Christoph Elschenbroich

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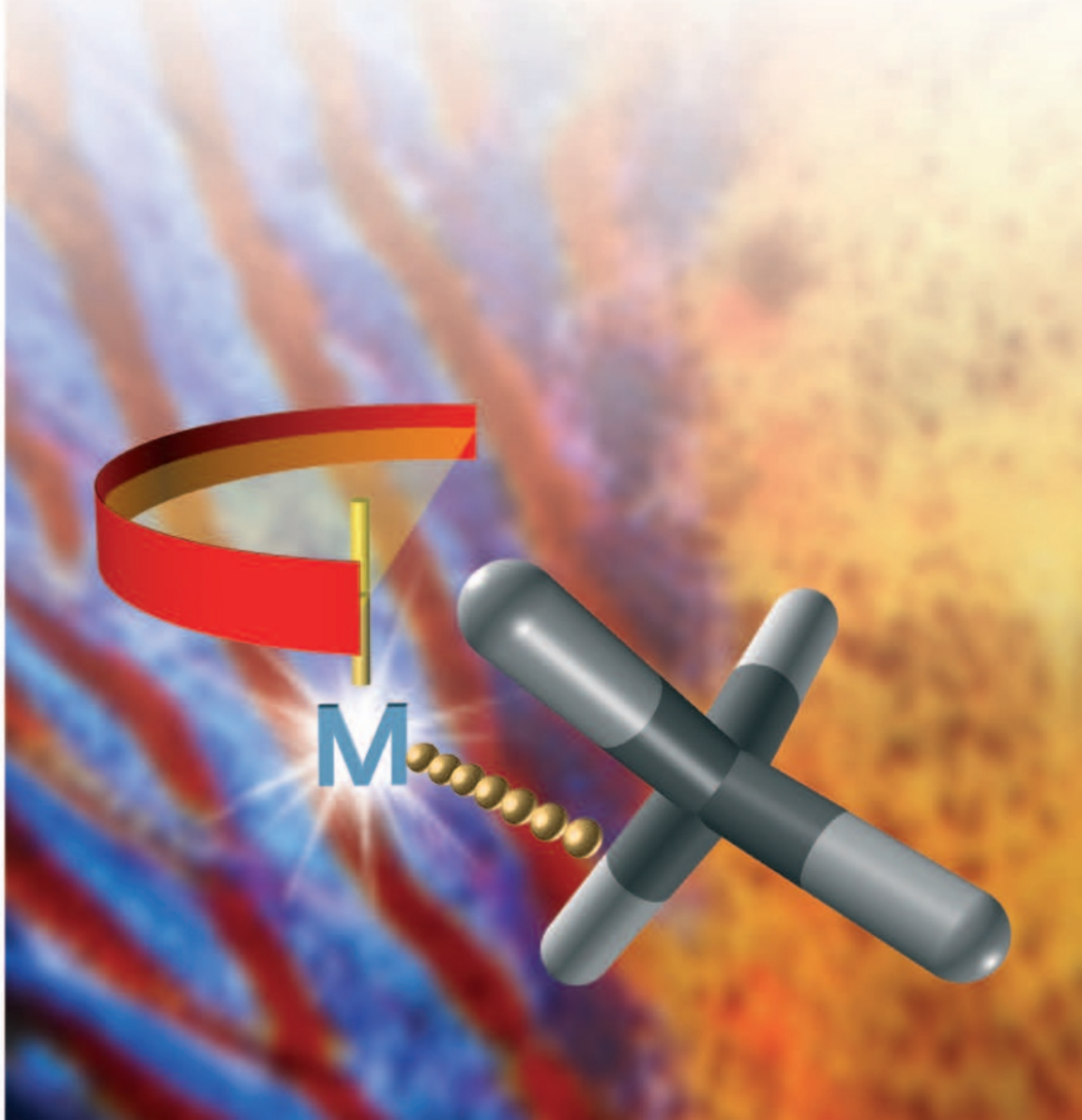
Organometallics

Third, Completely Revised and Extended Edition



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Organometallics

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Christoph Elschenbroich

Organometallics

Translated by
José Oliveira
and
Christoph Elschenbroich

Third, Completely Revised and Extended Edition

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The Author

Prof. Dr. Christoph Elschenbroich
Fachbereich Chemie
Philipps-Universität Marburg
Hans-Meerwein-Str.
35043 Marburg
Germany

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Cover Picture
From the disordered liquid or gaseous phase a methane molecule approaches a coordinatively unsaturated highly reactive metal atom and is about to form an M···CH_4 σ complex. Oxidative addition to yield a hydrido–metal–methyl unit eventually follows. The low-valent metal atom may either be stabilized by π coordination to an allyl or pentadienyl ligand (the red ribbon) or may be part of a metal surface (the maroon/blue band pattern). If the northwestern C–H bond is replaced by a C–C bond that is connected to the ligand, the intermolecular C–H activation described in the scenario above becomes instead intramolecular C–H activation as encountered in agostic interactions.

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Preface to the Third Edition

Whereas the Second Edition of this book followed only three years after the first, the Third Edition had to wait 14 years to go into print. In a field as flourishing as that of organometallic chemistry this time span borders to infinity. Since the former coauthor *Albrecht Salzer* reconsidered his priorities, Organometallics, 3rd Ed. has become a single author book, a fact that did not speed up the process of preparing it. If the Third Edition does not look completely alien to the reader this must be traced to the invaluable contributions Albrecht made to previous editions and which have kept their place in the most recent version.

Another obvious change is the considerably increased volume of the Third Edition, which appears simultaneously with the Fifth Edition of the German version. This growth reflects the impressive advances made in the field to which, among others, Nobel prizes awarded to six leading organometallic chemists during the last decade attest. Spectacular new achievements include synthetic masterpieces of fundamental importance, particularly in main-group organoelement chemistry, increased attention to the f-block elements as bonding partners to carbon, and the elaborate use of organotransition-metal complexes in homogeneous catalysis, serving laboratory-scale preparations as well as industrial processes. Bioorganometallic chemistry has emerged recently as a fascinating new discipline; the complexity of this topic often likens it to searching for a needle in a haystack. These highly disparate endeavors are now aided by access to sophisticated, yet routine, methods of structural analysis in solution and in the solid state as well as by the rapidly expanding use of computational quantum chemistry. Attempts to convey to the reader a little bit of all of this without a significant page increase would have been doomed to failure. Admittedly, the often cited excuse put forward by *Blaise Pascal* more than three centuries ago also applies in the present case: "I have made this a rather long letter because I haven't had time to make it shorter."

Organometallics 3rd Edition is thought to contain sufficient material for a one-year course meeting twice a week. Compared to previous editions only Chapter 16, which deals with metal-metal bonds and metal-atom clusters, has remained virtually unchanged as no principally new perspectives have turned up and a systematic approach to cluster synthesis does not appear to be in sight.

The selection of citations in the running text is based more on utility considerations than on historical fidelity. Often a full paper or a review article is more useful

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for the reader than the earlier short communication that protects priority interests. For "milestones" of pivotal importance, however, the appropriate primary references are generally given. In view of the vast amount of published work, the choice of articles for further reading collected in Appendix A-4 to some extent reflects "careful arbitrariness". Notwithstanding, the literature accessible through the author index should be fairly representative of modern organometallic chemistry.

I am grateful to numerous colleagues who offered valuable hints. Taking the risk of incompleteness I would like to name *A. Ashe III, A. Berndt, M. Bickelhaupt, G. Boche, M. Brookhart, K.H. Dötz, J. Ellis, R.D. Ernst, H. Fischer, G. Frenking, A. Hafner, J. Heck, G. Herberich, R.W. Hoffmann, P. Jutzi, W. v. Philipsborn, K. Pörschke, Ch. Reichardt, P. Roesky, H. Schwarz, W. Siebert, J. Sundermeyer, R. Thauer, W. Uhl, M. Weidenbruch, H. Werner,* and *N. Wiberg.* To ex-coauthor *Albrecht Salzer* I am indebted for the splendid cooperation in the past. New formulae and schemes were drawn with insight and proficiency by *Andrea Nagel*; the author and subject indexes were converted for the English Edition by *José Oliveira*. More importantly, it is a pleasure to acknowledge the linguistic contributions of *José Oliveira*, who translated the new sections from the German Fifth Edition and who commented on those parts which I had translated myself. Cooperation with Project Editor *Bettina Bems* was both efficient and pleasant. Production Manager *Hans-Jochen Schmitt* must be commended for creating an attractive layout and for tolerating several last-minute corrections.

Last but not least I thank those colleagues and students who pointed out errors in previous editions and made suggestions for improvements. Hopefully, this practice will continue in future.

Marburg, December 2005 *Christoph Elschenbroich*

Preface to the First Edition

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 indispensible 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 from 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". Rigor-

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ous 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 Bernd Riedel (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	March	*A. Salzer*
Marburg	1989	Zürich
Germany		Switzerland

Contents

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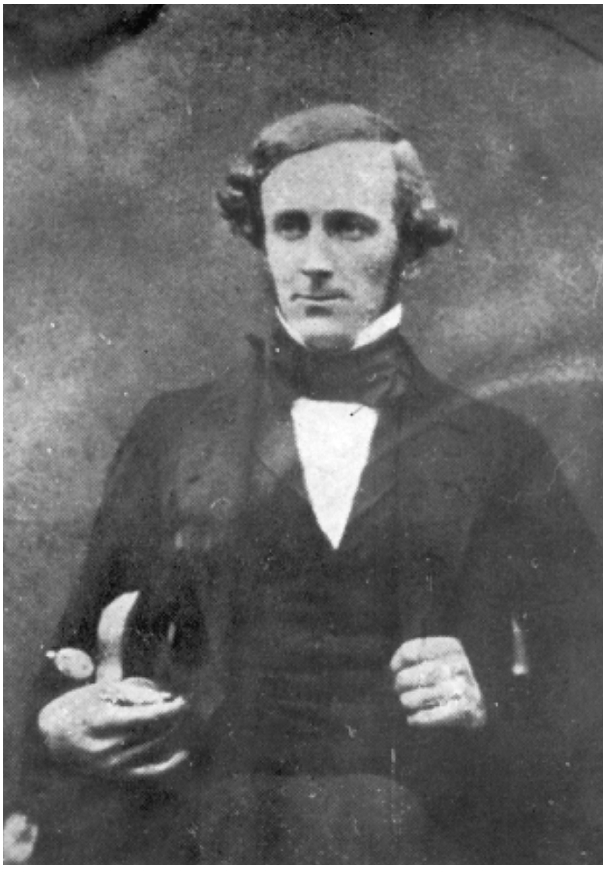

Sir Edward Frankland (1825–1899)
pioneer and inventor of the term ‘organometallic’,
around 1849, the year he earned his PhD
from the University of Marburg.
[Reproduced with permission from the Royal Society
of Chemistry]

Introduction

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1
Milestones in Organometallic Chemistry

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

$$As_2O_3 + 4\,CH_3COOK \longrightarrow \text{“Cadet's fuming liquid”}$$

contains cacodyloxide $[(CH_3)_2As]_2O$
($\kappa\alpha\kappa\omega\delta\eta\varsigma$ = malodorous)
first organometallic compound

1827 *Zeise*'s salt, $Na[PtCl_3C_2H_4]$: the **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 $R_2As–AsR_2$ leads to a profusion of derivatives such as $(CH_3)_2AsCN$, whose taste (!) is checked by *Bunsen*.

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

$$3\,C_2H_5I + 3\,Zn \begin{cases} \not\longrightarrow ZnI_2 + 2\,C_2H_5 \\ \longrightarrow (C_2H_5)_2Zn \text{ (a pyrophoric liquid)} \\ \qquad + C_2H_5ZnI \text{ (solid)} + ZnI_2 \end{cases}$$

Frankland is admirably skilled in the manipulation of air-sensitive compounds. He uses hydrogen gas as a protective atmosphere!

1852 *Frankland* prepares the important alkylmercury halides:

$$CH_3I + Hg \xrightarrow{\text{sunlight}} CH_3HgI$$

additionally: $(C_2H_5)_4Sn$, $(CH_3)_3B$ (1860).

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

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

1852 *C. J. Löwig* and *M. E. Schweizer* in Zürich first prepare $(C_2H_5)_4Pb$ from ethyl iodide and Na/Pb alloy. In a similar manner, they also obtain $(C_2H_5)_3Sb$ and $(C_2H_5)_3Bi$.

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

$$2\,Al + 3\,RI \longrightarrow R_2AlI + RAlI_2$$

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

$$SiCl_4 + m/2\ ZnR_2 \longrightarrow R_mSiCl_{4-m} + m/2\ ZnCl_2$$

1866 *J. A. Wanklyn* develops a method for the synthesis of halide-free alkylmagnesium compounds:

$$(C_2H_5)_2Hg + Mg \longrightarrow (C_2H_5)_2Mg + Hg$$

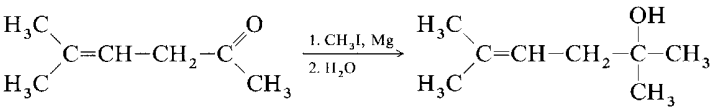
1868 *M. P. Schützenberger* obtains $[Pt(CO)Cl_2]_2$, the **first metal–carbonyl complex**.

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

Known:	**Predicted:**	**Found**:
$Si(C_2H_5)_4$	Eka-$Si(C_2H_5)_4$	$Ge(C_2H_5)_4$ (C.Winkler, 1887)
	$d = 0.96$	$d = 0.99$
$Sn(C_2H_5)_4$	bp: 160 °C	bp: 163.5 °C

1890 *L. Mond*: $Ni(CO)_4$, **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 Zn by Mg in reactions with alkyl iodides:



The reaction is 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 $(C_6H_5)_2SiO$, suspects its high molecularity, yet calls the material **diphenylsilicone**.

1909 *W. J. Pope*: formation of $(CH_3)_3PtI$, the **first σ-organotransition-metal compound.**

1909 *P. Ehrlich* (developer of chemotherapy, Nobel Prize 1908) introduces Salvarsan for the treatment of syphilis.

1917 *W. Schlenk*: alkyllithium reagents through transalkylation.

$$2\,Li + R_2Hg \longrightarrow 2\,LiR + Hg$$
$$2\,EtLi + Me_2Hg \longrightarrow 2\,MeLi + Et_2Hg$$

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

1922 *T. Midgley* and *T. A. Boyd* introduce $Pb(C_2H_5)_4$ as an antiknock additive in gasoline.

1927 *A. Job* and *A. Cassal* prepare $Cr(CO)_6$.

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

$$Fe(CO)_5 + H_2NCH_2CH_2NH_2 \longrightarrow (H_2NCH_2CH_2NH_2)Fe(CO)_3 + 2\,CO$$
$$Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$$

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

1930 *K. Ziegler* encourages more extensive use of organolithium compounds in synthesis by developing a more simple preparation:

$$PhCH_2OMe + 2\,Li \longrightarrow PhCH_2Li + MeOLi \text{ (ether cleavage)}$$
$$H.\ Gilman: RX + 2\,Li \longrightarrow RLi + LiX \text{ (procedure used today)}$$

1931 *W. Hieber* prepares $Fe(CO)_4H_2$, the **first transition-metal–hydride complex**.

1935 *L. Pauling* provides a valence-bond description of the bonding in $Ni(CO)_4$.

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*: $2\,CH_3Cl + Si \xrightarrow{\text{Cu cat., } 300\,^\circ C} (CH_3)_2SiCl_2 + \ldots$
This "direct synthesis" triggers the large-scale production and use of **silicones**. Preliminary work by *R. Müller* (Radebeul, near Dresden) was interrupted by World War II.

1951 *M. J. S. Dewar* proposes a bond theory for complexes of alkenes with transition metals (elaborated on by *J. Chatt* and *L. A. Duncanson*, 1953).

1951 *P. Pauson* (UK) and S. A. Miller (USA) obtain ferrocene, $(C_5H_5)_2Fe$, the **first sandwich complex**.

1952 *H. Gilman* prepares $LiCu(CH_3)_2$, thereby establishing a now synthetically important class of compounds, the **organocuprates**.

1953 *G. Wittig* develops a new synthesis of olefins from phosphonium ylides and carbonyl compounds (Nobel Prize 1979).

1955 *E. O. Fischer*: rational synthesis of **bis(benzene)chromium**, $(C_6H_6)_2Cr$.

1955 *K. Ziegler*, *G. Natta:* **polyolefins** from ethylene or propylene in a **low-pressure process** employing mixed metal (transition-metal halide/AlR_3) catalysts (Nobel Prize 1963).

1956 *H. C. Brown*: **hydroboration** (Nobel Prize 1979).

1959 *J. Smidt*, *W. Hafner:* preparation of $[(C_3H_5)PdCl]_2$, installation of the field of π-allyl–transition-metal complexes.

1959 *R. Criegee*: stabilization of cyclobutadiene by complexation in $[(C_4Me_4)NiCl_2]_2$, thereby verifying a prediction by *H. C. Longuet-Higgins* and *L. Orgel* (1956).

1960 *M. F. Hawthorne* prepares the icosahedral *closo*-borane dianion $[B_{12}H_{12}]^{2-}$, predicted by *H. C. Longuet-Higgins* (1955).

1961 *D. Crowfood Hodgkins*: Based on X-ray crystal-structure analysis, vitamin B_{12} coenzyme contains a Co–C bond (Nobel Prize 1964).

1963 USA: Reports of the dicarba-*closo*-borane $C_2B_{10}H_{12}$ are issued by several industrial laboratories.

1963 *L. Vaska*: *trans*-$(PPh_3)_2Ir(CO)Cl$ reversibly binds O_2.

1964 *E. O. Fischer*: $(CO)_5WC(OMe)Me$, the first **carbene complex.**

1965 *G. Wilkinson*, *R. S. Coffey*: $(PPh_3)_3RhCl$ acts as a homogeneous catalyst in the hydrogenation of alkenes.

