

7.1: Transition Metal Alkyl Complexes

Learning Objectives

In this lecture you will learn the following

- Get a general prospective on the historical background of transition metal organometallic compounds with particular emphasis on metal alkyls.
- Know more about stable metal alkyls.
- Get introduced to transition metal agostic alkyls.
- Develop an understanding of reactions of relevance to metal alkyls like the reductive eliminations, oxidative additions and the halide eliminations.

Transition metal σ -bonded organometallic compounds like the metal alkyls, aryls and the hydrides derivatives are by far the most common organometallic species encountered in the world of chemistry. Yet, these compounds remained elusive till as late as the 1960s and the 1970s.

Historical background

Metal alkyls of the main group elements namely, Li, Mg, Zn, As and Al, have been known for a long time and which over the years have conveniently found applications in organic synthesis whereas development on similar scale and scope in case of the transition metal counterparts were missing till only recently. The origin of the organometallic compounds traces back to 1757, when Cadet prepared a foul smelling compound called cacodyl oxide from As_2O_3 and CH_3COOK , while working in a military pharmacy in Paris. Years later in 1840, R. W. Bunsen gave the formulation of cacodyl oxide as $\text{Me}_2\text{As}-\text{O}-\text{AsMe}_2$. The next known transition metal organometallic compound happens to be Et_2Zn , which was prepared serendipitously in 1848 from the reaction of ethyl iodide (EtI) and Zn with the objective of generating free ethyl radical. Frankland further synthesized alkyl mercury halides like, CH_3HgI , from the reaction of methyl iodide (CH_3I) and Hg in sunlight. It is important to note that the dialkyl mercury, R_2Hg , and the dialkyl zinc, R_2Zn , have found applications as alkyl transfer reagents in the synthesis of numerous main group organometallic compounds.

Another notable development of the time was of the preparation of Et_4Pb from ethyl iodide (EtI) and Na/Pb alloy by C. J. Lowie and M. E. Schweizer in 1852. They subsequently extended the same method for the preparation of the Et_3Sb and Et_3Bi compounds. In 1859, aluminumalkyl iodides, R_2AlI , were prepared by W. Hallwachs and A. Schafarik from alkyl iodide (RI) and Al. The year 1863 saw the preparation of organochlorosilanes, $\text{R}_m\text{SiCl}_{4-m}$, by C. Friedel and J. M. Crafts while the year 1866 saw the synthesis of halide-free alkyl magnesium compound, Et_2Mg , by J. A. Wanklyn from the reaction of Et_2Hg and Mg. In 1868, M. P. Schutzenberger reported the first metal-carbonyl complex in the form of $[\text{Pt}(\text{CO})\text{Cl}_2]_2$. In 1890, the first binary metal-carbonyl compound, $\text{Ni}(\text{CO})_4$ was reported by L. Mond, who later founded the well-known chemical company called ICI (Imperial Chemical Industries). In 1909, W. J. Pope reported the first σ -organotransition metal compound in the form of $(\text{CH}_3)_3\text{PtI}$. In 1917, the alkyllithium, RLi , compounds were prepared by W. Schlenk by transalkylation reactions. In 1922, T. Midgley and T. A. Boyd reported the utility of Et_4Pb as an antiknock agent in gasoline. A. Job and A. Cassal prepared $\text{Cr}(\text{CO})_6$ in 1927. In 1930, K. Ziegler showed the utility of organolithium compounds as alkylating agent while in the following year in 1931, W. Heiber prepared $\text{Fe}(\text{CO})_4\text{H}_2$ as the first transition metal-hydride complex. O. Roelen discovered the much renowned hydroformylation reaction in 1938, that went on to become a very successful industrial process worldwide.

