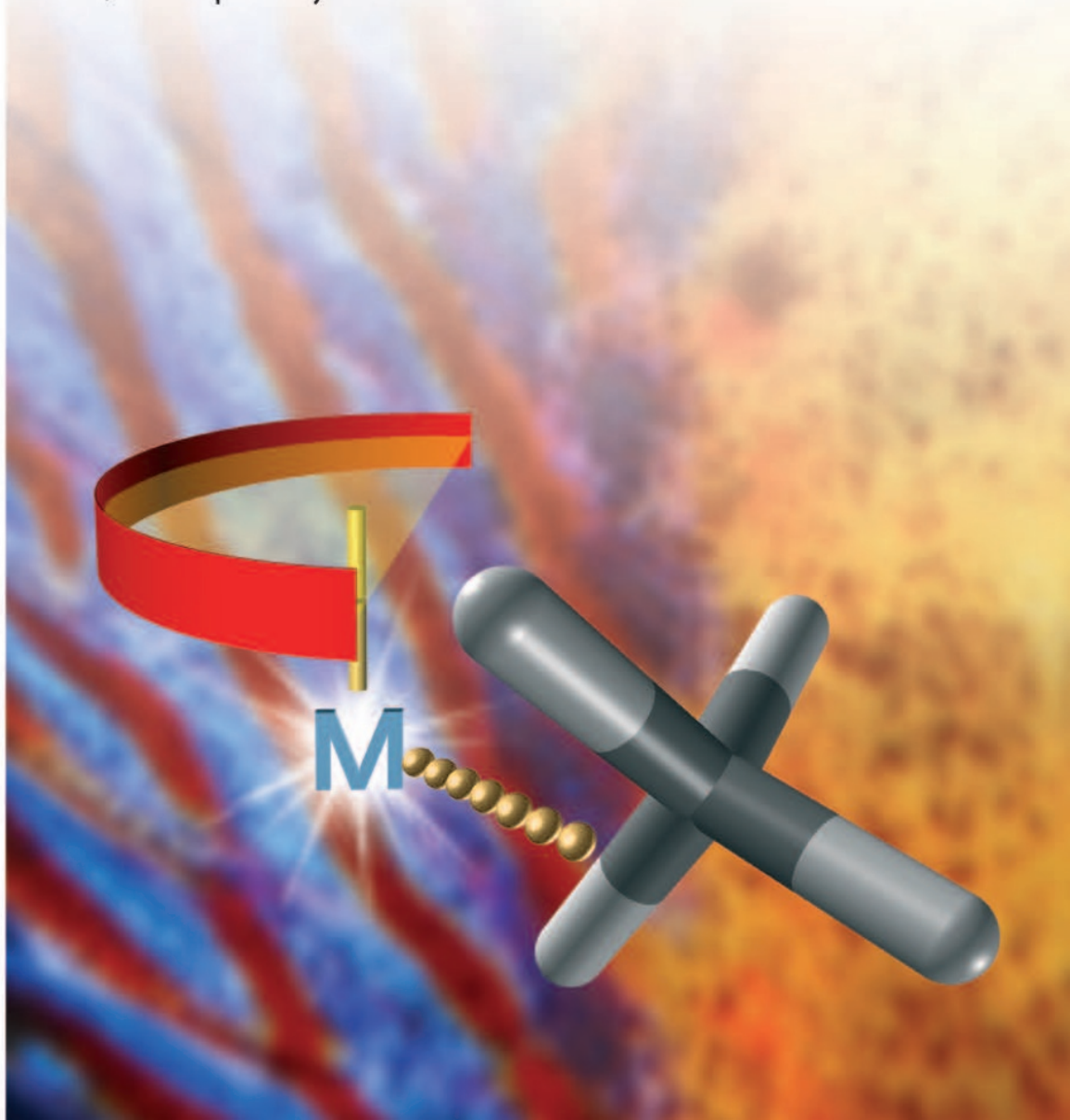


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*Christoph Elschenbroich*

## **Organometallics**

*Translated by*  
*José Oliveira*  
*and*  
*Christoph Elschenbroich*

Third, Completely Revised and Extended Edition



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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  $M \cdots CH_4$   $\sigma$  complex. Oxidative addition to yield a hydrido–metal–methyl unit eventually follows. The low-valent metal atom may either be stabilized by  $\pi$  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*, 3<sup>rd</sup> 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* 3<sup>rd</sup> 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

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 “Organometalchemie – Eine kurze Einführung”; corrections and a few results of very recent origin were included but otherwise the body was left unchanged.