1965 *R. Petit*: Synthesis of $(C_4H_4)Fe(CO)_3$, stabilization of the antiaromatic cyclobutadiene through complexation.

1965 *J. Tsuji* discovers the first Pd-mediated C–C coupling.

1967 *G. Wilkinson* stabilizes the highly reactive carbon monosulfide in the rhodium complex $(Ph_3P)_2Rh(Cl)CS$.

1968 *A. Streitwieser*: preparation of uranocene, $U(C_8H_8)_2$.

1969 *P. L. Timms*: synthesis of organotransition-metal complexes by means of metal-atom–ligand-vapor cocondensation.

1969 *A. E. Shilov* discovers the Pt^{II}-catalyzed H/D exchange of alkenes with solvent protons in homogeneous solution, thereby laying the foundation for the now flourishing field of **C–H activation**.

1970 *G. Wilkinson*: kinetically inert transition-metal alkyl compounds by blocking β-elimination.

1972 *R. F. Heck* discovers the palladium-catalyzed substitution of vinylic H atoms with aryl, benzyl, and styryl halides which he subsequently develops into one of the most important named reactions in organometallic chemistry.

1972 *H. Werner*: $[(C_5H_5)_3Ni_2]^+$, the first **triple-decker sandwich complex**.

1973 *E. O. Fischer*: $I(CO)_4Cr(CR)$, the 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 the structure and bonding in boranes.

1976 *M. F. Lappert* opens the field of main-group-element **dimetallenes** with the synthesis of $[(Me_3Si)_2CH]_2Sn{=}Sn[CH(SiMe_3)_2]_2$.

1979 *H. Köpf* and *P. Köpf-Maier* discover the cancerostatic action of titanocene dichloride, $(C_5H_5)_2TiCl_2$.

1980 *H. Bock*: synthesis and studies of silabenzene C_5H_5SiH in the gas phase (matrix isolation: *G. Maier*, 1982).

1981 *R. West*: $(Mes)_2Si{=}Si(Mes)_2$, the first stable compound with a **silicon–silicon double bond**.

1981 Nobel Prize to *R. Hoffmann* and *K. Fukui*: semiempirical MO concepts in a unified discussion of the structure and reactivity of inorganic, organic, and organometallic molecules (**isolobal analogy**).

1981 *G. Becker* synthesizes *t*Bu-C≡P, the first compound with a carbon–phosphorus triple bond.

1982 *R. G. Bergman*: intermolecular reactions of organotransition-metal compounds with alkanes (**C–H activation**).

1985 *W. Kaminsky* and *H. Brintzinger* introduce the "chiral zirconocene dichloride/methyl alumoxane (MAO)" as a new generation of catalysts for the isotactic polymerization of propene.

1986 *R. Noyori* develops the catalytic, enantioselective addition of organozinc reagents ZnR_2 to carbonyl compounds.

1989 *P. Jutzi*: preparation of decamethylsilicocene, **Cp^*_2Si**.

1989 *H. Schnöckel* synthesizes AlCl(solv), which he uses in the development of the organometallic chemistry of monovalent aluminum, for example, $Cp^*_4Al_4$ (1991).

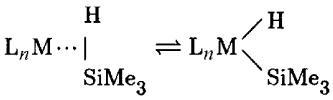
1991 *W. Uhl*: synthesis of anionic $[i\text{-}Bu_{12}Al_{12}]^{2-}$, an icosahedral *closo*-alane.

1993 *D. Milstein* reports the insertion of Rh into a C–C bond (**C–C activation**).

1994 *S. Harder* prepares the lightest metallocene, the lithocene anion $[Li(C_5H_5)_2]^-$.

1995 *A. H. Zewail* studies M–M and M–CO bond cleavage in Mn_2CO_{10} in a molecular beam on the femtosecond timescale (10^{-15} s) by means of a pulsed laser (Nobel Prize 1999).

1995 *G. Kubas* synthesizes the first σ-complex of a silane and studies the tautomerism with the hydridosilyl form:



This observation contributes to the understanding of the mechanism of C–H activation.

1996 *P. P. Power* prepares the first germyne complex with a molybdenum–germanium triple bond.

1997 *C. C. Cummins*: the C atom as the ultimate ligand in an organometallic compound: $[(R_2N)_3MoC]^-$, a "carbon complex".

1997 *G. M. Robinson* synthesizes the salt Na_2[ArGaGaAr] and postulates a gallium–gallium triple bond for the diaryldigallyne anion. (Extreme example of the steric protection of a labile structural element!)

1999 *W. Ho* monitors the dehydrogenation of single ethylene molecules on a Ni(110) surface by means of scanning tunneling microscopy (STM) and inelastic electron tunneling spectroscopy (IETS).

2001 Nobel Prize to *K. B Sharpless*, *W. S. Knowles*, and *R. Noyori* for pioneering work in the field of enantioselective catalysis.

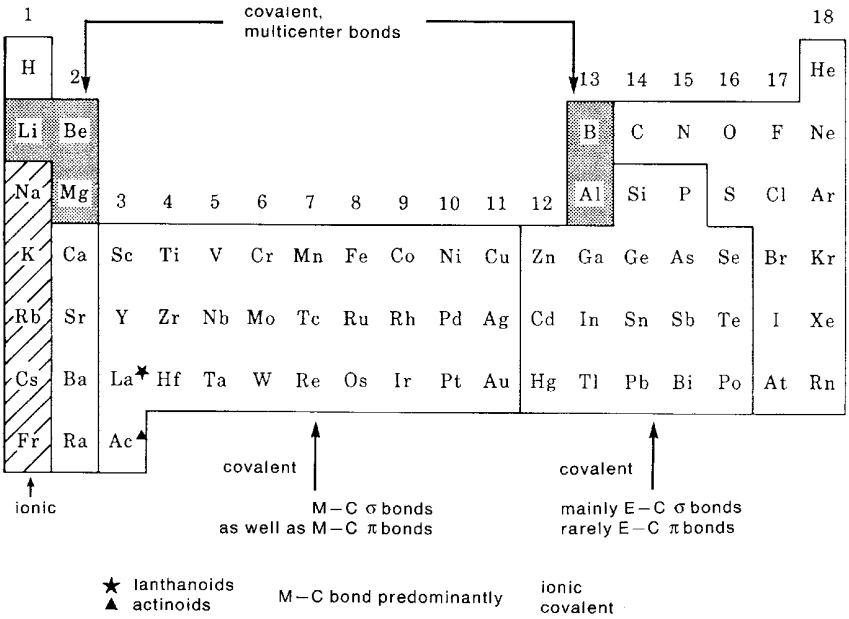
2004 *E. Carmona* reports on decamethyldizincocene Cp*Zn–ZnCp*, the first molecule with an unsupported Zn^{I}–Zn^{I} bond.

2005 *A. Sekiguchi* fully characterizes R–Si≡Si–R, the first compound with a **silicon–silicon triple bond.**

2005 Nobel Prize to *Y. Chauvin*, *R. R. Schrock*, and *R. H. Grubbs* for mechanistic and applications-oriented studies on catalysts active in **olefin metathesis**.

2
Organoelement Compounds: Classification and Electronegativity Considerations

Organometallic compounds (metal organyls, organometallics) are characterized by 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, As, Se, and Te resembles the chemistry of their metallic homologues. Therefore, the term "organoelement compounds" is used occasionally in order to include the aforementioned non- and semimetals. A convenient classification of organometallic compounds is based on the bond type:



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

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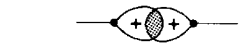
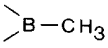
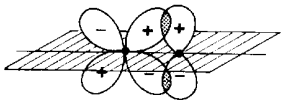
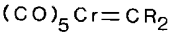
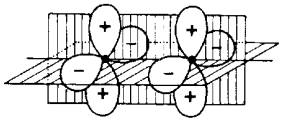
The designations σ, π, and δ bond are defined as follows:

Overlap	Number of nodal planes including the bond axis	Bond type	Example
	0	σ	
	1	π	
	2	δ	

To evaluate the **polarity** of a bond, the **electronegativity** difference between the neighboring atoms is usually employed. The electronegativity values in the table below are based on the Pauling thermochemical method of determination.

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, 3rd Ed.,* **1960**, Ithaca; A. L. Allred, *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.

The concept of electronegativity is complex, not only with respect to the method of derivation of the diverse electronegativity scales, but also to the choice of a scale that is suitable for a particular problem (*Huheey*, 1995). In this section, only a few aspects that are important for application in organometallic chemistry are discussed.

- In contrast to the element hydrides, the fact that EN(C) is dependent on the extent of **hybridization** of the C atom must be considered in the case of element–carbon compounds. As s electrons experience a stronger effective nuclear charge than p electrons of the same principal quantum number, EN(C) increases with increasing s character of the hybrid orbital: Whereas $EN(C_{sp^3}) = 2.5$ for sp^3-hybridized carbon atoms, higher values have been proposed for larger s ratios (*Bent*, 1961), so that $EN(C_{sp^2}) = 2.7$ (comparable to S) and $EN(C_{sp}) = 3.29$ (comparable to Cl). This gradation is reflected in the increasing CH acidity ($C_2H_6 < C_2H_4 \ll C_2H_2$) and suggests that the M–C bond in alkynyl–metal complexes (Chapter 14.1) is considerably more polar than in alkyl–metal species.
- The electronegativity of an element increases with increasing **oxidation number**. However, the degree of this dependence varies between the different EN scales. For example, $EN(Tl^{I}, Tl^{III}) = 1.62, 2.04$ (*Pauling*); 0.99, 2.55 (*Sanderson*).
- A related effect is the dependence of the electronegativity of an atom on the nature of its substituents, which can induce a partial charge on the atom. This fact justifies the introduction of **group electronegativity** EN_G (*Bratsch*, 1985). For example, $EN_G(CH_3) = 2.31$, $EN_G(CF_3) = 3.47$. Thus, the different group electronegativities of the Et_3Ge and Cl_3Ge groups in Et_3GeH and Cl_3GeH lead to the umpolung of the Ge–H bond (p. 174). L_nM fragments can be considered in an analogous manner in transition-metal chemistry: $EN(L_nM)$ increases with increasing π-acceptor and decreasing π-donor character of L.
- *Mulliken* proposed a scale in 1934 in which he attempted to relate electronegativity to the electronic properties of individual atoms: $EN_M = (IP_V + EA_V)/2$ (IP_V is the ionization potential and EA_V is the electron affinity of an atom in its **valence state**). Although the approach is intuitively plausible, the problem with this scale lies in the concept of the valence state, which is not a stationary state and is not directly observable by spectroscopy. Instead, the valence state, which differs from the ground state by the promotion energy, must be represented as a weighted average of several stationary states (*Bratsch*, 1988). As reliable EA values are now more readily available owing to modern experimental techniques, the EN_M scale is becoming increasingly significant.
- A more refined concept based on *Mulliken*'s original definition of EN_M is that of **orbital electronegativity** (*Hinze*, *Jaffe*, 1963, 1996): $EN_i = -(\delta E/\delta n_i) = (\delta E/q_i)$; n_i is the occupation number, q_i is the charge in the atomic orbital i, and E is the energy of the atom in the valence state. The EN_i value has the dimension of an electric potential of the atom i to attract electrons before bond formation. This is in accordance with the *Pauling* definition of electronegativity EN_P as a measure of the power of an atom in a molecule to draw bonding electrons towards itself. The fact that atoms generally have several valence orbitals leads to several (different) EN_i values per atom. However, this "complication" is reflected in reality, as shown in an example from organo-P, As, and Sb chemistry (*Michl*, 1989). The heteroarenes phosphinine C_5H_5P, arsenine C_5H_5As, and stibine C_5H_5Sb (pp. 229 ff.), which are homologues of pyridine C_5H_5N, are interesting study objects with regard to the involvement of the heavy elements P, As, and Sb in aromatic π conjugation. The interpretation of the UV and MCD spectra of these heteroarenes called for the

assumption that the perturbation of the aromaticity of the π system is caused by the π-acceptor effect of the P, As, and Sb atoms. This led to the conclusion that the effective π-orbital electronegativity of the elements P, As, and Sb is greater than that of carbon, in contrast to the values listed in the various EN scales. The apparent contradiction is resolved when one considers that in a σ-bond framework P acts as an electron donor towards C. The resulting decreased shielding of the nuclear charge of the P atom leads to a decrease in energy of the P(pπ) orbital, that is, its electronegativity increases.

When considering the **usefulness of the concept of electronegativity** in organometallic chemistry, one needs to differentiate between main-group and transition elements. In the organometallic chemistry of **s- and p-block elements**, qualitative discussions based on the EN values of the bonding partners are quite appropriate. However, the group electronegativity of the organic residue must be considered, as the EN value of the C atom can lie in a very broad range owing to its dependence on the degree of hybridization and on the nature of the substituents. The variation in bond type and the attendant gradation in chemical reactivity within a main group are also accounted for in the EN values. As mentioned before, it is necessary to distinguish between σ and π electronegativity.

The applicability of electronegativity to **d- and f-block elements** is much more restricted. A limiting factor is already the small variation in EN values between the transition metals and especially between the lanthanoids and actinoids. More importantly, it is imperative that the group electronegativity rather than the atom electronegativity be considered. This is due to the fact that the characteristic bonding in transition-metal complexes can have an exceptionally strong effect on the electronegativity of the L_nM fragments. An example can be taken from coordination chemistry: the redox potential E^o [L_nCo(III/II)] depends on the nature of the ligands and ranges from –0.80 V ($L = CN^-$) to +1.83 V ($L = H_2O$). It would be totally inappropriate and of no practical value to rationalize this parameter in terms of an inherent electronegativity of isolated cobalt ions.

The limited use of the concept of electronegativity in its rudimentary form in the discussion of organometallic chemistry can be demonstrated by comparing the reactivity of a pair of isostoichiometric compounds of a main-group and a transition element: beryllocene $(C_5H_5)_2Be$ is an extremely air- and water-sensitive compound, whereas in stark contrast, ferrocene $(C_5H_5)_2Fe$ is inert, even though the electronegativities of the central metal atoms, $EN_P(Be) = 1.6$ and $EN_P(Fe) = 1.8$, are very similar!

By way of generalization, it may be stated that the chemistry of main-group organometallic compounds is governed by the group that the metal belongs to, whereas the chemistry of organotransition-metal species is dominated by the nature of the ligand. Consequently, the material in Chapters 4–11 is arranged in conformity with the periodic table, whereas 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 on the properties of organometallic compounds it is important to distinguish between **thermodynamic** (stable, unstable) and **kinetic** (inert, labile) factors.

Metal–carbon single bonds are encountered throughout the periodic table (*examples:* $MgMe_2$, PMe_3, MeBr, $[LaMe_6]^{3-}$, WMe_6). For organotransition-metal compounds special considerations 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, $r = d - r_{carbon} = d - 77$.

Group												
2, 12			13			14			15		
M	*d*	*r*	M	*d*	*r*	M	*d*	*r*	M	*d*	*r*
Be	179	102	B	156	79	C	154	77	N	157	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 **1982**, *1*, 10.

3.1
Stability of Main-Group Organometallic Compounds

Compared with M–N, M–O, and M–Hal bonds, M–C bonds must be deemed **weak**. This bond weakness is reflected in the uses that organometallic reagents find in synthesis. As standard entropies are seldom known for organometallic compounds, enthalpies of formation ΔH_f^o are often used instead of free enthalpies of formation ΔG_f^o when evaluating thermodynamic stabilities. A decisive factor that gives rise to the low (negative or positive) ΔH_f^o values of organometallic compounds is the high bond energy of the constituent elements (M, C, H) in their respective standard states.

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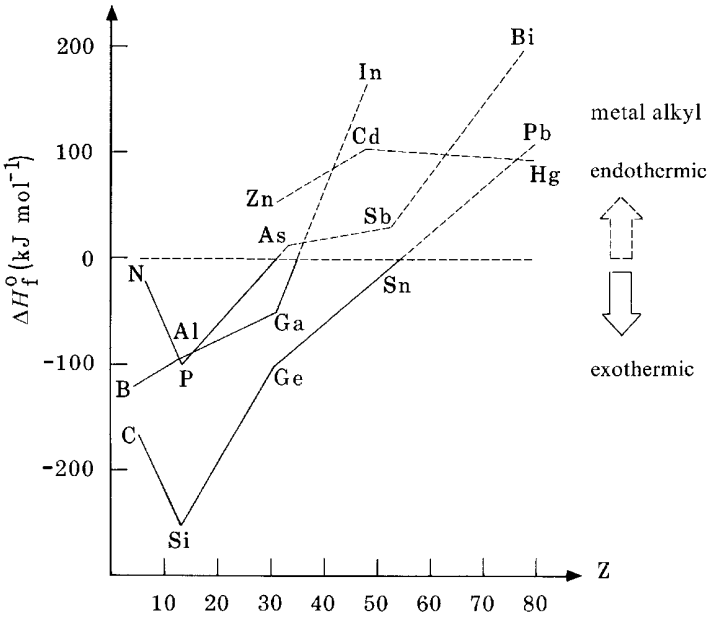
Comparison of standard enthalpies ΔH_f^0 in kJ/mol and mean bond enthalpies $\bar{D}$ (M – C) in kj/mol of methyl derivatives in the gas phase with values $\bar{D}$ (M – X), X = Cl, O

Group												
12 MMe_2			13 MMe_3			14 MMe_4			15 MMe_3			
M	ΔH_f^0	$\bar{D}$	M	ΔH_f^0	$\bar{D}$	M	ΔH_f^0	$\bar{D}$	M	ΔH_f^0	$\bar{D}$	
			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	
cf.			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*, **1982**, *1*, 5.
Data for M – X: J. E. Huheey, *Inorganic Chemistry, 3rd Ed.*, A-32.



