INORGANIC CHEMISTRY

Organometallics

Prof. Tarlok S. Lobana
Department of Chemistry
Guru Nanak Dev University
Amritsar 143005

(19.06.2006)

CONTENTS

Keywords
Organolithium, organoaluminium, organomercury, organotin and organotitanium, metal-alkene, metal carbonyls, nomenclature

Introduction

A metal atom can form bonds with one or more carbon atoms (M–C bond) such as $M–CH_3$, M–CO, M–CN, M-(η^5-C_5H_5) (η^5-C_5H_5 = cyclopentadienyl binding via its π-electrons) and so on. An organometallic compound is defined as one which contains at least one metal–carbon bond. The carbon compounds of boron, arsenic, silicon and germanium (metalloids) are also considered as organometallic compounds, excluding those of phosphorus (P–C) and more electronegative elements. Traditionally metal carbonyls are considered as organometallic compounds, while metal-cyanides and metal-carbides as inorganic compounds.

The organometallic compounds have $M^{\delta+}– C^{\delta-}$ bond polarity, which make them different from organic compounds. The organic compounds have $M^{\delta-}– C^{\delta+}$ bond polarity in which carbon is at the positive end of bonds to nonmetallic elements (M = O, N, F, Cl, Br). The bond polarity ($M^{\delta+}– C^{\delta-}$) of organometallic compounds such as metal alkyls and aryls, MR_n, makes R group carbanionic and susceptible to attack by electrophiles (affinity for negative center). The metal center on the other hand, which generally has vacant orbitals, is susceptible to attack by nucleophiles (affinity for positive center). The vacant orbitals can accommodate electronic charge from nucleophiles, and thus help to stabilize a transition state in the reactions of organometallic compounds.

Historical Background

Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, prepared in 1827, is the first organometallic compound known, and is now established as the first metal-alkene complex (C_2H_4 = ethylene). Edward Frankland prepared ethylzinc(II) iodide and diethylzinc(II) in 1849, and methylmercury(II) iodide, the first organomercury compound in 1852. Ethylsesquiiodide (a 1:1 mixture of $EtAlI_2$ and Et_2AlI) were reported in 1859 by Hallwachs and Schafarik.Various other organometallic compounds discovered are as follows: metal carbonyls $\{M(CO)_n\}$ by Schützenberger in 1868; organomagnesium halides (Grignard reagents) in 1900; trimethylplatinum(IV) chloride, $(CH_3)_3PtCl$ by Pope et al in 1907; bis(cyclopentadiney)iron(II) known as ferrocene, (π-$C_5H_5)_2Fe$, by Wilkinson in 1951. The organometallic compounds such as diethylzinc(II), ferrocene, Zeise salt etc. helped in understanding the formation of chemical bonds. Each element has a definite combining capacity (known as its valency), and that both sigma (σ) and pi-bonding (π) are crucial in the formation of various compounds including organometallics. The discovery of Grignard reagents led to a variety of organic and organometallic syntheses. The $TiPh(OPr^i)_3$ (σ-bonded) was isolated in 1952 as the first organotitanium compound, even though attempts were made as early as 1861 (from $TiCl_4$ and $ZnEt_2$). The use of alkyl aluminium(III) – titanium(IV) chloride as catalysts in the alkene polymerization by Ziegler and Natta led to enormous developments in polymer industry.

Classification of Organometallic Compounds

The organometallic compounds are classified into different types based on the nature of metal-carbon bonding. Carbon can form both ionic bonds with electropositive elements as well as covalent bonds with several main group and d-block elements.

(i) Metal-carbon Ionic Bonds : The most electropositive elements (Na, K etc.) form ionic organometallic compounds. For example, the crystalline solid (close packed hexagonal) of methylpotassium ($K^+CH_3^-$) has isolated methyl anions (CH_3^-) and metal cations (K^+).

Generally, the stability of anion is very important for the formation of ionic compounds. The stable anions are encountered among aromatic rings and unsaturated organic groups, due to the possibility of delocalization of anionic charge on the entire ring, or unsaturated chain systems. In the formation of sodium cyclopentadienyl salt ($Na^+C_5H_5^-$), the radical $\{C_5H_5\}^{\cdot}$ readily accepts electron from Na atom to form $C_5H_5^-$ anion with a delocalized aromatic ring system. Similarly, the anion of $Na^+Ph_3C^-$ has aromatic ring system for delocalization of electron accepted from Na atom. The negative charge in sodium ethynyl ($Na^+CH{\equiv}C^-$) is stabilized mainly due to higher electronegativity of sp versus sp^3 hybridized carbon atoms. In all the examples cited above, there is high degree of ionic character in M^+R^- compounds.

(ii) Metal-Carbon Bridge Bonding : The light electropositive elements (e.g. Li, Be, Mg, Al) form organometallic compounds such as MeLi, Me_2Mg , Ph_3Al etc. These compounds do not exist as monomers rather form oligomers, or polymers, namely, $(MeLi)_4$, $(Me_2Mg)_n$, $(Ph_3Al)_2$ involving bridging by alkyl or aryl groups. This bridge formation is similar to that in boranes which involve two electron-three center bonds. The metal-carbon bonds have considerable covalent character.

(iii) Metal-Carbon Two Electron Covalent Bonds: The main group elements form binary alkyls and aryls, MR_n which have single two electron M–C bonds, the polarity of which depends on their electronegativity differences. For example, Al–C bonds in Me_3Al are more polar (χ_C-χ_{Al} = 2.5–1.6 = 0.9) than B–C bonds in Me_3B ((χ_C-χ_B = 2.5–2.1 = 0.4). The M–C bond strength decreases with increase in atomic number among main group elements. This difference is due to more effective overlap of carbon (2s/2p) orbitals with the metal in the same row, rather than with the metal down the group, which has more diffuse s and p-orbitals.

The alkyl and aryl derivatives of transition elements with M–C bonds are also known; however their isolation and stability varies with the organic group and nature of metal. For instance, Me_4Ti has been isolated but is unstable and decomposes readily, while Et_4Ti is too unstable to be isolated. This lability is not due to weakness of Ti–C bonds, rather it is attributed to kinetic instability. The M–C bond strength among transition elements increases down the group, a trend opposite to that observed in the main group elements. This is explained as follows: The 3d orbitals (first transition series) are more contracted than 4d (second transition series) or 5d (third transition series) orbitals, and thus M–C orbital overlap increases in the order: 5d > 4d > 3d.