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

An apparent omission is the absence of a chapter specifically dealing with organometallic reaction mechanisms. It is our contention, however, that mechanistic organometallic chemistry has not yet reached the stage which would warrant a short overview 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 organo-transition 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-

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*  
Marburg  
Germany

March  
1989

*A. Salzer*  
Zürich  
Switzerland

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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]



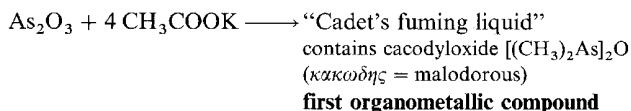
## Introduction



## 1

## Milestones in Organometallic Chemistry

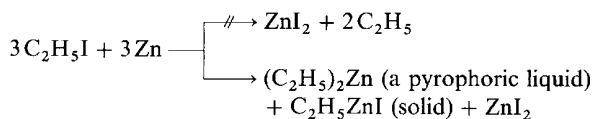
1760 The cradle of organometallic chemistry is a Paris military pharmacy. It is there that Cadet works on invisible inks based on cobalt salt solutions. For their preparation, he uses cobalt minerals that contain arsenic.



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

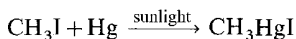
1840 *R. W. Bunsen* continues the study of cacodyl compounds, which he names “alkarsines”. The weakness of the As–As bond in molecules of the type  $\text{R}_2\text{As–AsR}_2$  leads to a profusion of derivatives such as  $(\text{CH}_3)_2\text{AsCN}$ , whose taste (!) is checked by *Bunsen*.

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



*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:



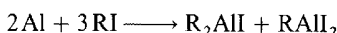
additionally:  $(\text{C}_2\text{H}_5)_4\text{Sn}$ ,  $(\text{CH}_3)_3\text{B}$  (1860).

In the following years, **alkyl-transfer reactions** with  $\text{R}_2\text{Hg}$  and  $\text{R}_2\text{Zn}$  serve in the synthesis of numerous main-group organometallic compounds.

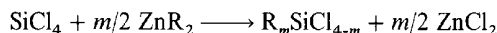
*Frankland* also introduced the concept of valency (“combining power”) and the term “organometallic”.

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

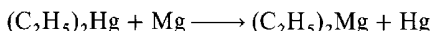
1859 *W. Hallwachs* and *A. Schafarik* generate alkylaluminum iodides:



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



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



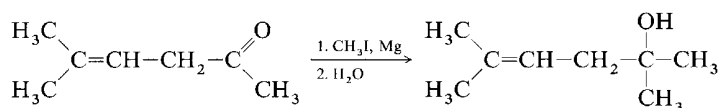
1868 *M. P. Schützenberger* obtains  $[\text{Pt}(\text{CO})\text{Cl}_2]_2$ , the **first metal–carbonyl complex**.

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

<b>Known:</b>	<b>Predicted:</b>	<b>Found:</b>
$\text{Si}(\text{C}_2\text{H}_5)_4$	Eka-Si( $\text{C}_2\text{H}_5$ ) <sub>4</sub> $d = 0.96$	$\text{Ge}(\text{C}_2\text{H}_5)_4$ (C. Winkler, 1887) $d = 0.99$
$\text{Sn}(\text{C}_2\text{H}_5)_4$	bp: 160 °C	bp: 163.5 °C

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

1899 *P. Barbier* replaces 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  $\text{ZnR}_2$ ,  $\text{RMgX}$  is a more potent alkyl-group-transfer reagent.