A limitation in the use of mean bond enthalpies $\bar{D}$(M–C) when assessing the reactivity of organometallic compounds is the fact that stepwise bond dissociation energies $D_{1,2\ldots n}$ may deviate strongly from the mean value $\bar{D} = 1/n\sum_i^n D_i$. Dimethylmercury serves as a good example (see p. 79 ff.):

$$(CH_3)_2Hg \longrightarrow CH_3Hg + CH_3 \qquad D_1(CH_3Hg-CH_3) = 214\ kJ/mol$$
$$CH_3Hg \longrightarrow Hg + CH_3 \qquad D_2(CH_3-Hg) = 29\ kJ/mol$$

The data for methyl derivatives presented in the table above are prototypical inasmuch as they may require slight modification in different chemical environments. As should be expected, the energy of an L_nM-CX_3 bond depends on the oxidation state and ligand sphere L_n of the metal atom as well as on the nature of the substituent X at the carbon atom. Furthermore, steric (e.g. $X = CH_3$) and electronic effects (e.g. L = π-acceptor ligand, X = F) also contribute to this variability.

Generalizations:

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

Compound	$(CH_3)_3B$	$(CH_3)_3As$	$(CH_3)_3Bi$
$\bar{D}$(M–C) (kJ/mol)	365	229	141
bond	"strong"	"medium"	"weak"

- **The mean bond energy** $\bar{D}(M-C)$ within a main group decreases with increasing atomic number. This trend also applies to the bonds of M to other elements of the second period. 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 when M is particularly electropositive and/or the carbanion is especially stable. *Examples:*

  $Na^+[C_5H_5]^-$, $K^+[CPh_3]^-$, $Na^+[C\equiv CH]^-$.

- **Multicenter bonds** ("electron-deficient bonds") are formed when the valence shell of M is less than half filled and the M^{n+} cation is strongly polarizing, that is, it has a large charge/radius ratio (z/r). *Examples:*

  $[LiCH_3]_4$, $[Be(CH_3)_2]_n$, and $[Al(CH_3)_3]_2$ form M–C–M 2e3c bonds,
  but $K^+[C_nH_{2n+1}]^-$ are predominantly ionic in nature.

3.2 Lability of Main-Group Organometallic Compounds

Predictions of the thermal behavior of organometallic compounds that are based on standard enthalpies of formation meet with limited success because these compounds generally do not decompose into their elements, but follow other more complicated pathways.

Example:

$$Pb(CH_3)_4(g) \longrightarrow Pb(s) + 2\,C_2H_6(g) \quad \Delta H = -307\ kJ/mol \qquad (1)$$

Factors that contribute to the driving force of this reaction include the enthalpy of formation $\Delta H_f^o(C_2H_6)$ 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:

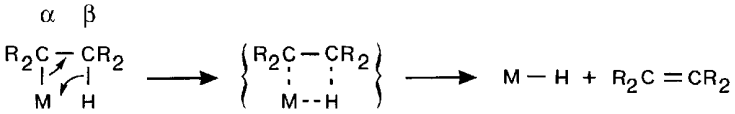
$$Pb(CH_3)_4(g) \longrightarrow Pb(s) + 2\,CH_4(g) + C_2H_4(g) \qquad \Delta H = -235\ kJ/mol \qquad (2)$$

$$Pb(CH_3)_4(g) \longrightarrow Pb(s) + 2\,H_2(g) + 2\,C_2H_4(g) \qquad \Delta H = -33\ kJ/mol \qquad (3)$$

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

$$R_3M-R \longrightarrow \{R_3M^{\cdot} + R^{\cdot}\} \longrightarrow \text{products} \qquad (4)$$

is accompanied by **β elimination**:



(5)

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 the β position. This reaction explains why the temperature of decomposition is higher for $Pb(CH_3)_4$ than for $Pb(C_2H_5)_4$ (p. 200).

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 C_β–H bond. It is for this reason that the β elimination mechanism plays a more important role for organometallic compounds of groups 1, 2, and 13 (valence configurations s^1, s^2, and s^2p^1, respectively) than for those of groups 14, 15, and 16 (s^2p^2, s^2p^3, and s^2p^4, respectively). If a binary organometallic species has an empty coordination site at its disposal, β elimination can be blocked and thermal stability increased through the formation of a Lewis base adduct (e.g. (bipy)$Be(C_2H_5)_2$, bipy = 2,2′-bipyridyl). β Elimination plays a central role in the chemistry of organotransition-metal compounds (Chapter 13.2).

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 organometallic species are encountered that may be traced back to differences in **kinetic inertness**. *Example:*

	Heat of combustion	Thermodynamics	Property	Kinetics
$Zn(C_2H_5)_2$	−1920 kJ/mol	unstable	pyrophoric	labile
$Sn(CH_3)_4$	−3590 kJ/mol	unstable	airstable	inert

Particularly labile against O_2 and H_2O are organometallic molecules with free electron pairs, low-lying empty orbitals, and/or highly polar M–C bonds. Compare:

	In air:	In water:	Relevant factors:
Me_3In	pyrophoric	hydrolyzed	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.
$(Me_3Al)_2$	pyrophoric	hydrolyzed	electron gap at Al in the monomer, nucleophilic attack through 3 d(Al) or σ^*(Al–C) in the dimer, high bond polarity.
SiH_4	pyrophoric	hydrolyzed	Si steric shielding ineffective, relatively electron rich.
$SiCl_4$	inert	hydrolyzed	Si relatively electron-poor, high polarity of Si–Cl bonds, nucleophilic attack through 3 d(Si) or σ^*(Si–Cl).
$SiMe_4$	inert	inert	Si shielded effectively, low polarity of Si–C bonds.

This brief survey is only intended to provide a few qualitative arguments, which have to be weighed up against each other in individual cases.

Excursion 1: Where does our knowledge of M–C bond energies come from?

Whereas detailed information on structure, spectroscopy, and reactivity of organometallic molecules is available, our knowledge of their thermodynamic properties (e. g. bond energies), is quite restricted. Occasionally, it is not even clear whether one is dealing with the kinetically or thermodynamically controlled product of a reaction. In this section, five examples demonstrate the versatility of the methods employed in the determination of M–C bond energies (*Marks*, 1990).

1. Classical Calorimetry (*Skinner*, 1982)

The classical procedure is combustion calorimetry, which already provided the standard enthalpy of formation of dimethylzinc shortly after its first synthesis (*Guntz*, 1887). In this approach, the known standard enthalpies of formation of the products are subtracted from the measured heat of combustion to yield the standard enthalpies of formation of the reactants. The latter provide the unknown bond enthalpies ΔH(M–C). This method requires a stoichiometric reaction. In the application to organometallic molecules, problems arise from uneven combustion and from difficulties in product analysis. Furthermore, apportioning the sum total bond enthalpy to individual M–C bonds in the molecule is often proble-

matic. A variant on the classical combustion calorimetry is the thermochemical monitoring of reactions in solution, such as the bromination of organometallic molecules.

$$L_nM{-}R + Br_2 \longrightarrow L_nM{-}Br + RBr \qquad \Delta H_{reac}$$
$$D(L_nM{-}R)_{solv} = \Delta H_{reac} + D(L_nM{-}Br)_{solv} + D(R{-}Br)_{solv} - D(Br_2)_{solv}$$

By varying R, one can use the measured heats of reaction ΔH_{reac} to determine relative bond energies $D(L_nM{-}R)$ or absolute values when $D(L_nM{-}Br)$ is known.

2. Photoacoustic Microcalorimetry (PAC) (*Peters*, 1988)

A solution of the substrate is exposed to a laser pulse of energy $E_{h\nu}$ (typical duration: 10 ns). The radiation is absorbed by the substrate, and homolytic cleavage results:

$$L_nM{-}R \xrightarrow{E_{h\nu}} L_nM^{\bullet} + R^{\bullet} \qquad \Delta H_{obs}$$
$$\Delta H_{obs} = E_{h\nu} - \Delta H_R \Phi$$

The difference between the energy of the incident photons $E_{h\nu}$ and the bond dissociation energy ΔH_R is released to the medium as thermal energy. This gives rise to a compression wave, which is detected by means of a piezoelectric wave transducer at the cell wall. The amplitude of this compression wave is proportional to the released thermal energy ΔH_{obs}. The quantum yield Φ is used to correct for the proportion of absorbed light that is likely not involved in photoinduced dissociation. Some advantages of this method include:

- The specific determination of the enthalpy of an *individual* bond in the molecule. Classical calorimetry, on the other hand, requires that the total enthalpy be apportioned to several bonds present.
- A comparison with data from gas-phase experiments provides information on solvation effects.
- Time-resolved photoacoustic experiments provide not only thermodynamic but also kinetic information, provided that consecutive reactions also liberate reaction heat to the medium and generate compression waves.

Problems with the application to organometallic molecules lie with quantum yields Φ that are too low or are not known beforehand. Furthermore, nonuniform photochemistry of organotransition-metal compounds may also preclude the use of PAC techniques.

An actual example of the application of PAC is the determination of the energy of the Co–C bond (150 kJ mol^{-1}) in molecules of the vitamin B_{12} family under physiological conditions (*Grabowski*, 1999).

3. Temperature Dependence of the Equilibrium Position

An analysis of the temperature-dependent composition of an equilibrium mixture provides a value for the reaction enthalpy ΔH^o by means of the van't Hoff equation:

$$d(\ln K)/dT = \Delta H^o/RT^2$$

Such a study on metathesis reactions,

$$L_nM{-}R + R'{-}H \rightleftharpoons L_nM{-}R' + R{-}H \qquad \Delta H^o$$

(e.g. R = H, alkyl, alkenyl, aryl, alkynyl; R′–H = C_6H_6)

with various R groups, should provide a scale of relative bond enthalpies D(M–R). This method was used successfully on organometallic compounds of the early transition metals (*Bercaw*, 1988). A broad application of this method in organometallic chemistry is hampered by the difficulty in finding suitable, rapidly equilibrating systems that also show sufficient thermal stability in the required temperature range.

4. Kinetic Methods

The measurement of the activation parameters of a homolytic cleavage *in solution* by monitoring the temperature dependence of the reaction rate is also suitable for the determination of M–C bond enthalpies (*Halpern*, 1988).

$$M{-}R \underset{k_1}{\overset{k_1}{\rightleftharpoons}} M^{\bullet} + R^{\bullet} \qquad (1)$$

$$R^{\bullet} + T \xrightarrow{k_T} R{-}T^{\bullet} \qquad (2)$$

$$M{-}R + T \longrightarrow M^{\bullet} + R{-}T^{\bullet} \qquad (3)$$

$$D(M{-}R) = \Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger} \qquad (4)$$

Once it has been established with certainty that the reaction does indeed proceed as a homolytic cleavage and not, as is typical in organometallic molecules, as an alkene elimination, it should, in principle, be possible to measure the activation enthalpy for the cleavage ($\Delta H_1^{\ddagger}$) and for the recombination ($\Delta H_{-1}^{\ddagger}$). The difference between these two values (4) is the bond enthalpy D(M–R). This method is rarely used as the experimental determination of $\Delta H_{-1}^{\ddagger}$ is difficult. Instead, the recombination (k_{-1}) is suppressed by the addition of a radical trap T. (As a bonus, the nature of the spin-trapped product R–T$^{\bullet}$ is proof of the homolytic character of the cleavage.) The bond enthalpy D(M–R) is then approximately equal to the activation enthalpy $\Delta H_1^{\ddagger}$ of the forward reaction. The relationship

$\Delta H_1^{\neq} \simeq D(\mathrm{M-R})$ is also justified by the endothermic nature of the bond cleavage (k_1) which results in a small activation barrier for the reverse reaction and thus a low $\Delta H_{-1}^{\neq}$; in this case the transition state is said to resemble the product (Hammond postulate). Should no suitable spin-trap reagent T be available, $\Delta H_{-1}^{\neq}$ in (4) can be approximated by the activation enthalpy of the solvent viscosity (8–20 kJ/mol), as the recombination (k_{-1}) is generally diffusion-controlled. This method found broad application in the determination of the bond energy $D(\mathrm{Co-C})$ in a series of model complexes for the vitamin B_{12} coenzyme. A corresponding investigation on natural substrates was reported by *Brown* (1984) in which Co–C bond homolysis was induced by a B_{12}-dependent ribonucleotide reductase.

In a related application, the bond enthalpy $D(\mathrm{M-CO})$ is equated to the activation enthalpy $\Delta H_1^{\neq}$ of the laser-induced pyrolysis of metal carbonyls $M(CO)_n$ in the gas phase (*Smith*, 1984).

An estimate of the parameter $D(\mathrm{M-CO})$ may already be derived from the activation enthalpy of carbonyl substitution in solution

$$M(CO)_n + L \longrightarrow M(CO)_{n-1}L + CO$$

based on the assumption that the mechanism is dissociative. However, associative contributions can often not be excluded which affects the reliability of this determination. Less ambiguity exists in the gas phase, in which only unimolecular M–CO bond cleavage is encountered.

$$M(CO)_n \xrightarrow[k_1]{\Delta} M(CO)_{n-1} + CO \quad (1)$$

$$M(CO)_{n-1} \xrightarrow[k_2]{\Delta} M(CO)_{n-2} + CO \quad (2)$$

$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

$$M(CO) \xrightarrow[k_n]{\Delta} M + CO \quad (n)$$

In general (but not exclusively!), the first CO molecule to be cleaved from $M(CO)_n$ is the most tightly bound. Thus k_1 represents the rate-determining step in $M(CO)_n$ pyrolysis. The reverse reaction (k_{-1}) is negligible as $k_1 < k_2$, $k_3, \ldots k_n$, and the steady-state concentrations of the subsequent fragments are very low. Furthermore, the decomposition kinetics are not influenced by the addition of CO; the reverse reactions thus do not play a role. Therefore the relationship $\Delta H_1^{\neq} \simeq D(\mathrm{M-C})$ also holds in this case. The kinetic analysis of the gas-phase pyrolysis is advantageous in that it yields a $D(\mathrm{M-CO})$ value for an individual bond, whereas classical thermochemical methods provide a mean value $\bar{D}(\mathrm{M-CO})$ for all bonds present. These values can differ significantly. *Example:* $Fe(CO)_5$: $D[(CO)_4Fe\text{–}CO] = 174$ kJ/mol, $\bar{D}[Fe(CO)_5] = 117$ kJ/mol. The application of both

techniques to the same molecule thus draws a complete picture of the relative enthalpies of consecutive M–CO bond-cleavage reactions.

A further differentiation is effected by the introduction of the concept of the bond enthalpy term *E* (*Beauchamp*, 1990).

$$\begin{array}{lllll} MR_n\,(g) & \rightarrow & MR^*_{n-1}\,(g) + R^*\,(g) & \Delta H_{nr} & = E(M\text{–}R) \\ & & & \downarrow\ \Delta H_{reorg.} & \\ MR_n\,(g) & \rightarrow & MR_{n-1}\,(g) + R\,(g) & \Delta H^\circ_r & = D(M\text{–}R) \end{array}$$

The difference between *D* and *E* is the reorganization energy ΔH_{reorg} of the fragments that arise from the bond cleavage. In this example, the fragment labeled with an asterisk* has the same configuration as the initial molecule, whereas the unlabeled fragment adopts the equilibrium configuration after reorganization (e. g. R = methyl: $CH_3^{\bullet *}$ pyramidal, $CH_3^\bullet$ trigonal planar, $\Delta H_{reorg} = 24$ kJ mol^{-1}). The term bond energy generally refers to the fragments in their relaxed equilibrium configuration. In the correlation with other parameters such as bond lengths or force constants, the *E* values are superior to the *D* values.

5. Mass Spectrometry

Thermochemical data for gas-phase reactions can be collected by means of tandem mass spectrometry with a focused ion beam (*Armentrout*, 1985). The setup consists of the sequence: ion source – mass spectrometer (MS1) – reaction zone – mass spectrometer (MS2) – ion detector. In a typical experiment, ions are produced in MS1, of which one type M^+ with a certain mass is selected. The selected ions are accelerated to a defined kinetic energy and they react with a neutral gaseous reagent RL. The product ions are separated in MS2 according to mass and analyzed with respect to their energy (*Armentrout*, 1989). In the practical application of this technique, two variants are followed:

Variant a: In order to determine the metal–ligand bond energy for ML^+ or ML, the endothermic reaction

$$\begin{array}{lll} M^+ + RL & \rightarrow & ML^+ + R \\ & \rightarrow & ML\ + R^+ \end{array}$$

is carried out and the kinetic energy available to the system is varied to the threshold value E_T at which product formation is first observed. The desired thermochemical parameters can be deduced from the measured E_T value. It should be noted that whereas the energy content of the neutral partner RL is well defined by the reaction temperature, this is not necessarily true for the M^+ ions, which could have electronic excitation energy from their generation. This fact should be considered in the energy balance. An example of the application of variant **a** is the determination of the bond energy $D(Fe^+\text{–}CH_3) = 243$ kJ mol^{-1} from the gas-phase reaction between Fe^+ and CH_4 (*Armentrout*, 1988).

Variant b: In this variant of the method (*Armentrout*, 1995), the organometallic species MR_n of interest is ionized in MS1. The MR_n^+ ions are provided with a defined kinetic energy by exposure to a variable acceleration voltage and they then react with an inert gas, usually Xe. At a particular energy threshold E_T, collision-induced dissociation (CID) of MR_n^+ occurs, and the resulting ions are analyzed in MS2 according to mass and energy.

$$MR_n \xrightarrow{-e^-} MR_n^+ \xrightarrow{E_T} \{MR_n^+\} \xrightarrow{Xe} MR_{n-1}^+ + R + Xe$$

The desired bond-dissociation energy for MR_n^+ can again be obtained by considering the energy balance. Bond energies for the corresponding neutral molecules MR_n can be deduced by taking measured ionization energies IE(MR_n) into account.