(iv) Metal – Carbon Multiple bonds: The multiple bond formation between carbon and other main group elements is uncommon. Phopshorus and silicon form $R_3P{=}CH_2$ and $R_2C{=}SiR_2'$ compounds. The latter however, do not exist as monomers, rather form oligomers or polymers. However, the use of bulky R/R' groups help to prepare monomers. Multiple bonds are more common with transition elements. Tungsten compounds of type, $(OC)_5W{=}C(OMe)Me$, and $(Bu^tO)_3W{\equiv}Cet$, represent some examples. The suitable metal d-orbitals and carbon 2p orbitals for π-overlap are engaged in multiple bonding.

(v) Metal–Carbon π- Bonds with Unsaturated Hydrocarbons: Organic compounds are known to form bonds via filled π electrons, as for example, first observed in ferrocene, and Zeise's salt. It is essential that metal should have filled suitable orbitals which can form back-bonds (π-bonds) to empty π* orbitals centered on the organic ligand. A large number of π

complexes have been prepared with d-block elements, to a lesser extent with the lanthanides and actinides, and only small number with main group elements. Cyclopentadiene and cyclooctatetraene are some organic compounds which have formed a number of complexes with various elements. The bonding is predominantly ionic in case of main group, polar in case of f-block, and covalent in case of d-block elements.

Properties

The physical properties of organometallic compounds resemble with those of organic compounds. For example, organometallic compounds are soluble in solvents of low polarity such as toluene, ethers etc. Several of them exist as low melting solids, liquids or gases at ordinary temperatures. Thermal stability of compounds depends on the nature of compounds. While some decompose at room temperature and form metal oxide, CO_2 and H_2O, others are stable at higher temperature. For example, $SiMe_4$ is stable at 500^oC for several days; $TiMe_4$ decomposes rapidly at room temperature. The differences exist in kinetic stability to oxidation as well, $HgMe_2$, $FeCp_2$ are not attacked by oxygen at room temperature, while BMe_3, $CoCp_2$ are spontaneously inflammable. Finally, some compounds are readily attacked by water, while others are inert to water attack. For example, $AlMe_3$ is readily attacked by water, while BMe_3 is not affected by water. The hydrolysis depends on the polarity of M-C bond which is more for Al than for B.

Nomenclature

In order to understand how various organometallic compounds are named, some examples and rules in this section will give an idea about the nomenclature. Nomenclature for lithium compounds is the simple matter. Since only one R group is attached to Li metal to form RLi, the resulting compound is organolithium. For R = Me, it is methyllithium, for R = Ph, it is phenyllithium and so on. If RLi is not a monomer and has oligomerized, then it is called dimer, trimer, tetramer and so on. For example, MeLi is a tetramer, $(MeLi)_4$, while, Pr^iLi is hexamer, $(Pr^iLi)_6$.

Two systems (A and B) are used for naming various compounds. Some examples notably of Al are used to bring home this method of nomenclature and rules/conventions used hold true for other organometallic compounds. According to system A, the organic groups/ hydrogen atoms bonded to Al are named in alphabetical order with no space between groups followed by the word aluminium. The hydrogen attached to Al is designated with the prefix, 'hydrido', and the number of identical organic groups indicated by the prefixes, di, tri, tetra etc. or using prefixes bis, tris etc for complex groups. Some examples below illustrate this system.

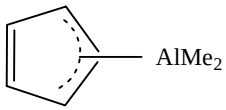
- $(Me_3Al)_2$, trimethylaluminum;
- $(Me_3Si)_3Al$, tris(trimethylsilyl)aluminium;
- $(Bu^i_2AlH)_3$, hydrido(diisobutyl)aluminium;
- $(EtMePhAl)_2$, ethyl(methyl)phenylaluminium.

In system B, organic, hydrogen, anionic or neutral groups attached to Al are listed in alphabetical order with prefixes used to indicate the number of identical groups. Two more rules can be used to name fully various compounds. If a number of C atoms of organic group are bonded to Al, the prefix η (read as eta or hapto) is used and is precede by the arabic numbers

indicating the first and last bonded C atoms. Further groups bridging two aluminum centers are given a prefix, μ.
di-μ.-methyl(tetramethyl)dialuminium, $(Me_3Al)_2$;

butyl(diphenyl)pyridinealuminium, $BuPh_2Al.(NC_5H_5)$;

1-3-η-cyclopentadienyl(dimethyl)aluminum



tetra-μ.-methyltetralithium, $(MeLi)_4$

$(PhLi.tmen)_2$ di-μ.-diphenylbis(tetramethylethylenediamine)dilithium

Compounds such as, PhAl(Br)Cl can be named as phenylaluminium bromide chloride or by using system A, as bromo(chloro)phenylaluminum. $(Bu^i_2AlH)_3$ can also be named as diisobutylaluminium hydride. Likewise, organoaluminium anions such as, $[Ph_3AlH]^-$ can be named as hydridotriphenylaluminate(III) or as triphenylaluminum hydride anion. $[Bu^i_3AlMe]^-$ is named as triisobutyl(methyl)aluminate(III) anion. Compounds bearing π-boded cyclopentadienyl and other aromatic ring systems can be named in the analogous maner. For example, Cp_2Fe is named as di-π-cyclopentadienyliron or di-η^5-cyclopentadienyliron and like wise, $(C_6H_6)_2Cr$ is named as di-π-benzene chromium or di-η^6-bezenechromium.

Compounds of Hg, Sn and Ti can be similarly named.

Me_2Hg is named as dimthylmercury,

MeHgCl is named both as chloro(methyl)mercury or methylmercury chloride.

Me_4Sn is named as tetramthyltin.

$CpTiCl_3$ is named as trichloro(π-cyclopentadienyl)titanium or (π-cyclopentadienyl)titanium trichloride or (η^5-cyclopentadienyl)titanium trichloride.
Cp_4Ti , di(η^5-cyclopentadienyl) di(η^1-cyclopentadienyl)titanium or di(π-cyclopentadienyl)di(σ-cyclopentadienyl)titanium.

Organometallic Compounds of Lithium
Preparation:
(a) Direct Method: Reaction of lithium metal with an organic halide in a suitable organic solvent leads to the preparation of an organolithium reagent (equation 1).

$$2Li + RX \longrightarrow RLi + LiX \qquad \text{Eq. 1}$$

Here R may be alkyl or aryl group. The organolithium compounds rapidly react with oxygen and moisture and thus for their preparation dry solvents and apparatus should be used and also air should be excluded by using an inert atmosphere. For inert atmosphere, dinitrogen (N_2) or argon gas is normally used. Further, lithium metal should be in reactive state, and thus its surface should be free from any corrosive product - usually metal oxide. Lithium is often stored in dry kerosene oil, benzene or toluene, and is washed with dry n-hexane under inert atmosphere before use.