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

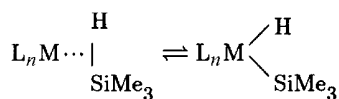
- 1909 *W. J. Pope*: formation of  $(\text{CH}_3)_3\text{PtI}$ , the **first  $\sigma$ -organotransition-metal compound**.
- 1909 *P. Ehrlich* (developer of chemotherapy, Nobel Prize 1908) introduces Salvarsan for the treatment of syphilis.
- 1917 *W. Schlenk*: alkyllithium reagents through transalkylation.
- $$2 \text{Li} + \text{R}_2\text{Hg} \longrightarrow 2 \text{LiR} + \text{Hg}$$
- $$2 \text{EtLi} + \text{Me}_2\text{Hg} \longrightarrow 2 \text{MeLi} + \text{Et}_2\text{Hg}$$
- 1919 *F. Hein* synthesizes polyphenylchromium compounds, now known to be sandwich complexes, from  $\text{CrCl}_3$  and  $\text{PhMgBr}$ .
- 1922 *T. Midgley* and *T. A. Boyd* introduce  $\text{Pb}(\text{C}_2\text{H}_5)_4$  as an antiknock additive in gasoline.
- 1927 *A. Job* and *A. Cassal* prepare  $\text{Cr}(\text{CO})_6$ .
- 1928 *W. Hieber* inaugurates his systematic study of metal carbonyls:
- $$\text{Fe}(\text{CO})_5 + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \longrightarrow (\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)\text{Fe}(\text{CO})_3 + 2 \text{CO}$$
- $$\text{Fe}(\text{CO})_5 + \text{X}_2 \longrightarrow \text{Fe}(\text{CO})_4\text{X}_2 + \text{CO}$$
- 1929 *F. A. Paneth* generates alkyl radicals through pyrolysis of  $\text{PbR}_4$ ; 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:
- $$\text{PhCH}_2\text{OMe} + 2 \text{Li} \longrightarrow \text{PhCH}_2\text{Li} + \text{MeOLi} \text{ (ether cleavage)}$$
- $$\text{H. Gilman: } \text{RX} + 2 \text{Li} \longrightarrow \text{RLi} + \text{LiX} \text{ (procedure used today)}$$
- 1931 *W. Hieber* prepares  $\text{Fe}(\text{CO})_4\text{H}_2$ , the **first transition-metal-hydride complex**.
- 1935 *L. Pauling* provides a valence-bond description of the bonding in  $\text{Ni}(\text{CO})_4$ .
- 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*:  $2 \text{CH}_3\text{Cl} + \text{Si} \xrightarrow{\text{Cu cat., } 300^\circ\text{C}} (\text{CH}_3)_2\text{SiCl}_2 + \dots$   
 This “direct synthesis” triggers 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  $\pi$ -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. Crowfoot 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  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{Cl})\text{CS}$ .
- 1968 *A. Streitwieser*: preparation of uranocene,  $\text{U}(\text{C}_8\text{H}_8)_2$ .
- 1969 *P. L. Timms*: synthesis of organotransition-metal complexes by means of metal-atom–ligand-vapor cocondensation.
- 1969 *A. E. Shilov* discovers the  $\text{Pt}^{\text{II}}$ -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  $\beta$ -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*:  $[(\text{C}_5\text{H}_5)_3\text{Ni}_2]^+$ , the first **triple-decker sandwich complex**.
- 1973 *E. O. Fischer*:  $\text{I}(\text{CO})_4\text{Cr}(\text{CR})$ , 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  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ .
- 1979 *H. Köpf* and *P. Köpf-Maier* discover the cancerostatic action of titanocene dichloride,  $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ .
- 1980 *H. Bock*: synthesis and studies of silabenzene  $\text{C}_5\text{H}_5\text{SiH}$  in the gas phase (matrix isolation: *G. Maier*, 1982).
- 1981 *R. West*:  $(\text{Mes})_2\text{Si}=\text{Si}(\text{Mes})_2$ , 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  $t\text{Bu-C}\equiv\text{P}$ , 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  $\text{ZnR}_2$  to carbonyl compounds.
- 1989 *P. Jutz*: preparation of decamethylsilicocene,  $\text{Cp}^*_2\text{Si}$ .
- 1989 *H. Schnöckel* synthesizes  $\text{AlCl}(\text{solv})$ , which he uses in the development of the organometallic chemistry of monovalent aluminum, for example,  $\text{Cp}^*_4\text{Al}_4$  (1991).
- 1991 *W. Uhl*: synthesis of anionic  $[\textit{i}\text{-Bu}_{12}\text{Al}_{12}]^{2-}$ , 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  $[\text{Li}(\text{C}_5\text{H}_5)_2]^-$ .
- 1995 *A. H. Zewail* studies M–M and M–CO bond cleavage in  $\text{Mn}_2\text{CO}_{10}$  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  $\sigma$ -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:  $[(\text{R}_2\text{N})_3\text{MoC}]^-$ , a “carbon complex”.