Variant **b** can also be used to determine sequential bond energies for MR_n. The gradation obtained can provide clues on structural transformations as well as changes in the spin state that may accompany a chain of bond dissociations. Finally, the thermodynamic characterization of coordinatively unsaturated species is important in discussions of mechanisms in homogeneous catalysis (Chapter 18).

In summary it can be said that the thermodynamic aspects of organometallic (and inorganic) reactions are considerably more complex than those of organic processes, for which the additive combination of bond increments (C–C, C–H, C–O, etc.) often allows the reliable prediction of heats of reaction.

6. Computational Thermochemistry

As the number of laboratories specialized in the determination of thermochemical parameters stagnates but quantum chemical calculations become more reliable and economical, the latter are increasingly used. In applications to thermochemistry density functional theory (DFT) appears to stand out; according to *Ziegler* (1998) bond energies can be calculated with a ± 25 kJ mol^{-1} error if all elements of the periodic table are tolerated as bonding partners. However, these calculations furnish values for processes in the gas phase; reactions in solution, strongly influenced by solvation, and heterogeneous reactions important in catalysis cannot yet be treated computationally.

Strictly speaking, the term "bond energy" deserves a more detailed treatment as the multiplicity of symbols and definitions encountered in the literature suggests. In this text we simplify by universally using the term bond energy D in order to rationalize trends in chemical behavior. A recent introduction into refined thermochemical discussion is given by *Ellison* (2003): *What are bond strengths?*

Main-Group Organometallics

Organometallics. 3rd Ed. C. Elschenbroich

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4
Overview of Preparation Methods

Procedures for the formation of bonds between main-group elements 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:

$$2\,M + n\,RX \longrightarrow R_nM + MX_n \text{ (or } R_nMX_n)$$

$$2\,Li + C_4H_9Br \longrightarrow C_4H_9Li + LiBr$$

$$Mg + C_6H_5Br \longrightarrow C_6H_5MgBr$$

The high enthalpy of formation of the salt MX_n generally renders this type of reaction exothermic. This is, however, not true for elements of high atomic number (M = Tl, Pb, Bi, Hg), which form weak M–C bonds. In these cases, $\Delta H_f^\circ(R_nM) > 0$ is not compensated for by $\Delta H_f^\circ(MX_n) < 0$, 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

$$2\,Na + Hg + 2\,CH_3Br \longrightarrow (CH_3)_2Hg + 2\,NaBr \qquad \Delta H = -530\ \text{kJ/mol}$$

$$4\,NaPb + 4\,C_2H_5Cl \longrightarrow (C_2H_5)_4Pb + 3\,Pb + 4\,NaCl$$

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

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:*

$$Pb^{II}I_2 + CH_3I \longrightarrow CH_3Pb^{IV}I_3$$

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Metal + Organometal **Transmetalation** [2]

$$M + RM' \longrightarrow RM + M'$$
$$Zn + (CH_3)_2Hg \longrightarrow (CH_3)_2Zn + Hg \quad \Delta H = -35\ kJ/mol$$

This general method may be applied to M = Li–Cs, Be–Ba, Al, Ga, Sn, Pb, Bi, Se, Te, Zn, Cd. RM′ should be weakly exothermic or, preferentially, endothermic (e.g. $(CH_3)_2Hg$, $\Delta H_f = +94$ kJ/mol). The decisive factor in its feasibility really is the difference in the free enthalpies of formation $\Delta(\Delta G_f^\circ)$ RM, RM′.

Organometal + Organometal **Metal Exchange** [3]

$$RM + R'M' \longrightarrow R'M + RM'$$
$$4\,PhLi + (CH_2{=}CH)_4Sn \longrightarrow 4\,(CH_2{=}CH)Li + Ph_4Sn$$

Precipitation of Ph_4Sn shifts this equilibrium to the right and good yields of vinyllithium are obtained.

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

$$RM + M'X \longrightarrow RM' + MX$$
$$3\,CH_3Li + SbCl_3 \longrightarrow (CH_3)_3Sb + 3\,LiCl$$

The equilibrium lies to the side of the products if M is more electropositive than M′. This procedure is widely applicable to organoalkali-metal compounds RM, as the formation of MX makes a large contribution to the driving force. Occasionally, this reaction is also referred to as a "transmetalation".

Organometal + Aryl Halide **Metal–Halogen Exchange** [5]

$$RM + R'X \longrightarrow RX + R'M \qquad M = Li$$
$$n\text{-BuLi} + PhX \longrightarrow n\text{-BuX} + PhLi$$

The equilibrium is shifted to the right if R′ is superior to R in stabilizing a negative charge. Therefore, this reaction is only practical for **aryl** halides (X = I, Br, rarely Cl, never F). F in C_6H_5F does not exchange directly with Li. Instead, the reaction follows a different sequence that includes *ortho* metalation, elimination of LiF to yield an aryne, and addition of RLi to the C≡C triple bond to afford the coupling product PhR upon hydrolysis.

Competing reactions to metal–halogen exchange are alkylation and metalation of R′X. Metal–halogen exchange is, however, a relatively fast reaction and is favored at low temperatures (**kinetic control**). This allows the use of substrates with reactive substituents, such as NO_2, $CONR_2$, COOR, $SiCl_3$, etc, which are not attacked by RLi at these low reaction temperatures. The metal–halogen exchange of *t*BuLi with primary alkyl iodides is faster than the deprotonation of methanol!

Current mechanistic proposals (*Bailey*, 1988) include the intermediate formation of radicals. Accordingly, metal–halogen exchange is initiated by a single-electron-transfer step (SET):

$$RLi + R'X \longrightarrow \underbrace{\left\{\begin{matrix} R^{\cdot} \; Li^{+} \\ R'^{\cdot} \; X^{-} \end{matrix}\right\}}_{\text{(solvent cage)}} \longrightarrow RX + R'Li$$

Evidence for radicals in the reaction medium was obtained by EPR and CIDNP. However, this in no way proves their role as mechanistic intermediates. An alternative mechanism involves the nucleophilic attack of R–Li at R′–X with the intermediate formation of a halogen "ate complex"

$$R\text{–}Li + R'\text{-}X \rightleftharpoons [R\text{–}\overset{\ominus}{X}\text{–}R'\ \overset{\oplus}{Li}] \rightleftharpoons R\text{–}X + R'\text{–}Li$$

In one case, an "ate complex" of this type, $[Li(TMEDA)_2]^+[(C_6F_5)_2I]^-$, was isolated and characterized by X-ray crystallographic analysis (*Farnham*, 1986). Whether the reaction proceeds through one or the other mechanism or even through a parallel, competitive combination of the two is still a matter of debate. However, the observation that iodine "ate complexes" can decompose, generating radicals in the process (*Bailey*, 1998), suggests that the boundaries between the two alternatives are not well-defined and that an overriding mechanism is at play that leads to different experimental observations, depending on the nature of the substrate.

Organometal + C – H Acid **Metalation** 6

$$RM + R'H \rightleftharpoons RH + R'M \qquad M = \text{alkali metal}$$
$$PhNa + PhCH_3 \rightleftharpoons PhH + PhCH_2Na$$

Metalations (**replacement of H by M**) are acid–base equilibria ($R^- + R'H \rightleftharpoons RH + R'^-$), which are shifted to the products with increasing acidity of R′H. The practical success of a metalation is intimately linked to the **kinetic CH acidity** (p. 45). Substrates with an exceptionally high CH acidity (acetylenes, cyclopentadienes) may also be metalated by alkali metals in a redox reaction:

$$C_5H_6 + Na \xrightarrow{THF} C_5H_5Na + \tfrac{1}{2}\,H_2$$

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

$$HgX_2 + RH \xrightarrow[-\,HX]{} RHgX \xrightarrow[-\,HX]{+\,RH} R_2Hg$$

By their very nature, mercurations are also metalations. In the case of **aliphatic substrates**, they are confined to molecules of high CH acidity (carbonyl, nitro, halo and cyano compounds, alkynes, etc.).

$$Hg[N(SiMe_3)_2]_2 + 2\,CH_3COCH_3 \longrightarrow (CH_3COCH_2)_2Hg + 2\,HN(SiMe_3)_2$$

If $Hg(CH_3COO)_2$ 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**:

$$Hg(CH_3COO)_2 + ArH \xrightarrow[\text{cat. } HClO_4]{MeOH} ArHg(CH_3COO) + CH_3COOH$$

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

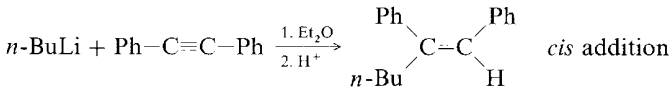
Metal Hydride + Alkene (Alkyne) **Hydrometallation** 8

M = B, Al; Si, Ge, Sn, Pb; Zr

$$(C_2H_5)_2AlH + C_2H_4 \longrightarrow (C_2H_5)_3Al \quad \text{hydroalumination}$$

Propensity for addition: Si–H < Ge–H < Sn–H < Pb–H; *cis* addition is favored.

Organometal + Alkene (Alkyne) **Carbometallation** 9



As in the case of hydrometalation, carbometalation also proceeds as a *cis* addition. However, in contrast to M–H, the addition of M–C to alkenes or alkynes proceeds only if M is very electropositive (M = alkali metal, Al).

Organometal + Carbene **Carbene Insertion** 10

$$PhSiH_3 + CH_2N_2 \xrightarrow{h\nu} PhSi(CH_3)H_2 + N_2$$
$$Me_2SnCl_2 + CH_2N_2 \longrightarrow Me_2Sn(CH_2Cl)Cl + N_2$$
$$Ph_3GeH + PhHgCBr_3 \longrightarrow Ph_3GeCBr_2H + PhHgBr$$
$$RHgCl + R'_2CN_2 \longrightarrow RHgCR'_2Cl + N_2$$

Notably, insertions of carbenes into M–C bonds are avoided; insertions into M–H or M–X bonds are strongly favored.

Pyrolysis of Carboxylates **Decarboxylation** [11]

$$HgCl_2 + 2\,NaOOCR \longrightarrow Hg(OOCR)_2 \xrightarrow{\Delta} R_2Hg + 2\,CO_2$$

The group R should contain electron-withdrawing substituents ($R = C_6F_5$, CF_3, CCl_3, etc.). Decarboxylation of organoelement formates leads to hydrides:

$$(n\text{-}Bu)_3SnOOCH \xrightarrow[\text{reduced pressure}]{170\,^\circ C} (n\text{-}Bu)_3SnH + CO_2$$

Arylation via Diazonium Salts [12]

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

$$ArN_2^+Cl^- + HgCl_2 \longrightarrow ArN_2^+HgCl_3^- \xrightarrow[-N_2]{} \underset{\text{(depending on the catalyst)}}{ArHgCl,\ Ar_2Hg}$$

$$ArN_2^+X^- + As(OH)_3 \longrightarrow ArAsO(OH)_2 + N_2 + HX \text{ (Bart reaction)}$$

5
Organometallic Chemistry of Alkali Metals (Group 1)

5.1
Organolithium Compounds

Preparation: General methods [1], [2], [3], [5], [6], [9]

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

$$CH_3Br + 2\,Li \xrightarrow[20\,^\circ C]{Et_2O} CH_3Li + LiBr \qquad [1]$$

$$C_5Me_5H + n\text{-BuLi} \xrightarrow[-78\,^\circ C]{THF} C_5Me_5Li + n\text{-BuH} \qquad [6]$$

Perlithiated hydrocarbons are formed in the cocondensation of Li vapor with chlorohydrocarbons, for example, CLi_4 from CCl_4 and Li (*Lagow*, 1972). The air sensitivity of organoalkali compounds requires that they be manipulated under a **protective atmosphere** of an inert gas (N_2, Ar). Whereas *Grignard* reagents must be prepared in ethers for reasons of solubility, the preparation and reaction of organolithium compounds may be carried out more economically in inert hydrocarbons such as hexane.

Volumetric methods are available for the **assay of RLi** solutions. A simple acid–base titration with HX

$$RLi + H_2O \longrightarrow RH + LiOH$$
$$LiOH + HX \longrightarrow LiX + H_2O$$

is inapplicable as alkoxides ROLi (from the reaction of RLi with O_2 or from ether cleavage) would suggest too high an RLi content. Therefore, a double-titration method was developed (*Gilman*, 1964). The concentration of RLi can be calculated by determining the difference $(m + n) - n$:

1. $m\,RLi + n\,ROLi + (m + n)\,HX \longrightarrow m\,RH + n\,ROH + (m + n)\,LiX$
2. $m\,RLi + n\,ROLi + m\,BrCH_2CH_2Br \longrightarrow m\,RBr + m\,LiBr + m\,C_2H_4 + n\,ROLi$
   $n\,ROLi + n\,HX \longrightarrow n\,ROH + n\,LiX$

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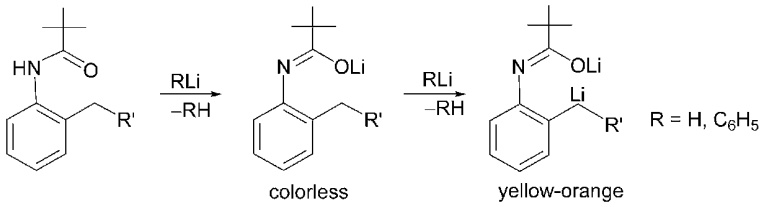
However, newer methods involving the use of self-indicating reagents such as *N*-pivaloyl-*o*-toluidine (R′ = H) (*Suffert*, 1989) allow direct titrations:



This technique is not hampered by lithium alkoxides. *N*-Pivaloyl-*o*-benzylaniline (R′ = C_6H_5) is the reagent of choice for the titration of phenyllithium in solution.

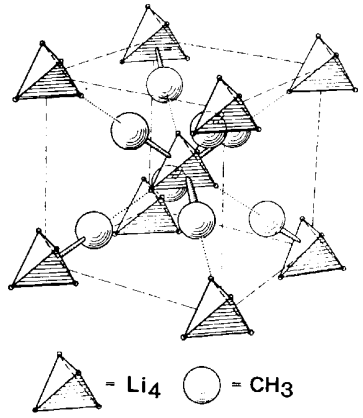
An especially versatile method takes advantage of the color change that occurs upon the cleavage of ditellurides (*Ogura*, 1989). This method is also suitable for the quantitative determination of the weakly basic alkynyllithium and Grignard reagents.

PhTeTePh + RM ⟶ RTePh + PhTeM
red (M = Li, MgBr) pale yellow

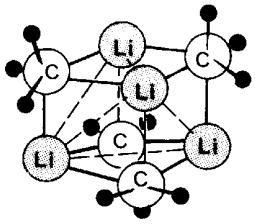
Structure and Bonding

A conspicuous feature of organolithium compounds is their tendency to form **oligomeric units** in solution as well as in the solid state. For example, the structure of solid **methyllithium** is best described as a cubic body-centered packing of $(LiCH_3)_4$ units (a), which consist of Li_4 tetrahedra with methyl groups capping the triangular faces (*Weiss*, 1964).

(a) Unit cell of $(LiCH_3)_4$ (s)



(b) Schematic drawing of the unit $(LiCH_3)_4$



d(Li–C) = 231 pm $(LiCH_3)_4$
d(Li···C) = 236 pm $(LiCH_3)_4$
d(Li–Li) = 268 pm $(LiCH_3)_4$
compare: d(Li–Li) = 267 pm Li_2 (g)
d(Li–Li) = 304 pm Li (s)

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 **$[AB]_4$** species.

A closer inspection of the Li–C distances reveals that the methyl groups of one $[LiCH_3]_4$ unit interact with the Li atoms of a neighboring Li_4 tetrahedron. These intermolecular forces of the agostic interaction type (see p. 301) are responsible for the low volatility and the insolubility of $LiCH_3$ in nonsolvating media.

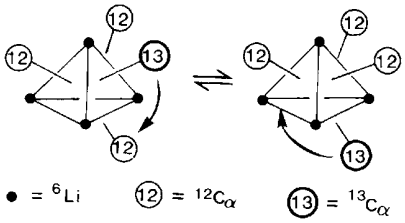
The structure of *tert*-butyllithium is very similar to that of methyllithium. However, the intermolecular forces are weaker. In contrast to MeLi, *t*-BuLi is soluble in hydrocarbons and sublimes at 70 °C/1 mbar.

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

LiR	Solvent	Aggregation
$LiCH_3$	hydrocarbon	hexamer (Li_6 octahedron)
	THF, Et_2O	tetramer (Li_4 tetrahedron)
	$Me_2NCH_2CH_2NMe_2$(TMEDA)	monomer
Li(*n*-C_4H_9)	cyclohexane	hexamer
	Et_2O	tetramer
Li(*t*-C_4H_9)	hydrocarbon	tetramer
LiC_6H_5	THF, Et_2O	dimer
$LiCH_2C_6H_5$ (benzyl)	THF, Et_2O	monomer
LiC_3H_5 (allyl)	Et_2O	highly aggregated ($n \geq 10$)
	THF	monomer

The presence of oligomers $[LiR]_n$ in solution is substantiated by osmometric molar-weight measurements, by Li NMR spectroscopy, and by EPR experiments (p. 57). The observation of the fragment ion $[Li_4(t\text{-}Bu)_3]^+$ by mass spectrometry shows that the association is maintained in the gas phase.

Thorough NMR spectroscopic studies by *Brown* (1970) and by *Fraenkel* (1984) established that, much like *Grignard* reagents (p. 66), solutions of organolithium compounds represent complicated equilibrium mixtures. The dynamic processes in these solutions also involve **intramolecular bond fluctuation**:



etc.