Methyl halides (MeX) (X = Cl, Br, I) react with lithium metal in diethyl ether; however, alkyl iodides are not used since they undergo side reaction (equation 2), and are not suitable reagents. Benzyl chloride ($C_6H_5CH_2Cl$) also undergoes similar side reaction to generate 1, 2-diphenylethane (equation 3). The n-butyllithium, obtained from reaction of n-butyl chloride or bromide with lithium metal in hexane or ether, is most frequently used reagent. Its solution in hexane is commercially available. Phenyllithium can be readily prepared in good yield from the reaction with bromobenzene or iodobenzene; chlorobenzene reaction is very slow and often not used. Bromobenzene is more commonly used as compared to iodobenzene.

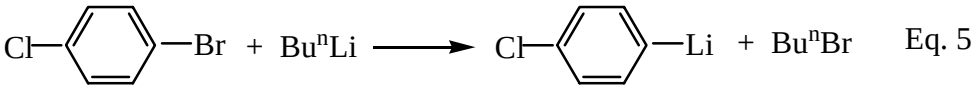
$$RI + RLi \longrightarrow R{-}R + LiI \qquad \text{Eq. 2}$$

$$C_6H_5CH_2Cl + C_6H_5CH_2Li \longrightarrow C_6H_5CH_2CH_2C_6H_5 + LiCl \qquad \text{Eq. 3}$$

It may be pointed out that organolithium reagents often react with ethers, although reactions are very slow, for example, MeLi reacts very slowly with diethyl ether. Where possible, alternative reagents such as Grignard reagents may be used, depending on the reaction requirements.

(b) Metal-Halogen Exchange: In this method, an organolithium compound reacts with an organic halide (equation 4). The formation of R'Li occurs if R' is more electronegative than R and it varies with the unsaturation in the organic group ($C_{sp} > C_{sp2} > C_{sp3}$). The unsaturation leads to the formation of more stable carbanion. Reactions of butyllithium with $Ph_2C{=}CHBr$ and PhBr form $Ph_2C{=}CHLi$ and PhLi respectively. Among aryl halides, the reactivity order is I > Br >Cl > F. Interestingly, reaction of BuLi with ClC_6H_4Br gives 90% ClC_6H_4Li (equation 5). It may be pointed out that the metal-halogen exchange reactions are regiospecific.

$$RLi + R'X \longrightarrow R'Li + RX \qquad \text{Eq. 4}$$



Eq. 5

(c) Metal-Hydrogen Exchange - Metallation : The exchange of metal with hydrogen is known as metal-hydrogen exchange and this process is known as metallation. The process of metallation involves nucleophilic attack of an organolithium reagent on the acidic hydrogen. For example, reaction of organolithium RLi with hydrocarbon R'H gives R'Li and RH (equation 6); also reaction of R_2NLi with R'H gives R'Li (equation 7).

$$R'H + RLi \longrightarrow R'Li + RH \qquad \text{Eq. 6}$$

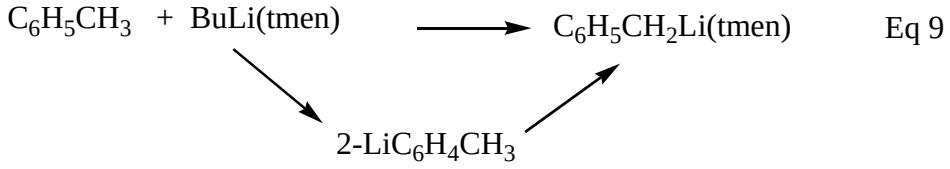
$$R'H + R_2NLi \longrightarrow R'Li + R_2NH \qquad \text{Eq. 7}$$

The reactions will procced to right only if hydrocarbon R'H is more acidic than RH or R_2NH. For example, reaction of phenylethyne (PhC_2H) with PhLi gives PhC_2Li and PhH, because PhC_2H is more acidic than PhH (equation 8).

$$PhC{\equiv}CH + PhLi \longrightarrow PhC{\equiv}CLi + PhH \qquad \text{Eq 8}$$

It may be interesting to note that the coordination of the lithium to a base increases nucleophilic character of carbon bonded to lithium. Thus the reactivity of organolithium compounds is more in ethers than in hydrocarbons because ethers with oxygen donor atoms bind to lithium. However, some times ethers themselves get metallated or cleaved by organolithium reagents (*vide infra*). However, tertiary amines such as $Me_2NCH_2CH_2NMe_2$ (tmen) are not readily

metallated. Thus tmen chelates to lithium in BuLi and the chelate complex BuLi(tmen) is very soluble in hydrocarbons. It is a strong chelating agent and metallates toluene readily at room temperature and to benzene slowly.



Eq 9

Methoxybenzene ($MeOC_6H_5$) with electron attracting methoxy group is readily metallated by BuLi at 2-position forming *ortho*-lithium, o-$MeOC_6H_4Li$.

(d) Metal-Metal Exchange: In this method, an organolithium reagent is used to prepare other organolithium compounds of organic compounds. For example, phenyl lithium reacts with tetravinyltin in ether to generate vinyllithium reagents. Here tin bonded to vinyl moiety is exchanged by Li bonded to phenyl (equation 10). Similarly, allyllithium can be prepared.

$$(H_2C{=}CH)_4Sn + 4PhLi \longrightarrow 4(H_2C{=}CHLi) + Ph_4Sn \quad \text{Eq 10}$$

Properties: Organolithium compounds are soluble in hydrocarbons such as n-hexane, ethers etc. They are highly volatile and can be sublimed in vacuum. They readily react with water and air, and are often flammable. The high polarity of R^-Li^+ bonds leads to strong association of organolithium moieties in their solid, liquid and gas states. Mostly, lithium alkyl and aryl compounds exist as aggregates in the solid, solution, and even gas states. In the solid state, methyllithium and ethyllithium (RLi) exist as tetramers, $(RLi)_4$ (R = Me, Et). Methyl lithium is tetramer in diethyl ether and thf, but insoluble in cyclohexane, toluene and benzene. Ethyllithium exists as an hexamer in cyclohexane, toluene and benzene, but is tetramer in diethyl ether and thf. Bu^nLi is tetamer in diethyl ether and thf, hexamer in toluene, benzene and cyclohexane. Bu^tLi is tetramer in each of the above mentioned solvents. Phenyl lithium is a dimer in Et_2O and thf, and also $Li_2\{C(SiMe_3)_3\}_2$ is a dimer.

