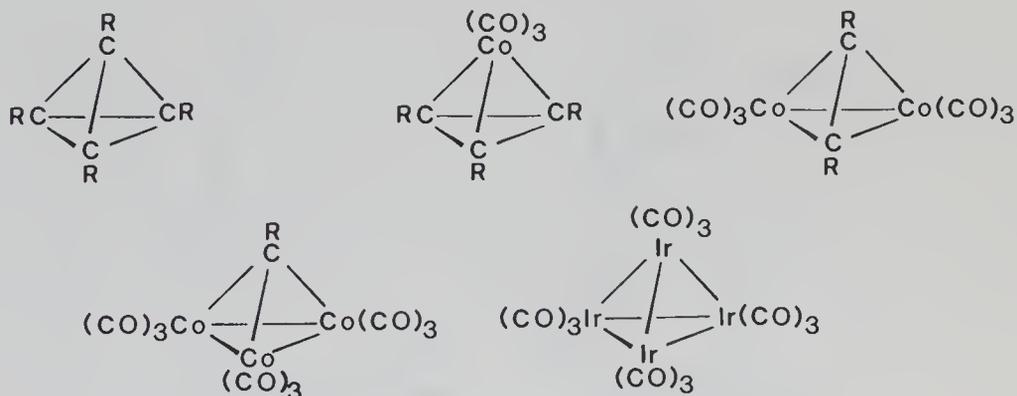


Therefore, the following compounds are related:





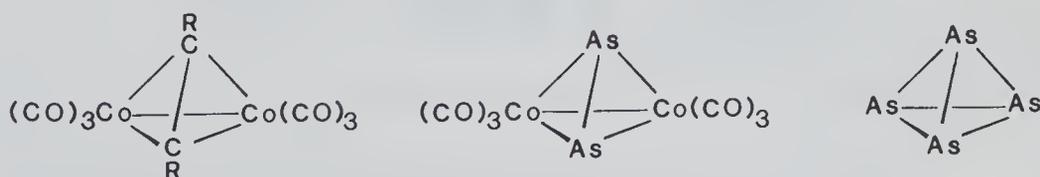
This leads to the following series of analogous clusters:



Even the molecules P_4 , As_4 and Sb_4 may be included into a larger family:



hence the following tetrahedranes are analogous:



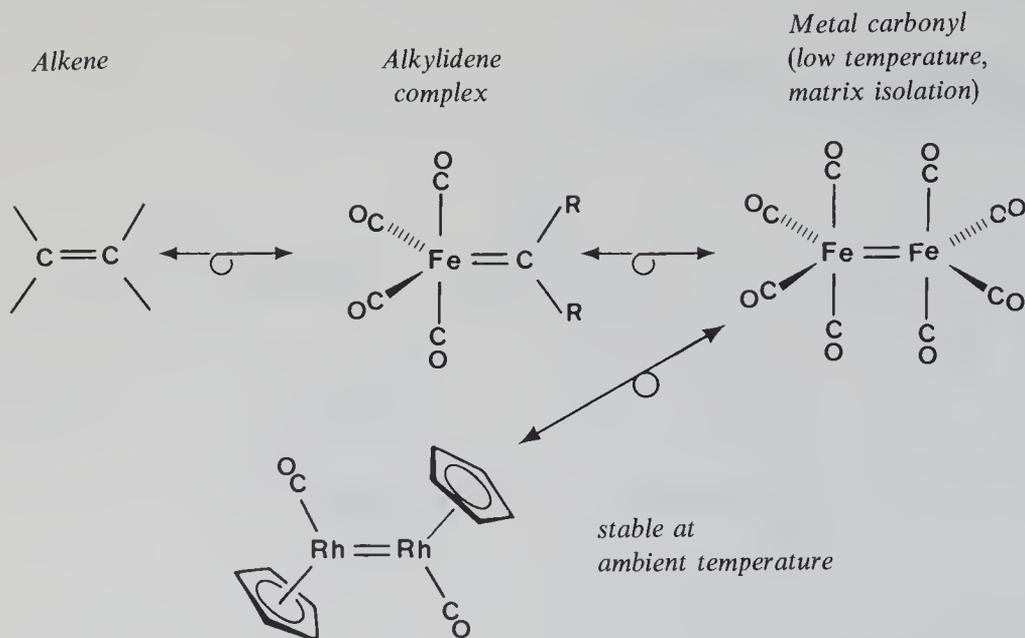
Structural relationships between boranes and carbaboranes (p. 70) stem from the isobal analogy



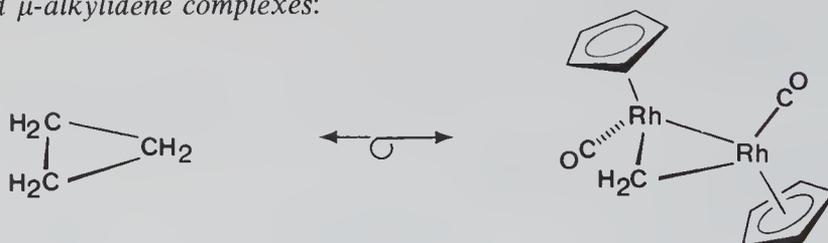
Inclusion of the ligand $\eta^5\text{-C}_5\text{H}_5^-$ which, as a donor of three π -electron pairs formally occupies three coordination sites, yields the analogies



The following molecules then are related:



Another analogy is that between cyclopropane and μ -alkylidene complexes:

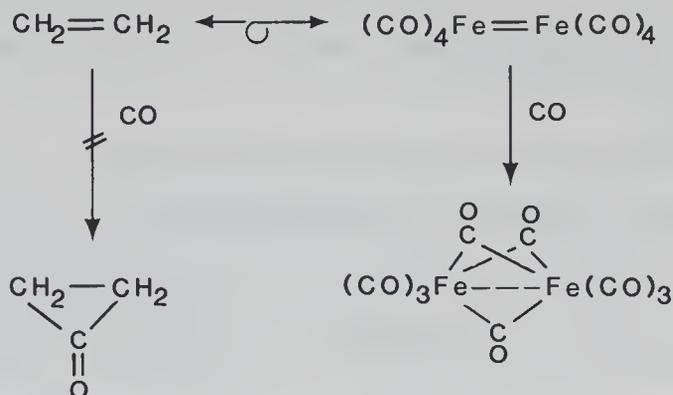


The realm of isolobal connections is considerably extended if the mutual replacement of σ -donor ligands and metal electron pairs is introduced:

Organic fragment	Coordination number of the metal on which the derivation of the isolobal fragments is based				
	9	8	7	6	5
CH_3	$d^1\text{-ML}_8$	$d^3\text{-ML}_7$	$d^5\text{-ML}_6$	$d^7\text{-ML}_5$	$d^9\text{-ML}_4$
CH_2	$d^2\text{-ML}_7$	$d^4\text{-ML}_6$	$d^6\text{-ML}_5$	$d^8\text{-ML}_4$	$d^{10}\text{-ML}_3$
CH	$d^3\text{-ML}_6$	$d^5\text{-ML}_5$	$d^7\text{-ML}_4$	$d^9\text{-ML}_3$	

Not for all of these general types have fragments yet been recognized. As a caveat it should also be stressed that applications of the isobal principle do not necessarily furnish stable molecules: according to the relation $\text{CH}_2 \leftarrow \text{O} \rightarrow \text{Fe}(\text{CO})_4$ the existence of a molecule $(\text{CO})_4\text{Fe}=\text{Fe}(\text{CO})_4$ would be

predicted. However, $\text{Fe}_2(\text{CO})_8$ has only been observed in low temperature matrices; it readily accepts CO to yield the stable molecule $\text{Fe}_2(\text{CO})_9$. Its analogue cyclopropanone, on the other hand, does not form spontaneously from $\text{H}_2\text{C}=\text{CH}_2$ and CO; it has to be prepared in a different way.



"That's Dr. Arnold Moore. He's conducting an experiment to test the theory that most great scientific discoveries were hit on by accident."

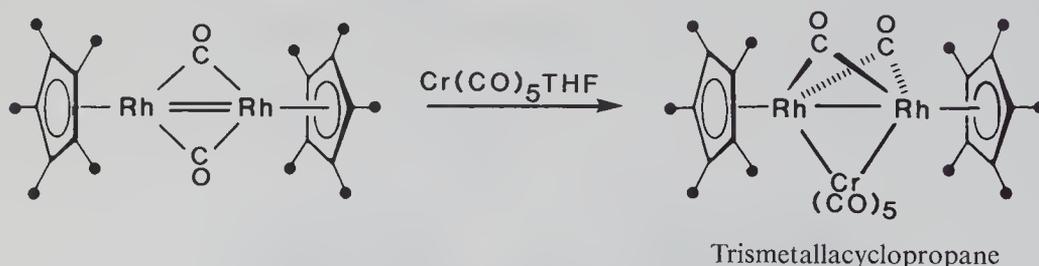
(Hoff, © 1957, The New Yorker Magazine, Inc.)

16.5 Approaches to Systematic Cluster Synthesis

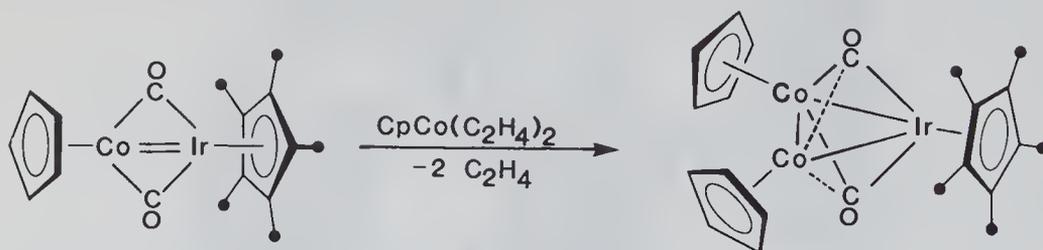
As opposed to the formation of carbon–carbon bonds, the methods of cluster synthesis have not yet reached a stage where far-reaching generalizations would be warranted. Rather, many new cluster molecules owe their existence to serendipity, and writing balanced equations for their formation is fraught with difficulties. In an attempt to plan cluster synthesis, the conceptional assembly of a cluster from fragments with distinct frontier orbital characteristics is translated into a preparative reaction sequence. Since the structural chemistry of metal atom clusters is extremely varied, the role of organic chemistry as a supplier of models is limited. In the following paragraphs, a few promising approaches are sketched. They are arranged according to the reaction types build-up (I), expansion (II) and exchange (III).

I Cluster build-up starting from $M\equiv M$ and $M\equiv C$ multiple bonds

- Addition of carbene-like fragments to $M=M$ (Stone, 1983)



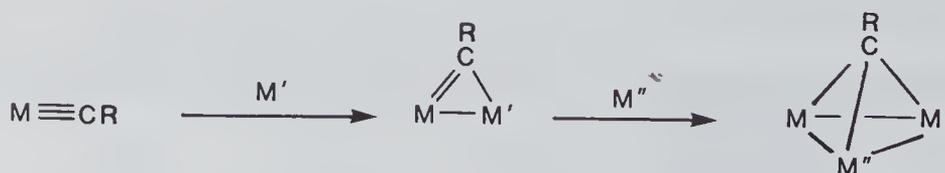
Because of the isolobal connection $Cr(CO)_5 \leftarrow \sigma \rightarrow CH_2$ this type of reaction corresponds to the formation of cyclopropane from ethylene and methylene.



The two CO ligands engage in unsymmetrical bridging (Herrmann, 1985).

- Addition of carbene-like fragments to $M\equiv C$ and to $M=C$ (Stone, 1982)

Principle:

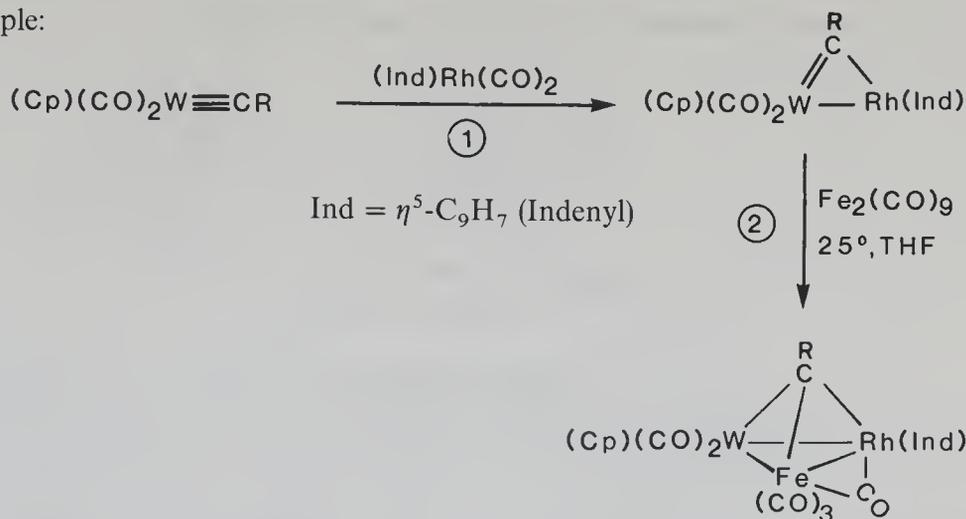


$M, M' =$ coordinatively
unsaturated fragment

Dimetalla-
cyclopropene

Trimetalla-
tetrahedrane

Example:



In reaction ① the fragment $(\text{Ind})\text{Rh}[d^8\text{-ML}_3]$ behaves like a carbene although it is a species of the type $d^8\text{-ML}_4$ which were introduced as carbene analogues (p. 398). The propensity of the late transition metals (d^8, d^{10}) to form stable 16 VE complexes calls for a **corollary in the classification of isolobal fragments**. Accordingly, the fragments $d^8\text{-ML}_3$ and $d^{10}\text{-ML}_2$ also are carbene-like and can add to multiple bonds.

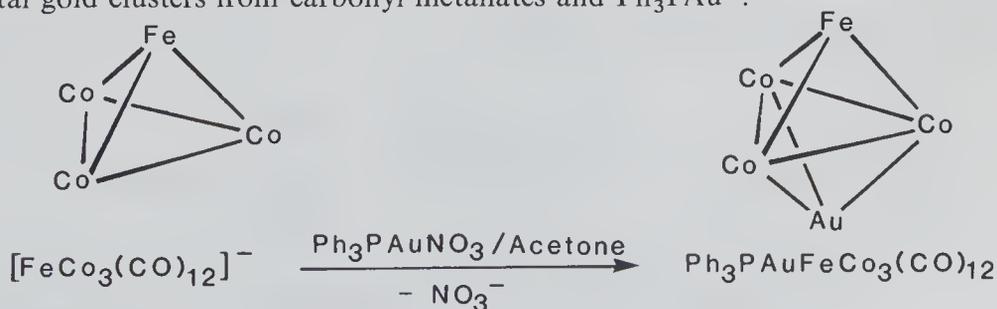
Carbene analogues	but also
$d^8\text{-ML}_4$	$d^8\text{-ML}_3$
$\text{Cp}(\text{CO})\text{Co}, (\text{CO})_4\text{Fe}$	$\text{CpRh}, (\text{acac})(\text{CO})\text{Ir}$
and $d^6\text{-ML}_5$	$d^{10}\text{-ML}_2$
$\text{Cp}(\text{CO})_2\text{Re}, (\text{C}_6\text{H}_6)(\text{CO})_2\text{Cr}$	$(\text{R}_3\text{P})_2\text{Pt}, (1,5\text{-COD})\text{Pt}$

The cluster formed in reaction ② contains one element each of the three transition series and is chiral. Clusters of this kind show extremely high values of optical rotation (up to 10^4 degrees).

II Cluster expansion

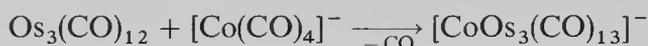
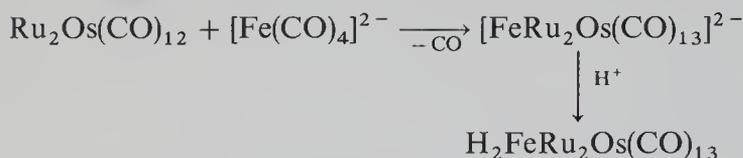
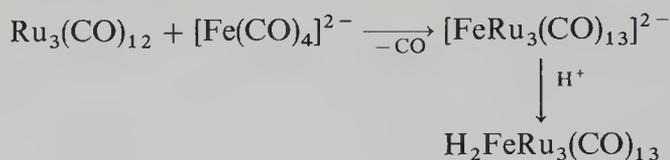
● Addition of the fragment Ph_3PAu (Lauher, 1981)

The moieties H and Ph_3PAu can mutually replace each other in carbonyl metallates ($\text{Ph}_3\text{PAu}^+ \leftarrow \text{O} \rightarrow \text{H}^+$). Examples are the pairs $(\text{CO})_4\text{CoH}$, $(\text{CO})_4\text{CoAuPPh}_3$ and $(\text{CO})_4\text{FeH}_2$, $(\text{CO})_4\text{Fe}(\text{AuPPh}_3)_2$. This finding led to a general synthesis of transition-metal gold clusters from carbonyl metallates and Ph_3PAu^+ :



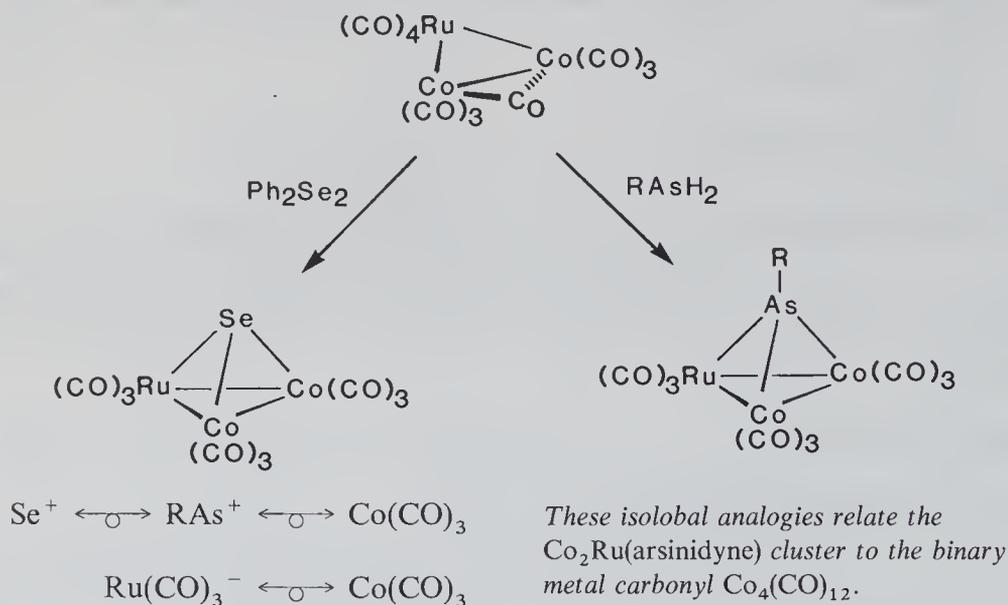
This procedure has wide applicability.