$^{13}C\{^1H\}$NMR ([(*t*-Bu)Li]$_4$):
T < –22 °C: $^1J(^{13}C, 3\ ^6Li) = 5.4$ Hz
T < –5 °C: $^1J(^{13}C, 4\ ^6Li) = 4.1$ Hz
(*Thomas*, 1986)

as well as **intermolecular exchange**:

$$\left.\begin{matrix} R_4Li_4 \rightleftharpoons 2\,R_2Li_2 \\ + \qquad\quad + \\ R'_4Li_4 \rightleftharpoons 2\,R'_2Li_2 \end{matrix}\right\} \rightleftharpoons 2\,R_2R'_2Li_4 \rightleftharpoons 4\,RR'Li_2 \rightleftharpoons \left\{\begin{matrix} R_3R'Li_4 \\ + \\ RR'_3Li_4 \end{matrix}\right.$$

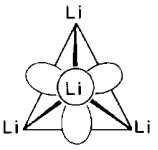
It was demonstrated by means of mass spectrometry that these scrambling reactions proceed through cleavage of the Li_4 units rather than through ligand transfer, whereby the integrity of the Li_4 units would be maintained (*Brown*, 1970):

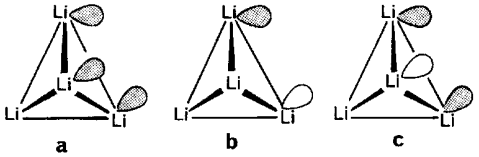
$$t\text{-}Bu_4{}^6Li_4 + t\text{-}Bu_4{}^7Li_4 \xrightarrow{\text{cyclopentane}} t\text{-}Bu_4{}^6Li_3{}^7Li + t\text{-}Bu_4{}^6Li_2{}^7Li_2 + \ldots .$$

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

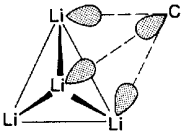
The tendency of organolithium compounds to associate in the solid state as well as in solution is due to the fact that in a single molecule LiR, the number of valence electrons is too low to use all the available Li valence orbitals for two-electron two-center (2e2c) bonding. In the aggregates $[LiR]_n$ this "electron deficiency" is compensated for by the formation of **multicenter bonds**, for example, 2e4c. This is illustrated for the tetrahedral species $(LiCH_3)_4$:

Li_4 skeleton with 4 Li sp^3-hybrid orbitals per Li atom.
Directional properties of the Li valence orbitals:
1 × **axial**, identical with one of the threefold axes of the tetrahedron.
3 × **tangential**, pointing towards the normals of the triangular faces.





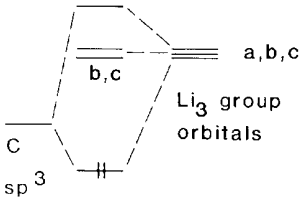
Group orbitals formed from three tangential Li(sp^3) hybrid orbitals originating at the corners of the Li_3 triangle.



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

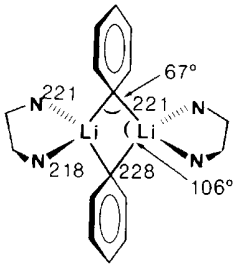
The electronegativity difference between lithium and carbon should manifest itself in the 2e4c bonding pair of electrons being located closer to the carbon than to the lithium atoms. The **bond polarity** $Li^{\delta+} \blacktriangleleft C^{\delta-}$ can be demonstrated experimentally, for example, by means of NMR spectroscopy. $LiCH_3$ molecules in matrix isolation were reported to have a dipole moment of about 6 Debye (*Andrews*, 1967); a value of 9.5 Debye would be expected in 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 are favored by some authors (*Lipscomb*, 1980; *Ahlrichs*, 1986) and essentially ionic character by others (*Streitwieser*, 1976;

Schleyer, 1988, 1994). More-recent quantum-chemical investigations on methyllithium oligomers (*Bickelhaupt*, 1996) provided a picture of a strong, polar electron-pair bonding that involves two components of different polarities: 1) a covalent electron-pair bond between the bonding C–C and Li–Li fragment orbitals, which arise from the $(CH_3^{\bullet})_4$ and $(Li^{\bullet})_4$ units; and 2) a strong polar interaction between the respective antibonding C–C and Li–Li fragment orbitals (thus the Li_4 cluster is stabilized by the withdrawal of antibonding electron density from the $(Li)_4^*$ orbital.



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

The axial Li sp^3-hybrid orbitals, which are unoccupied in an isolated molecule of $[LiCH_3]_4$, are used in the crystal for interaction with methyl groups of neighboring $[LiCH_3]_4$ units (p. 34) and in solution for coordination to σ donors (Lewis bases, solvent molecules). An example is the tetrameric etherate of **phenyllithium**, $[(\mu^3\text{-}C_6H_5)Li{\cdot}OEt_2]_4$.



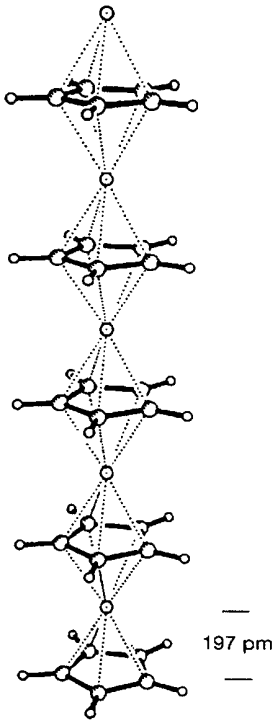
$d(\text{Li}-\text{Li}) = 249$ pm

In the presence of the chelating ligand *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, $\overline{NN}$), however, phenyllithium crystallizes as a dimeric structure reminiscent of triphenylaluminum (Al_2Ph_6, p. 115) (*Weiss*, 1978); *d*(Li–Li) = 249 pm.

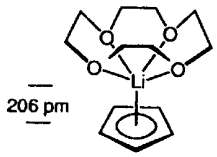
A totally different type of association is encountered for organolithium compounds in which the carbanion contains a delocalized π system. Instead of Li_n clusters (n = 2,4,6), columnar structures are formed whose geometric features depend on the coordination of solvating molecules. Solvate-free cyclopentadienyllithium, LiC_5H_5 (LiCp), crystallizes in the form of a polydecker sandwich complex (p. 570) in which the Li^+ cations are arranged almost linearly with alternating, parallel, eclipsed Cp rings. In contrast, monomeric building blocks are found in the crystal structure in the presence of potential ligands. *Example:* $[Li([12]crown\text{-}4)]C_5H_5$.

A portion of the polymeric structure of LiCp can be found in the lithocene anion $[Li(C_5H_5)_2]^-$, whose existence had already been deduced long before based on conductivity measurements (*Strohmeier*, 1962). This suggests that an equilibrium exists in solution from which the lithocene anion can be precipitated with large cations:

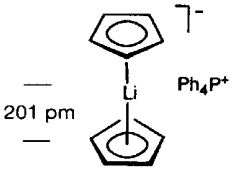
$$2\ LiC_5H_5 \rightleftharpoons Li^+ + [Li(C_5H_5)_2]^- \xrightarrow[THF]{Ph_4PCl} Ph_4P[Li(C_5H_5)_2] + LiCl$$



Polymeric structure of LiC_5H_5 in the crystalline state (high-resolution powder diffraction (*Olbrich*, 1997)

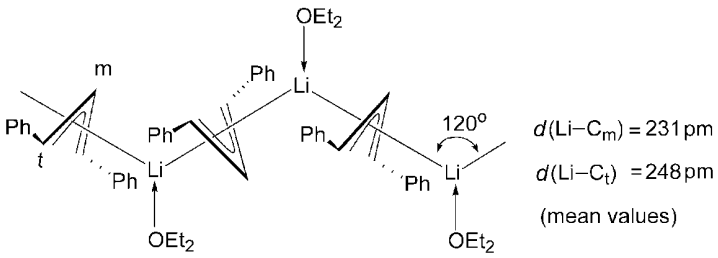


Structure of the sandwich-type complex [Li([12]crown-4)] C_5H_5 (*Power*, 1991)



Structure of the lithocene anion in the crystalline state, staggered rings, D_{5d} symmetrie (*Harder*, 1994)

In contrast to the heavy alkali metals, zigzag chains with bent sandwich units are not found in lithium cyclopentadienyl compounds. This can be attributed to steric reasons as a result of the small ionic radius of Li^+. However, zigzag chains are found with Li compounds of open allyl ligands. *Example:* $(Ph(CH)_3Ph)Li{\cdot}Et_2O$ (*Boche* 1986).



Excursion 2: ^{6}Li and ^{7}Li NMR Spectroscopy 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. Magnetic isotopes fall into one of two classes based on the magnitude of the nuclear spin quantum number I:

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

For small molecules, nuclei with $I = 1/2$ usually give rise to sharp resonance lines with halfwidths $W_{1/2}$ (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, respectively) may result (e.g. T_1(^{109}Ag) up to 10^3 s). This severely complicates the detection of these resonances.

2) Nuclei with Spin Quantum Number $I \geq 1$

These nuclei have electric quadrupole moments (deviations of the distribution of nuclear charge from spherical symmetry), which can cause extremely short nuclear relaxation times and concomitant large halfwidths $W_{1/2}$ (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 reorientation (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 regular cubic symmetry, for example, tetrahedral or octahedral ligand arrangements. In these cases, an important relaxation path is blocked owing to the absence of an electric-field gradient q_{zz}. 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** with respect to that of the proton ($D_p^X = 1.000$), is defined as follows:

$$D_X^p = \frac{\gamma_X^3 N_X I_X (I_X + 1)}{\gamma_p^3 N_p I_p (I_p + 1)}$$

$$\gamma = \frac{\text{magnetic moment}}{\text{angular momentum}} = \frac{\mu_X}{I \cdot h/2\pi} \left(\frac{\text{rad}}{\text{s T}}\right)$$

I = nuclear spin
N = natural abundance (%)
μ_X = magnetic moment [JT^{-1}]
γ = magnetogyric ratio [rad s^{-1} T^{-1}]

In the following table, the properties of "unconventional" nuclei are compared with the routine cases ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P:

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

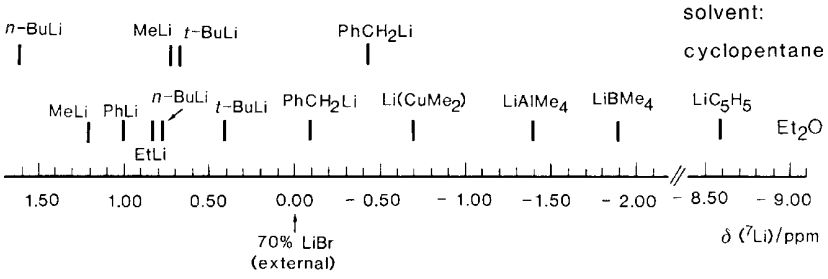
Nucleus	N in %	I	μ_x pos. + neg. –	Q in 10^{-28} m^2 (barn)	NMR frequency in MHZ at 2.35 T	Standard	Relative receptivity D_x^p
^{1}H	99.9	1/2	+		100	Me_4Si	1.000
^{2}H	0.015	1	+	2.73×10^{-3}	15.4		1.45×10^{-6}
^{6}Li	7.4	1	+	-8.0×10^{-4}	14.7	Li^+ (aq)	6.32×10^{-4}
^{7}Li	92.6	3/2	+	-4.5×10^{-2}	38.9	Li^+ (aq)	0.27
^{11}B	80.4	3/2	+	3.55×10^{-2}	32.1	$BF_3 \cdot OEt_2$	0.13
^{13}C	1.1	1/2	+		25.1	Me_4Si	1.76×10^{-4}
^{15}N	0.37	1/2	–		10.14	$MeNO_2$, NO_3^{-3}	3.85×10^{-6}
^{19}F	100	1/2	+		94.1	CCl_3F	0.83
^{23}Na	100	3/2	+	0.12	26.5	Na^+ (aq)	9.25×10^{-2}
^{25}Mg	10.1	5/2	–	0.22	6.1	Mg^{2+} (aq)	2.71×10^{-4}
^{27}Al	100	3/2	+	0.15	26.1	$Al(acac)_3$	0.21
^{29}Si	4.7	1/2	–		19.9	Me_4Si	3.7×10^{-4}
^{31}P	100	1/2	+		40.5	H_3PO_4	6.63×10^{-2}
^{51}V	99.8	7/2	+	0.3	26.3	$VOCl_3$	0.38
^{57}Fe	2.19	1/2	+		3.2	$Fe(CO)_5$	7.39×10^{-7}
^{59}Co	100	7/2	+	0.4	23.6	$[Co(CN)_6]^{3-}$	0.28
^{71}Ga	39.6	3/2	+	0.11	30.5	Ga^3 (aq)	5.62×10^{-2}
^{77}Se	7.6	1/2	+		19.1	Me_2Se	5.26×10^{-4}
^{103}Rh	100	1/2	–		3.2	$Rh(acac)_3$	3.12×10^{-5}
^{119}Sn	8.6	1/2	–		37.3	Me_4Sn	4.44×10^{-3}
^{125}Te	7.0	1/2	–		31.5	Me_2Te	2.2×10^{-3}
^{183}W	14.4	1/2	+		4.2	WF_6	1.04×10^{-5}
^{195}Pt	33.8	1/2	+		21.4	$[Pt(CN)_6]^{2-}$	3.36×10^{-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 spectroscopy. The choice between the two isotopes ^{6}Li ($I = 1$) and ^{7}Li ($I = 3/2$) must take the nature of the specific problem into account. ^{7}Li displays higher receptivity owing to the larger quadrupole moment; however, the lines are broad. ^{6}Li presents narrower linewidths, albeit at the cost of lower receptivity (*Wehrli*, 1978). Therefore, **^{7}Li NMR** offers **higher sensitivity**, whereas **^{6}Li NMR** provides **superior resolution** of coupling patterns. (^{6}Li carries the smallest of all known nuclear quadrupole moments.) (Cf. *Günther*, 1996.)

Organolithium compounds are not only the most widely used organoalkali-metal reagents in the laboratory but also boast the greatest variety of structures and bonding types. The study of organolithium compounds in solution has greatly benefited from the application of Li NMR spectroscopy. The NMR spectra of the heavier organoalkali-metal compounds of Na–Cs reflect the nature of the M^+–solvate complex, as ionic bonding dominates and the organic counterion does not contribute significantly to the shielding of M^+. On the other hand, Li NMR spectra are much more diverse because the bonding modes range from mainly covalent (e. g. alkyllithium compounds LiR) to ion pairs (e. g. lithium tetraorganometallates and lithium compounds with strongly resonance-stabilized organic anions such as triphenylmethyl and cyclopentadienyl). As would be expected, solvent effects play an important role in Li NMR spectroscopy in that the solvating power affects the polarity of the Li–C bond and governs the degree of association (p. 35).

The NMR shifts $\delta(^7\text{Li})$ cover a small range of only 10 ppm, which shrinks to about 2 ppm in essentially covalently bonded organolithium compounds. The strong solvent dependence and the narrow shift range mean that $\delta(^7\text{Li})$ values are used much less routinely in structure determination than the corresponding NMR parameters of other nuclei.



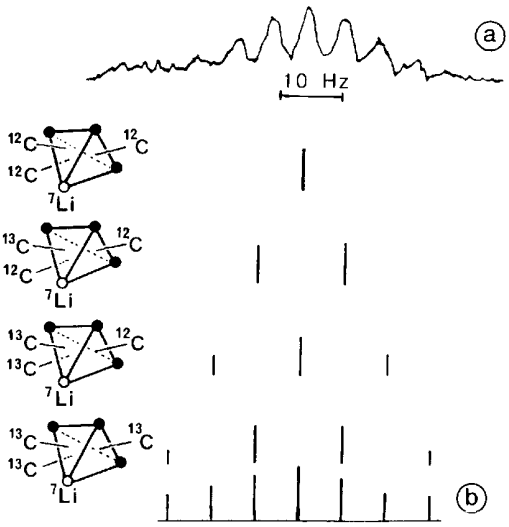
However, the following generalizations may be made:

- ^{7}Li NMR signals for more-covalent organolithium compounds appear at low magnetic field, whereas those for species with a large ionic contribution to the bond are shifted upfield.
- 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 in alkyllithium compounds.

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

Examples of Applications

a) Confirmation of the Tetrameric Structure of *tert*-Butyllithium in Solution



The reconstruction ⓑ of the experimental spectrum ⓐ [**^{7}Li NMR** of *t*-BuLi (0.1 M) in cyclohexane, RT, 57% ^{13}C-enriched at the α positions] is a superposition of isotopomeric species in which the observed nucleus ^{7}Li is coupled to 0, 1, 2, and 3 neighboring ^{13}C nuclei, $^{1}J(^{13}C, ^{7}Li) = 11$ Hz. The agreement between ⓐ and ⓑ demonstrates that the association of $(t\text{-BuLi})_4$ units, which structural analysis revealed for the solid state, is maintained in solution. This also applies to methyllithium in the solid state and in THF at –70 °C (*McKeever*, 1969).

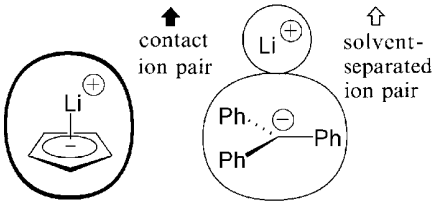
b) Type and Structure of Ion Pairs $Li^{+}C_mH_n^{-}$

If the group $C_mH_n^{-}$ of an organolithium compound is endowed with significant resonance stabilization, ionic bonding will dominate, and the role of the solvent will be to favor one of two main kinds of structures known as **contact ion pairs** and **solvent-separated ion pairs.** Since the environment of the Li^{+} cation strongly differs for the two structure types, characteristic ^{7}Li NMR shifts result. Thus, in addition to the diagnosis of the prevailing bond type, ^{7}Li NMR shifts furnish information on the position of the Li^{+} cation relative to the organic anion. This is illustrated for cyclopentadienyllithium and triphenylmethyllithium (*Cox*, 1974).