Lithium alkyls are often considered to be carbanionic (R^-) in reactions. The reactivity of organolithium compounds depends on differences in aggregation and nature of solvent. The reactivity of methyllithium $(MeLi)_4$ towards a substrate in THF is 10^4 times less than that of benzyllithium ($LiCH_2Ph$). Further, Bu^tLi is tetrameric in noncoordinating solvents, and in THF it exists in equilibrium as shown in equation 11. The nucleophilic character of organolithium compounds is increased remarkably by the addition of a base such as tmen which coordinates to Li^+ ion. The property of lithium to interact with π-electrons of alkene, alkynes and arenes explains the ability of lithium alkyls to initiate polymerization of dienes.

$$(Bu^tLi)_4 \rightleftharpoons 2(Bu^tLi)_2 \quad \text{Eq 11}$$

Reactions: Organolithium undergo thermal decomposition to form different products. For example, Bu^nLi in boiling octane involves α-elimination reaction forming butene-1 (equation 12). Methyllithium decomposes at 250°C to give CH_4 and CH_2Li_2 (equation 13), while at higher temperature, LiC ≡CLi, LiH and Li are formed. The ease of decomposition of organoalkali metal compounds has been found to be potassium > sodium > lithium.

$$BuLi \longrightarrow CH_3CH_2CH{=}CH_2 + LiH \quad \text{Eq 12}$$

$$2MeLi \longrightarrow CH_4 + CH_2Li_2 \qquad \text{Eq 13}$$

Organolithium compounds undergo a variety of reactions which illustrate their versatility in organic synthesis. Some general reactions are described below. They are highly reactive towards oxygen. For example, methyl, ethyl and phenyl derivatives ignite in air. In general, sodium and potassium compounds are more easily oxidized than the lithium compounds, and a two step scheme 1 depicts the oxidation route. Hydrolysis of RO_2Li and ROLi will yield RO_2H and ROH respectively. For example, $(BuLi)_4$ in diethyl ether at -78^oC gave BuOOH after hydrolysis; and likewise, $(BuLi)_6$ in benzene gave BuOH. Other oxidants such as iodine and sulfur also react with organolithium compounds (RLi) to form R-I and R-S_x-R compounds (equations 14 and, 15).

$$RLi + O_2 \longrightarrow RO_2Li$$

$$RO_2Li + RLi \longrightarrow 2ROLi$$

Scheme 1

$$RLi \xrightarrow{I_2} RI + LiI \qquad \text{Eq 14}$$

$$RLi \xrightarrow{S} RSxR + Li_2S \qquad \text{Eq 15}$$

Organolithium compounds readily react with a variety of proton sources to give hydrocarbon, RH. Reaction of methyllithium with ethanol in diethyl ether forms CH_4 and EtOLi and with HBr(g), it forms CH_4 and LiBr (equations 16 and 17). Similarly, reactions of RLi with H_2O, R'SH, $R_2'NH$ and Ph_2CH_2 forming hydrocarbons RH, and lithium salts (equations 18-21). Organic halides such as bromobenzene undergo exchange reaction with RLi forming PhLi and RBr (equation 22). Organolithium compounds react with some solvents and deprotonate them. For example, Et_2O reacts with RLi to give RH, $CH_2=CH_2$ and $LiOCH_2CH_3$. Similarly, BuLi rapidly cleaves tetrahydrofuran after metallating it at 2-position (equation 23). Organometal halides R'_3ECl (E = Si, Sn, Pb) react with organolithium compounds to generate R'_3ER (equation. 24), and also undergo Wurtz coupling (equation 25).

$$MeLi + EtOH \longrightarrow CH_4 + EtOLi \qquad \text{Eq 16}$$

$$MeLi + HBr \longrightarrow CH_4 + LiBr \qquad \text{Eq 17}$$

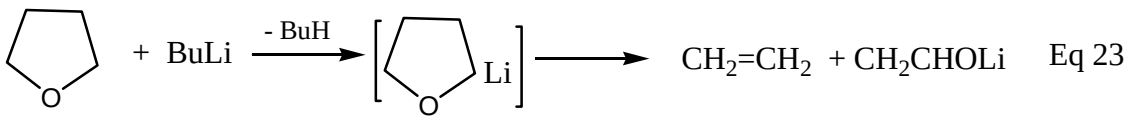
$$RLi \xrightarrow{H_2O} RH + LiOH \qquad \text{Eq 18}$$

$$RLi \xrightarrow{R'SH} RH + LiSR' \qquad \text{Eq 19}$$

$$RLi \xrightarrow{R_2'NH} RH + LiNR_2' \qquad \text{Eq 20}$$

$$RLi \xrightarrow{Ph_2CH_2} RH + LiCHPh_2 \qquad \text{Eq 21}$$

$$RLi \xrightarrow{PhBr} PhLi + RBr \qquad \text{Eq 22}$$



$$CH_2=CH_2 + CH_2CHOLi \qquad \text{Eq 23}$$

$$RLi + R'ECl \longrightarrow R'ER + LiCl \qquad \text{Eq 24}$$

$$RLi + R'X \longrightarrow R\text{-}R' + LiCl \qquad \text{Eq 25}$$

Bonding and Structure: Organolithium compounds form oligomers - low molecular weight polymers. This oligomerization can be explained in terms of multicenter two electron bonds. The structure of $(MeLi)_4$ tetramer can be described in two ways : According to one description, Li atoms lie at the corners of a tetrahedron, and four methyl groups are centered over the facial planes in μ_3-modes. And according to second description, Li and C atoms occupy alternate corners of a cube and each Me group is similarly bonded in μ_3-mode (Fig. 1). The structures of $(EtLi)_4$ and thf /diethyl ether adducts, namely, $(MeLi{\cdot}thf)_4$, and $(PhLi{\cdot}Et_2O)_4$ are similar, except each Li is bonded in addition to O atoms from thf (C_4H_8O), or Et_2O. Fig. 2 shows overlap of orbitals - a simplified view of bonding. $\{PhLi{\cdot}(tmen)\}_2$ is a dimer with Li bonded to N, N-chelating, tmen ($Me_2N\text{-}CH_2\text{-}CH_2\text{-}NMe_2$) ligands (Fig. 3). The thf (C_4H_8O), Et_2O and tmen are Lewis bases which are forming coordinate bonds to Li center.