The large scale production and the use of silicones were triggered by E. G. Rochow, when he reported the 'direct synthesis' from methyl chloride (CH_3Cl) and Si using Cu catalyst at 300 °C in 1943. The landmark compound, ferrocene (C_5H_5) $_2\text{Fe}$, known as the first sandwich complex was obtained by P. Pauson and S. A. Miller in 1951. H. Gilman introduced the important utility of organocuprates when he prepared $\text{LiCu}(\text{CH}_3)_2$, in 1952. In the subsequent year 1953, G. Wittig found a new method of synthesizing olefins from phosphonium ylides and carbonyl compounds that fetched him a Nobel prize in 1979. The year 1955 turned out to be a year of path breaking discoveries with E. O. Fischer reporting the rational synthesis of bis(benzene)chromium, $(\text{C}_6\text{H}_6)_2\text{Cr}$ while K. Ziegler and G. Natta announcing the ground breaking polyolefin polymerization process that subsequently gave them the Nobel prizes, E. O. Fischer sharing with G. Wilkinson in 1973 while K. Ziegler and G. Natta shared the same in 1963. In 1956, H. C. Brown reported hydroboration for which he too received the Nobel prize in 1979. In 1963, L. Vaska reported the famous Vaska's complex, $\text{trans}-(\text{PPh}_3)_2\text{Ir}(\text{CO})\text{Cl}$, that reversibly binds to molecular oxygen. In 1964, E. O. Fischer reported the first carbene complex, $(\text{CO})_5\text{W}(\text{OMe})\text{Me}$. In 1965, G. Wilkinson and R. S. Coffey reported the Wilkinson catalyst, $(\text{PPh}_3)_3\text{RhCl}$, for the hydrogenation of alkenes. In 1973, E. O. Fischer synthesized the first carbyne complex, $\text{I}(\text{CO})_4\text{Cr}(\text{CR})$.

After the early 1970s, there were tremendous outburst in activity, in the area of transition metal organometallic chemistry leading to phenomenal developments having far-reaching consequences in various branches of the main stream and interfacial chemistry. Several Nobel prizes that have been awarded to the area in recent times fully recognized the significance of these efforts with Y. Chauvin, R. R. Schrock, and R. H. Grubbs winning it in 2005 for olefin metathesis and Akira Suzuki, Richard F Heck and E. Negishi receiving the same for the Pd catalyzed C–C cross-coupling reactions in organic synthesis in 2010.

Metal alkyls

In day to day organic synthesis, particularly from the application point of view, the metal alkyls are often perceived as a source of stabilized carbanions for reactions with various electrophiles. The extent of stabilization of alkyl carbanions in metal alkyl complexes depend upon the nature of the metal cations. For example, the alkyls of electropositive metals like that of Group 1 and 2, Al and Zn are regarded as polar organometallics as the alkyl carbanions remain weakly stabilized while retaining strong nucleophilic and basic character of a free anion. These polar alkyls are extremely air and moisture sensitive as in their presence they often get hydrolyzed and oxidized readily. Similar high reactivity was also observed in case of the early transition metal organometallic compounds particularly of Ti and Zr. On the contrary the late transition metal organometallic compounds are much less reactive and stable. For example, the Hg–C bond of (Me–Hg)⁺ cation is indefinitely stable in aqueous H₂SO₄ solution in air. Thus, on moving from extremely ionic Na alkyls to highly polar covalent Li and Mg alkyls and to essentially covalent late-transition metal alkyls, a steady decrease in reactivity is observed. This trend can be correlated to the stability of alkyl carbanions that also depended on the nature of hybridization of the carbon center, with *sp*³ hybridized carbanions being the least stable and hence most reactive, followed by the *sp*² carbanions being moderately stable while the *sp* carbanions being the least reactive and most stable. The trend also correlates well with the respective pK_a values observed for CH₄ (pK_a = ~50), C₆H₆ (pK_a = ~43) and RC≡CH (pK_a = ~25).

Stable alkyls

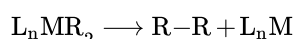
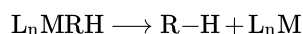
As has been mentioned earlier, that the β-elimination is a crucial destabilizing influence on the transition metal organometallic complexes. Hence, inhibition of this decomposition pathway leads to increased stabilities of organometallic compounds. Thus, many stable alkyl transition metal complexes do not possess β-hydrogens like W(Me)₆ and Ti(CH₂Ph)₄. In some cases despite the presence of the β-hydrogens the organometallic complexes are stable as the β-hydrogens are deposited away from the metal center like in, Cr(CHMe₂)₄, and Cr(CMe₃)₄. In this category of stable transition metal organometallic compounds also falls the ones that contain β-hydrogens but cannot β-eliminate owing to the formation of a olefinic bond at a bridgehead, which is unfavorable, like in Ti(6-norbornyl)₄ and Cr(1-adamantyl)₄. Lastly, some 18 VE metal complexes are stable, again despite having β-hydrogens, for reasons of being electronically as well as coordinatively saturated at the metal center owing to attaining the stable 18 electron configuration.