In the case of $Li^{+}C_5H_5^{-}$, the strong upfield shift of the ^{7}Li 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. The shielding

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

Organo-Li compound	Solvent			
	Et_2O	THF	DME	HMPA
$Li^+C(C_6H_5)_3^-$		−1.11	−2.41	−0.88
$Li^+C_5H_5^-$	−8.60	−8.37	−8.67	−0.88



increases when the Li^+ ion is located between two $C_5H_5^-$ ligands. Indeed, the **^{7}Li-MAS-NMR** spectrum of the lithocene anion in solid $Ph_4P[Li(C_5H_5)_2]$ shows a peak with a large $\delta(^7Li)$ value of –12.9 ppm. This parameter can now be applied as a structural criterion (*Johnels*, 1998). The value $\delta(^7Li) = -13.1$ ppm was measured for solid LiCp, with its polydecker sandwich structure (p. 38). Furthermore, Li NMR spectroscopy allows the study of the position and dynamics of Li^+ exchange in the equilibrium

$$\begin{array}{lccc} & 2\ LiCp & \rightleftharpoons & [Li(THF)_4]^+ + [LiCp_2]^- \\ \delta(^6Li) & -7.64 & & -1.10 \qquad -12.78\ ppm \end{array}$$

Above 80 °C, the ^{6}Li NMR signals coalesce (*Paquette*, 1990).

Whereas $Li^+C(C_6H_5)_3^-$ and $Li^+C_5H_5^-$ form different types of ion pairs in the weakly solvating medium tetrahydrofuran (THF), both compounds exist as solvent-separated ion pairs in the strongly solvating medium hexamethylphosphoric trisamide (HMPA), as inferred from the identical chemical shifts $\delta(^7Li)$.

An interesting new NMR technique for structure analysis of dissolved organolithium compounds is **^{6}Li,^{1}H-HOESY** (2D heteronuclear Overhauser spectroscopy, *Schleyer*, 1987). As the nuclear Overhauser effect is related to dipole–dipole relaxation, its action decreases by r^{-6}. Thus the distance between ^{6}Li and ^{1}H nuclei can be derived from the intensity of their cross-peaks. Among other uses, ^{6}Li,^{1}H-HOESY is suitable for differentiating between contact and solvent-separated ion pairs. Another application is the structure determination of organolithium cuprates $LiCuR_2$ in solution (pp. 254, 255).

Reactions of Organolithium Compounds

Organolithium compounds LiR resemble *Grignard* reagents RMgX in their behavior; they are, however, more reactive. This advantage is offset by certain limitations imposed by their shelf-life. Decomposition by LiH elimination with the formation of alkenes generally only occurs at higher temperatures (50–150 °C). An exception is 2-butyllithium, whose decomposition already sets in at 0 °C. More critical is the reactivity towards ethereal solvents. The following table (*Schlosser*, 1994) shows temperature/solvent combinations for which various organolithium reagents have half-lives of at least 100 hours for decomposition by ether cleavage.

(°C)	Diethyl ether DEE	Tetrahydrofuran THF	Dimethoxyethane DME
+ 50	Li–CH_3		
+ 25	Li–C_6H_5		
0	**Li–$CH_2C_3H_7$**	Li–CH_3	
– 25	Li–CH(CH_3)(C_2H_5)	Li–C_6H_5	
– 50	Li–$C(CH_3)_3$	**Li–$CH_2C_3H_7$**	Li–CH_3
– 75		Li–CH(CH_3)(C_2H_5)	
– 100		Li–$C(CH_3)_3$	**Li–$CH_2C_3H_7$**
– 125			Li–CH(CH_3)(C_2H_5)
– 150			Li–$C(CH_3)_3$

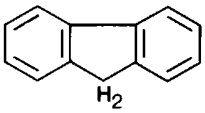
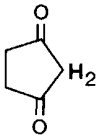
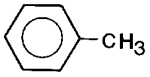
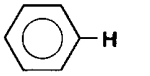
a) Metalation and Subsequent Reactions

$$R-Li + R'-H \rightleftharpoons R-H + R'-Li$$

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, the metalation equilibrium is shifted to the right with increasing **CH acidity** of R′–H.

In the following table, pK_a values for organic CH acids in non-aqueous media are listed and contrasted with inorganic acids. The pK_a(CH) values are linked to the conventional scale in aqueous media by means of a conversion factor.

CH acid exponents for organic CH acids in non-aqueous media* and values of inorganic acids for comparison:

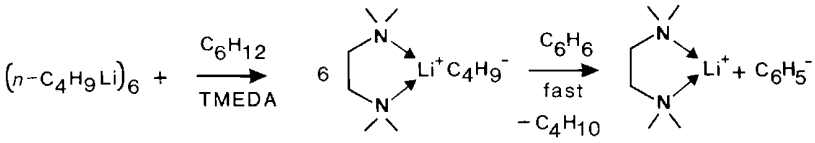
Compound	pK_a	Compound	pK_a
$(CN)_3C-H$	−5		21
H_2SO_4	−2		
$(NO_2)_3C-H$	0	$HC\equiv C-H$	24
$HClO_3$	0	Ph_3C-H	30
	4.5		~35
CH_3COOH	4.7		
HCN	9.4		~37
O_2N-CH_3	10		
	15	$C_3H_7CH_2-H$ (alkanes)	~44
H_2O	15.7		

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

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

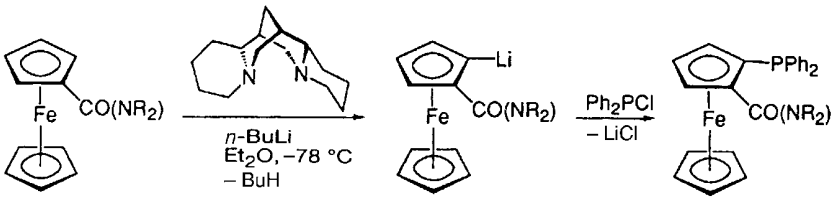
$$C_6H_6 + n\text{-}C_4H_9Li \rightleftharpoons C_6H_5Li + n\text{-}C_4H_{10}$$

This reaction is immeasurably slow. Rapid Li/H exchange only occurs upon addition of a strong σ donor such as TMEDA or *tert*-butoxide (*t*-BuO$^-$), which increases the "kinetic CH acidity":



TMEDA effects both the cleavage of *n*-BuLi oligomers and, through complexation of the Li^+ cation, polarization of the Li–C bond. In this way, the carbanionic character and therefore the reactivity of the butyl group increases. The fact that monomerization is essential for the metalation reaction to proceed smoothly is indicated by the observation that the rates of metalation by $PhCH_2Li$ (monomeric in THF) exceed those of CH_3Li (tetrameric in THF) by a factor of 10^4, although CH_3^- is a stronger base than $PhCH_2^-$.

The following example of (–)-sparteine-mediated **enantioselective lithiation** (*Hoppe*, 1997) describes the formation of a chiral ferrocenyl phosphane. Such ligands are important building blocks for catalysts for enantioselective synthesis.



Metalations of geminal dichlorides are followed by elimination of LiCl, resulting in **chlorocarbene** formation:

$$CH_2Cl_2 + n\text{-BuLi} \xrightarrow[-C_4H_{10}]{} LiCHCl_2 \xrightarrow[-LiCl]{} :CHCl \quad \text{follow-up reactions}$$

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

$$Ph_3PCH_3^+ + RLi \rightarrow RH + \left\{ \underset{\text{ylide}}{Ph_3\overset{\oplus}{P}-\overset{\ominus}{\underline{C}}H_2} \longleftrightarrow \underset{\text{ylene}}{Ph_3P=CH_2} \right\} + Li^+$$

$$\downarrow R_2CO \quad \text{Wittig reaction}$$

$$Ph_3P=O + R_2C=CH_2$$

This *Wittig* reaction is employed in the synthesis of terminal olefins.

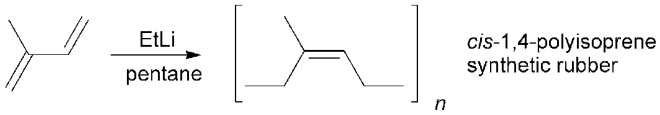
c) Addition to Multiple Bonds (Carbolithiation)

Organolithium compounds lie between *Grignard* reagents and organoboron/organoaluminum compounds in their tendency to add to **C–C multiple bonds**: $RMgX < RLi < R_3B$, $(R_3Al)_2$. Under mild conditions, organolithium compounds only add to conjugated dienes and to styrene derivatives. As in the case of metala-

tion, the presence of strong σ donors such as TMEDA exerts an activating effect on RLi additions.

Example: *n*-BuLi/TMEDA initiates the polymerization of ethylene.

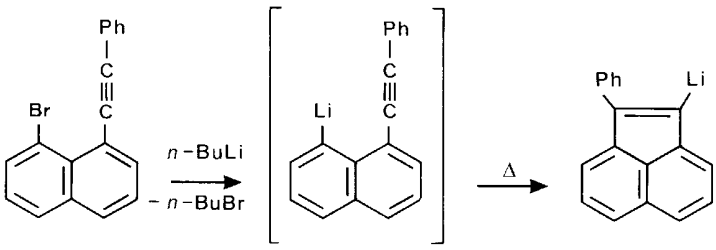
The alkyllithium-initiated polymerization of isoprene produces a synthetic rubber that mimics the natural product in many respects (*Hsieh*, 1957). This discovery led to the first large-scale application of organolithium compounds.



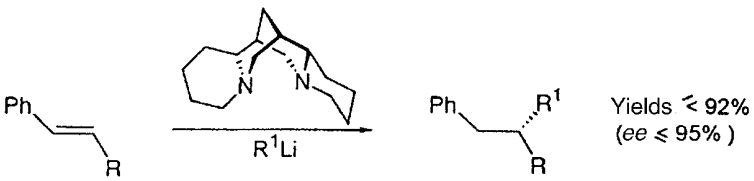
cis-1,4-polyisoprene
synthetic rubber

The use of Et_2O or THF as solvent favors the the undesired *trans*-l,4-, -3,4-, and -1,2-additions.

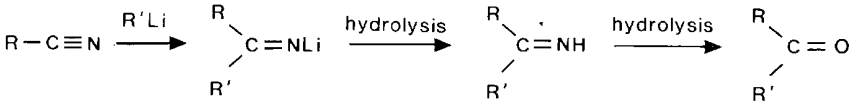
Carbolithiations of C–C multiple bonds may also proceed in an intramolecular fashion:



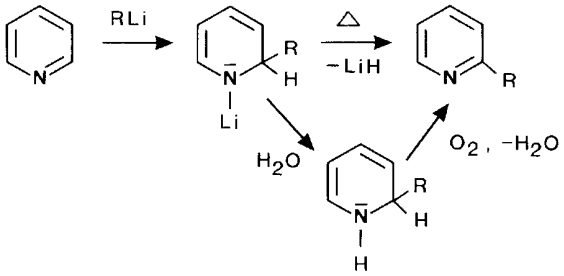
Analogous to deprotonation by RLi, carbolithiation can also proceed enantioselectively (*Normant*, 1999):



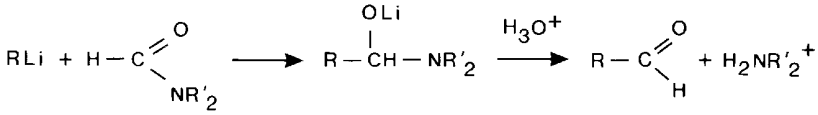
Among the additions of RLi to **C–N multiple bonds**, the reaction with nitriles deserves mention as it constitutes a versatile method for the preparation of ketones:



Equally notable is the reaction with pyridine which, similarly to the *Chichibabin* reaction, gives rise to 2-substituted pyridine derivatives:



Additions of organolithium compounds to **C=O and 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, affords aldehydes:



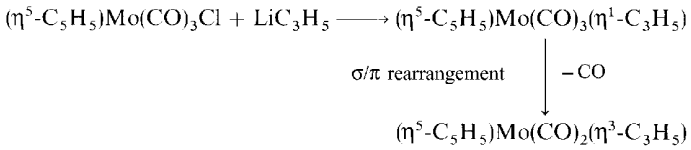
Whereas reactions of organolithium compounds with free carbon monoxide are nonspecific and have found little use, additions of RLi to complexes of CO with transition metals are of great importance from a theoretical as well as from a practical point of view, as this reaction led to the discovery of transition-metal–carbene complexes (Chapter 14.3).

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

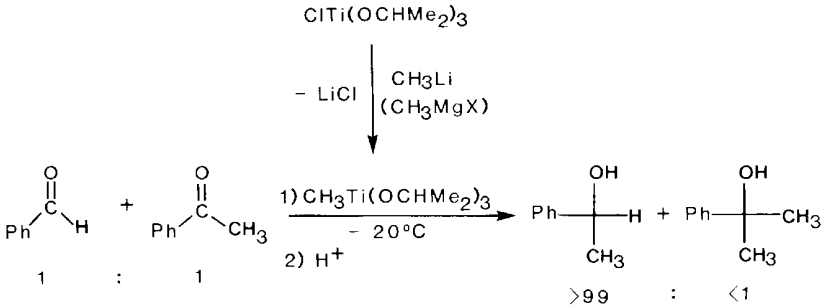
Conversions of the type RLi + MX → MR + LiX have already been introduced as synthetic procedure [4] for **main-group organometallic compounds** (p. 28); owing to their wide applicability, these may well be the most frequently conducted reactions in organometallic chemistry. For the halides of high-valent elements, the reaction proceeds in several steps, which do not always lend themselves to efficient control, and therefore requires separations of product mixtures. In some cases, addition of excess RLi leads to the formation of "ate-complexes".

		Examples:
$n\,RLi + MX_n$	$\longrightarrow R_nM + n\,LiX$	Me_3Sb, Ph_4Sn
$RLi + MX_n$	$\longrightarrow RMX_{n-1} + LiX$	$RMgCl$, $MeSnCl_3$
$RLi + R'MX_{n-1}$	$\longrightarrow RR'MX_{n-2} + LiX$	$Ph(Me)SnCl_2$
$RLi + R_nM$	$\longrightarrow (R_{n+1}M)^- + Li^+$	Ph_4B^- "ate-complex"

In the case of transition metals, which exhibit a larger variety of bonding types to organic groups than do main-group elements, the coupling reactions are often followed by ligand displacement:



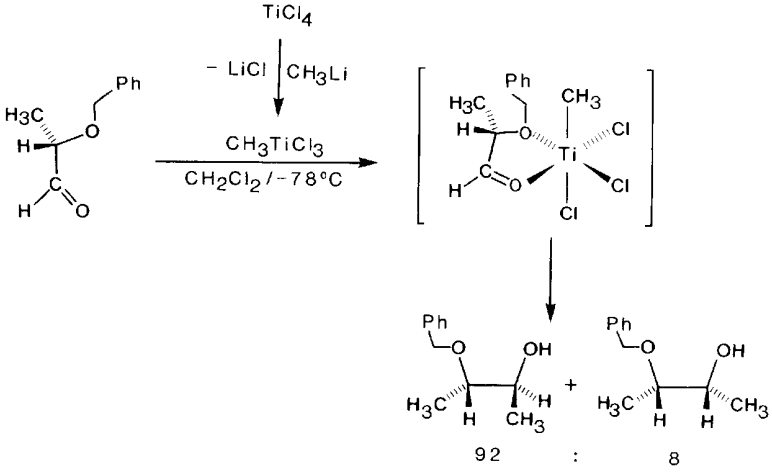
The intermediate alkylation of titanium is the basis of a procedure that results in high **chemo- and stereoselectivity in carbanion addition** to carbonyl groups (*Reetz*, *Seebach*, 1980). In contrast to RLi or RMgX, the organotitanium reagent $RTi(O\text{-}i\text{-}Pr)_3$ attacks aldehyde functions 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 these mild reaction conditions, other functional groups such as CN, NO_2, and Br remain unaffected.

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

An example for stereoselectivity is the reaction of CH_3TiCl_3 with α-alkoxy aldehydes:



In contrast to the titanium alkoxides, CH_3TiCl_3 still acts as a Lewis acid. Presumably, during the course of this reaction, an octahedral chelate complex is formed as an intermediate in which intra- or intermolecular transfer of the methyl group to the less-hindered side of the coordinated aldehyde is favored (*Reetz*, 1987).

5.2 Organometallic Compounds of the Heavier Alkali Metals

Compared with the eminent importance of organolithium compounds in almost every branch of organometallic chemistry, the organometallic compounds of the heavier alkali metals, with the exception of C_5H_5Na (NaCp), play only a limited role.

Preparation

$$2\,Na_{(dispersion)} + n\text{-}C_5H_{11}Cl \longrightarrow n\text{-}C_5H_{11}Na + NaCl \quad [1]$$

$$2\,K_{(mirror)} + (CH_2{=}CHCH_2)_2Hg \longrightarrow 2\,CH_2{=}CHCH_2K + Hg \quad [2]$$

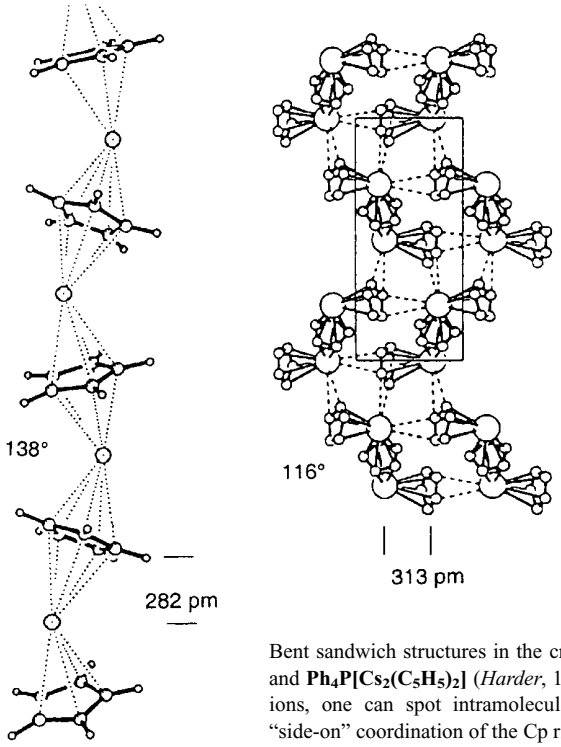
$$Na + C_5H_6 \longrightarrow C_5H_5Na + 1/2\,H_2 \quad [6]$$

(NaCp)

Structure and Bonding

In the group of organoalkali-metal compounds, the ionic character of the M–C bond increases from Li to Cs, as the larger alkali-metal cations are less polarizing. **$NaCH_3$** has the structure of $LiCH_3$. **KCH_3**, **$RbCH_3$**, and **$CsCH_3$** are best described as ionic lattices of the NiAs type (CH_3^- with a trigonal-prismatic environment of six M^+ cations, M^+ surrounded by an octahedron of six CH_3^- anions; *Weiss*, 1993). This change in lattice type reflects the trend in the ionic radius ratios M^+/CH_3^-, as the ionic radii $r(M^+)$ can be divided into two groups: Li^+ 69, Na^+ 97 pm and K^+ 133, Rb^+ 147, Cs^+ 167 pm.