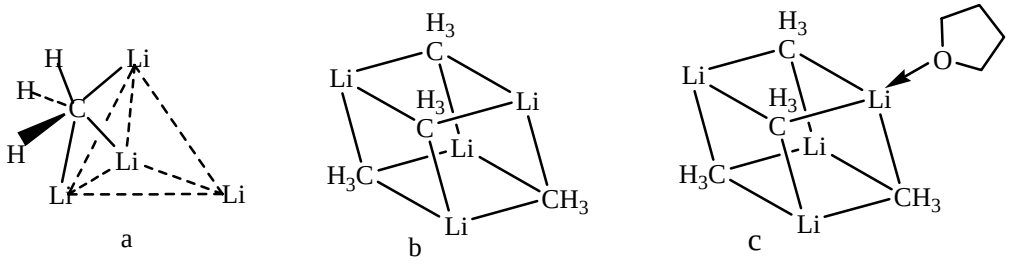


Fig. 1. Structure of tetramethyllithium $(MeLi)_4$ (a, b) and $(MeLi.thf)_4$ (c)

The formation of bonds may be understood as follows. Consider the bonding of CH_3 over the plane formed by three Li atoms as shown in Figure 1a. If CH_3 is treated as a radical with C atom considered sp^3 hybridized, and again each Li atom is treated as sp^3 hybridized, then one sp^3 orbital with one electron from C atom , one sp^3 from one Li with one unpaired electron, and two empty sp^3 orbitals from two lithium atoms combine as shown Fig. 2 forming four center two electron (4c-2e) bonds. Same process repeats with other three methyl groups over remaining three faces of the tetrahedron. In $\{PhLi{\cdot}(tmen)\}_2$, sp^2 orbital of C of Ph group with one electron, one Li atom with one electron, and one empty orbital of second Li atom form 3c-2e bond (Li-C-Li bond). Alkali metals (Li^+, Na^+, K^+) are also known to form π - complexes with rings such as cyclopentadienyl (Cp, $C_5H_5^-$).

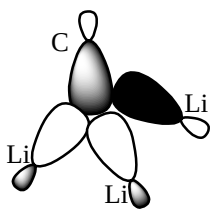


Fig. 2. Orbital overlap along one face formed by three Li atoms.

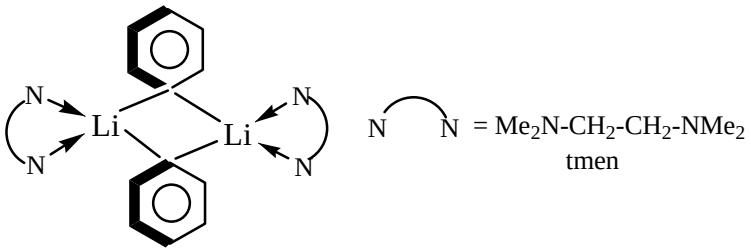


Fig. 3. Structure of phenyllithium dimer $(PhLi.tmen)_2$

Organometallic Compounds of Aluminium

Preparation: The alkylaluminium halides and aluminium alkyls can be synthesized by direct reaction of an alkyl halide with aluminium (equation 26). The sesquihalide mixture (R_2AlX and $RAlX_2$) can be separated into its components, or can be further reacted with Na metal to get trialkylaluminium. This method is very useful for the synthesis of trimethylaluminium. Reactions of aluminium halides with organomagnesuim halides (RMgX) or organolithium (RLi) in Et_2O lead to the formation of an etherate complex of R_3Al, and thermal heating removes Et_2O forming R_3Al (equation 27). But if R_3Al is thermally unstable, then it may be difficult to remove Et_2O by heating.

$$RX + Al \longrightarrow R_2AlX + RAlX_2 \xrightarrow[-NaX]{Na} R_3Al \qquad \text{Eq. 26}$$

$$3RMgX + AlX_3 \xrightarrow[-3MgX_2]{} R_3Al(OEt_2) \xrightarrow[-Et_2O]{\Delta} R_3Al \qquad \text{Eq. 27}$$

Organoaluminium compounds can be prepared in the laboratory by gently heating aluminium metal with diorganomercury(II) (R_2Hg), and this transfer of R groups from Hg to Al is known as transmetallation (equation 28). Here R may be alkyl, or aryl group. This method requires that both organomercury and resulting organoaluminium compounds are thermolabile. The unsymmetrical aluminium compounds R_2AlR' can be prepared by the reaction of organoaluminium halides by reacting alkalimetal hydrides, and which can be readily added to unsaturated hydrocarbons such as alkenes, or alkynes (equation 29). The reaction of R_2AlCl with organolithium also gives unsymmetrical organoaluminium R_2AlR' compounds (equation 30). In these methods higher temperature can lead to disproportionation and should be avoided.

$$3R_2Hg + 2Al \longrightarrow 2R_3Al + 3Hg \qquad \text{Eq. 28}$$

$$R_2AlCl \xrightarrow[-LiCl]{LiH} R_2AlH \xrightarrow{CH_2=CHR'} R_2AlCH_2CH_2R' \qquad \text{Eq. 29}$$

$$R_2AlCl + R'Li \xrightarrow[-LiCl]{} R_2AlR' \qquad \text{Eq. 30}$$

Direct reaction of aluminium metal with hydrogen in the presence of trialkyl aluminium (R_3Al) gives R_2AlH, which reacts with alkene to yield R_3Al (equation 31). This method is very useful for an alkene with high reactivity such as ethylene ($CH_2=CH_2$). The use of alkene $CH_2=CR_2$ directly in place of R_3Al also gives $(R_2CHCH_2)_3Al$ (equation 32). Both these methods used for large scale synthesis of organoaluminium compounds stemmed from the studies of K. Ziegler

and need heating in the range 110-160^{o}C. It may pointed out that Al does not react with H_2 to form AlH_3, but in presence of aluminium alkyl, it picks up hydrogen to form, R_2AlH as shown in equation 31. For R = Et and R′ = H, triethyl aluminium will be formed.

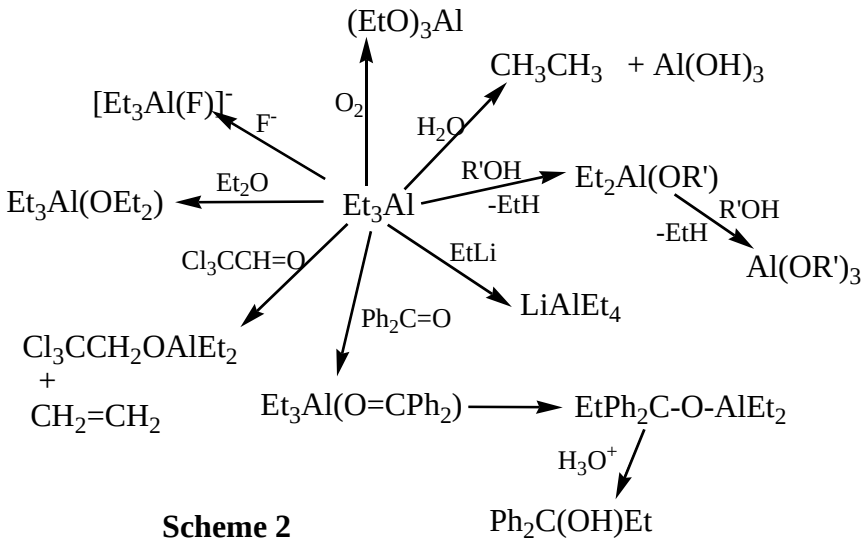
$$2Al + 3H_2 + 4R_3Al \longrightarrow 6R_2AlH \xrightarrow{CH_2=CHR'} 6R_2AlCH_2CH_2R') \quad \text{Eq. 31}$$