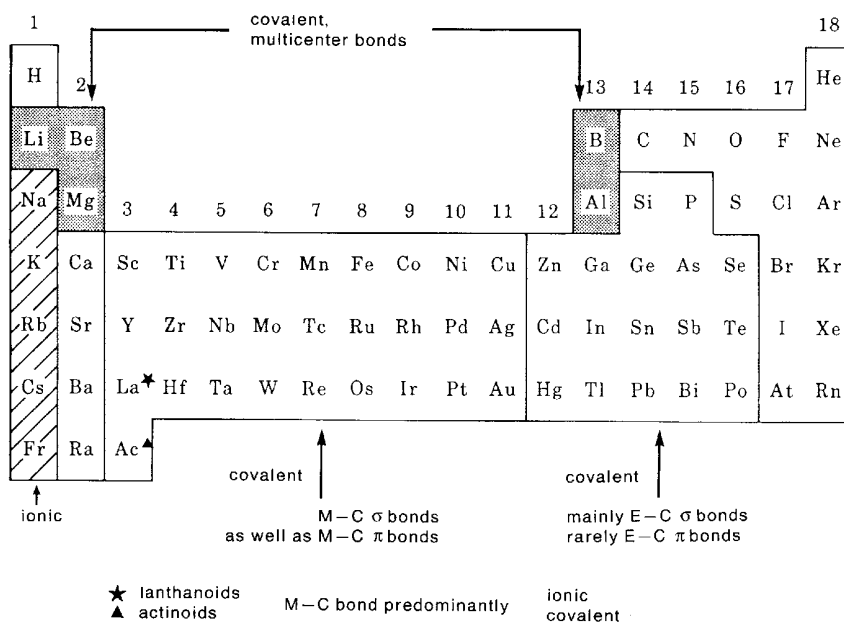
- 1997 *G. M. Robinson* synthesizes the salt  $\text{Na}_2[\text{ArGaGaAr}]$  and postulates a gallium–gallium triple bond for the diaryldigallyne anion. (Extreme example of the steric protection of a labile structural element!)
- 1999 *W. Ho* monitors the dehydrogenation of single ethylene molecules 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  $\text{Cp}^*\text{Zn}-\text{ZnCp}^*$ , the first molecule with an unsupported  $\text{Zn}^{\text{I}}-\text{Zn}^{\text{I}}$  bond.
- 2005 *A. Sekiguchi* fully characterizes  $\text{R}-\text{Si}\equiv\text{Si}-\text{R}$ , 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

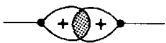
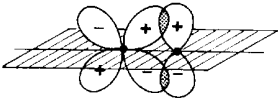
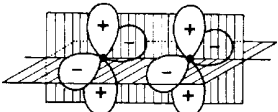
## Organoelement Compounds: Classification and Electronegativity Considerations

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.