● **Addition of carbonyl metallates to $M_3(CO)_{12}$** (Geoffroy, 1980 R)

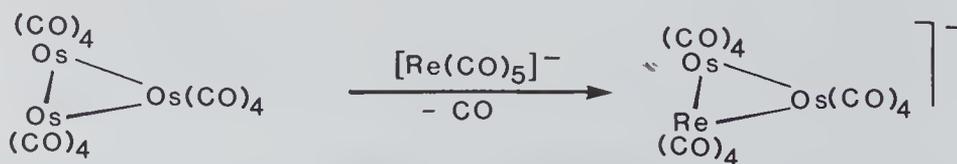


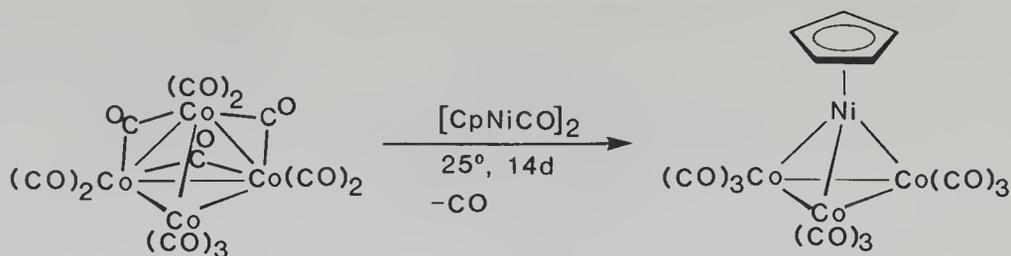
In this way triangular 48 VE clusters may be transformed into tetrahedral 60 VE clusters which contain various combinations of the elements Fe, Ru, Os, and Co in their frame. These reactions rarely proceed in a uniform fashion and product composition is very sensitive to reaction temperature and duration.

● **Cluster expansion by main-group elements** (Vahrenkamp, 1983)



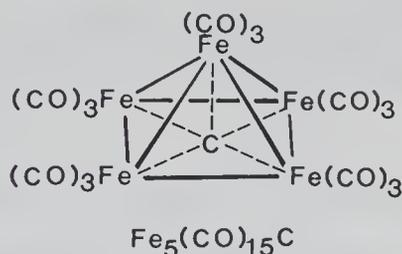
III Metal exchange using isolobal fragments



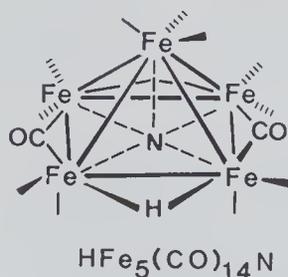


In contrast to the pyrolytic procedures used in the infancy of cluster synthesis, these reactions proceed under mild conditions and consequently are more specific. In the examples stated above, the high nucleophilicity of the carbonyl metallate $[\text{Re(CO)}_5]^-$ and the reactivity of the 17 VE species CpNi(CO) , which exists in equilibrium with its dimer, are decisive. The mechanistic study of this type of metal exchange reaction is still at an early stage – among the three conceivable sequences, cluster fragmentation/reconstitution, elimination/addition and addition/elimination, the third variant is currently best supported by experimental evidence (Vahrenkamp, 1985 R).

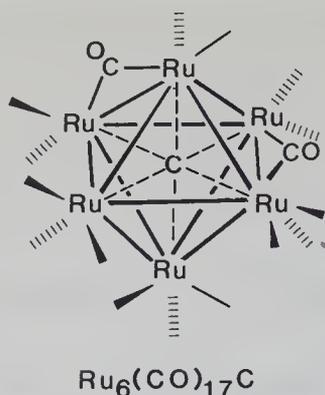
16.6 Pentanuclear and Higher Nuclearity Clusters



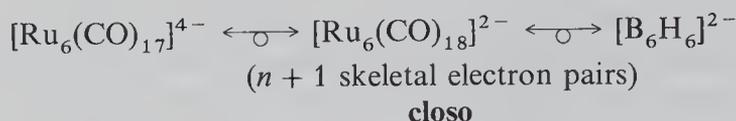
The *carbido-cluster* $\text{Fe}_5(\text{CO})_{15}\text{C}$ is formed in low yield if $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ are heated in hydrocarbon solvents in the presence of alkynes like 1-pentyne (Hübel, 1962). According to IR spectroscopy, bridging CO ligands are absent. The five-coordinate C atom is located slightly below the Fe_4 plane. Formyl dissection into $[\text{Fe}_5(\text{CO})_{15}]^{4-}$ and C^{4+} followed by an application of the isolobal principle and Wade's rules leads to a *nido* structure for the Fe_5 frame:



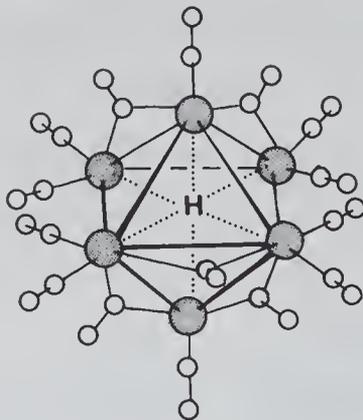
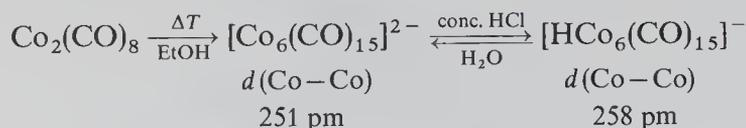
The *nitrido-cluster* $[\text{Fe}_5(\text{CO})_{14}\text{N}]^-$ and its protonated form $\text{HFe}_5(\text{CO})_{14}\text{N}$ also display *nido* structures. They are prepared from NaFe(CO)_4 , Fe(CO)_5 and NOBF_4 at 145°C (Muetterties, 1980).



The *carbido-cluster* $\text{Ru}_6(\text{CO})_{17}\text{C}$ (Bianchi, 1969) – dissection into $[\text{Ru}_6(\text{CO})_{17}]^{4-}$ and C^{4+} – possesses a *closo* structure which can be rationalized on the basis of isolobal relationships in the following way:

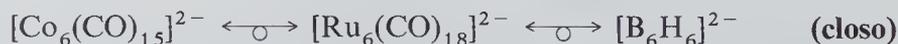


In the context of the bonding mode of hydrogen in interstitial metal hydrides, the preparation and structural characterization of the **hydrido cluster** $[\text{HCo}_6(\text{CO})_{15}]^-$ is relevant (Longoni, Bau, 1979):



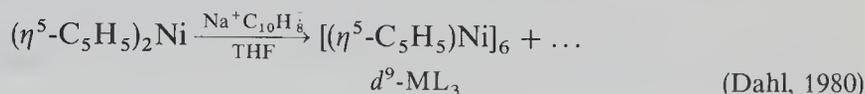
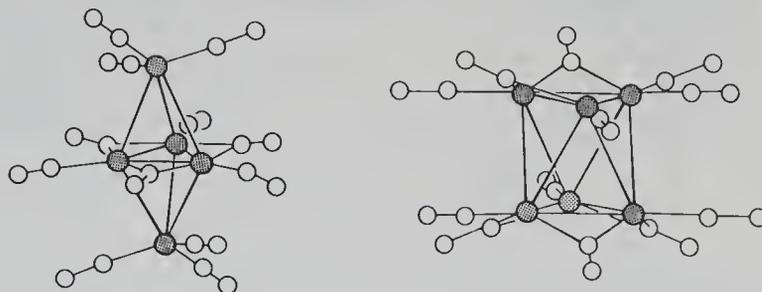
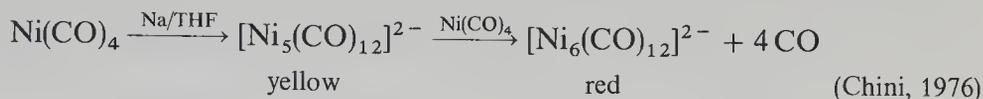
Structure (neutron diffraction) of the cluster anion $[\text{HCo}_6(\text{CO})_{15}]^-$ in the crystal: the Co_6 octahedron holds ten terminal CO ligands, four unsymmetrical CO bridges and one symmetrical CO bridge. Upon raising the pH, the H atom readily leaves the center of the Co_6 octahedron. As opposed to conventional carbonyl metal hydrides, the H atom in the cluster center is strongly deshielded, $\delta^1\text{H} = 23$ ppm (see p. 306).

The octahedral structure (*closo*) of the ion $[\text{Co}_6(\text{CO})_{15}]^{2-}$ and of its protonated form $[\text{HCo}_6(\text{CO})_{15}]^-$ is concordant with Wade's rules because of the analogies

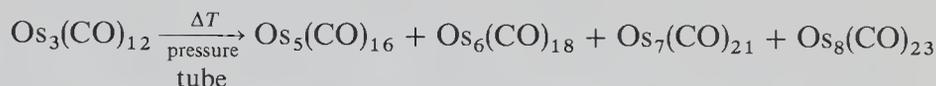


Note the unusual coordination numbers of C, N, and H in these clusters!

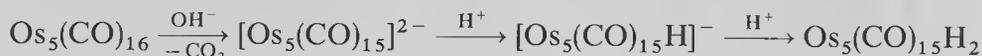
A path of access to **higher nuclearity clusters** is, inter alia, the **reductive aggregation** of mononuclear precursors:



Another method of synthesis is **thermally induced aggregation**:



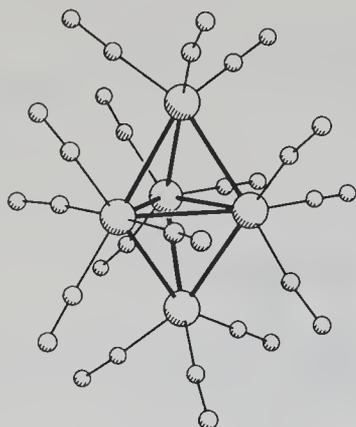
A conversion of the ligand sphere by means of a Hieber base reaction may follow:



For these higher nuclearity clusters the 18 VE rule, which starts from the premise of localized $2e2c$ bonds, is no longer reliable. Instead, one attempts to rationalize the structures in such a way that the $d^x\text{-ML}_y$ fragments of the framework are “translated” into the corresponding $\text{BH}^{+,0,-}$ fragments, using isolobal analogies, and Wade’s rules are employed thereafter. The plethora of cluster geometries calls for an extension of the relations between the number n of apical units, the number of skeletal bonding electron pairs and the corresponding structural type:

Skeletal bonding electron pairs	Wade type	Cluster geometry
$n - 1$		$(n - 2)$ polyhedron, 2 caps
n		$(n - 1)$ polyhedron, 1 cap
$n + 1$	closo	(n) polyhedron
$n + 2$	nido	$(n + 1)$ polyhedron, 1 apex unoccupied
$n + 3$	arachno	$(n + 2)$ polyhedron, 2 apices unoccupied
$n + 4$	hypho	$(n + 3)$ polyhedron, 3 apices unoccupied

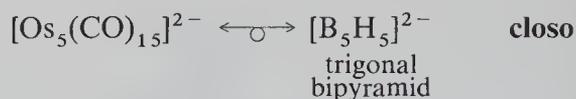
Examples:



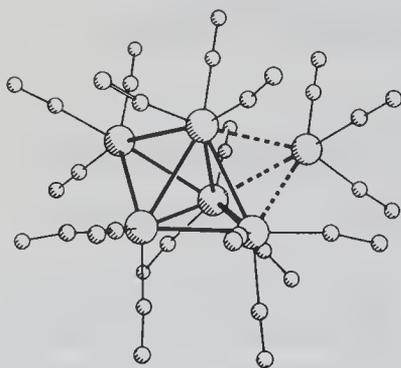
$\text{Os}_5(\text{CO})_{16}$



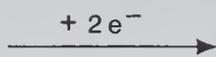
hence



A skeletal structure analogous to that of the dianion $[\text{Os}_5(\text{CO})_{15}]^{2-}$ is displayed by the protonated forms $[\text{Os}_5(\text{CO})_{15}\text{H}]^-$ and $\text{Os}_5(\text{CO})_{15}\text{H}_2$ as well as by the iso(valence)electronic neutral molecule $\text{Os}_5(\text{CO})_{16}$.



$\text{Os}_6(\text{CO})_{18}$



$[\text{Os}_6(\text{CO})_{18}]^{2-}$

$\text{Os}_6(\text{CO})_{18}$ for an octahedral structure is "short of one electron pair". Therefore, a structure with a higher degree of M–M connectivity is encountered: monocapped trigonal bipyramid.

$[\text{Os}_6(\text{CO})_{18}]^{2-}$ is a *regular octahedron* since $n = 6$ apical units dispose of $(n + 1) = 7$ skeletal electron pairs (*close structure*).

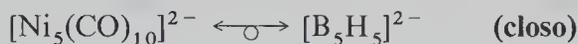
Accordingly:

$\text{Os}_7(\text{CO})_{21}$ monocapped octahedron from $6 + 1$ Os atoms

$\text{Os}_8(\text{CO})_{23}$ bicapped octahedron from $6 + 2$ Os atoms,
verified for the iso(valence)electronic anion $[\text{Os}_8(\text{CO})_{22}]^{2-}$.

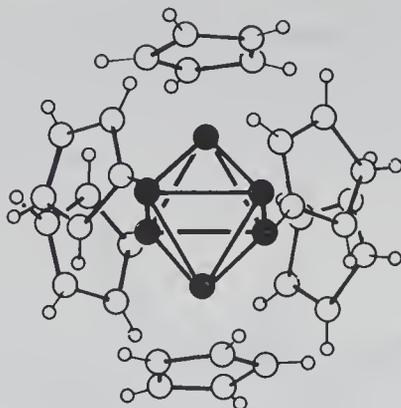
The reliability of predictions which are based on the analogy of TM carbonyl clusters to equiangular borane polyhedra is limited. Whereas the structural chemistry of **higher boranes** is dominated by **icosahedral geometry**, which is also found in elemental boron, **higher nuclearity TM clusters** tend to form **closest packed structures** mimicking the metallic state.

It is already with $[\text{Ni}_5(\text{CO})_{12}]^{2-}$ that a comparison with the corresponding borane leads to inconsistencies. This cluster anion was found to have trigonal bipyramidal structure (p. 407) which according to



would be predicted for the – hitherto unknown – anion $[\text{Ni}_2(\text{CO})_{10}]^{2-}$.

The unique cluster $(\text{CpNi})_6$ (p. 407) with an electron count of 90 VE in the spirit of Wade's rules is "in excess of two electron pairs" for its octahedral frame:



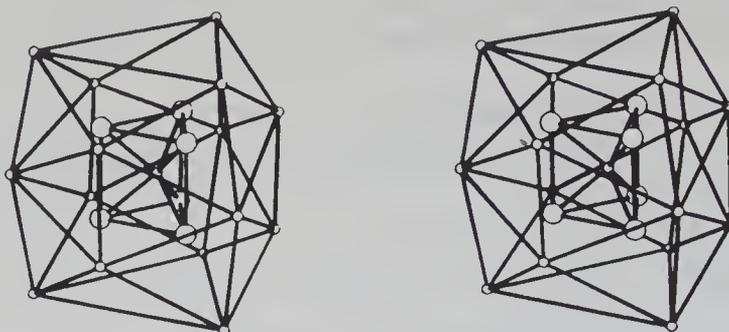
An analogy between $(\text{CpNi})_6$ and $[\text{B}_6\text{H}_6]^{6-}$ – contrary to experimental evidence – would suggest for this Ni_6 cluster an arachno structure derived from a square antiprism. Apparently, in this particular case the steric requirement of the ligands C_5H_5 must be considered which favors the highly symmetrical closo structure.

A trigonal prismatic arrangement of six metal atoms is realized in the carbido cluster anion $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ (Albano, 1973):



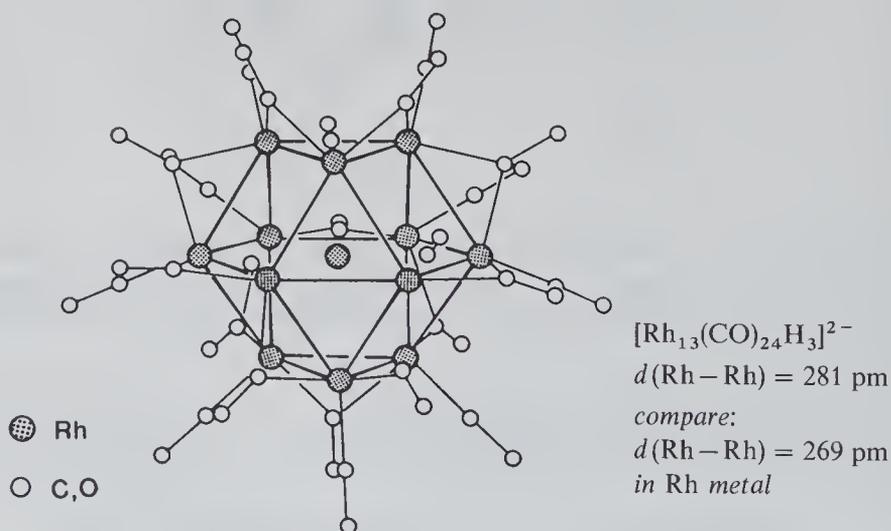
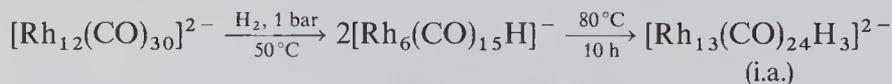
The carbon atom is situated in the center of a trigonal Rh_6 prism with bridging and terminal CO ligands at the edges and corners, respectively. Contrarily, in the binary metal carbonyl $\text{Rh}_6(\text{CO})_{16}$ the Rh atoms span an octahedron (=trigonal antiprism). It would appear that the central carbido C atom triggers the unusual disposition of the metal atoms in $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$. The following stereoview of this cluster anion also serves to

demonstrate an alternative way of looking at the structure of oligonuclear metal carbonyls (B. F. G. Johnson, 1981 R):



One recognizes a concentric arrangement of one C atom, an Rh₆ prism and a (CO)₁₅ deltahedron (= polyhedron with triangular faces). The positions of the terminal and the bridging CO groups are easily spotted. In this structural approach, it is assumed that the geometry of the ligandsphere is governed by a sterically optimal distribution of the external CO molecules (effective radius ≈ 300 pm) on the surface of a sphere as well as by the steric demands of the internal M_n cluster.