$$2Al + 3H_2 + 6CH_2=CR_2 \longrightarrow 2(R_2CHCH_2)_3Al \quad \text{Eq. 32}$$

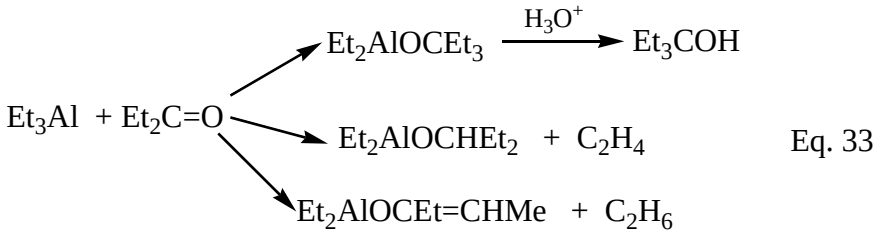
The mixed organoaluminium compounds of the type R_nAlX_{3-n} can be prepared by reacting R_3Al with AlX_3 (X = halide or other anions, such as OR or OR′).

Properties : Organoaluminium compounds are sensitive to air, water, alcohols and many other compounds. Despite the fact that these compounds are extremely susceptibile to oxidation and hydrolysis and handling being hazardous, still they are industrially prepared on very large scale. Organoaluminium compounds are generally liquid, or low-melting solids and are often miscible with hydrocarbons solvents. They are volatile at moderate temperatures. Lower alkyls are extremely reactive liquids and are spontaneously flammable. The Al-C and Al-H bonds have considerable covalent character, although electronegativity suggest that bonds are polar. Organoaluminium compounds have tendency to oligomerize into dimers, trimers or tetramers.

Reactions: Organoaluminium compounds undergo a wide variety of reactions, some of which are given in Scheme 2, using Et_3Al as an example. It can be seen that reaction with oxygen gave triethoxyaluminium, and that with water, it formed aluminum hydroxide. It is possible water may initially form an adduct, $Et_3Al(OH_2)$ in Lewis-acid base terminology, followed by hydrolysis to form, $Et_2Al(OH)$ and ethane, and finally, $Al(OH)_3$. Similar arguments appear to hold true for the reaction with R′OH. Reaction with EtLi transfers Et^- group to Al to generate $LiAlEt_4$, and likewise, fluoride ion and diethyl ether form adducts. The reaction with diphenyl ketone involves transfer of Et^- group from Al metal center to electrophilic carbon center of ketone; corresponding reaction with an aldehyde led to evolution of ethylene. However, reaction of Et_3Al with $Et_2C=O$, a ketone having β-hydrogen, such as ethyl group undergoes different reactions such as shown in equation 33.



Scheme 2



Eq. 33

Structure and Bonding: Trimethylaluminium is a dimer, Me_6Al_2, in solid as well as vapour states.unlike Me_3B which is a monomer. Dimerization is attributed to bigger size of Al versus B atoms which poses less steric problem for the former than for the latter element. The association nature of other organoaluminium compounds is as follows: Et_3Al, $Pr^n{}_3nAl$, $Bu^n{}_3Al$, Ph_3Al, Me_2AlX (X = H, Cl, Br, I), are dimers, $Bu^t{}_3Al$ and $Bu^i{}_3Al$ are monomers, and Me_2AlF is a tetramer. Triorganoaluminium compounds, R_3Al dimerize via alkyl or aryl groups, and R_2AlX dimerize via X groups.

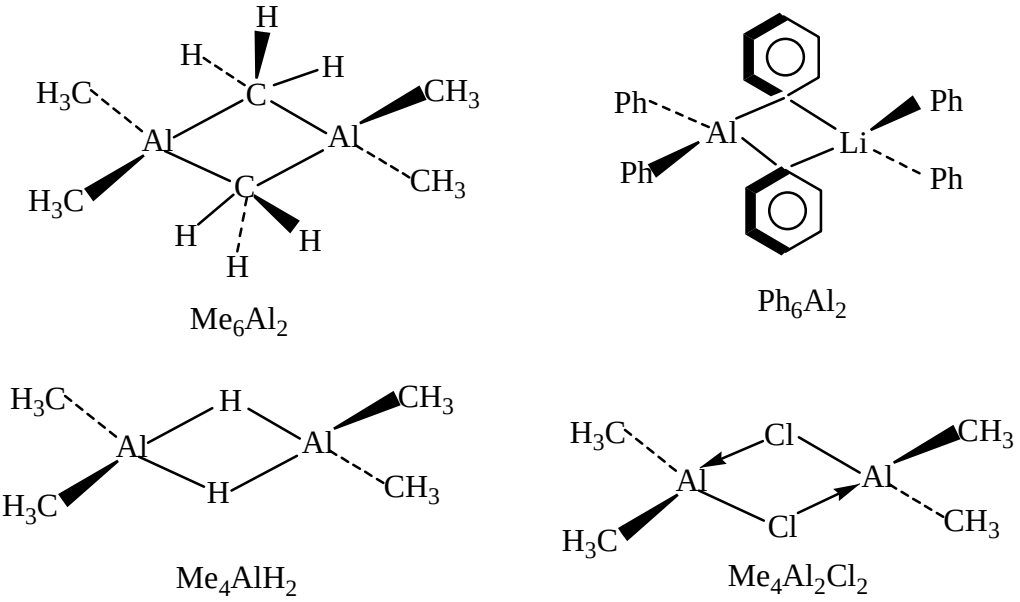


Figure 4. Structures of some organoaluminium compounds

The structures of some dimeric organoaluminium compounds are shown in Fig. 4. The bonding in Me_6Al_2 and analogous compounds can be readily understood as follows. Dimeric Me_6Al_2 is made from dimerization of two Me_3Al units. Each of four terminal methyl groups forms 2c-2e (two center two electron) Al-C bonds and two bridging methyl groups form 3c-2e Al-C-Al bonds (three center two electron). If each CH_3 group bridging two Al centers is treated as a radical with C atom considered sp^3 hybridized, and again each Al atom is treated as sp^3 hybridized, then one sp^3 orbital with one electron from C atom, one sp^3 orbital of one Al with one electron, and one empty sp^3 orbital of second Al atom combine as shown Fig. 5 forming three center two electron (3c-2e) bonds. The second Al-C-Al bridge is similarly formed except first Al sp^3 orbital will be empty and second Al sp^3 orbital will have one electron. The hydride bridging in $Me_4Al_2H_2$ can be similarly explained in terms of 3c-2e bonds. Here one H atom shares its s-orbital (containing

one electron) with one sp^3 orbital from one Al atom (containing one electron) and one empty sp^3 orbital of second Al atom. The bridging groups like Cl^- form one covalent bond with one Al atom and a coordinate bond using lone of electron to second Al atom (Fig. 4) The bridging pattern of Ph groups in Ph_6Al_2 is similar to that shown in Fig. 3.