The designations  $\sigma$ ,  $\pi$ , and  $\delta$  bond are defined as follows:

Overlap	Number of nodal planes including the bond axis	Bond type	Example
	0	$\sigma$	$\text{B}-\text{CH}_3$
	1	$\pi$	$(\text{CO})_5\text{Cr}=\text{CR}_2$
	2	$\delta$	$[\text{R}_4\text{Re}\equiv\text{ReR}_4]^{2-}$

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  $\pi$ -acceptor and decreasing  $\pi$ -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  $\pi$  conjugation. The interpretation of the UV and MCD spectra of these heteroarenes called for the

assumption that the perturbation of the aromaticity of the  $\pi$  system is caused by the  $\pi$ -acceptor effect of the P, As, and Sb atoms. This led to the conclusion that the effective  $\pi$ -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  $\sigma$ -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( $p\pi$ ) 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  $\sigma$  and  $\pi$  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  $E^\circ$  [ $L_nCo(III/II)$ ] 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 ( $C_5H_5$ )<sub>2</sub>Be is an extremely air- and water-sensitive compound, whereas in stark contrast, ferrocene ( $C_5H_5$ )<sub>2</sub>Fe 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*:  $\text{MgMe}_2$ ,  $\text{PMe}_3$ ,  $\text{MeBr}$ ,  $[\text{LaMe}_6]^{3-}$ ,  $\text{WMe}_6$ ). 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,  $r = d - r_{\text{carbon}} = d - 77$ .

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

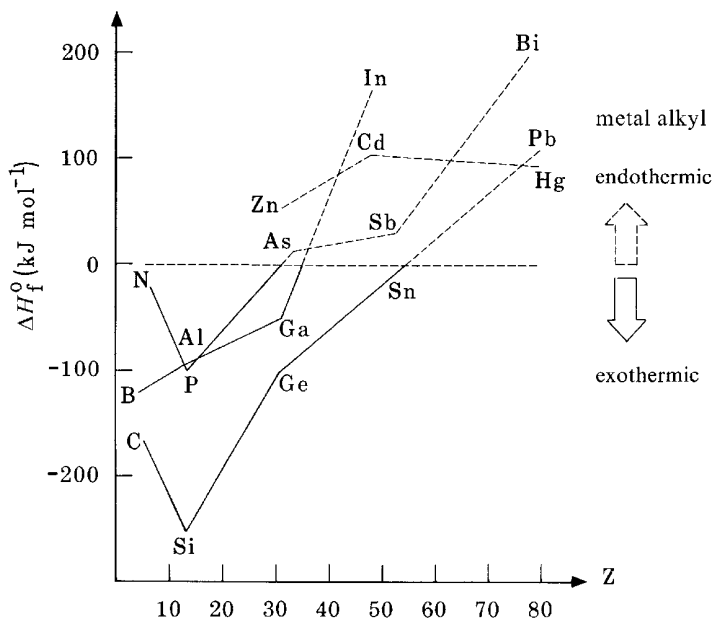
Compared with M–N, M–O, and M–Hal bonds, M–C bonds must be deemed **weak**. This bond weakness is reflected in the uses that organometallic reagents find in synthesis. As standard entropies are seldom known for organometallic compounds, enthalpies of formation  $\Delta H_f^\circ$  are often used instead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

Comparison of standard enthalpies  $\Delta H_f^\circ$  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

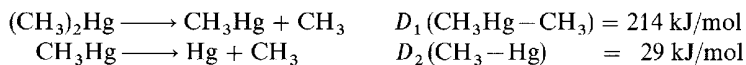
Group											
12 MMe <sub>2</sub>			13 MMe <sub>3</sub>			14 MMe <sub>4</sub>			15 MMe <sub>3</sub>		
M	$\Delta H_f^\circ$	$\bar{D}$	M	$\Delta H_f^\circ$	$\bar{D}$	M	$\Delta H_f^\circ$	$\bar{D}$	M	$\Delta H_f^\circ$	$\bar{D}$
			B	-123	365	C	-167	358	N	-24	314
			Al	-81	274	Si	-245	311	P	-101	276
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  $D_{1,2,\dots,n}$  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.):



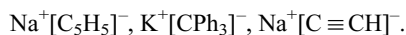
The data for methyl derivatives presented in the table above are prototypical inasmuch as they may require slight modification in different chemical environments. As should be expected, the energy of an  $L_n\text{M}-\text{CX}_3$  bond depends on the oxidation state and ligand sphere  $L_n$  of the metal atom as well as on the nature of the substituent X at the carbon atom. Furthermore, steric (e.g. X =  $\text{CH}_3$ ) and electronic effects (e.g. L =  $\pi$ -acceptor ligand, X = F) also contribute to this variability.