One of the most interesting aspects of multiatomic clusters is the **gradual transition from the molecular to the sub-microcrystalline metallic state**. By way of conclusion this is exemplified for another higher cluster of rhodium (Chini, 1975):



The 13 Rh atoms lie in three parallel planes; they form a cluster of symmetry D_{3h} and display **hexagonal closest packing**. The central Rh atom is connected to additional Rh atoms only; one half of the CO groups is in terminal, the other half in bridging positions. This cluster ion may be regarded as the smallest conceivable metal crystal with carbon monoxide **chemisorbed** at its surface. The connection to heterogeneous catalysis is obvious.

17 Organometallic Catalysis

pro memoria:

A catalyst accelerates the rate of a thermodynamically feasible reaction by opening a lower activation energy pathway. If alternative routes exist, a catalyst can enhance product selectivity by accelerating just one of the competing reaction sequences.

MODE OF ACTION OF TRANSITION-METAL COMPLEXES IN CATALYSIS

- *The coordination of the reaction partners to a transition metal brings them into **close proximity**, thus promoting the reaction (Example: cyclooligomerization of alkynes, p. 276).*
- *Through coordination to a transition metal, a reaction partner can become **activated** for subsequent reactions (Example: hydrogenation of alkenes, p. 427).*
- *The coordination of an organic substrate to a transition metal can **facilitate nucleophilic attack** (Example: PdCl₂-catalyzed oxidation of ethylene to acetaldehyde, p. 425).*

Catalytically active systems therefore must possess **vacant coordination sites** or be able to generate them in a primary dissociation step.

HETEROGENEOUS CATALYSIS

The vacant coordination site is located at a phase boundary (solid/liquid, solid/gas), i.e., only the surface atoms are catalytically active. A principal advantage is the easy recovery of the catalyst. Disadvantages include low specificity, relatively high reaction temperatures and difficulties in the mechanistic study.

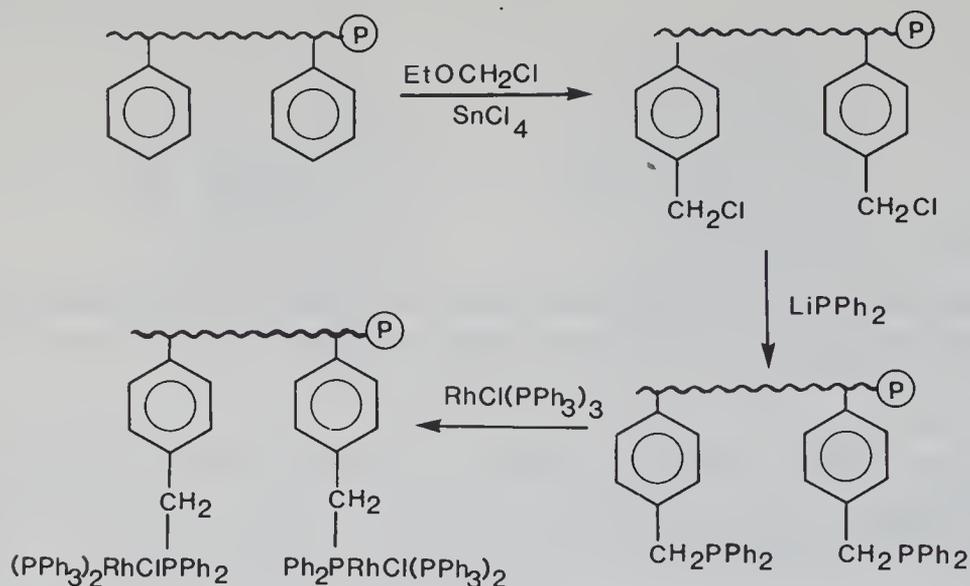
HOMOGENEOUS CATALYSIS

The catalyst can be tailor-made by ligand variation and is obtained reproducibly; high specificity is thus achieved and the catalysis can often be carried out at low temperatures. Ideally, the catalyst complex is stable in more than one coordination number and, through fine-tuning of chemical bond strength (variation of the ligands), capable of holding a substrate molecule **selectively but not too tightly**.

The readiness of a particular metal to exist in a coordinatively unsaturated state is pronounced at the end of the transition series (M d^8 , d^{10} , p. 189). Thus, the most important complexes which are active in homogeneous catalysis are those which contain the "late transition metals" Ru, Co, Rh, Ni, Pd and Pt.

The mechanisms of catalysis are studied more easily in the homogeneous than in the heterogeneous case; catalyst recovery is, however, fraught with difficulties. A possible

remedy is to attach a homogeneously active complex to a **polymeric support** (Pittman, 1974):



Supported Wilkinson's catalyst (cf. p. 427)

Another variant, already in industrial usage, is the **catalysis in a liquid/liquid two-phase system**. In this approach, the ligand tris(metasulfonato)triphenylphosphane is employed, which renders the catalyst water-soluble. The catalyst can be recovered quantitatively from the organic products (Application: hydroformylation of propene to give *n*-butyraldehyde, the Ruhrchemie/Rhone-Poulenc process, cf. p. 437).

17.1 Catalytic Reactions and the 16/18 VE Rule

Discussions of organometallic reaction sequences may be systematized by the definition of five general reaction types and their reverse reactions (Tolman, 1972). Characteristic variables pertaining to these reaction types are:

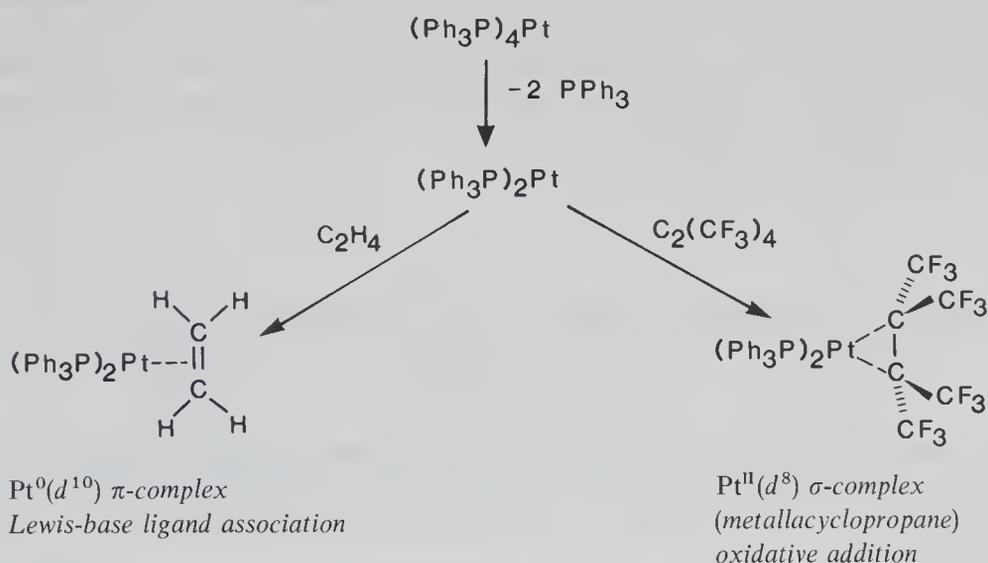
- ΔVE *Change in the number of valence electrons at the central metal*
- ΔOS *Change in the oxidation state of the metal (usual convention: -hydride, -alkyl, -allyl and -cyclopentadienyl are regarded as anions)*
- $\Delta\text{C.N.}$ *Change in the coordination number*

For olefinic ligands, the classifications Lewis-base ligand association and oxidative addition are limiting cases for a continuum of intermediate types. Which term most adequately describes the bonding situation has to be decided either on the basis of the electronic properties of the incoming alkene or through inspection of structural details of the product as determined by X-ray analysis (Example, p. 413).

Elementary organometallic reaction steps

Reaction	ΔVE	ΔOS	$\Delta C.N.$	Example
→ Lewis-acid ligand dissociation	0	0	-1	} $CpRh(C_2H_4)_2SO_2 \rightleftharpoons CpRh(C_2H_4)_2 + SO_2$
← Lewis-acid ligand association	0	0	+1	
→ Lewis-base ligand dissociation	-2	0	-1	} $NiL_4 \rightleftharpoons NiL_3 + L$
← Lewis-base ligand association	+2	0	+1	
→ Reductive elimination	-2	-2	-2	} $H_2Ir^{III}Cl(CO)L_2 \rightleftharpoons H_2 + Ir^I Cl(CO)L_2$
← Oxidative addition	+2	+2	+2	
→ Insertion (migratory)	-2	0	-1	} $MeMn(CO)_5 \rightleftharpoons MeCOMn(CO)_4$
← Extrusion	+2	0	+1	
→ Oxidative coupling	-2	+2	0	} $(C_2F_4)_2 Fe^0(CO)_3 \rightleftharpoons (CF_2)_4 Fe^II(CO)_3$
← Reductive decoupling	+2	-2	0	

Example:



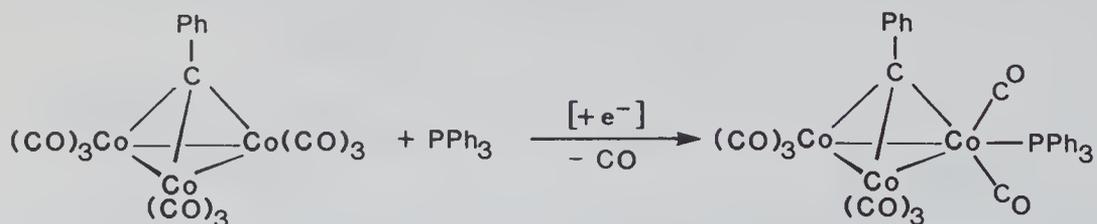
The formulation of a plausible reaction mechanism for an organometallic catalysis is assisted by the 16/18 VE rule (Tolman, 1972):

- ① Diamagnetic organometallic complexes of the transition metals exist in significant amounts at normal temperatures only if the central metal atom has 18 or 16 valence electrons. A concentration can be regarded as "significant" if it is detectable by spectroscopy or in kinetic studies.
- ② Organometallic reaction sequences proceed by elementary steps which involve intermediates having 18 or 16 valence electrons.

The conditions ① and ② considerably limit the number of possible reactions which a particular complex is likely to undergo:

Elementary step	expected for complexes with the configuration:
Lewis-acid ligand dissociation	16, 18 VE
Lewis-acid ligand association	
Lewis-base ligand dissociation	18 VE
Reductive elimination	
Insertion	
Oxidative coupling	
Lewis-base ligand association	16 VE
Oxidative addition	
Extrusion	
Reductive decoupling	

It should be stressed, however, that the 16/18 VE criterion is increasingly regarded as an undue restraint (Kochi, 1985 R). Thus, associatively activated CO substitution at $\text{Mn}_2(\text{CO})_{10}$ proceeds via the 17 VE intermediate $\cdot\text{Mn}(\text{CO})_5$ (p. 247), and **electron-transfer(ET) catalysis** (p. 233) of substitution reactions at 18 VE species is explained by intermediates with 17 VE (oxidatively initiated) or 19 VE (reductively initiated). The ET-catalyzed substitution of CO by phosphanes in (methylidyne)cobaltcarbonyl clusters is a good example (P. H. Rieger, 1981). The reaction is initiated by a mere 0.01 equivalents of electrons, supplied either by electrochemical reduction or through the addition of minute amounts of benzophenone ketyl:



Since in organometallic reaction mixtures traces of O_2 can generate 17 VE radical cations or, likewise, reducing components 19 VE radical anions, a radical pathway cannot be excluded a priori, even in those cases which currently are rationalized on the basis of the 16/18 VE criterion.

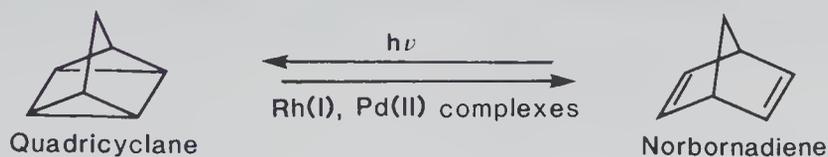
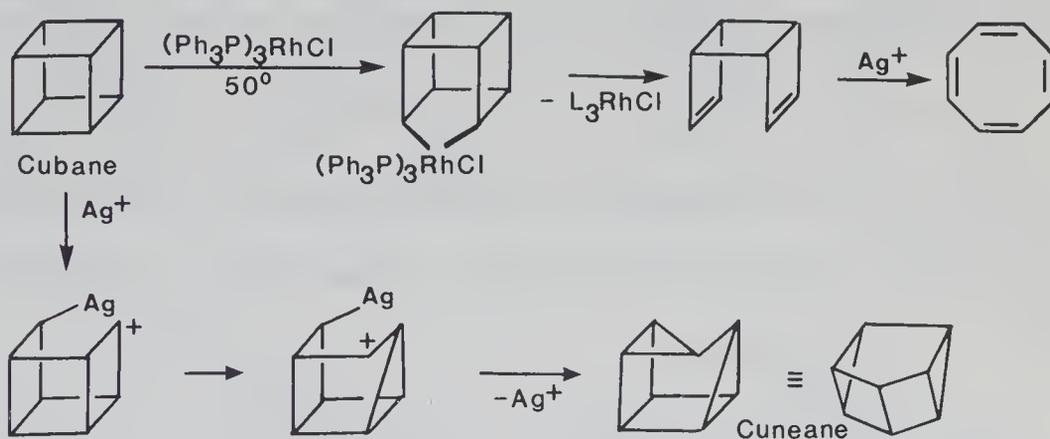
Homogeneous catalysis proceeds via a series of organometallic reaction steps, coupled to each other in such a way that they form a loop. This will be illustrated in the following sections for several reactions, some of which are of vast industrial importance. The discussion will be organized according to increasing number of components involved in the catalyzed reaction. These cycles have not always have been worked out in detail; often they take on the character of plausible assumptions, of working hypotheses or even caricatures.

When referring to a "catalyst", it should be borne in mind that the actual catalyst of a reaction is not always known. The term catalyst in this book therefore often refers to the

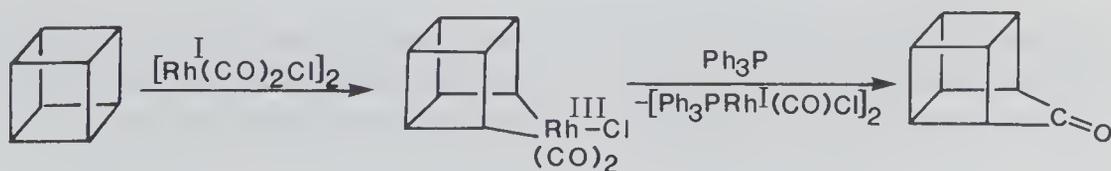
“precatalyst”, usually a well-known substance like $(\text{PPh}_3)_3\text{RhCl}$, which reacts with H_2 , CO or other substrates in solution to generate the active catalyst. In industrial processes, the catalyst sometimes forms directly in the reactor from simple precursors like a metal salt and the appropriate ligands, e.g. phosphanes, or from the bulk chemicals employed in the process.

17.2 Transition-Metal Assisted Valence Isomerizations

These reactions entail the rearrangements of σ frameworks in small hydrocarbon rings (**skeletal rearrangements**) with relief of ring strain. They are usually initiated by the oxidative addition of a C–C bond to a transition metal. Examples:



As concerted processes, the transformations quadricyclane \rightarrow norbornadiene and cubane \rightarrow cyclooctatetraene would be symmetry-forbidden (Woodward-Hoffmann rules). The presence of transition-metal ions may, however, open up low-energy multistep routes, rendering these rearrangements possible. In some cases, organometallic intermediates can be isolated. Example:



Cyclopropane

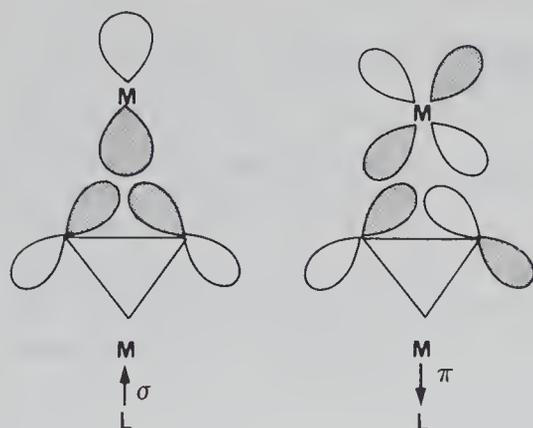


C₃ bonding,
occupied

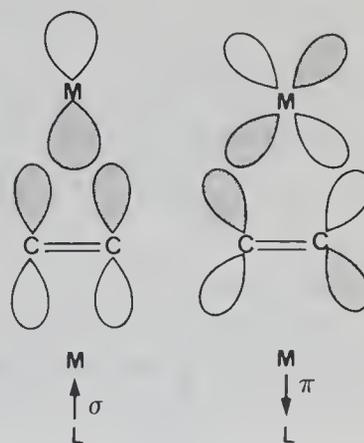
C₃ antibonding,
unoccupied

The small bond angle in the three-membered ring induces a higher *p* character for the σ bond relative to sp^3 hybridization and an overlap region lying outside the C–C axis (so-called *Walsh orbitals*).

Cyclopropane complex

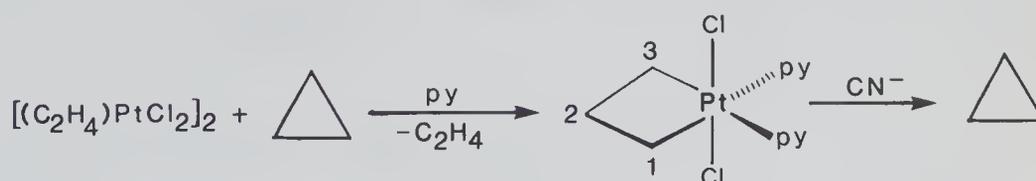


Olefin complex



While in the case of metal-olefin coordination, the $C^{\sigma}C$ bond of the ligand is retained, it is virtually lost on metal-cyclopropane coordination: structural data for transition-metal cyclopropane complexes point to metallacyclobutane character.