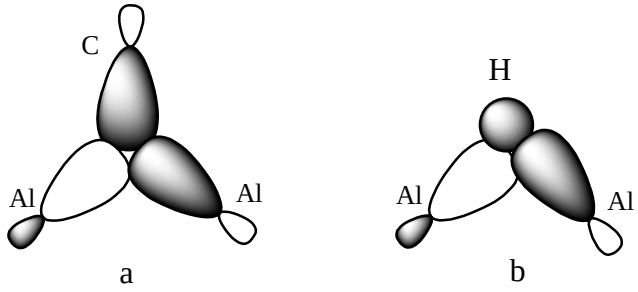


Fig. 5. Orbital overlap along one Al-C-Al bridge (a) and one Al-H-Al bridge (b)

Organometallic Compounds of Mercury

Preparation: There are several methods for the preparation of organomercury(II) compounds and some of these are delineated below.

(a) Transmetallation : Organolithium and organomagnesium reagents have been extensively used for the preparation of organomercury(II) compounds by reacting them with mercury(II) halides or other mercury(II) salts (equations 34 and 35). Here organic groups from RLi or RMgX substrates are transferred to Hg metal center and the process is known as transmetallation. The range of organomercury(II) compounds will depend upon the available organolithium or organo- magnesium reagents. For example, reaction of phenyllithium with $HgCl_2$ forms phenyl - mercury(II) chloride. Similarly, reaction of PhMgBr (from PhBr and Mg in diethyl ether) with $HgCl_2$ yields PhHgCl. Organometallic compounds of other metals (B, Sn etc.) have also transferred organic groups to mercury for the preparation of organomercury compounds (equations 36 and 37).

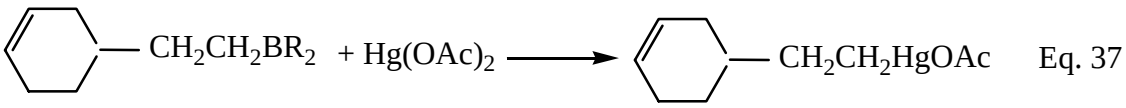
$$RLi + HgX_2 \longrightarrow RHgX + LiX \qquad \text{Eq. 34}$$

X = Cl, Br, I

$$RMgX + HgX_2 \longrightarrow RHgX + MgX_2 \qquad \text{Eq. 35}$$

X = Cl, Br, I

$$Ph_3Sn(CH_2)SR + HgCl_2 \longrightarrow PhHgCl + Ph_2ClSn(CH_2)SR \qquad \text{Eq. 36}$$



Eq. 37

(b) Mercury-Hydrogen Exchange – Mercuration: The replacement of hydrogen of an organic compound (e. g. R-H) by mercury is known as mercuration, and this process is electrophilic substitution reaction. For aliphatic hydrocarbons, it is limited to hydrocarbons with acidic hydrogen atoms, and this process occurs readily with aromatic hydrocarbons. Equation 38 shows

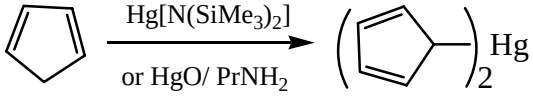
that both RHgX and R_2Hg can be obtained; the latter compound requires more forcing conditions.

$$RH + HgX_2 \xrightarrow{-HX} RHgX \xrightarrow[-HX]{RH} R_2Hg \qquad \text{Eq. 38}$$

The choice of X depends on the organic substrate and its should be more easily replaced by R group. Thus usually X = Cl, OAc, NO_3, NR_2 (R = $SiMe_3$) are used. A few examples given below demonstrate the use of this method. Reactions of $Hg[(N(SiMe_3)_2]_2$ with phenyl acetylene (PhC≡CH), acetone (MeCOMe) and cyclopentadiene form $(PhC{\equiv}C)_2Hg$, $(MeCOCH_2)_2Hg$ and $(C_5H_5)_2Hg$ respectively (equations 39-41). The use of excess $HgCl_2$ in presence of NaOAc in equation 41 yields permercurated $C_5(HgCl)_6$ (here all hydrogen atoms are replaced by six HgCl moieties).

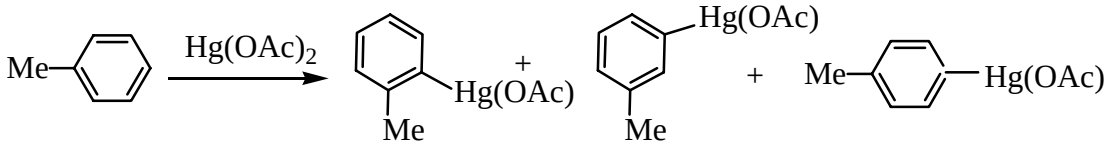
$$Hg[N(SiMe_3)_2] + PhC{\equiv}CH \longrightarrow [PhC{\equiv}C]_2Hg \qquad \text{Eq. 39}$$

$$Hg[N(SiMe_3)_2] + MeCOMe \longrightarrow (MeCOCH_2)_2Hg \qquad \text{Eq. 40}$$

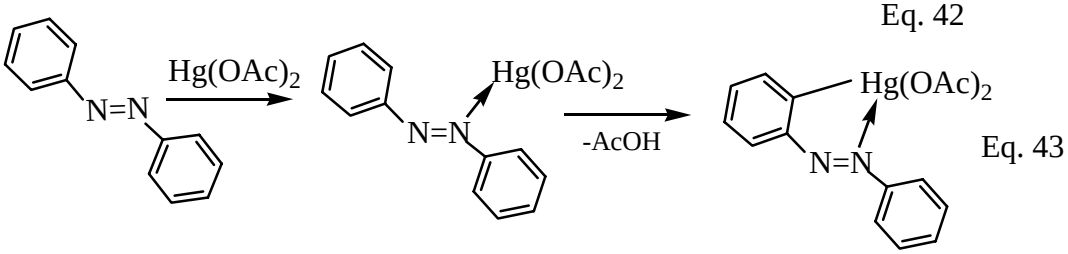


Eq. 41

The mercuration of arenes, an electrophilic substitution, lacks selectivity and results in all possible ring substituted products. For example, mercuration of toluene with $Hg(OAc)_2$ under refluxing conditions yields a mixture of o-, m- and p-$CH_3C_6H_4Hg(OAc)$ isomers (equation 42) and addition of HBr to resulting isomers can convert them into o-, m-, & p-$CH_3C_6H_4HgBr$ compounds. The reaction conditions change the amounts of each isomer. Mercuration of benzene occurs at 110°C in presence of glacial acetic acid. The mercuration of azobenzene occurs at ortho position due to coordination of Hg by N donor atom followed by formation of Hg-C bond as shown in equation. 43.