Generalizations:

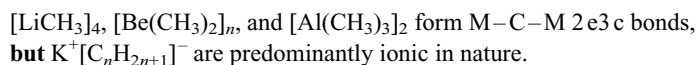
- **M–C bond energies cover a wide range**

Compound	$(\text{CH}_3)_3\text{B}$	$(\text{CH}_3)_3\text{As}$	$(\text{CH}_3)_3\text{Bi}$
$\bar{D}(\text{M}-\text{C})$ (kJ/mol)	365	229	141
bond	“strong”	“medium”	“weak”

- **The mean bond energy  $\bar{D}(\text{M}-\text{C})$**  within a main group decreases with increasing atomic number. This trend also applies to the bonds of M to other elements of the second 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:*



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



### 3.2

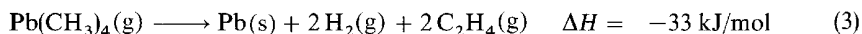
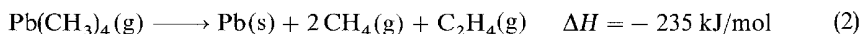
#### Lability of Main-Group Organometallic Compounds

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.

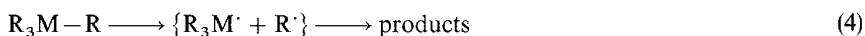
*Example:*



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



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



is accompanied by  **$\beta$  elimination**:



The concerted nature of decomposition pathway (5) entails a lowering of the activation energy. However, this path is limited to molecules with hydrogen atoms in the  $\beta$  position. This reaction explains why the temperature of decomposition is higher for  $\text{Pb}(\text{CH}_3)_4$  than for  $\text{Pb}(\text{C}_2\text{H}_5)_4$  (p. 200).

A further condition for  $\beta$  elimination to occur is the availability of an empty valence orbital on M to interact with the electron pair of the  $\text{C}_\beta\text{--H}$  bond. It is for this reason that the  $\beta$  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,  $\beta$  elimination can be blocked and thermal stability increased through the formation of a Lewis base adduct (e.g.  $(\text{bipy})\text{Be}(\text{C}_2\text{H}_5)_2$ ,  $\text{bipy} = 2,2'$ -bipyridyl).  $\beta$  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  $\text{MO}_n$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ . 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
$\text{Zn}(\text{C}_2\text{H}_5)_2$	–1920 kJ/mol	unstable	pyrophoric	labile
$\text{Sn}(\text{CH}_3)_4$	–3590 kJ/mol	unstable	airstable	inert

Particularly labile against O<sub>2</sub> and H<sub>2</sub>O 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 <sub>3</sub> In	pyrophoric	hydrolyzed	electron gap at In, high bond polarity.
Me <sub>4</sub> Sn	inert	inert	Sn shielded well, low bond polarity.
Me <sub>3</sub> Sb	pyrophoric	inert	free electron pair on Sb.
Me <sub>3</sub> B	pyrophoric	inert	electron gap at B is closed by means of hyperconjugation, low bond polarity.
(Me <sub>3</sub> Al) <sub>2</sub>	pyrophoric	hydrolyzed	electron gap at Al in the monomer, nucleophilic attack through 3 d(Al) or $\sigma^*(\text{Al}-\text{C})$ in the dimer, high bond polarity.
SiH <sub>4</sub>	pyrophoric	hydrolyzed	Si steric shielding ineffective, relatively electron rich.
SiCl <sub>4</sub>	inert	hydrolyzed	Si relatively electron-poor, high polarity of Si–Cl bonds, nucleophilic attack through 3 d(Si) or $\sigma^*(\text{Si}-\text{Cl})$ .
SiMe <sub>4</sub>	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.

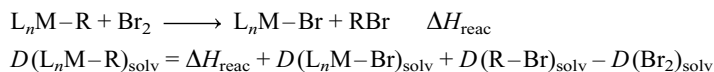
### Excursion 1: Where does our knowledge of M–C bond energies come from?