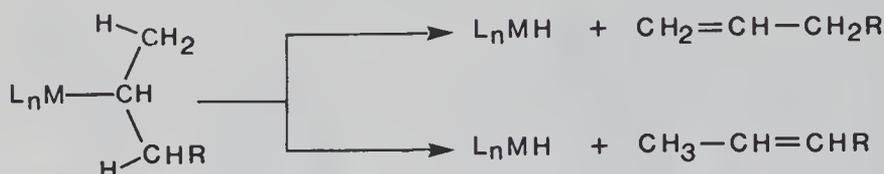
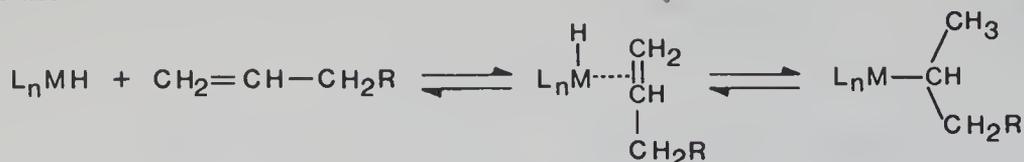
The following reaction can therefore be classified as an oxidative addition to Pt(II) or as an insertion of Pt(II) into cyclopropane, respectively, ring strain being diminished. Besides their role in valence isomerizations, metallacyclobutanes also qualify as intermediates in the olefin metathesis mechanism (p. 419).



* $C_1C_2C_2/C_3PtC_1 = 168^\circ$,
 $C_1-C_3 = 255$ pm, $Pt-C_2 = 269$ pm

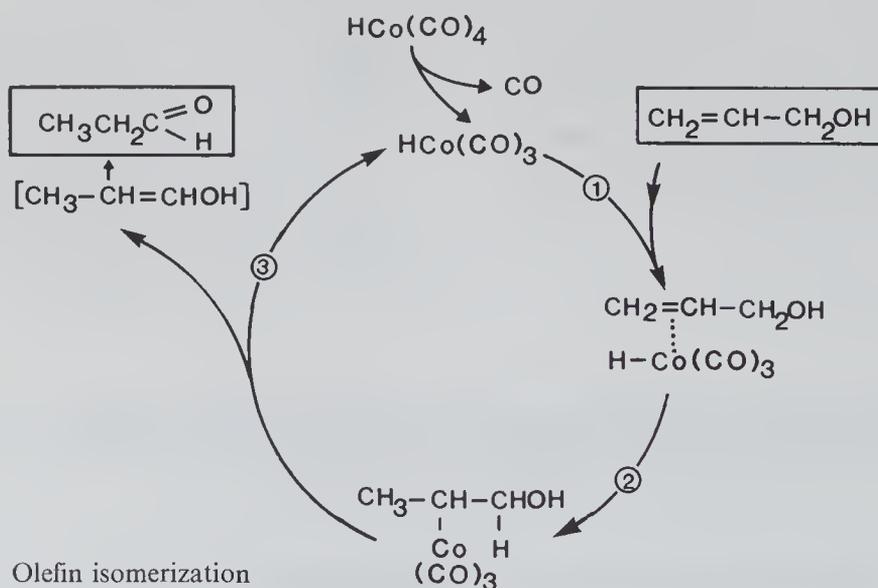
17.3 Isomerization of Unsaturated Molecules

Catalysts of composition L_nMH or combinations of the type $(R_3P)_2NiCl_2 + H_2$ can accelerate a rearrangement to the thermodynamically most stable olefin, i.e. they can catalyze the transformations terminal \rightleftharpoons internal and isolated \rightleftharpoons conjugated. Essential steps are:



After hydrometallation according to Markovnikov's rule (H adds to the carbon bearing the most hydrogen atoms), two ways for β -elimination exist, either leading back to the starting material or to the isomerized product. This cycle accelerates the establishment of the equilibration terminal \rightleftharpoons internal.

Practical example: allyl alcohol \rightarrow propionaldehyde

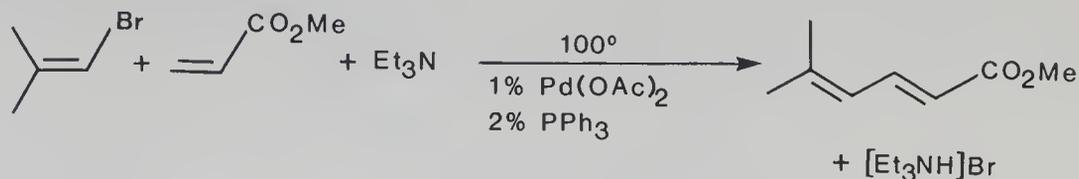


Since $HCo(CO)_3$ is the actual catalyst here, $HCo(CO)_4$ is an example of a "precatalyst" (p. 415).

If $DCo(CO)_4$ is introduced into the cycle, the only deuterated product found is CH_2DCH_2CHO . This proves the Markovnikov direction of the olefin insertion (2).

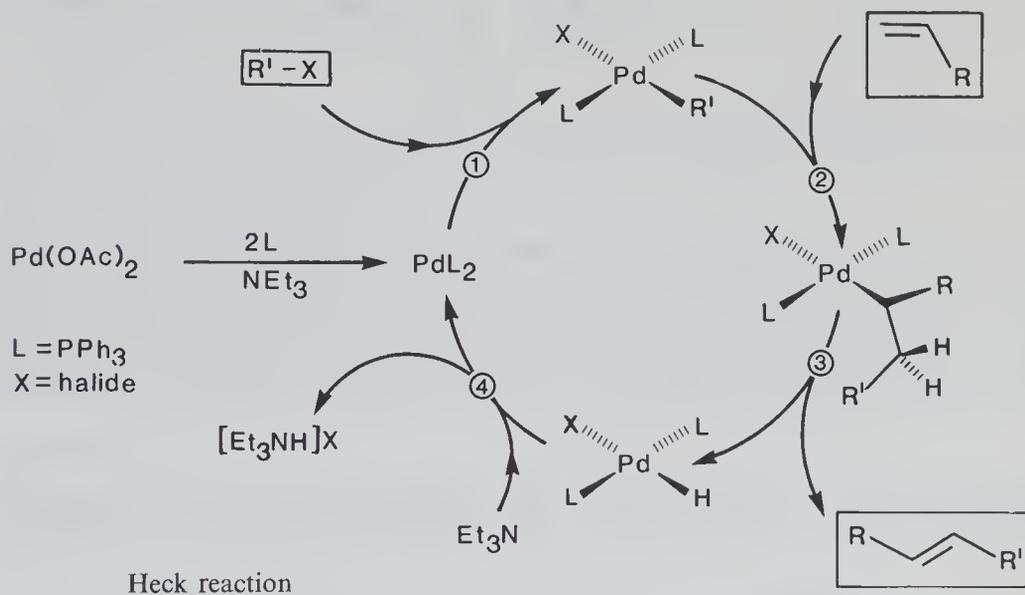
17.4 Arylation/Vinylation of Olefins (Heck Reaction)

In this reaction, a vinylic hydrogen atom is replaced by a vinyl-, benzyl- or aryl group. Example:



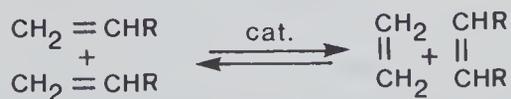
The catalyst is a Pd^0 complex, formed *in situ* from $\text{Pd}(\text{OAc})_2$, Et_3N and PPh_3 .

With regard to the mechanism of the Heck reaction (1982 R), the following cycle has been proposed: oxidative addition (1) of $\text{R}'\text{X}$ to the Pd^0 species first gives *trans*- $\text{R}'\text{PdL}_2\text{X}$. In order to prevent rapid decomposition of this intermediate by β -elimination, $\text{R}'\text{X}$ can only be an aryl-, benzyl- or vinyl halide. After olefin insertion (2) into the $\text{Pd}-\text{C}$ bond, the β -elimination (3) proceeds, the substituted olefin being released. The catalyst PdL_2 is regenerated in step (4) by reaction with Et_3N , which is consumed in stoichiometric amounts:



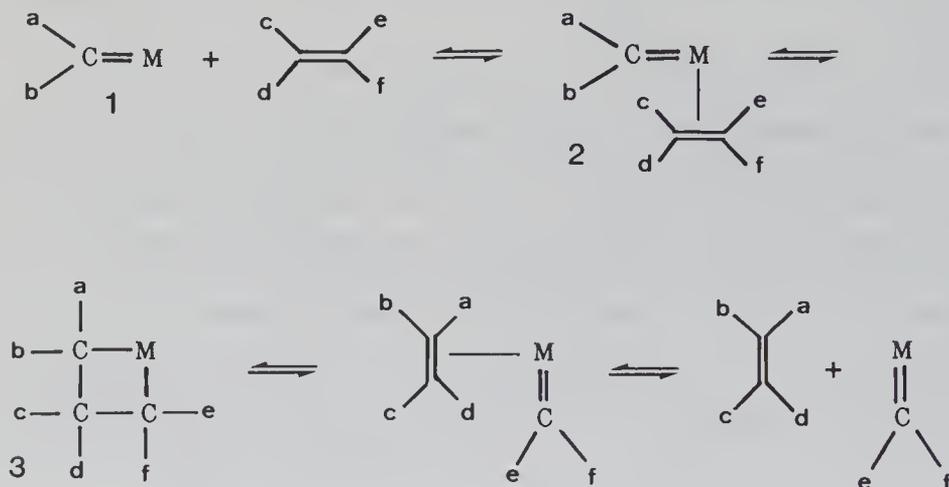
17.5 Alkene Metathesis

Principle:

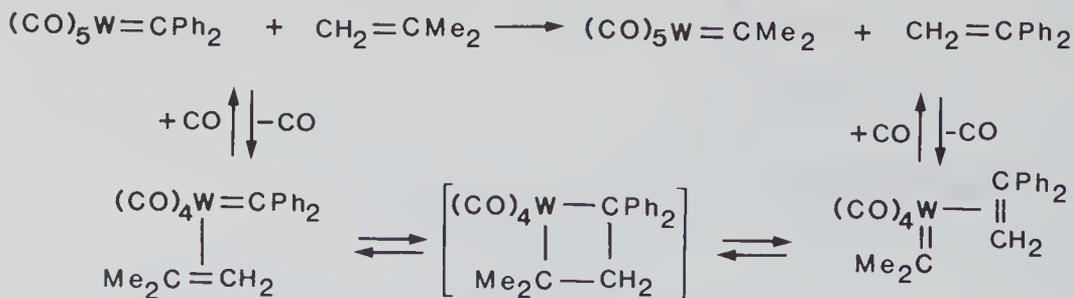


A possible application of olefin metathesis is the catalytic conversion of propene into ethylene (for ensuing polymerization) and pure 1-butene (to be used in the production of

C₅ aldehyde via an oxo process). This reaction type is of less technical importance than, for instance, hydroformylation or olefin oxidation (Wacker process). Alkene metathesis is, however, intriguing from a mechanistic point of view, since it is the first homogeneous catalysis for which **carbene complex intermediates** have been established. Typical catalysts are Mo(CO)₆ on Al₂O₃ (heterogeneous) and WCl₆/EtOH/2 Et₂AlCl (homogeneous). The mechanism of alkene metathesis has been intensively studied in recent years. Currently, the following sequence is favored (**Chauvin mechanism**):

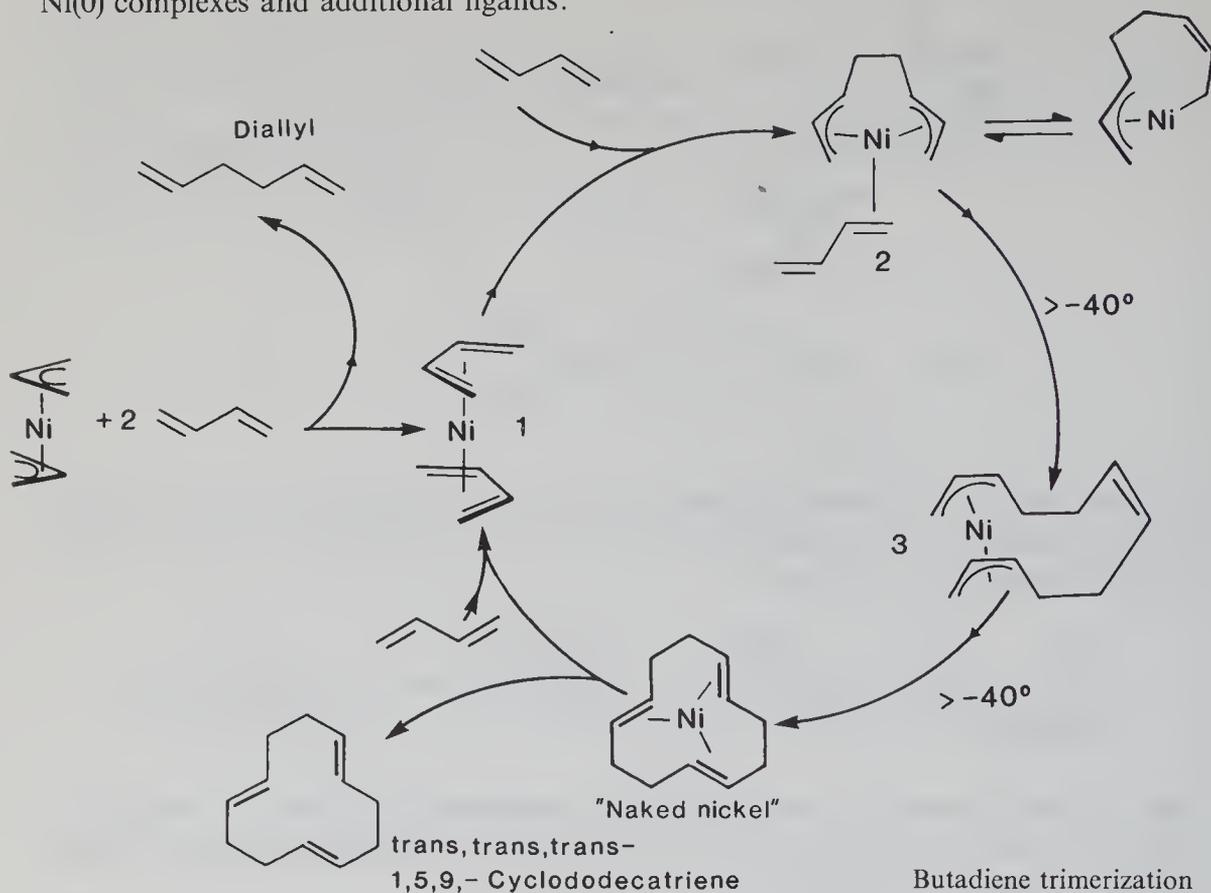


The catalytically active species is the carbene complex **1**. The metallacyclobutane intermediate **3** has two possibilities for ring opening. If the ring opens in a way which differs from the reverse reaction of its formation, the result is a metathesis (redistribution of alkylidene units). In support for the Chauvin mechanism, the following stoichiometric reaction may be cited (Casey, 1974):



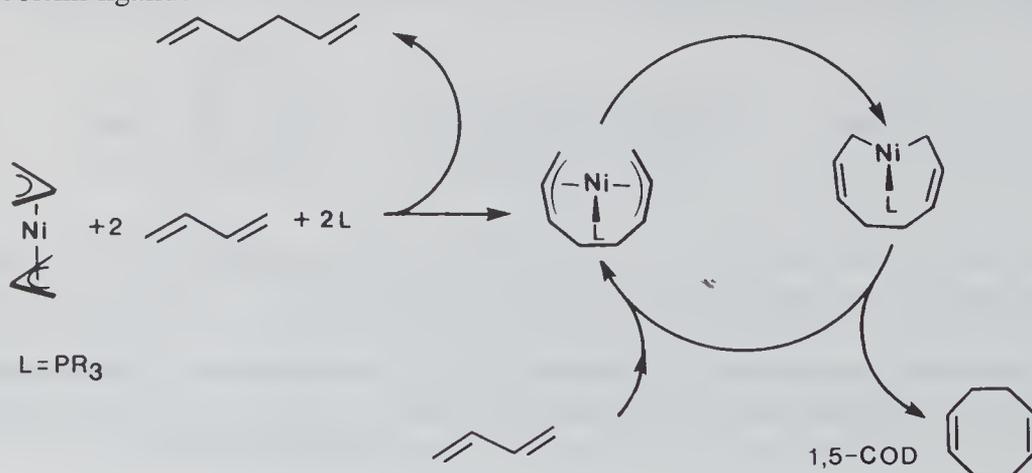
The tungstacyclobutane intermediate in this mechanism has not yet been isolated. The likely role of a metallacycle in the alkylidene redistribution is, however, supported by the following result (Puddephatt, 1976):

A topic of high complexity is the sequence of events in systems consisting of butadiene, Ni(0) complexes and additional ligands:

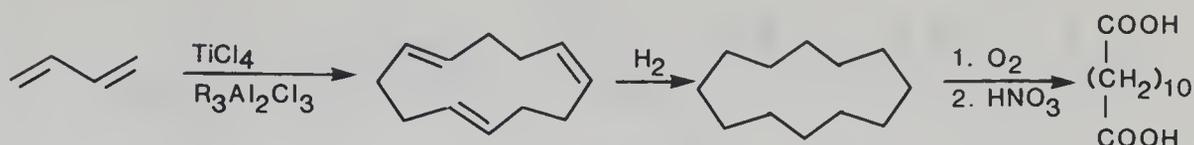


This **cyclotrimerization of butadiene** to cyclododecatriene, initiated by bis(η³-allyl)nickel, was one of the first organometallic reactions subjected to careful mechanistic study (Wilke, from 1960 onwards). Compound 3 can be synthesized independently and channeled into the catalytic cycle. Note the change in coordination number (3, 4), oxidation state (Ni⁰, Ni^{II}) and valence electrons (18, 16) during the course of this cycle.

Complexes of type 2, bearing a phosphane ligand L instead of η²-C₄H₆, effect the **cyclodimerization of butadiene** to 1,5-cyclooctadiene (COD), a frequently used chelating cycloolefin ligand:



An alternative catalytic cyclotrimerization of butadiene leads to *cis,trans,trans*-1,5,9-cyclododecatriene (10,000 t/a, Chem. Werke Hüls), which is subsequently converted into dodecane-1,12-dicarboxylic acid, a polyamide building block:



OLEFIN POLYMERIZATION

The “growth reaction” (Ziegler)

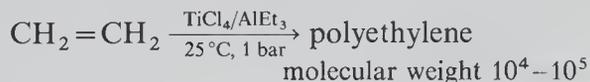


competes with the dehydroalumination



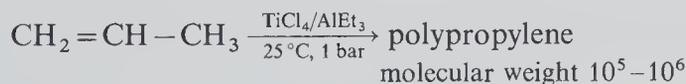
and is limited to the formation of linear aliphatics with a maximum chain length of about C_{200} (cf. p. 77). During a series of systematic studies aimed at producing higher-chain polymers by means of the growth reaction, one particular batch gave the opposite result, namely the quantitative formation of 1-butene from ethylene. A trace of a nickel compound, adventitiously present in the autoclave, was discovered as the cause. In the ensuing search for other transition-metal complexes which would also lead to premature termination of chain growth, a highly polymeric product was unexpectedly obtained when using zirconium acetylacetonate and triethylaluminum.