Agostic alkyls

Agostic alkyls are extremely rare but very interesting species that represents a frozen point in a β-elimination pathway that have fallen short of the completion of the decomposition reaction. Thus, these agostic alkyl complexes can be viewed as snap shots of a β-elimination trajectory thereby providing valuable mechanistic understanding of the decomposition reaction. The agostic interaction has characteristic signatures in various spectroscopic techniques as observed from the decreasing J_{C–H} coupling constant values in the ¹H NMR and the ¹³C NMR spectra and the lowering of the ν_{C–H} stretching frequencies in the IR spectroscopy. The agostic alkyl complexes can be definitively proven by X-ray diffraction or neutron diffraction studies. The agostic alkyls thus have activated C–H bonds which are of interest for their utility in chemical catalysis. Quite interestingly, many *d*⁰ Ti agostic alkyl complexes do not β-eliminate primarily for the metal center being too electron deficient to donate electron to the σ* C–H orbital as required for the subsequent β-elimination process.

Reductive elimination

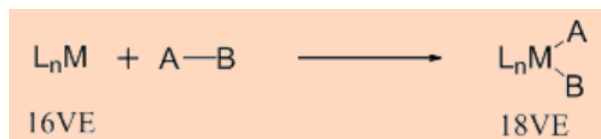
Reductive elimination represents a major decomposition pathway of the metal alkyls. Opposite of oxidative addition, the reductive elimination is accompanied by the decrease in the oxidation state and the valence electron count of the metal by two units. The metal alkyl complexes may thus reductively eliminate with an adjacent hydrogen atom to yield an alkane, (R–H) or undergo the same with an adjacent alkyl group to give an even larger alkane (R–R) as shown below.



The reductive elimination is often facilitated by an electron deficient metal center and by sterically demanding ligand systems. Often d^8 metals like Ni(II), Pd(II), and Au(III) and d^6 metals in high oxidation state like, Pt(IV), Pd(IV), Ir(III), and Rh(III) exhibit reductive elimination.

Oxidative addition

Unlike the reductive elimination that represents a decomposition pathway of metal alkyls, the oxidative addition reaction represents a useful method for the formation of the metal alkyl complexes. The oxidative addition thus leads to increase in valence electron count and the oxidation state of the metal center by two units. The oxidative addition reactions are often facilitated by low valent electron rich metal centers and by less sterically demanding ligands.



Halide elimination

β -halide elimination is observed for the early transition metals and the f -block elements resulting in the formation of stable alkyl halides. The phenomenon is mostly seen in case of the metal fluorides and arise owing to the very high alkyl-fluoride bond strengths that favor the halide elimination.

Problems

1. Who elucidated the structure of cacodyl oxide?
Ans: R. W. Bunsen in 1840
2. Give the example of the first olefin bound transition metal complex?
Ans: Zeise's salt, $Na[PtCl_3(C_2H_4)]$
3. Who discovered olefin polymerization?
Ans: K. Ziegler and G. Natta
4. What kind of metal center promotes oxidative addition reactions?
Ans: Electron rich
5. The 18 VE complex would favor/disfavor oxidative addition reactions?
Ans: Disfavor

Self Assessment test

1. O. Roelen discovered which famous reaction?
Ans: Hydroformylation
2. What is the first binary metal-carbonyl complex?
Ans: $Ni(CO)_4$
3. Who discovered the hydroboration reaction?
Ans: H. C. Brown
4. Reductive elimination reaction is favored by what kind of ligands?
Ans: Sterically demanding
5. β -halide elimination is mainly observed for what type of metal halide complexes?
Ans: Metal fluorides

Summary

A broader outlook on metal alkyls is obtained from the study of its historical background thus dispelling many myths about these compounds like them being inherently unstable. It also establishes newer founding principles like these compounds indeed being thermodynamically stable under certain experimental conditions and thus facilitating further attempts to take up the synthesis of these compounds. Another important class of transition metal organometallic compounds are the agostic alkyls, which can be viewed as the ones that have proceeded along but have fallen short of the final sequence of the β -elimination step. While oxidative addition reaction remains a key method for synthesizing metal alkyls, the complementary reaction, *i.e.*, the reductive elimination, represents a decomposition reaction of these compounds. β -halide elimination reactions are observed for early transition metal elements and *f*-block elements.

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