The larger K^+, Rb^+, and Cs^+ ionic radii also affect the structural chemistry of the cyclopentadienyl compounds, which show similarities as well as differences to the lithium compounds. LiCp and NaCp have the same solid-state structure, and the sodocene anion $[NaCp_2]^-$ corresponds to the lithocene anion $[LiCp_2]^-$ (*Harder*, 1996). KCp, on the other hand, crystallizes in the form of a zigzag chain in which the bond vectors for every three K^+ ions form angles of 138° (*Olbrich*, 1997). This deformation as well as the larger distance between the K^+ ion and the center of the ring (282 pm) allow η^2-interactions between the K^+ ions and the Cp rings of neighboring chains. However, these interactions should not be thought of as the cause of the deformation, as this tilting angle seems to be common to sandwich structures of heavier main-group elements, even in the case of the isolated molecule in the gas phase (p. 71). The bent sandwich structure is also found in the triple-decker $[Cs_2Cp_3]^-$ anion. The particularly large coordination sphere of the Cs^+ cation also favors intermolecular interactions.



Bent sandwich structures in the crystals of **KC_5H_5** (*Olbrich*, 1997) and **$Ph_4P[Cs_2(C_5H_5)_2]$** (*Harder*, 1996). Within a layer of $[Cs_2Cp_3]^-$ ions, one can spot intramolecular "face-on" and intermolecular "side-on" coordination of the Cp rings.

Chemical Reactivity

The heavier alkali-metal organometallic compounds are extremely reactive and can even slowly metalate saturated hydrocarbons (in which they are insoluble). Solubility in other media is usually accompanied by attack of the solvent. The high reactivity of these organoalkali-metal compounds is caused by the pronounced carbanionic character. Ethers are slowly metalated at the α position with subsequent elimination of an alkoxide (**ether cleavage**). Ether cleavage is particularly rapid with cyclic ethers such as THF.

$$CH_3CH_2OCH_2CH_3 + KC_4H_9 \longrightarrow C_4H_{10} + K^{\oplus}[\overset{\ominus}{C}H(CH_3)-O-C_2H_5] \longrightarrow KOC_2H_5 + H_2C=CH_2$$

Additional modes of reaction that limit the stability are self-metalation:

$$2\,C_2H_5Na \longrightarrow C_2H_4Na_2 + C_2H_6 \longrightarrow \cdots$$

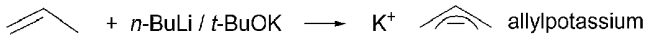
and β-hydride elimination:

$$C_2H_5Na \longrightarrow NaH + C_2H_4$$

More-stable products are obtained if the carbanion is resonance-stabilized, that is, if the negative charge is delocalized effectively as in C_5H_5Na or in Ph_3CK.

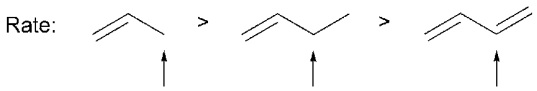
Whereas the use of binary alkali-metal organometallic reagents MR (M = Na, K, Rb, Cs) is of limited practical use, the combination of *n*-butyllithium with potassium *tert*-butoxide (known as the **Lochmann–Schlosser superbase** (LSB)) has found widespread use in organic synthesis (*Schlosser*, 1988). Despite the utility of this reagent, the actual active species is not clearly known. The proposal that *tert*-butylpotassium (which would be formed by metathesis) is involved has been disproved by several experimental studies. Some characteristics of the LSB system include:

- High reactivity in metalation reactions, even of weak CH acids

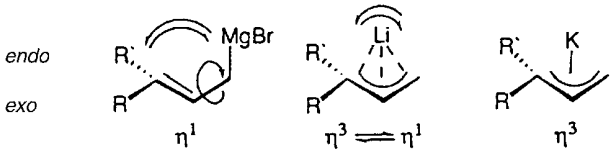


In contrast, pure *t*-BuLi results in carbolithiation (addition to the C–C double bond)

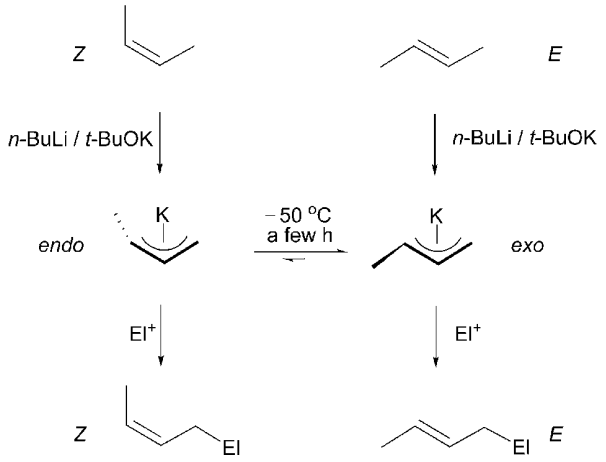
- Regioselectivity of metalation



- Configurational stability of allylpotassium



Whereas $\eta^3 \rightleftharpoons \eta^1$ rearrangement **(metallotropy)** and rotation about a C–C single bond for allyl–MgBr and allyl–Li leads to rapid face exchange of the metal ("top/bottom" relative to the C_3 plane) as well as to *exo*/*endo* isomerization, allylpotassium is significantly more configurationally stable. Thus, stereoselective syntheses are possible when the rate of *endo* $\rightleftharpoons$ *exo* equilibration is considered (*Schlosser*, 1993):



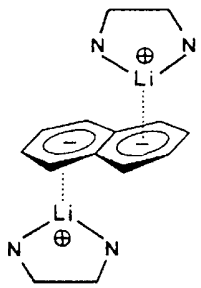
Addition compounds of the alkali metals

Besides organoalkali-metal reagents, whose generation involves the cleavage of a bond in the organic starting material, there is a second class of compounds that is formed by an electron transfer from the alkali metal to the organic partner, with no bonds being cleaved:

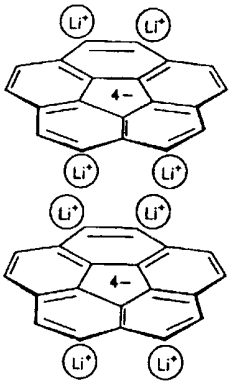
$$M + ArH \rightleftharpoons M^+ + ArH^{\bullet -}$$
$$2\,M + ArH \rightleftharpoons 2\,M^+ + ArH^{2-}$$

The **radical anions** $ArH^{\bullet -}$ and the mostly diamagnetic dianions ArH^{2-} generated in this way are of theoretical and practical significance. Sodium naphthalenide $Na^+C_{10}H_8^{\bullet -}$ forms moss-green solutions in ethers such as DME or THF and serves as a **self-indicating reducing agent** in the synthesis of metal complexes in low oxidation states. An attractive feature in this case is the availability of a very strong reducing agent that operates in the homogeneous phase ($E_{1/2}(C_{10}H_8^{0/-1}) = -2.5$ V versus a saturated calomel electrode). *Example:*

$$(n\text{-BuO})_4Ti + 2\,Na^+C_{10}H_8^- \xrightarrow{THF} (n\text{-BuO})_2Ti(THF)_2 + 2\,C_{10}H_8 + 2\,n\text{-BuONa}$$

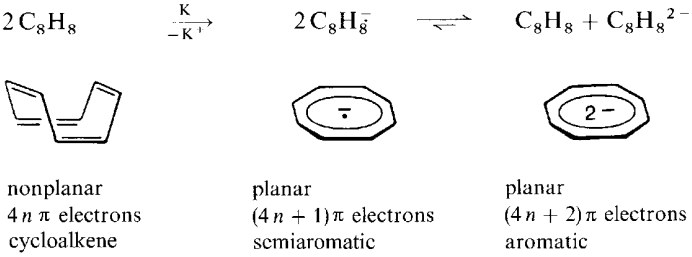


Alkali-metal–arene addition compounds have also been obtained in crystalline form. The compound **$[Li(TMEDA)]_2C_{10}H_8$** (*Stucky*, 1972) may be regarded as an arene complex of a main-group element; no decision on the prevailing bond type is implied by this designation!



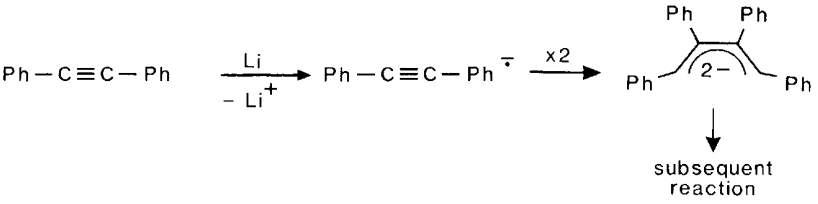
Higher polycyclic aromatic hydrocarbons can accommodate a surprisingly large number of extra electrons. For example, corannulene, which can be considered as one third of a C_{60} fullerene framework, forms $\mathbf{Li_8(C_{20}H_{10})_2}$, a sandwich with four endo- and (2 × 2) exo-located Li^+ cations (*Scott*, 1994).

Electron transfer to cyclic conjugated systems often has structural consequences:

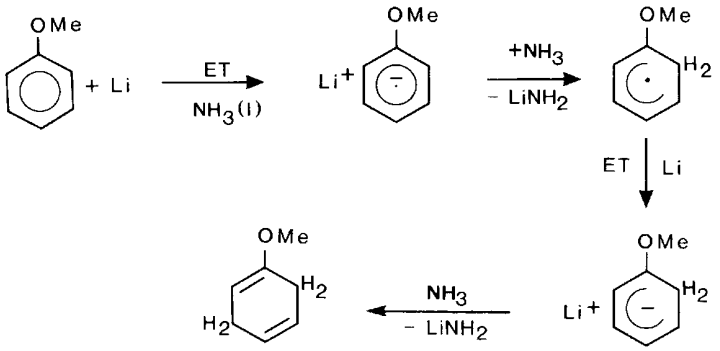


nonplanar	planar	planar
$4n\ \pi$ electrons	$(4n + 1)\pi$ electrons	$(4n + 2)\pi$ electrons
cycloalkene	semiaromatic	aromatic

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 pp. 96, 161, 231).



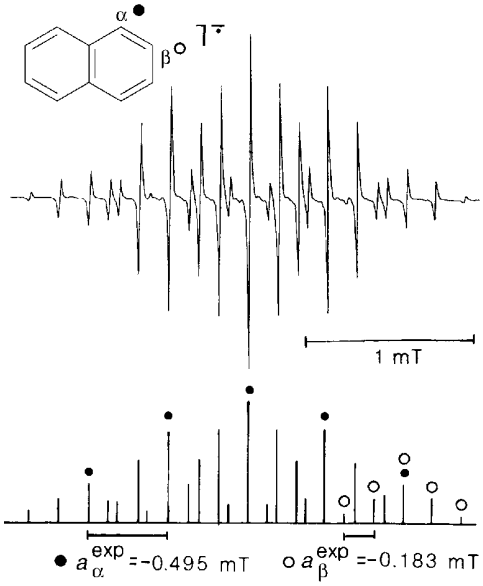
In the presence of proton donors, the addition compounds undergo follow-up reactions. The synthetically useful **Birch reduction** consists of a sequence of electron-transfer (ET) and protonation steps. *Example:*



Excursion 3: EPR Spectroscopy of Organoalkali-Metal Compounds

1) Radical Anions of Aromatic -Systems

In alkali-metal addition compounds $M^+ArH^{\bullet -}$, an unpaired electron resides in the lowest unoccupied molecular orbital (LUMO) of the neutral molecule ArH. Correspondingly, in radical cations $ArH^{\bullet +}$, the highest occupied molecular orbital (HOMO) contains an unpaired electron. The EPR spectra of $ArH^{\bullet +}$ and of $ArH^{\bullet -}$ provide **information about the composition of the HOMO and LUMO frontier orbitals** formed from the $C(p_\pi)$ atomic orbitals of the molecular frame. In view of the fact that the regioselectivity of chemical reactions can be a result of frontier-orbital control (*Fukui*), a knowledge of the shape of these molecular orbitals is of practical significance. *Example:*



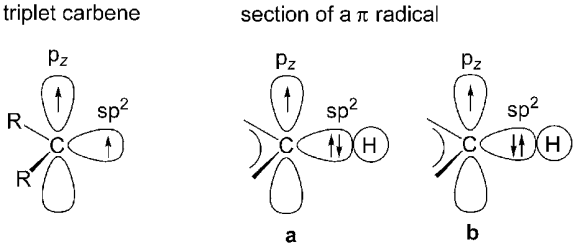
In the naphthalene radical anion $C_{10}H_8^{\bullet -}$, the LUMO ψ_6 is singly occupied. As the probability of finding the unpaired electron varies for the α and β positions, different electron–proton hyperfine coupling constants $a(^1H_\alpha)$ and $a(^1H_\beta)$ are observed.

The form of the singly occupied MO ψ_K can be derived from an analysis of the EPR spectrum **(McConnell equation)**:

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

$c_{K\mu}$ = coefficient of the π-AO at the atom C_μ in the singly occupied MO ψ_K
$a(^1\mathrm{H})$ = isotropic hyperfine coupling constant (fluid solution)
Q = –2.3 mT

The parameter Q describes the efficiency of **π–σ spin polarization**. This mechanism is responsible for the occurrence of spin density at the proton and thus for the observation of isotropic hyperfine coupling $a(^1\mathrm{H})$ in π radicals. The π–σ spin polarization mechanism can be seen as follows:

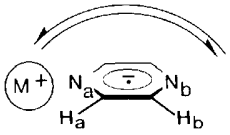


In a bent triplet carbene, the two orthogonal p_z and sp^2 orbitals are singly occupied (parallel spin). This is a manifestation of Hund's first rule in molecules. It can also be said that the two unpaired electrons in a triplet carbene are ferromagnetically coupled. The physical reason for Hund's first rule can be extended to doubly occupied sp^2 orbitals, as is the case in π radicals (prototype: $CH_3^{\bullet}$). The result is that of the two C–H bonding electrons, the one closer to the singly occupied p_z orbital prefers a local spin-parallel alignment (spin correlation). Thus spin configuration **a** is preferred over **b**, and a slight excess of negative spin density is present at the H atom which explains the negative sign of the hyperfine coupling constant $a(^1\mathrm{H})$. The preference for the triplet state of singly occupied orthogonal orbitals and spin polarization also provide arguments for the interpretation of macroscopic magnetic behavior (see p. 525 ff. and 582 ff.).

The McConnell equation (and its refined version) has been applied to a large number of π radicals and has confirmed quantum-chemical calculations of the 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, EPR spectroscopy yields unambiguous information about the structure of the ion pair $M^+ArH^{\bullet-}$ (contact or solvent-separated).

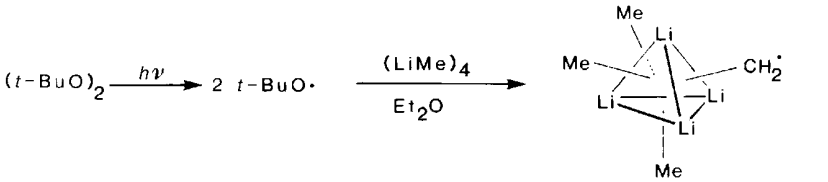
Like NMR, EPR spectroscopy lends itself to the study of dynamic processes. The ion pair M^+pyrazine$^{\bullet-}$ (M = alkali metal) in THF may serve as an example (*Atherton*, 1966).

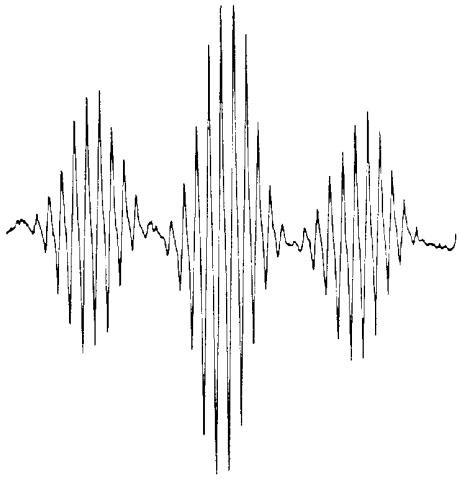


Li^+ is firmly coordinated to one of the two N atoms. This follows from the hyperfine pattern, which is governed by unequal coupling constants $a(^1H_a) \neq a(^1H_b)$ and $a(^{14}N_a) \neq a(^{14}N_b)$.