It was soon realized that the most effective catalyst resulted from the combination $TiCl_4/AlEt_3$ and that ethylene polymerization could be carried out at a pressure as low as 1 bar (**Mülheim normal-pressure polyethylene process**, K. Ziegler, 1955 R):

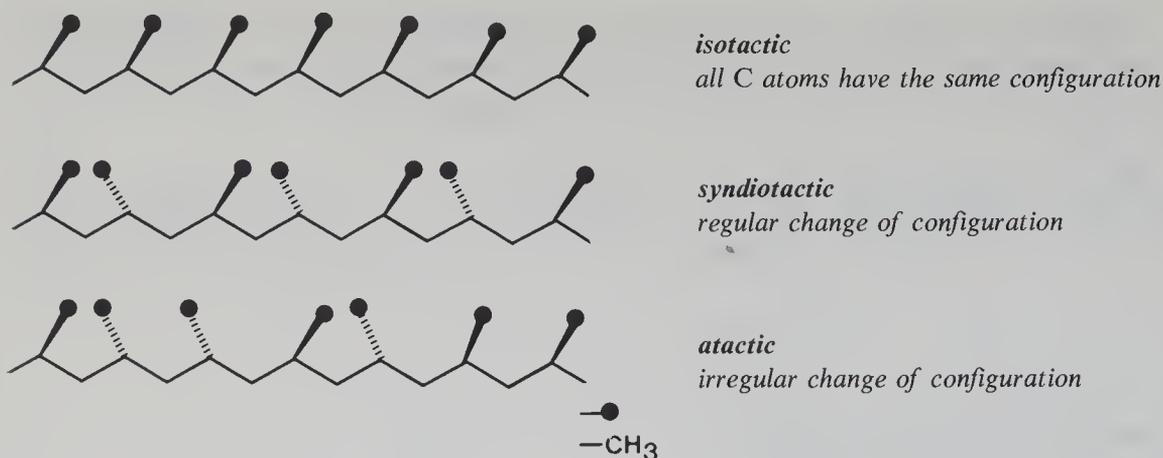


In contrast to high-pressure polyethylene (ICI, 1000–3000 bar, catalyst: max. 0.01 % O_2), low-pressure polyethylene is strictly linear.

The application of Ziegler-type catalysts to the polymerization of propylene and the establishment of a link between the stereochemical structure and the bulk properties of the polymer was the contribution of G. Natta (1955):

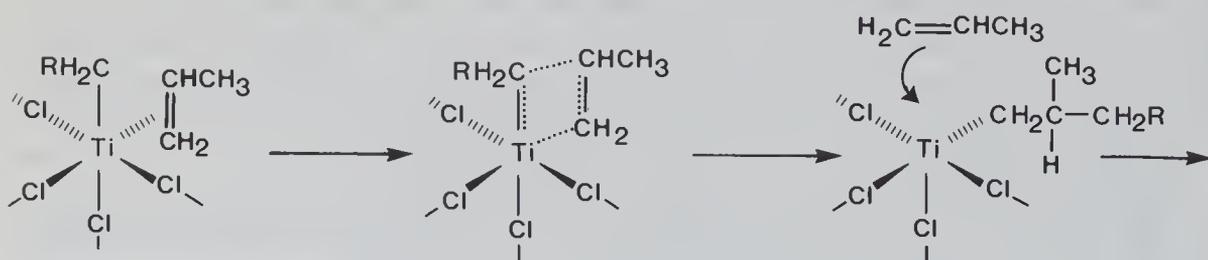


Owing to its stereoregular **isotactic structure**, low-pressure polypropylene has excellent material properties such as high density, hardness and tensile strength (Natta).

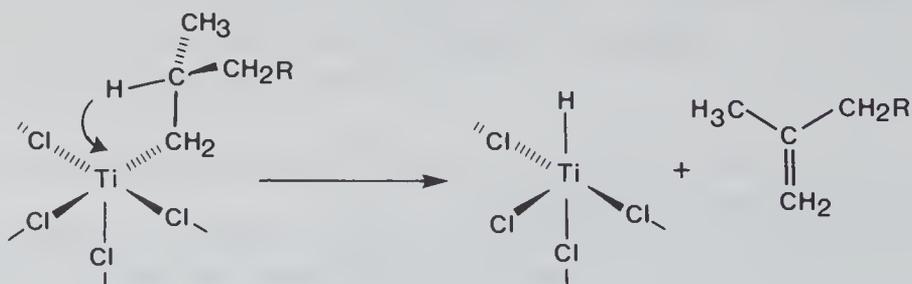


Although plausible conceptions about the mechanism of the **Ziegler-Natta polymerization** and, in particular, the regioselectivity exist, there is little experimental evidence. The reaction is a heterogeneous catalysis in which fibrous TiCl_3 , alkylated on its surface, is regarded as the catalytically active species.

Chain propagation:



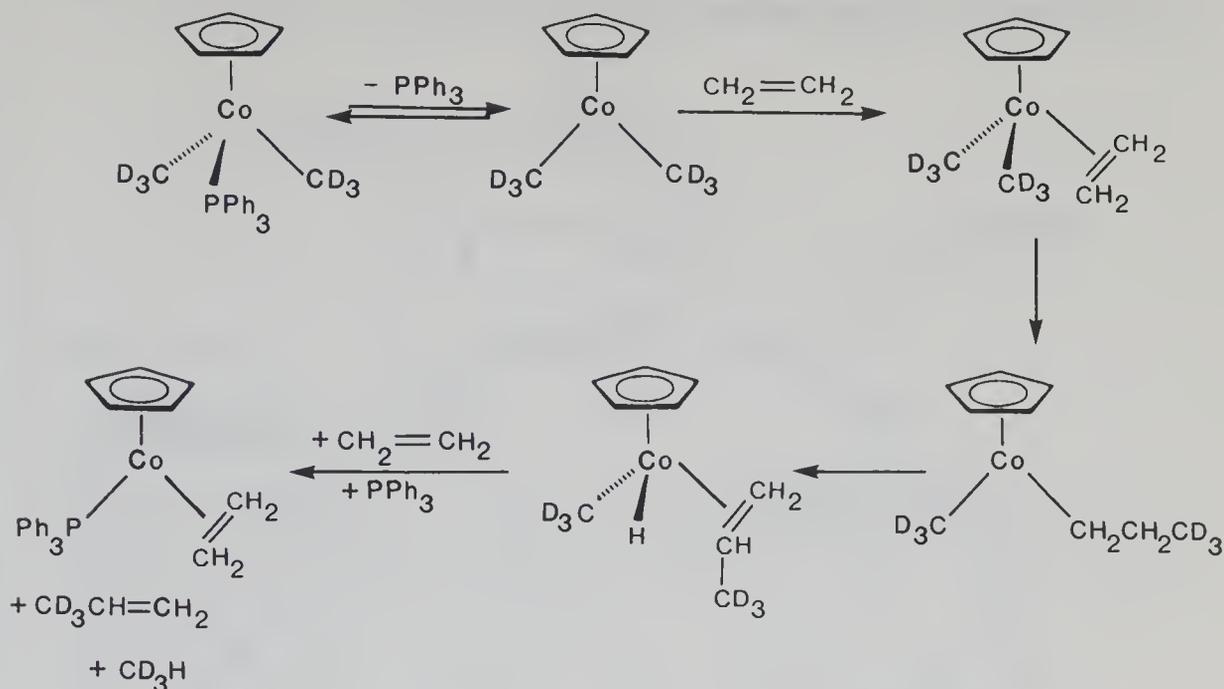
Chain termination:



Cossee (1964 R)

For the central step of the **Cossee mechanism**, namely the intramolecular insertion of an olefin into a transition-metal carbon bond, there is little precedent.

Example (Bergman, 1979):

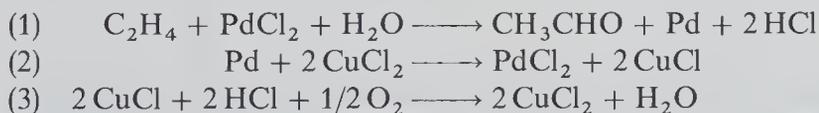


It may be noted in passing that insertions of CO into TM–C or >C=C< into TM–H are much more common.

17.7 Olefin Oxidation (Wacker Process)

The commercially important organic intermediates acetaldehyde, vinyl chloride and vinyl acetate can be produced from acetylene. However, for economic reasons, the switch to ethylene as a chemical feedstock was highly desirable.

The fact that ethylene-chloro complexes of palladium readily decompose in water to acetaldehyde and palladium metal has been known for a century. The reoxidation of Pd⁰ to Pd^{II} by O₂, mediated by the couple Cu⁺/Cu²⁺, finally led to the design of a catalytic cycle (Wacker process, Jira, 1962 R):

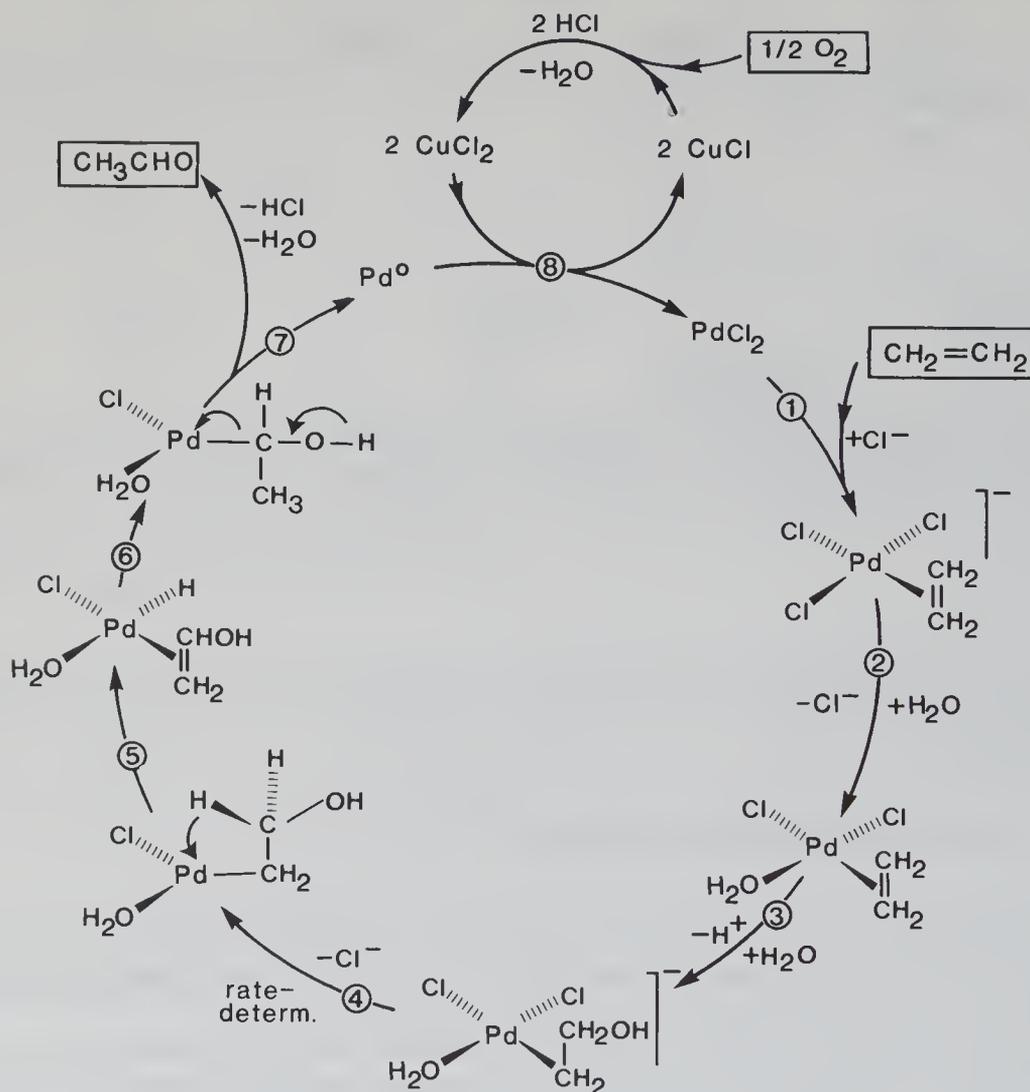


Alkenes of the type RCH=CHR' and RCH=CH₂ are converted to ketones (Example: propylene → acetone).

The following rate equation was derived for the Wacker process:

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = k \cdot \frac{[\text{C}_2\text{H}_4][\text{PdCl}_4^{2-}]}{[\text{H}^+][\text{Cl}^-]^2}$$

Based on detailed kinetic studies a catalytic cycle of the Wacker process which conforms with this rate law has been proposed by Baeckvall (1979):



Wacker process

Accordingly, the nucleophilic attack (3) at coordinated ethylene occurs by **external H₂O** and not by OH⁻ coordinated to palladium. By its very nature, step (3) is an **oxypalladation** (addition of Pd and OH⁻ across the C=C double bond). That acetaldehyde is formed in the final step (7) from the α-hydroxyethyl σ-complex rather than from the vinylalcohol π-complex intermediate is supported by the fact that no deuterium is found in the product if the catalysis is performed in D₂O. The formation of the α-hydroxyethyl palladium complex from the β-hydroxyethyl precursor probably occurs via β-hydride elimination (5) and migratory insertion (6).

The nature of the products of olefin oxidation depends on the reaction medium:

Solvent		Product
water	\longrightarrow $\left[\text{CH}_2 = \text{C} \begin{array}{l} \text{H} \\ \text{OH} \end{array} \right] \longrightarrow \text{CH}_3 - \text{C} \begin{array}{l} \text{O} \\ \text{H} \end{array}$	(acetaldehyde)
acetic acid	\longrightarrow $\text{CH}_2 = \text{C} \begin{array}{l} \text{H} \\ \text{OCOCH}_3 \end{array}$	(vinyl acetate)
alcohol	\longrightarrow $\text{CH}_2 = \text{C} \begin{array}{l} \text{H} \\ \text{OCH}_3 \end{array}$	(vinyl ether)
inert, non-aqueous	\longrightarrow $\text{CH}_2 = \text{C} \begin{array}{l} \text{H} \\ \text{Cl} \end{array}$	(vinyl chloride)

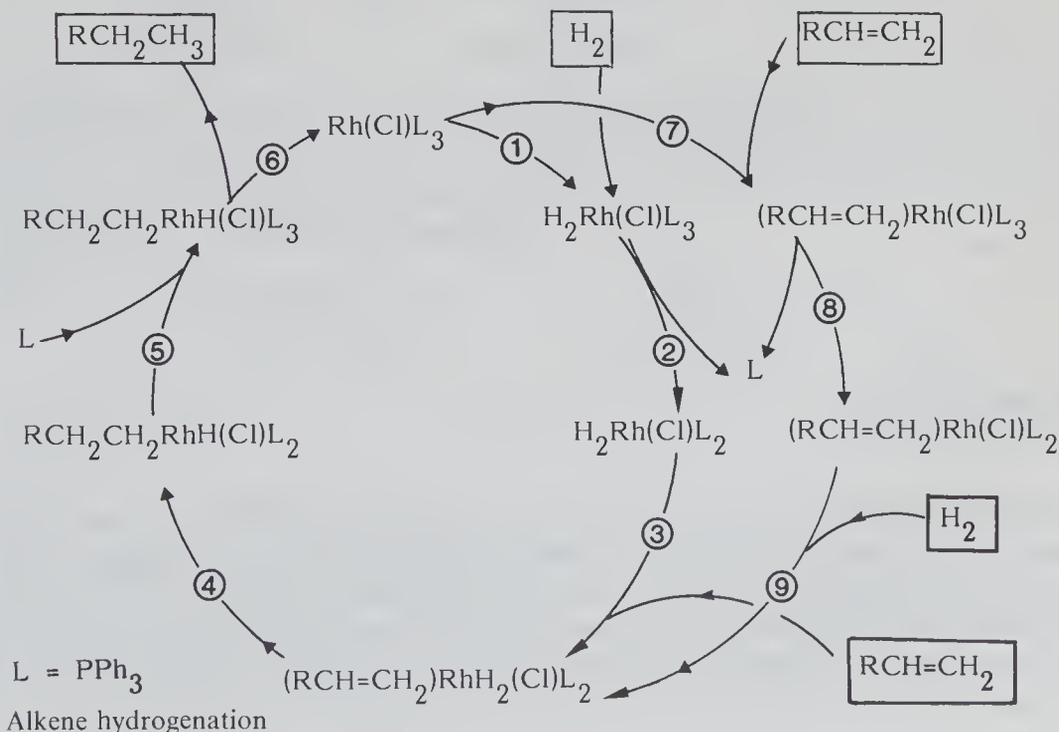
17.8 Hydrogenation of Alkenes

The activation of molecular hydrogen by transition-metal complexes in solution is long known. Intermediate hydride complexes could, however, rarely be isolated. The following three types of reaction present possible ways in which dihydrogen can be activated for hydrogenation in homogeneous solution:

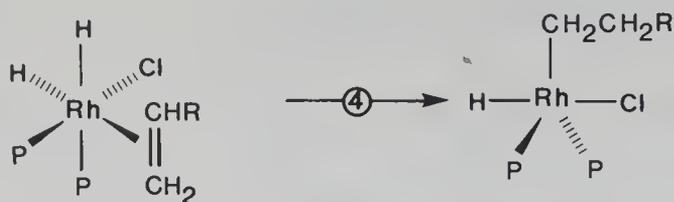
- *Oxidative addition:* $(\text{Ph}_3\text{P})_3\text{RhCl} + \text{H}_2 \longrightarrow (\text{Ph}_3\text{P})_3\text{Rh}(\text{H})_2\text{Cl}$
- *Heterolytic cleavage:* $[\text{RuCl}_6]^{3-} + \text{H}_2 \longrightarrow [\text{RuCl}_5\text{H}]^{3-} + \text{H}^+ + \text{Cl}^-$
- *Homolytic cleavage:* $2[\text{Co}(\text{CN})_5]^{3-} + \text{H}_2 \longrightarrow 2[\text{Co}(\text{CN})_5\text{H}]^{3-}$

The first complex to serve as a hydrogenation catalyst in homogeneous solution was the compound $(\text{Ph}_3\text{P})_3\text{RhCl}$ (**Wilkinson's catalyst**, 1965). This species catalyzes the hydrogenation of alkenes, alkynes and other unsaturated molecules at 25 °C and a pressure of 1 bar.