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  $\Delta H(\text{M}-\text{C})$ . 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-

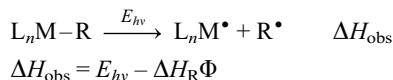
matic. A variant on the classical combustion calorimetry is the thermochemical monitoring of reactions in solution, such as the bromination of organometallic molecules.



By varying R, one can use the measured heats of reaction  $\Delta H_{\text{reac}}$  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  $E_{hv}$  (typical duration: 10 ns). The radiation is absorbed by the substrate, and homolytic cleavage results:



The difference between the energy of the incident photons  $E_{hv}$  and the bond dissociation energy  $\Delta H_R$  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  $\Delta H_{\text{obs}}$ . The quantum yield  $\Phi$  is used to correct for the proportion of absorbed light that is likely not involved in photo-induced 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  $\Phi$  that are too low or are not known beforehand. Furthermore, nonuniform photochemistry of organotransition-metal compounds may also preclude the use of PAC techniques.

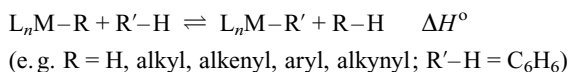
An actual example of the application of PAC is the determination of the energy of the Co–C bond ( $150 \text{ kJ mol}^{-1}$ ) in molecules of the vitamin B<sub>12</sub> family under physiological conditions (Grabowski, 1999).

### 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  $\Delta H^\circ$  by means of the van't Hoff equation:

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

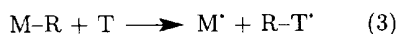
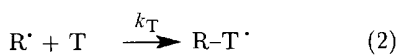
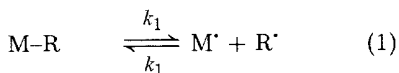
Such a study on metathesis reactions,



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).



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

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  $R-T^\cdot$  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

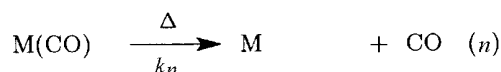
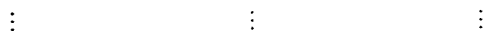
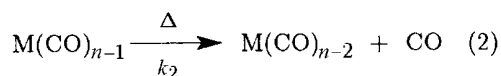
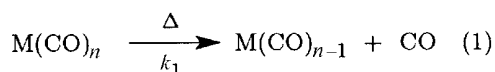
$\Delta H_1^\ddagger \approx D(\text{M}-\text{R})$  is also justified by the endothermic nature of the bond cleavage ( $k_1$ ) which results in a small activation barrier for the reverse reaction and thus a low  $\Delta H_{-1}^\ddagger$ ; in this case the transition state is said to resemble the product (Hammond postulate). Should no suitable spin-trap reagent T be available,  $\Delta H_{-1}^\ddagger$  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  $D(\text{Co}-\text{C})$  in a series of model complexes for the vitamin B<sub>12</sub> coenzyme. A corresponding investigation on natural substrates was reported by *Brown* (1984) in which Co–C bond homolysis was induced by a B<sub>12</sub>-dependent ribonucleotide reductase.

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

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



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.



In general (but not exclusively!), the first CO molecule to be cleaved from  $\text{M}(\text{CO})_n$  is the most tightly bound. Thus  $k_1$  represents the rate-determining step in  $\text{M}(\text{CO})_n$  pyrolysis. The reverse reaction ( $k_{-1}$ ) is negligible as  $k_1 < k_2, k_3, \dots, k_n$ , 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  $\Delta H_1^\ddagger \approx D(\text{M}-\text{C})$  also holds in this case. The kinetic analysis of the gas-phase pyrolysis is advantageous in that it yields a  $D(\text{M}-\text{CO})$  value for an individual bond, whereas classical thermochemical methods provide a mean value  $\bar{D}(\text{M}-\text{CO})$  for all bonds present. These values can differ significantly. *Example:*  $\text{Fe}(\text{CO})_5$ :  $D[(\text{CO})_4\text{Fe}-\text{CO}] = 174 \text{ kJ/mol}$ ,  $\bar{D}[\text{Fe}(\text{CO})_5] = 117 \text{ kJ/mol}$ . The application of both