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

2) Preservation of the Tetrameric Structure of $[LiCH_3]_4$ in Solution





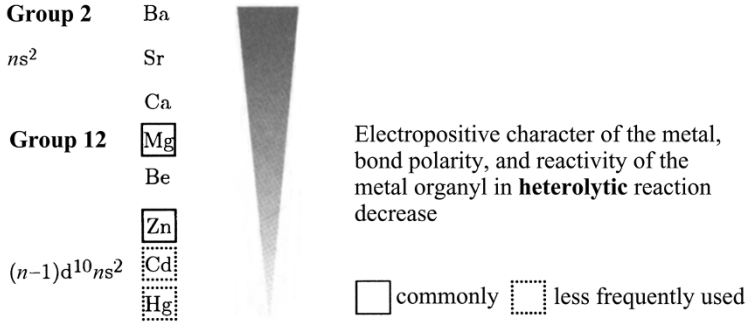
a(2 ^{1}H) = 1.83 mT
a(3 ^{7}Li) = 0.17 mT

Photolytically generated radicals *t*-$BuO^\bullet$ abstract an H atom from the $[LiCH_3]_4$ unit. The identity of the species $(CH_3)_3Li_4CH_2^\bullet$ is revealed by the EPR spectrum, which consists of a triplet (2 ^{1}H, I = 1/2) of decets (3 ^{7}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 Li–C bond.

6
Organometallic Compounds 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. Organocadmium and organomercury reagents have also found preparative use, albeit to a lesser extent. The reactivity of these compounds decreases with decreasing difference in electronegativity between metal and carbon:



Organomagnesium compounds combine in a unique way high reactivity and ease of access. The high reactivity of mercury organyls R_2Hg in transmetalations can be traced to the ready **homolytic** cleavage of the Hg–C bond.

6.1
Organometallic Compounds of the Alkaline-Earth Metals (Group 2)

6.1.1
Organoberyllium Compounds

Organoberyllium compounds are highly toxic and air- and moisture-sensitive materials that display a number of structural peculiarities.

Organometallics. 3rd Ed. C. Elschenbroich

ISBN: 3-527-29390-6

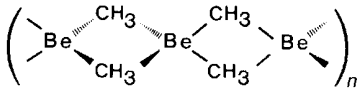
Preparation and Structures

$$Be + R_2Hg \longrightarrow R_2Be \longrightarrow Hg \qquad [2]$$

$$BeCl_2 + 2\,RLi\,(RMgX) \longrightarrow R_2Be + 2\,LiCl \quad (MgXCl) \qquad [4]$$

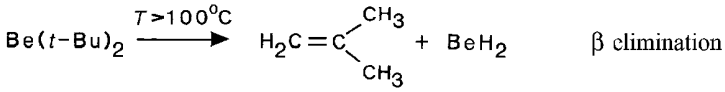
BeR_2 is a Lewis acid and forms stable etherates $(Et_2O)_2BeR_2$. It is therefore difficult to obtain these compounds free of solvent.

Like $BeCl_2$, the compound **$Be(CH_3)_2$** is a polymeric solid (structural type SiS_2). The bonding bridges in the chain resemble those in the alkylaluminum compounds (2e3c bonds, compare: $Al_2(CH_3)_6$), thereby reflecting the Be–Al "diagonal relationship".



$d(Be-Be) = 210$ pm,
angle Be–C–Be = 66°
(*Rundle*, 1951).

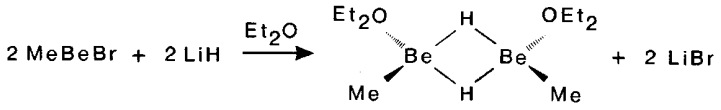
In the gas phase, BeR_2 is monomeric and linear and therefore suggests Be sp hybridization. For steric reasons, $Be(t\text{-}Bu)_2$ is monomeric even in the solid state. The thermolysis of $Be(t\text{-}Bu)_2$ yields pure, unsolvated beryllium hydride:



$Be(CH_3)_2$ has no β-hydrogen atoms, which are essential for elimination, and therefore only decomposes at T > 200 °C. As is the case with magnesium, organoberyllium compounds equilibrate with beryllium halides:

$$BeR_2 + BeX_2 \rightleftharpoons 2\,RBeX.$$

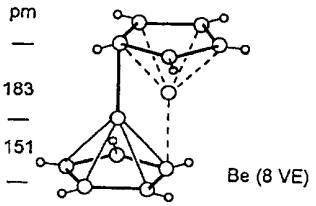
Organoberyllium hydrides, which can be prepared from RBeX and metal hydrides, feature hydride bridges and terminal methyl groups, according to their ^1H NMR spectra. The latter adopt *cis* and *trans* configurations. Thus, **a hydride bridge is favored over an alkyl bridge**. Isomerizations through intermediate cleavage of hydride bridges are slow on the NMR timescale.



The determination of the structure of **beryllocene** proved to be problematic for a long time, as investigations of different aggregation states led to different molecular geometries.

$$BeCl_2 + 2\ NaC_5H_5 \xrightarrow{Et_2O} (C_5H_5)_2Be$$

(*Fischer*, 1959)



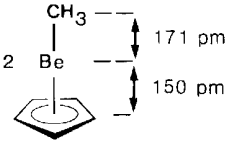
A low-temperature X-ray crystal-structure analysis (*Beattie*, 1984) clarified the situation. The results showed that **crystalline** beryllocene adopts a **slipped sandwich** structure in which the two Cp rings are staggered, corresponding to the formulation (η^1-C_5H_5)(η^5-C_5H_5)Be. The dashed lines in the figure indicate that the Be atom can occupy two equivalent positions between the staggered rings; in the crystal, the positions are occupied statistically. A bond angle of about 90° is formed between the plane of the Cp ring bound at the periphery and the C–Be bond vector: this ring is bound through a C(p_z) orbital of the $C_5H_5^-$ π system, which is only slightly distorted as a result of this Be coordination. A reinterpretation of the electron-diffraction data also leads to this type of structure for gaseous beryllocene.

In **solution**, $(C_5H_5)_2Be$ has a dipole moment ($\mu = 2.24$ D in cyclohexane). However, two equivalent C_5H_5 rings can be recognized in the ^{1}H NMR spectrum. Evidently, the exchange of the Be atom between the two positions is fast on the ^{1}H NMR timescale **(fluxional structure, haptotropy)**, which leads to a higher reactivity towards oxygen and hydrogen.

The bonding in beryllocene is essentially ionic. The structural peculiarities of this molecule arise from the fact that the optimal η^5-C_5H_5–Be bond length is smaller than half the van der Waals distance between two $C_5H_5^-$ ions. Di(pentamethyl-η^5-cyclopentadienyl)beryllium, Cp^*_2Be, adopts a "normal" η^5,η^5 sandwich structure (*Carmona*, 2000).

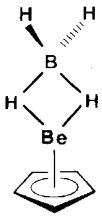
The reaction of beryllocene and dimethylberyllium leads to a half-sandwich compound, which in the spirit of Wade's rules (p. 101), may be referred to as a *nido* structure:

$$(C_5H_5)_2Be + Be(CH_3)_2 \longrightarrow 2\ CH_3Be(C_5H_5)$$



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 the propensity of both Be and B to engage in 2 e3 c bridge bonding:

$$(C_5H_5)BeCl + LiBH_4 \xrightarrow[-\ LiCl]{} (C_5H_5)BeBH_4$$



6.1.2 Organomagnesium Compounds

Preparation

$$Mg + RX \xrightarrow{Et_2O} RMgX(Et_2O)_n \quad X = Br, I \qquad \boxed{1}$$

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

$$Mg + PhCl \xrightarrow{\text{petroleum ether/THF}} PhMgCl(THF)_n \quad THF:Mg > 1$$

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

$$Mg(g) + RX(g) \xrightarrow[2.\ RT]{1.\ CC,\ -196\,^\circ C} RMgX$$

The ditelluride titration (p. 34) is one of several methods that are suitable for the **standardization** of *Grignard* reagents.

An extremely reactive form of magnesium is obtained by the method of *Rieke* (1977), in which anhydrous $MgCl_2$ is reduced with potassium. Rieke magnesium even reacts with inert fluoroalkanes:

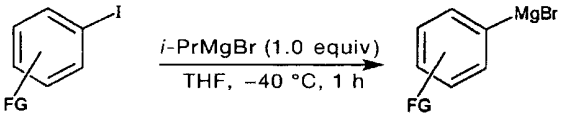
$$MgCl_2 \xrightarrow[-2\,KCl]{K,\ THF} Mg_{active} \xrightarrow[25^\circ C,\ 3\ h]{C_8H_{17}F} C_8H_{17}MgF \quad 89\%$$

Rieke magnesium is classified as an "**active metal**", which is defined as a state of the metal in which its reactivity has increased as a result of a physical or chemical manipulation (*Fürstner*, 1993).

Some **physical methods** include ultrasonic treatment of the reaction mixture, the use of metals condensed from the gas phase (in which case they react in the form of small metal clusters), or the formation of poorly aggregated metals by electrochemical reduction of solutions of anhydrous metals salts.

A **chemical method** is the preparation of active metals by reduction of metal compounds with alkali metals, or, more reliably, alkali metal addition compounds such as Li^+(naphthalene$^{\bullet -}$). Also suitable is the homolytic cleavage of labile adducts such as Mg–anthracene (thermal) or labile organotransition-metal compounds (photochemical, cf. p. 383). Metals deposited on inert support materials such as graphite are also highly reactive, and both surface bonding and intercalation are involved. An example is the commonly used potassium–graphite laminate C_8K. Upon treatment with MgI_2, magnesium–graphite is formed, which provides Grignard reagents in near-quantitative yield already at –78 °C.

Functionalized Grignard reagents are formed at low temperatures through iodine–magnesium exchange reactions:



This route bypasses a major problem encountered in the usual methods for the preparation of Grignard reagents in that they do not tolerate functional groups (FG) such as Br, $CONR_2$, CO_2Et (*Cahiez*, 1998).

Binary organomagnesium compounds can be prepared by transmetalation

$$Mg + R_2Hg \longrightarrow R_2Mg + Hg \qquad [2]$$

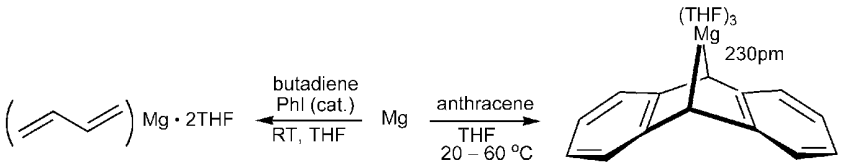
as well as by solvent-induced shifts in the equilibrium position:

$$\underset{\text{(solution)}}{2\,RMgX} + 2\ 1,4\text{-dioxane} \rightleftharpoons \underset{\text{(solution)}}{R_2Mg} + \underset{\text{(precipitate)}}{MgX_2(1,4\text{-dioxane})_2}$$

Superior to dioxane are the polyethers of the type $Me(OCH_2CH_2)_nOMe$, n = 2–5 (*Saheki*, 1987). The latter procedure may also lead to **magnesacycles**:

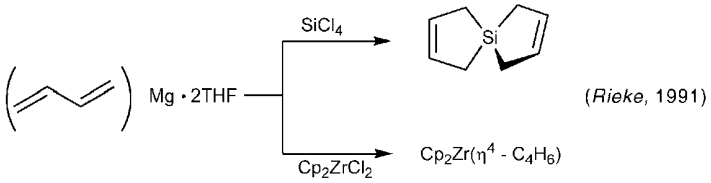
$$2\,BrMg(CH_2)_nMgBr \xrightarrow[n=4,5,6]{1,4\text{-dioxane}} \boxed{(CH_2)_n}\,Mg + MgBr_2(1,4\text{-dioxane})_2$$

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

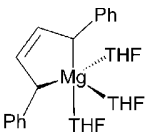


(*Yasuda*, 1976) (*Ramsden*, 1967)

Mg–butadiene [(2-butene-l,4-diyl)magnesium], a white, polymeric, sparingly soluble material of unknown structure, acts as a source of butadiene dianions $C_4H_6^{2-}$. It is used as a reagent for the introduction of the building block η^4-C_4H_6 (*Nakamura*, 1985).



(*Rieke*, 1991)



On the other hand, the structure of the [(1,4-diphenylbutadiene)magnesium] complex is known. The structure is a magnesacycle with a coordination number of 5 at the metal center, which is rare for magnesium (*Nakamura*, 1982).

Mg–anthracene (orange-yellow crystals, structure: *Raston*, 1988) reacts with anhydrous transition-metal halides to form catalysts that serve in the hydrogenation of magnesium under mild conditions (*Bogdanović*, 1980):

$$Mg + H_2\,(1-80\ \text{bar}) \xrightarrow[20-65\,^\circ C]{\text{Mg-anthracene}/MX_n/THF} MgH_2$$

$$MX_n = TiCl_4,\ CrCl_3,\ FeCl_2$$

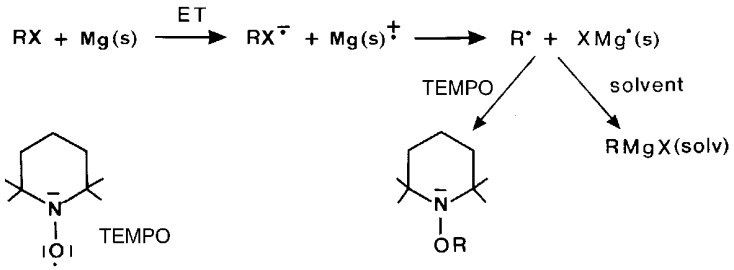
MgH_2 adds to l-alkenes (**hydromagnesation**)

$$MgH_2 + 2\ CH_2{=}CH{-}R \longrightarrow Mg(CH_2CH_2R)_2$$

and, upon cleavage above 300 °C, affords pyrophoric Mg free of solvent and halide for synthetic use. Furthermore, MgH_2 is a high-temperature storage medium for molecular hydrogen (*Bogdanović*, 1990).

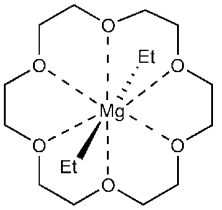
Mechanism of Formation and Constitution of Organomagnesium Compounds

Despite 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). Results by *Walborsky* (1990) suggest that the formation of "RMgX" is initiated by an electron-transfer step (ET). A hint as to the intermediacy of radicals $R^\bullet$ is furnished by the reaction with the trapping agent 2,2,6,6-tetramethylpiperidin-1-oxyl, TEMPO (*Whitesides*, 1989):



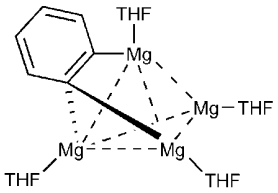
The possibility that ET reactions are involved and the knowledge that such processes are catalyzed by transition-metal ions dictate the use of ultrapure magnesium in mechanistic studies and invalidates many previous investigations in this field.

$Mg(C_2H_5)_2$, like $Be(C_2H_5)_2$, has a **polymeric chain structure** with $Mg\overset{Et}{\diagdown\diagup}Mg$ 2e3c bridge bonds. In contrast, organomagnesium compounds MgR_2 with bulky groups R crystallize as monomers (e.g. $Mg[C(SiMe_3)_3]_2$, *Eaborn*, 1989). In ethers, Grignard reagents crystallize as tetrahedral solvates, e.g. $RMgX \cdot 2\ Et_2O$. The chelate ligand [18]crown-6 gives rise to molecules of the rotaxane type, in which linear $MgEt_2$ species form the axis (*Ritchey*, 1988).



$MgEt_2 \cdot$ [18]crown-6

Mg – O 278 pm
Mg C 210 pm



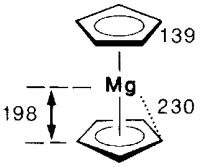
$(C_6H_4Mg \cdot THF)_4$

An original solution to the problem is offered by Nature in the structure of *o*-phenylenemagnesium $C_6H_4Mg \cdot THF$: Instead of a highly strained magnesacyclopropene ring, tetrameric units are formed in which the triangular surfaces of Mg_4 tetrahedra are capped with *o*-phenyl units; one carbon atom forms a 2e2c bond to a magnesium atom, and the neighboring carbon atom forms 2e3c bonds to the other two Mg atoms. A certain resemblance between the two heterocubane structures $[Mg^{2+}C_6H_4^{2-}]_4$ and $[Li^+CH_3^-]_4$ (p. 34) cannot be overlooked (*Bickelhaupt*, 1993).

The readily accessible **magnesocene**, $Mg(C_5H_5)_2$ (*Fischer*, *Wilkinson*, 1954), is a useful reagent for the introduction of C_5H_5 groups:

$$C_2H_5MgBr \xrightarrow[-C_2H_6]{C_5H_6,\ Et_2O} C_5H_5MgBr \xrightarrow[-MgBr_2]{x2,\ 220\,^\circ C,\ 10^{-4}\ mbar} \rightarrow Mg(C_5H_5)_2 \xrightarrow[-MgCl_2]{MCl_2} M(C_5H_5)_2$$

$$Mg + 2\,C_5H_6 \xrightarrow[-H_2]{500\,^\circ C} \rightarrow Mg(C_5H_5)_2$$



$Mg(C_5H_5)_2$ forms white, pyrophoric crystals that start to sublime at 50 °C/10^{-3} mbar, dissolve in nonpolar as well as in polar aprotic media, and undergo vigorous hydrolysis. The structural parameters apply to the crystalline state (X-ray diffraction; *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 $Mg(C_5H_5)_2$ 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, as in the case of purely ionic bonding an axially symmetric sandwich structure would also be the (electrostatically) favored configuration. Furthermore, a molecular crystal lattice does not necessarily imply covalent bonding within the $Mg(C_5H_5)_2$ units because, owing to the disparate sizes of Mg^{2+} and $C_5H_5^-$, this arrangement in which the lattice points are occupied by triple ions $Mg^{2+}(C_5H_5^-)_2$ is more favorable than a genuine ionic lattice. The high degree of polarity of the bonds in $Mg(C_5H_5)_2$ can be further seen in the electrical conductivity of solutions in NH_3 or in THF,