A thorough mechanistic study of this system was undertaken by Halpern (1976):

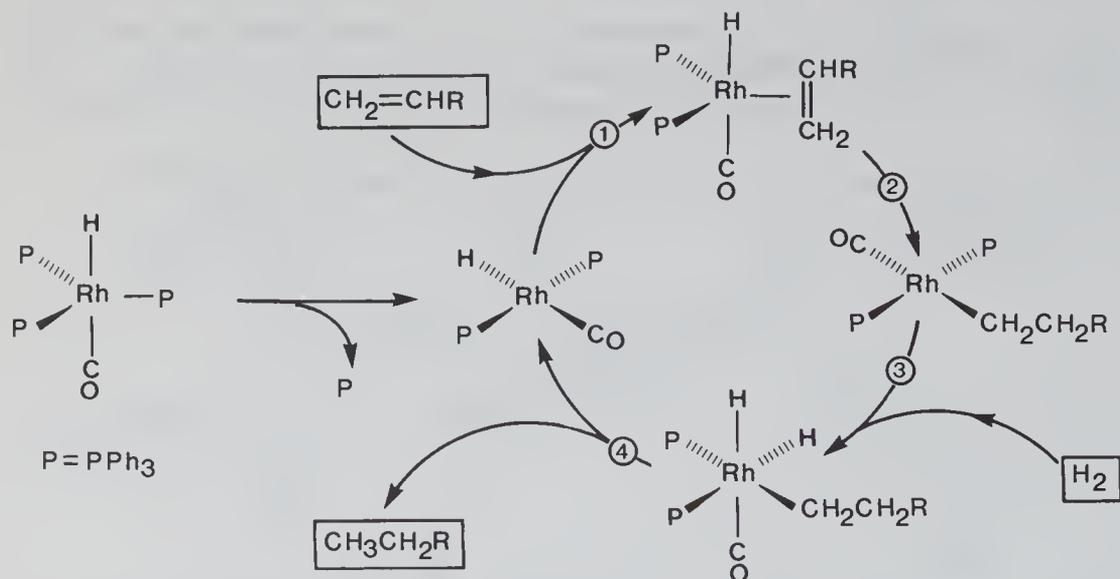


The simplified reaction scheme on p. 427 shows two routes which differ in the order in which H_2 and the olefin are taken up. As step ⑨ is slow, the sequence ① → ② → ③ should take preference over ⑦ → ⑧ → ⑨. The decisive step is the **insertion** ④:



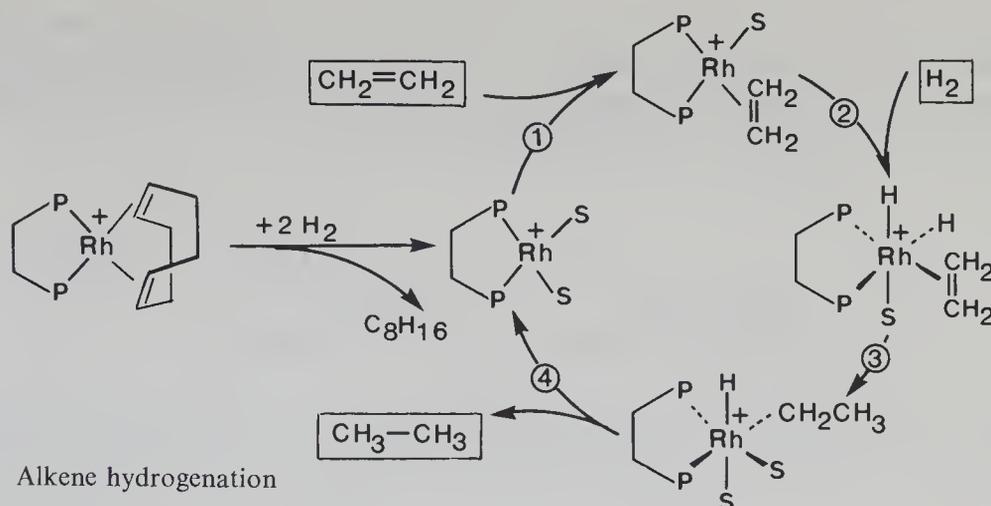
Cis-coordination of the phosphane ligands in these non-isolable intermediates is suggested by special NMR techniques (J. M. Brown, 1984). The rate determining nature of the intramolecular migratory insertion ④ also follows from an ab initio MO study of the full catalytic cycle (Morokuma, 1988).

While $(\text{Ph}_3\text{P})_3\text{RhCl}$ catalyzes the hydrogenation of terminal **and** internal olefins, $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{H}$ is **highly selective**, catalyzing hydrogenation of **terminal** olefins only (Wilkinson, 1968). A drawback of this catalyst is the concomitant isomerization of terminal to internal olefins, (cf. p. 418), the latter being hydrogenated very slowly (Strohmeier, 1973).



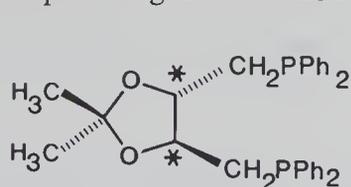
Alkene hydrogenation

Another class of catalysts is cationic and of the general type $[\text{L}_2\text{RhS}_2]^+$, where S represents a polar solvent molecule such as THF or CH_3CN (Osborn, 1976). These catalysts are generated *in situ* from the easily available diolefin complex $[(\text{COD})\text{RhL}_2]^+$ and H_2 . The addition of the olefin ① is followed by the oxidative addition of H_2 ② as the rate-determining step. Insertion ③ and elimination ④ complete the catalytic cycle (Halpern, 1977):



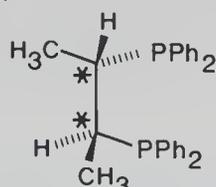
Asymmetric Hydrogenation

If the catalyst of the variety $(\text{L}_2\text{RhS}_2)^+$ bears an optically active diphosphane, prochiral unsaturated molecules can be hydrogenated to chiral products (asymmetric induction). In many cases, high optical purity has been achieved. Examples of chiral chelating diphosphane ligands are the following:



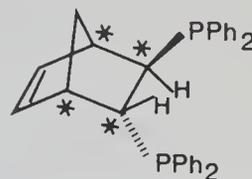
DIOP

(Kagan, 1972)



CHIRAPHOS

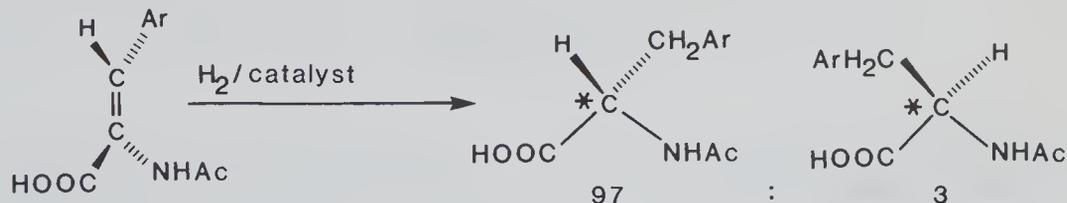
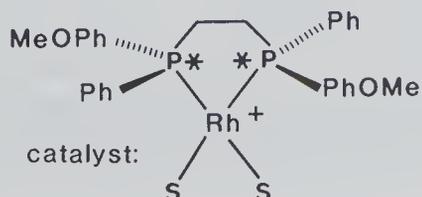
(Bosnich, 1977)



NORPHOS

(Brunner, 1979)

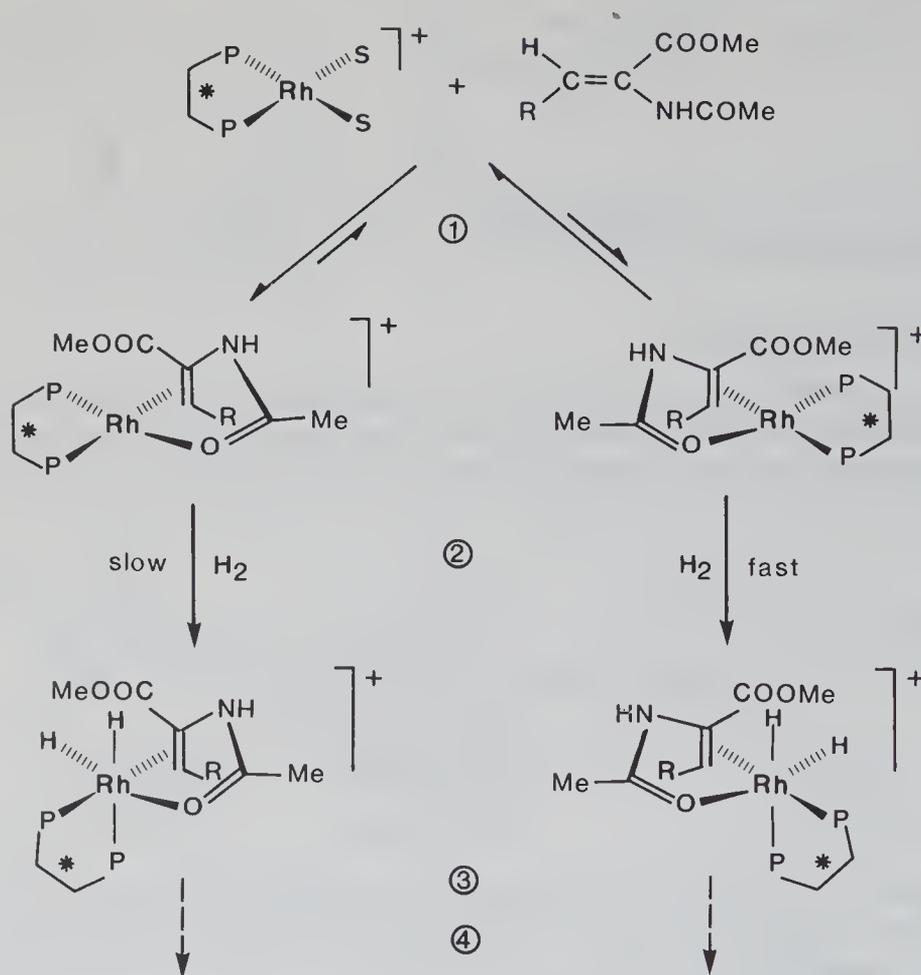
The chirality of the diphosphane ligand can be centered either at a carbon atom of the ligand framework or at phosphorus. A commercial application of asymmetric hydrogenation is the manufacture of a derivative of the chiral amino acid L-Dopa, which is effective in the treatment of Parkinson's disease:

Ar = 3,4- $\text{C}_6\text{H}_3(\text{OH})_2$ 

MONSANTO (1977)

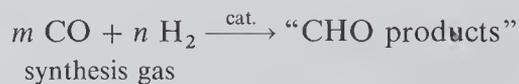
(Knowles, 1986 R)

The enantioselective step in this asymmetric hydrogenation is thought to be the oxidative addition (2) of H₂ to the diastereomeric η²-olefin complexes formed in step (1). The diastereomer less favored in the equilibrium reacts more rapidly with H₂ and therefore accounts for the enantiomeric excess (Halpern, 1983 R):



(p. 429)

17.9 Fischer-Tropsch Reactions



Depending on the reaction conditions, liquid alkanes, olefins, methanol and/or higher alcohols are formed. A common feature of all Fischer-Tropsch variants is the use of CO as the source of carbon (“C₁ chemistry”).

Generation of synthesis gas:

- *Controlled combustion of petroleum*
- “Reforming” natural gas (which consists mainly of CH₄)



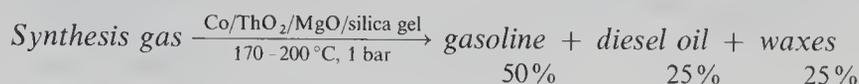
At present, this is the main source of syngas.

- *Coal gasification*

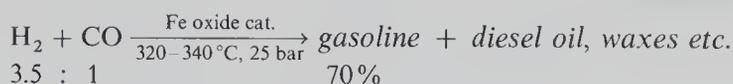


The production of syngas from coal in the (distant) future may well replace the process based on natural gas. This would, however, require that a catalysis of the water gas shift reaction be developed to enhance the H₂ content in syngas (cf. p. 432).

Classical Fischer-Tropsch processes are heterogeneously catalyzed. One problem is low product selectivity. Examples:

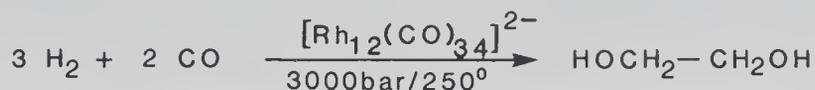


(Ruhchemie A.G., from 1936 on, discontinued in Germany after World War II)



The availability of cheap coal as a feedstock for syngas enables South Africa to satisfy about half of its gasoline demand in this manner (Sasol plant).

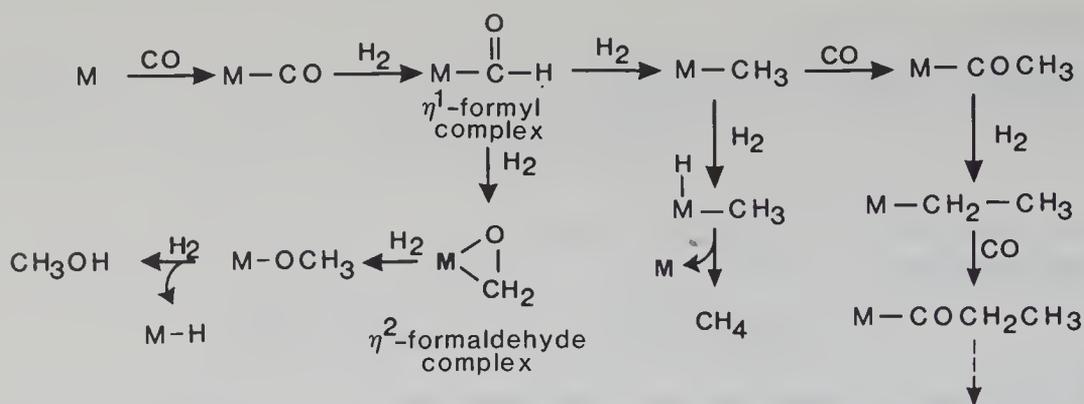
The introduction of homogeneous processes for the production of synthetic fuels from coal seems unlikely owing to the large plant size these processes would necessitate. With regard to the selective preparation of other Fischer-Tropsch products (short-chain olefins, glycols etc.), homogeneously catalyzed processes are potentially interesting, however (“New era of C₁ chemistry”). Example:



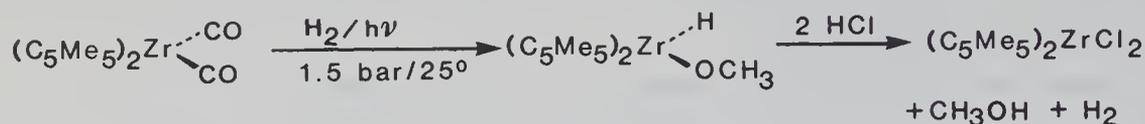
(Pruett, Union Carbide, 1974)

At lower pressures, methanol is formed rather than glycol. This homogeneously catalyzed reaction has not yet been implemented, largely due to the drastic conditions required. There remains, however, a heavy industrial demand for glycol (anti-freeze, building block for polyesters etc.).

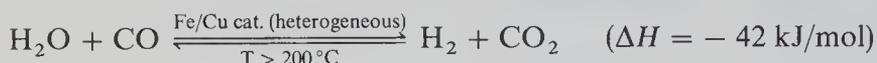
Mechanistic models of the Fischer-Tropsch reaction are based on the grossly simplified reaction sequences sketched on p. 432. M can be an active site on the catalyst surface (heterogeneous catalysis) or the vacant coordination site of a transition-metal complex in solution (homogeneous catalysis). In order to elucidate the detailed mechanisms, potential organometallic intermediates are synthesized and their reactivity patterns studied.



The first experimental proof for the reduction of coordinated CO by H₂ was supplied by Bercaw (1976):



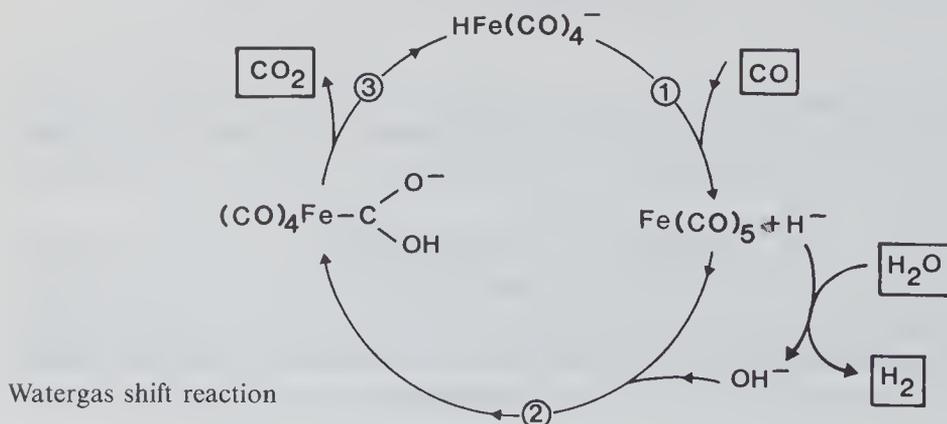
17.10 The Water-Gas Shift Reaction



The importance of this equilibrium, also known as “conversion”, lies in

- H₂ enrichment of synthesis gas for Fischer-Tropsch reactions
- Exploitation of the reducing power of CO to produce H₂ from H₂O under mild conditions
- Removal of CO from “mixed gas” (50% N₂, 30% CO, 15% H₂, 5% CO₂) for the Haber-Bosch process

The relatively high reaction temperature, unfavorable for the position of the equilibrium, is dictated by the non-optimal properties of the currently available catalysts. The development of a homogeneous catalysis for the water gas shift reaction has assumed high priority. The following cycle illustrates a possible approach (King, 1978):

