

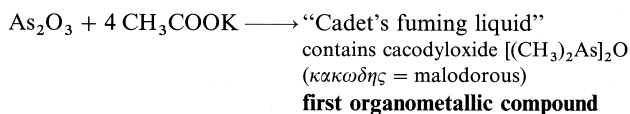
## Introduction



## 1

## Milestones in Organometallic Chemistry

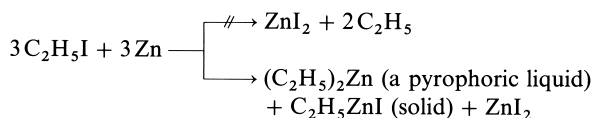
1760 The cradle of organometallic chemistry is a Paris military pharmacy. It is there that Cadet works on invisible inks based on cobalt salt solutions. For their preparation, he uses cobalt minerals that contain arsenic.



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

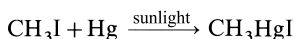
1840 *R. W. Bunsen* continues the study of cacodyl compounds, which he names “alkarsines”. The weakness of the As–As bond in molecules of the type  $\text{R}_2\text{As–AsR}_2$  leads to a profusion of derivatives such as  $(\text{CH}_3)_2\text{AsCN}$ , whose taste (!) is checked by *Bunsen*.

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:



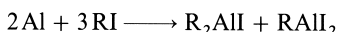
additionally:  $(\text{C}_2\text{H}_5)_4\text{Sn}$ ,  $(\text{CH}_3)_3\text{B}$  (1860).

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.

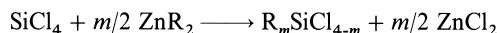
*Frankland* also introduced the concept of valency (“combining power”) and the term “organometallic”.

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:



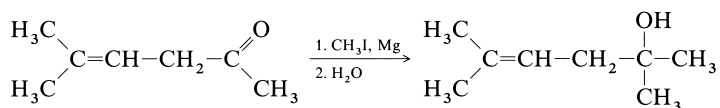
1868 *M. P. Schützenberger* obtains  $[\text{Pt}(\text{CO})\text{Cl}_2]_2$ , the **first metal–carbonyl complex**.

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.

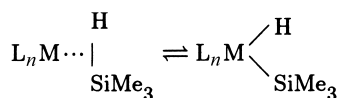
1901 *L. F. S. Kipping* prepares  $(\text{C}_6\text{H}_5)_2\text{SiO}$ , suspects its high molecularity, yet calls the material **diphenylsilicone**.

- 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**.