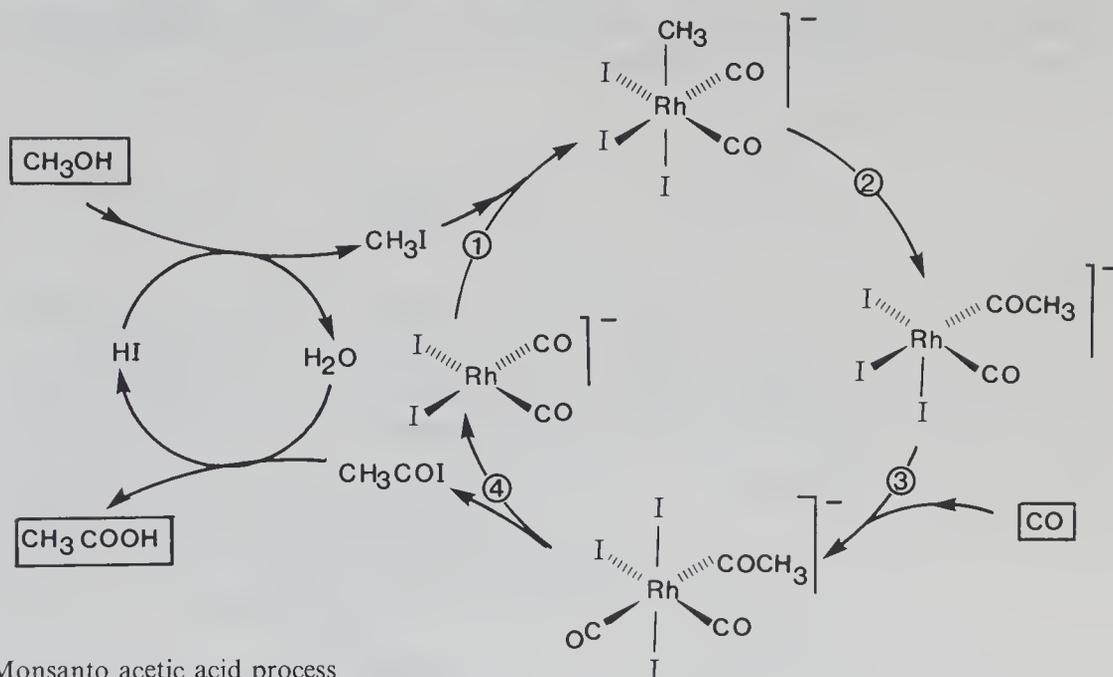


17.11 Monsanto Acetic Acid Process

This involves the homogeneously catalyzed **carbonylation of methanol** to yield acetic acid (“C₁ chemistry”):

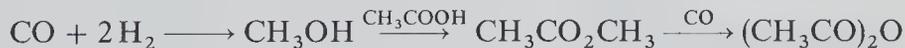


The catalysis most likely proceeds by the following mechanism (D. Forster, 1979 R):



Monsanto acetic acid process

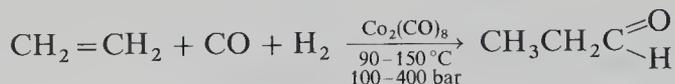
Since a large portion of the industrially produced acetic acid is converted into acetic anhydride to be used as an acetylation reagent, the direct formation of **acetic anhydride** by means of homogeneous catalysis is highly desirable. This target has been reached in the **Tennessee Eastman/Halcon SD process**, a carbonylation of methyl acetate in use since 1983:



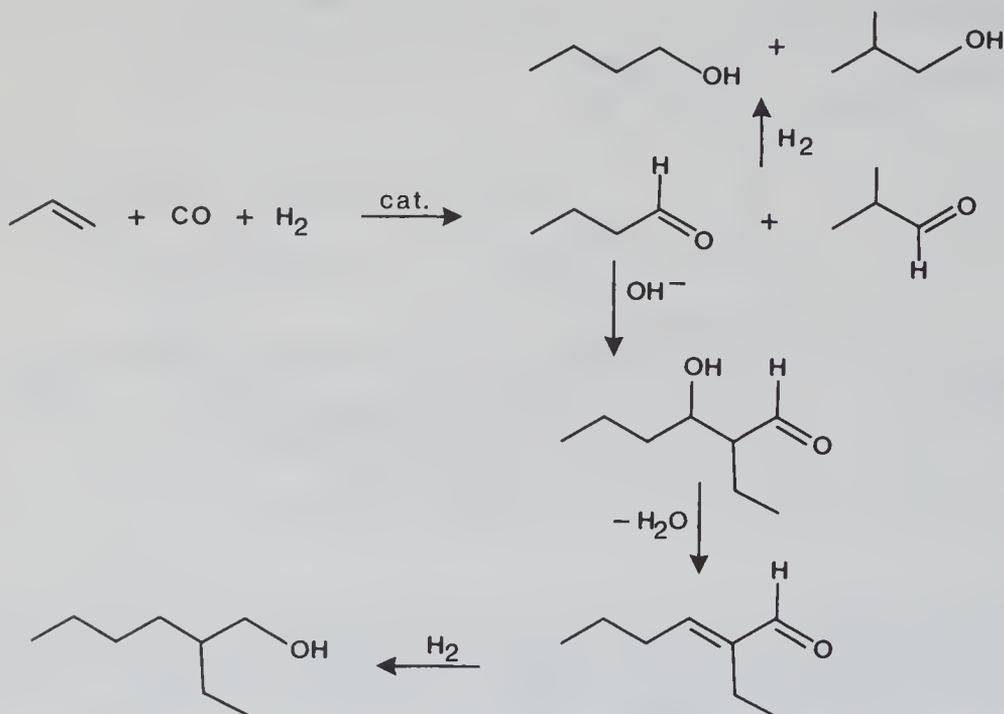
An outstanding feature of this process is the fact that its C₁ building blocks are derived exclusively from coal. The acetic acid required is obtained as a byproduct in the acetylation of cellulose. As in the Monsanto acetic acid process, $\text{cis}-(\text{CO})_2\text{RhI}_2^-$ serves as the catalyst and the overall cycle seems to share a certain similarity with that of the acetic acid process (Polichnowski, 1986).

17.12 Hydroformylation (Oxo Reaction)

The hydroformylation of olefins is the largest-scale industrial process that is homogeneously catalyzed, with a capacity of about 5×10^6 t/a in oxo compounds and their follow-up products. The reaction was discovered in 1938 by O. Roelen (Ruhchemie A.G.), who prepared propionaldehyde from ethylene and synthesis gas by means of a cobalt catalyst:



Today, $\text{C}_3 - \text{C}_{15}$ aldehydes are produced by the oxo process and subsequently converted into amines, carboxylic acids and, above all, primary alcohols. The most important oxo products are butanol and 2-ethylhexanol:

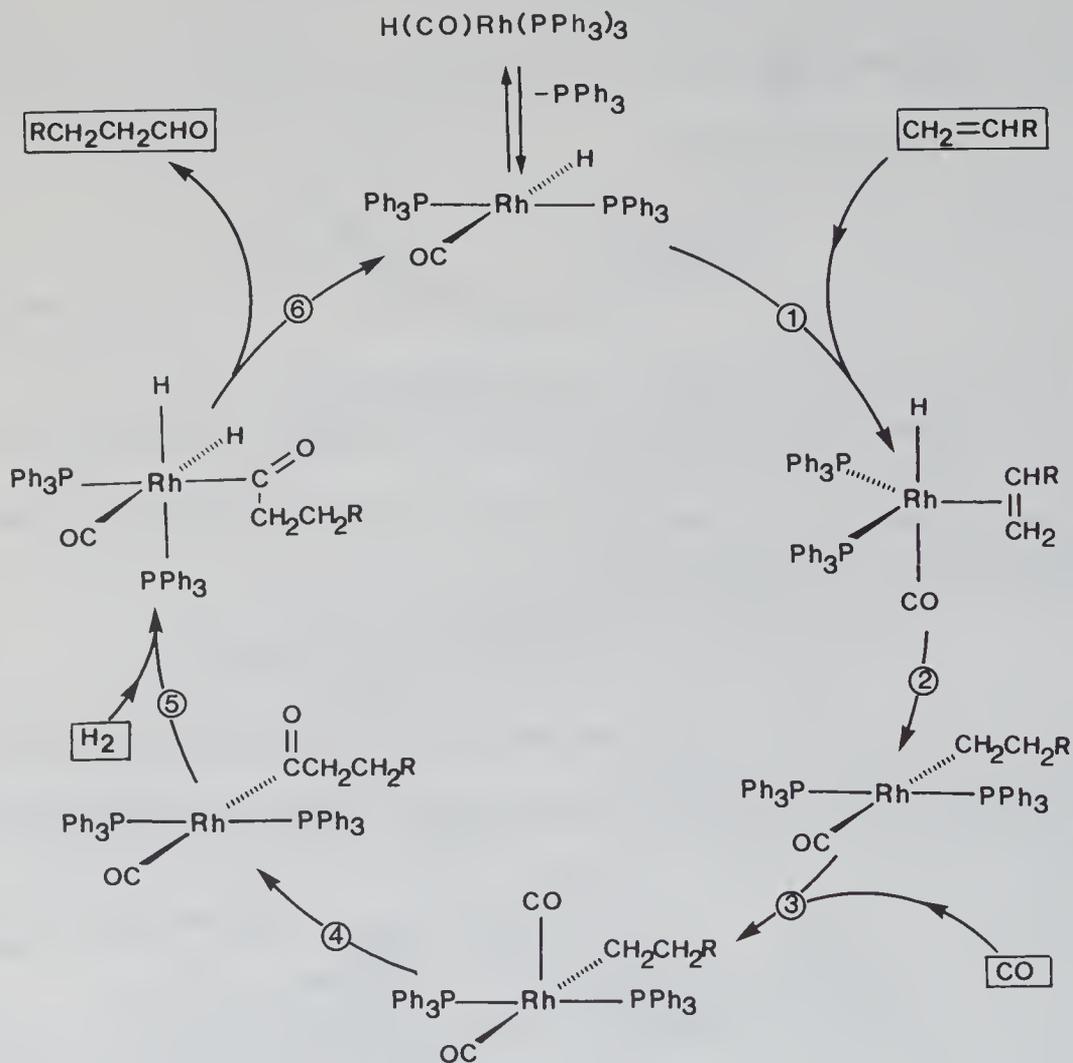


In the oxo reaction, **H and HCO are formally added** across a double bond; it is therefore referred to as “**hydroformylation**”.

A **mechanism** for the hydroformylation process was suggested by R.F. Heck and D.S. Breslow in 1961 (see p. 435 above). Experimental verification of this mechanism on the basis of kinetic measurements will be exceedingly difficult due to the large number of variables. The rate-determining step is possibly (6), the oxidative addition of H₂. Alternative mechanisms have been proposed by E. Oltay (1976, study under actual process conditions, assumption of a 20 VE intermediate) and by T. L. Brown (1980, radical mechanism).

Conclusion: The CO group of the acetyl group originates in the coordination sphere of $\text{CH}_3\text{Mn}(\text{CO})_5$; i.e., CO insertion proceeds intramolecularly. The stereochemistry observed implies that the alkyl group migrates to the cis-positioned CO group and that the vacant coordination site, thus created, is occupied by a new ligand like CO or phosphane (Calderazzo, 1977 R).

A more recent outgrowth, the **Union Carbide hydroformylation process**, utilizes $(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})\text{H}$ instead of $\text{HCo}(\text{CO})_4$ as a precatalyst. This procedure circumvents some of the disadvantages mentioned for $\text{HCo}(\text{CO})_4$:



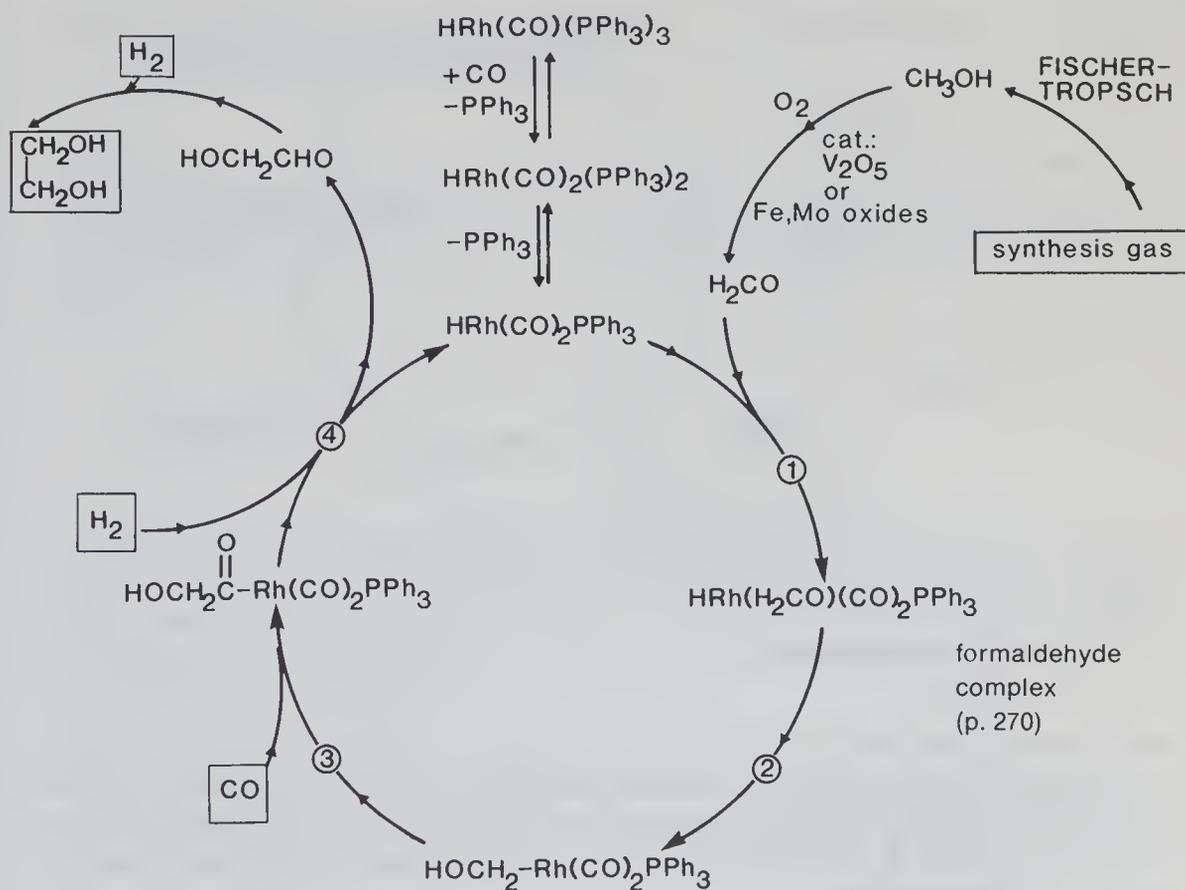
Union Carbide hydroformylation process

A goal of great commercial interest is the development of a catalytic oxo process which selectively yields **linear products**. In fact, replacement of cobalt by rhodium and the introduction of bulky phosphane ligands markedly increases the linear/branched product ratio. The reason for this could lie in the higher stability of the square-planar intermediate formed in step (2) with its *trans*-oriented phosphane ligands and a terminal alkyl group.

Compared to the cobalt-catalyzed oxo reactions, the rhodium-catalyzed process operates under rather mild conditions (100 °C, 10–20 bar).

An important further development of the Union Carbide oxo process is that of a two-phase liquid/liquid reaction system, made possible by the introduction of water soluble (phosphane)rhodium catalysts, mentioned on p. 412 (Rhone-Poulenc/Ruhrchemie, 1984).

The classical oxo reaction represents the hydroformylation of olefins. In an attempt to entirely switch to coal as a chemical feedstock, the **hydroformylation of the C₁ building block formaldehyde** is currently being explored. It is hoped that the drastic reaction conditions ($p = 3000$ bar) which have so far prevented the commercial application of the Union Carbide ethylene glycol process can be attenuated. The starting material formaldehyde itself is easily accessible from the Fischer-Tropsch product methanol. The following scheme traces the formation of **ethylene glycol from synthesis gas** (Monsanto, 1983):

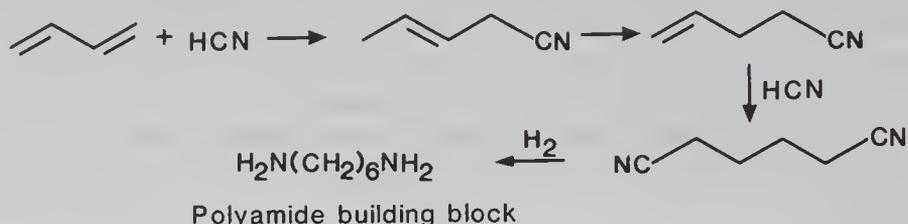


Ethylene glycol from synthesis gas (Monsanto, 1983)

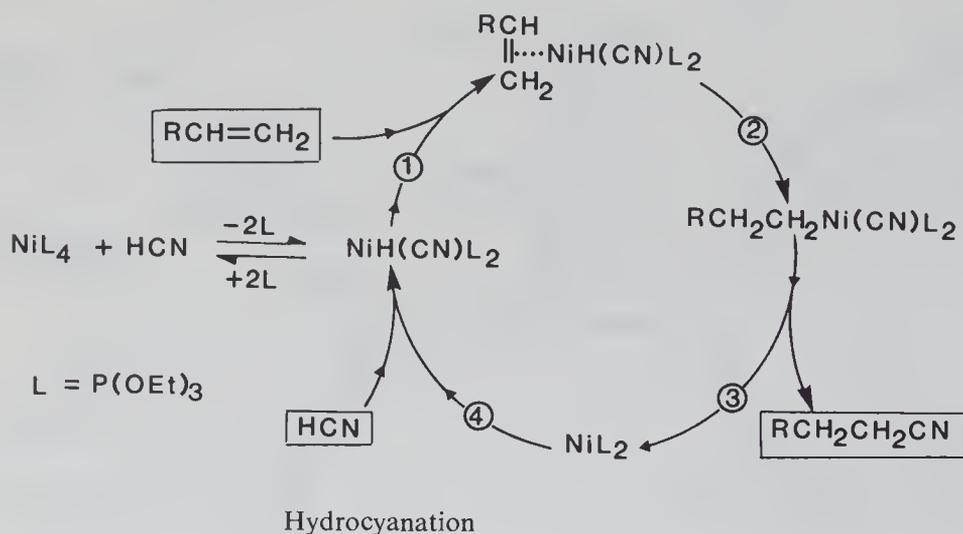
This process is still at an experimental stage.

17.13 Hydrocyanation

Certain complexes, mainly of nickel and palladium, catalyze the addition of HCN to olefins (Tolman, 1986 R). An important commercial application of this homogeneous catalysis is the production of adiponitrile $\text{NC}(\text{CH}_2)_4\text{CN}$ from butadiene and HCN (Du Pont):

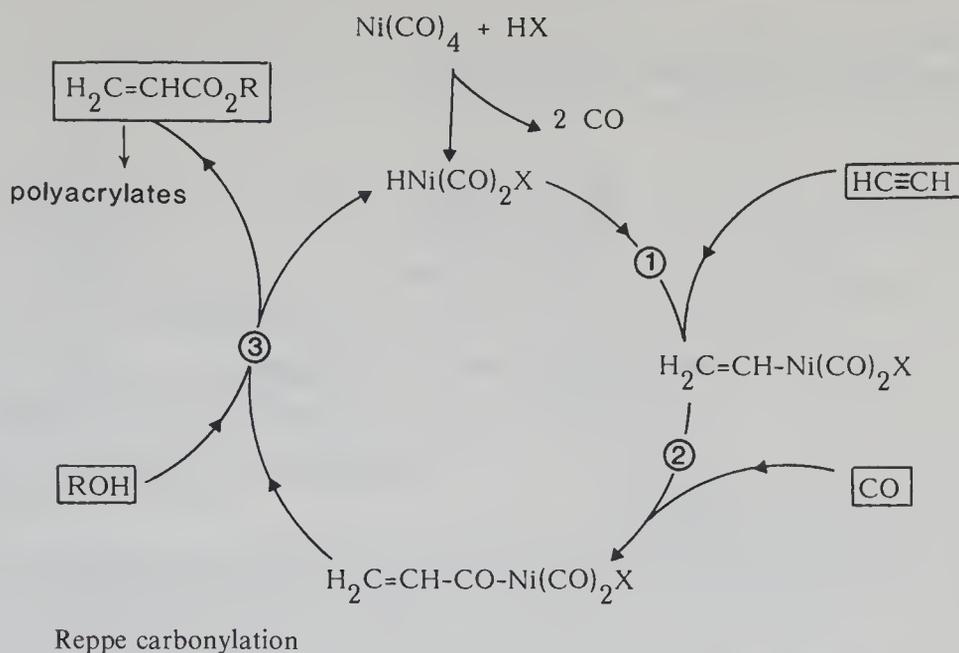


The active catalyst $\text{NiH}(\text{CN})\text{L}_2$ is formed from NiL_4 by ligand dissociation and oxidative addition of HCN:



17.14 Reppe Carbonylation

In this process, the carbonylation of alkenes and alkynes with the simultaneous addition of HX (molecule with active H) is achieved. $\text{HCo}(\text{CO})_4$, $\text{Ni}(\text{CO})_4$ or $\text{Fe}(\text{CO})_5$ can serve as the catalysts. An example is the production of acrylic ester from acetylene, CO, and ROH (BASF, Röhm & Haas, 140,000 t/a each). A disadvantage are the hazards encountered in handling acetylene.



17.15 Activation of C–H Bonds in Alkanes – a Topical Problem in Organometallic Research

One of the most exacting tasks facing homogeneous catalysis is the **intermolecular** activation of saturated hydrocarbons. The decisive step, the oxidative addition of C–H to the metal, formally resembles the addition of H₂, but in most cases is thermodynamically unfavorable due to the weaker nature of M–C as compared to M–H bonds (Halpern 1985 R):



Thus, (hydrido) σ -alkyl transition-metal complexes are known in small number only; they tend to decompose by reductive elimination of alkanes (cf. the mechanism of homogeneously catalyzed hydrogenation of alkenes, Section 17.8). Oxidative addition of **arene C–H bonds** to transition metals has been known for some time, however.

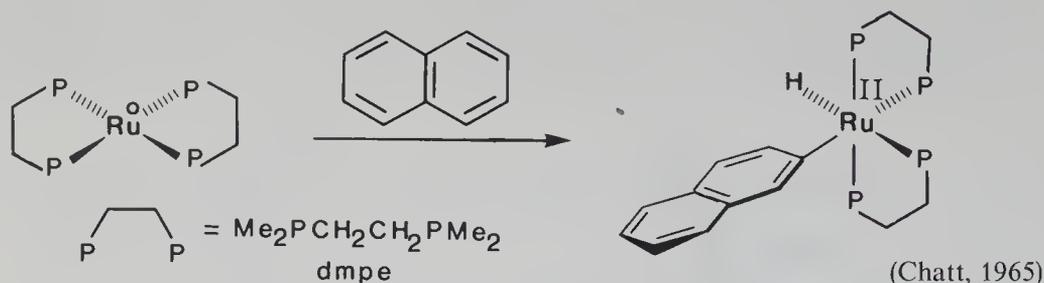
Intramolecular C–H addition:



This reaction type is called **orthometallation** or, more generally, **cyclometallation** (M. I. Bruce, 1977 R). The widespread occurrence of such cyclometallations reflects their

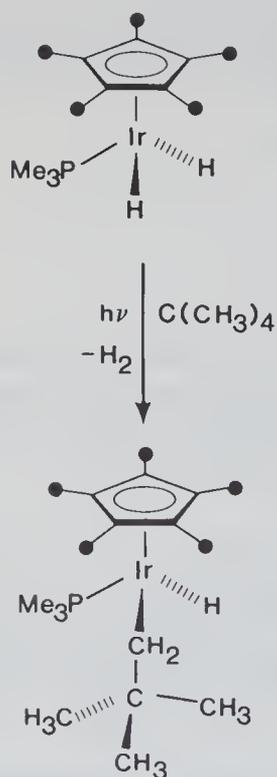
neutral entropic character. A prerequisite is that the C–H bonds are located so as to allow close approach to the central metal atom.

Intermolecular C–H addition:

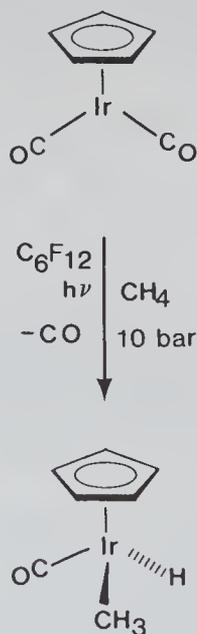


$(\text{dmpe})_2\text{RuH}(\text{C}_{10}\text{H}_7)$ is thermolabile and in equilibrium with a complex $(\text{dmpe})_2\text{Ru}(\text{C}_{10}\text{H}_8)$ of unknown structure.

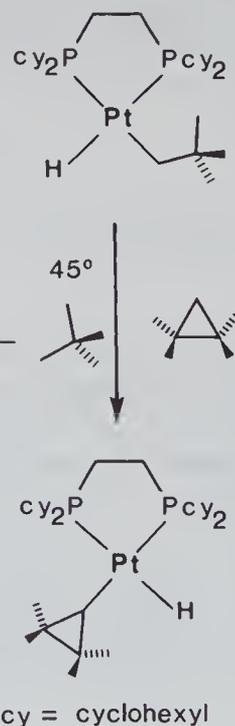
Of more recent origin are observations concerning the **intermolecular oxidative addition of alkanes** to transition metal centers. A common feature of these reactions is the prior generation of a complex of low coordination number and high electron density at the central metal. These coordinatively unsaturated species react readily even with non-activated aliphatic C–H bonds. What is particularly remarkable about this reaction is its high selectivity: the intermolecular reaction of the organometallic intermediate with saturated hydrocarbons is clearly favored over the reaction with the C–H bonds of its own ligands!



(R. G. Bergman, 1982)



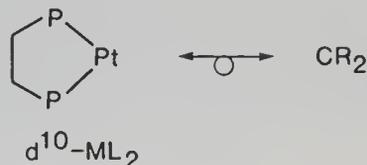
(W. A. G. Graham, 1983)



(G. M. Whitesides, 1986)

In the case of $[\text{cy}_2\text{P}(\text{CH}_2)_2\text{Pcy}_2]\text{PtH}(\text{C}_5\text{H}_{11})$, a coordinatively unsaturated Pt^0 complex is formed via reductive elimination of neopentane; this complex is especially suitable for illustrating important aspects of C–H activation:

- *Intramolecular cyclometallation is suppressed here since the incorporation of the organophosphanes into a chelating ligand prevents the C–H bonds from approaching the platinum atom.*
- *The Pt–C bond from the intermolecular reaction should be relatively strong as inter-ligand repulsion, which often weakens an M–C bond, is minimal here.*
- *The isolobal relationship likens the reaction of the fragment L_2Pt with C–H bonds to the insertion of singlet carbenes into C–H bonds.*
- *The exposure of the Pt atom in the fragment L_2Pt is reminiscent of that of the vertex atoms at heterogeneously active metal surfaces.*



These addition reactions have not yet found practical applications, as they have resisted incorporation into catalytic cycles. They demonstrate, however, that under appropriate conditions the reaction of non-activated C–H bonds with transition metal centers is thermodynamically and kinetically feasible and may therefore pave the way for further advances.

18 Literature

For a more detailed treatment of special topics in organometallic chemistry, students are referred to "Comprehensive Organometallic Chemistry" by Wilkinson, Stone and Abel. In keeping with the nature of the present text as a 'concise introduction', only a limited number of monographs and specialized review articles are included in the following list of references.

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Appendix

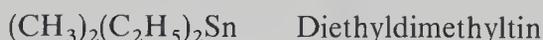
Symbols and Abbreviations

<i>a</i>	isotropic hyperfine coupling constant (ESR)	E	element
ab	antibonding	<i>E</i>	energy
Ac	acetyl	<i>E</i> ⁰	standard reduction potential for Ox + e ⁻ → Red
acac	acetylacetonate	EH	Extended Hückel
AIBN	azoisobutyronitrile	El	electrophile
AN	acetonitrile	\bar{E}	mean bond enthalpy (kJ/mol)
AO	atomic orbital	<i>EN</i>	electronegativity
Ar _F	perfluoroaryl	en	ethylenediamine
Ar	aryl	ET	electron transfer
b	bonding	ESR	electron spin resonance
bipy	2,2'-bipyridyl	2e3c	two electron three center bond
B.M.	Bohr magneton	EXT	extrusion (= deinsertion)
bp	boiling point (°C)	(g)	gas
Bu	1-butyl	<i>g</i>	<i>g</i> -value (ESR)
CC	cocondensation	γ	magnetogyric ratio
<i>c</i> -Hex	cyclohexyl	HMPA	hexamethylphosphoric trisamide
C.N.	coordination number	HOMO	highest occupied molecular orbital
COD	1,5-cyclooctadiene	INS	insertion
COMC	Comprehensive Organometallic Chemistry	<i>J</i>	scalar nuclear spin-spin coupling constant (NMR)
COT	cyclooctatetraene	(<i>l</i>)	liquid
Cp	cyclopentadienyl	LUMO	lowest unoccupied molecular orbital
Cp*	pentamethylcyclopentadienyl	M	metal
<i>D</i>	bond dissociation energy (kJ/mol)	Me	methyl
<i>d</i>	bond length (pm)	MGE	main-group element
dmpe	1,2-bis(dimethylphosphino)ethane	MO	molecular orbital (method)
dppe	1,2-bis(diphenylphosphino)ethane	mp	melting point (°C)
δ	chemical shift (NMR)	<i>n</i>	normal
Δ_0	splitting <i>t</i> _{2g} / <i>e</i> _g (octahedral field)	Nu	nucleophile
DBPO	di- <i>t</i> -butylperoxide	ν	stretching frequency (cm ⁻¹)
DME	1,2-dimethoxyethane	nb	nonbonding
DMF	dimethylformamide	OA	oxidative addition
DMSO	dimethylsulfoxide		

Ox	oxinate	<i>T</i>	temperature
OS	oxidation state	T	Tesla
Ph	phenyl	$t_{1/2}$	half life
Pr	1-propyl	THF	tetrahydrofuran
PE	petrol ether	TM	transition metal
py	pyridine	TMEDA	<i>N,N,N',N'</i> -tetramethyl- ethylenediamine
<i>r</i>	radius (pm)	Vi	vinyl
RE	reductive elimination	VSEPR	valence shell electron pair re- pulsion (Gillespie-Nyholm- model)
R _F	perfluoroalkyl	VE	valence electron
RT	room temperature	VB	valence bond (method)
σ	shielding (NMR)		
(s)	solid		
SCE	saturated calomel electrode		
<i>t</i>	tertiary, ton		

Nomenclature of Organometallic Compounds

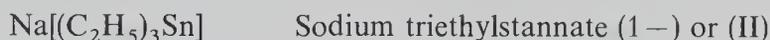
Organometallic compounds containing only $M-\overset{\sigma}{C}$ bonds are named according to the IUPAC Rules D-3. Ligands are listed in alphabetical order, followed by the name of the metal (cations taking precedence over anions):



Group 14 and 15 organyls can also be named by considering them to be derivatives of their binary hydrides (ending -ane, analogues to alkanes):



Anionic complexes are given the ending -ate, together with the charge on the anion or the oxidation number of the central metal atom:



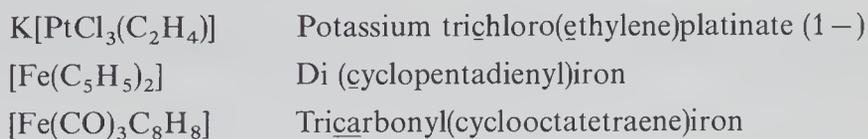
Cations are also characterized by a charge or oxidation number:



Complexes containing unsaturated hydrocarbons coordinated to a metal require a special nomenclature; this is also found in the IUPAC rules (volume 2, group 1, Rule 7.4). In π -complexes, at least two carbons of the ligand are bonded to the metal. However, use of the expression " π -coordinated" alone is too imprecise, since the exact nature of the bonding (σ , π) is often uncertain. Therefore, it seems wise to indicate the atoms bonded to the metal atom in a manner completely independent of theoretical implications (F. A. Cotton).

The precision with which a compound is named is largely determined by the complexity of its structure.

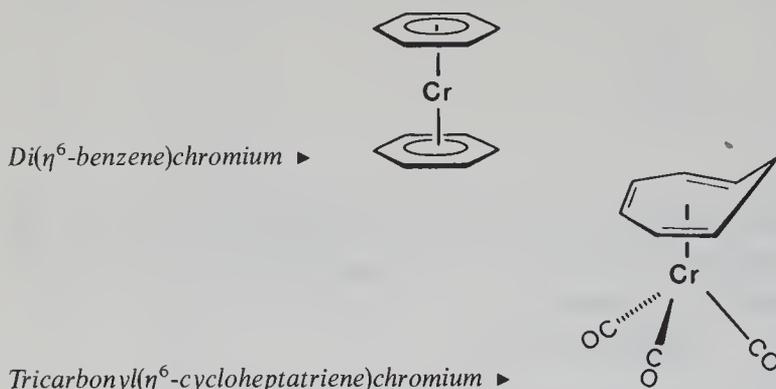
1. Designation of Stoichiometric Composition Only



2. Designation of Structure

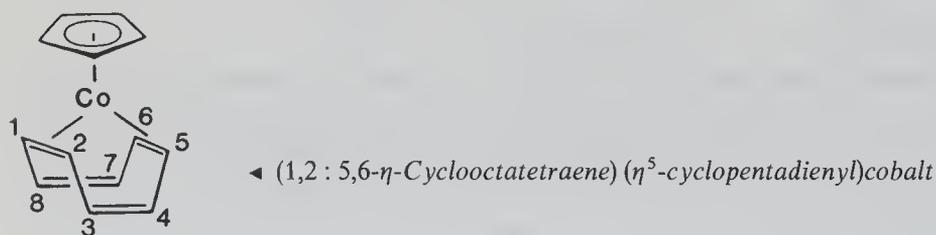
If all the unsaturated C atoms are coordinated to the metal, the name of the ligand is preceded by η - (pronounced eta). The number of coordinated C atoms can be addition-

ally indicated by a numerical right superscript and η then reads as -hapto (e.g., η^3 = trihapto, η^4 = tetrahapto, η^5 = pentahapto etc.).

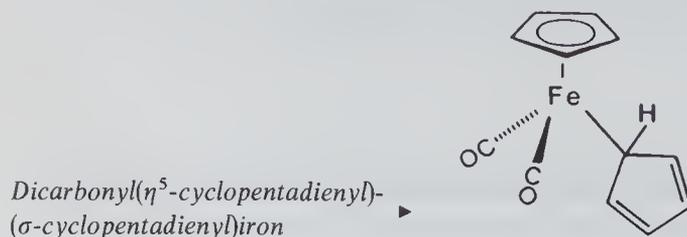


3. Exact Designation of the Coordinated Atoms

If not all the unsaturated C atoms of a ligand are involved in bonding, or if a ligand possesses several bonding modes, the locations of the ligating atoms appear in numerical sequence before the hapto symbol η . If the coordinated carbon atoms are in a consecutive sequence, only the first and last positions are indicated.

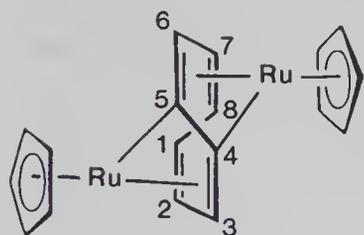
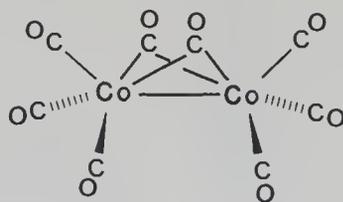


When it is desired to stress that a ligand is bonded to a single atom, the prefix σ - may be used:



Ligands which coordinate simultaneously to two or more metals (bridging ligands) are given the prefix μ (mu). A metal-metal bond is indicated by italicized atomic symbols enclosed in parentheses at the end of the name:

Di- μ -carbonyl-bis(tricarbonyl)-cobalt (Co-Co)



trans- μ [1-5 : 4-8- η -Cyclooctatetraene]-bis [(cyclopentadienyl)ruthenium]

For further details relating to stereochemical nomenclature and notation see T. E. Sloan in "Comprehensive Coordination Chemistry", Vol. 1, 1987, 109.

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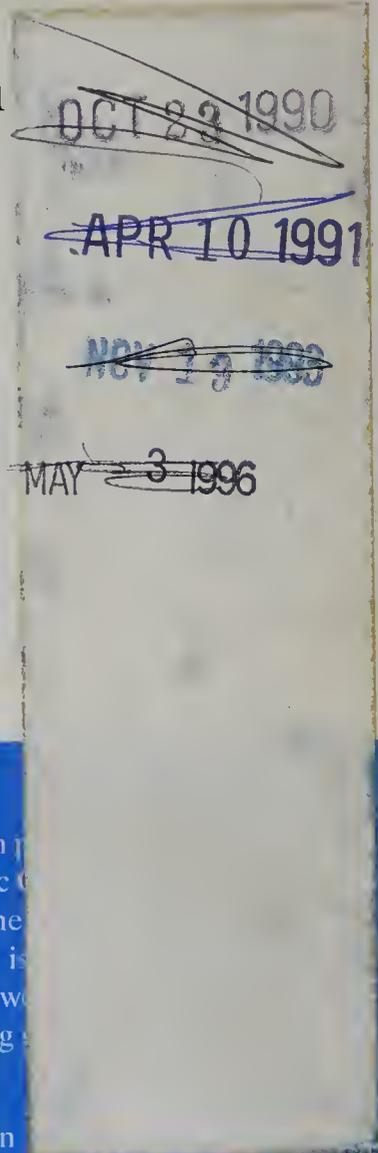
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