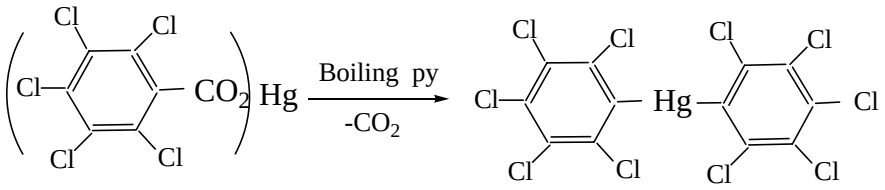
Eq. 42



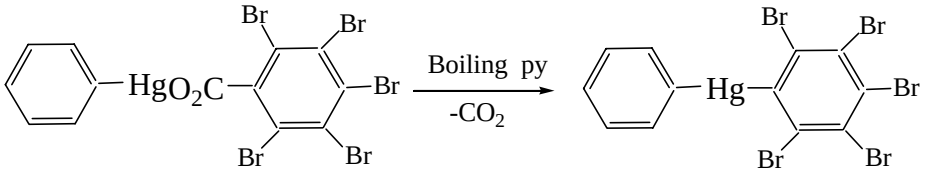
Eq. 43

(c) Decarboxylation: Organomercury compounds can also be prepared by the decarboxylation of alkyl, aryl, or heteroaryl carboxylates of mercury by thermal or UV irradiation methods. The presence of electronegative atoms present in aryl or aryl moieties bonded to Hg salts via O atoms, as well as addition of donor solvents such as H_2O, py etc. facilitate the decarboxylation. Equation 44-47 depict reactions of pentahalophenyl carboxylates and trifluoroacetate compounds of Hg(II), undergoing decarboxylation. It may be noted that photodecomposition of $(CF_3CO_2)_2Hg$ to $(CF_3)_2Hg$ occurs at much lower temperature (-160°C), unlike more forcing conditions as shown in equations 46 and 47. Other mercury carboxylates such as $Hg(O_2CC_6F_5)_2$,

$Hg(O_2CCCl_3)_2$, and $Hg(O_2CC_6H_2\text{-}2,4,6\text{-}NO_2)_2$ also undergo similar reactions to form, $Hg(C_6F_5)_2$, $Hg(CCl_3)_2$, and $Hg(C_6H_2\text{-}2,4,6\text{-}NO_2)_2$ respectively. Bis(trichloromethyl)mercury, $Hg(CCl_3)_2$, can be made also by the reaction of mercury halides with sodium trichloroacetate in 1, 2-dimethoxyethane (equation 48).



Eq 44



Eq 45

$$(CF_3CO_2)_2Hg \xrightarrow{300^oC} F_3C\text{-}Hg\text{-}OOCCF_3 \qquad \text{Eq 46}$$

$$(CF_3CO_2)_2Hg \xrightarrow[K_2CO_3]{200^oC} F_3C\text{-}Hg\text{-}CF_3 \qquad \text{Eq 47}$$

$$(Cl_3CCO_2)Na + HgCl_2 \xrightarrow[-CO_2]{-NaCl} Cl_3C\text{-}Hg\text{-}CCl_3 \qquad \text{Eq 48}$$

(d) Insertion Method: Organomercury compounds are also prepared by using azo compounds. Reaction of diazomethane with $HgCl_2$ under mild conditions in diethyl ether solvent involve insertion of CH_2 group between Hg and Cl (equation 49).

$$HgCl_2 + CH_2N_2 \xrightarrow[-N_2]{ether} ClCH_2\text{-}Hg\text{-}Cl \xrightarrow[-N_2]{CH_2N_2} ClCH_2\text{-}Hg\text{-}CH_2Cl \qquad \text{Eq 49}$$

Properties : Organomercury compounds such as RHgX with X = halide (Cl, Br, I), or pseudo halide (CN, SCN), or other anions such as OH, etc. are solid compounds and are soluble in various organic solvents such as methanol, ethanol etc. When anion X = NO_3^-, RCO_2^-, or SO_4^{2-}, the compounds are salt-like with weak Hg-anion covalent interaction. Dialkyl- and diaryl-mercury compounds are colorless solids. While dialkyl compounds are liquids, or low-melting solids, diarylmercury compounds are usually solids. Their solubility in water is limited, and in general they are unaffected by water and react very slowly with air. They are thermally and photochemically not very stable and should be stored in dark. They are toxic, particularly lower dialkyls such as Me_2Hg, Et_2Hg etc. and develop appreciable vapour pressure. Diarylmercury compounds such as Ph_2Hg are less toxic.

Reactions: The Hg-C bond or Hg-X bonds in organomercury compounds undergo a variety of reactions. Organomercury compounds are not very reactive towards oxygen, water, alcohols, carbonyl compounds, and simple alkyl halides. It may be noted that some organomercurials do

react with air and precautions need to be taken. Representative reactions of organomercurials are discussed below.

Organomercury compounds undergo alkylation, arylation and acylation reactions. It may be pointed out that organomercurials with simple organic groups have low nucleophilic character towards organic halides. The electrophilic alkylating reagents such as triarylmethyl halides react with nucleophilic organomercurials (having electron withdrawing groups such as α-carbonyl groups) (equation 50). The triarylmethyl halides and perchlorates can alkylate organomercurials to give coupled products; however, β–elimination occurs with t-Bu_2Hg (equations 51 and 52). In reaction 52, alkylating reagents such as Ph_3CX for X = BF_4 or $HgBr_3$ can also be used. The acyl halides are more reactive than alkyl halides and acylation of orgaomercurials occurs more readily (equation 53).

$$RCOCH_2HgCl + Ph_3CX \xrightarrow[PhH]{RT} RCOCH_2CCPh_3 + HgClX \qquad \text{Eq 50}$$

X =Cl, Br

$$Me_2Hg + Ph_3CClO_4 \xrightarrow{CH_2Cl_2} Ph_3CMe + MeHgClO_4 \qquad \text{Eq 51}$$

$$t\text{-}Bu_2Hg + Ph_3CClO_4 \xrightarrow{CH_2Cl_2} Ph_3CH + Me_2C{=}CH_2 + [t\text{-}BuHgX] \qquad \text{Eq 52}$$

$$(RC{\equiv}C)_2Hg + 2R'{-}\overset{\overset{O}{\|}}{C}{-}X \xrightarrow[\triangle]{\text{heptane}} 2RC{\equiv}C\overset{\overset{O}{\|}}{C}\text{-}R' \qquad \text{Eq 53}$$

The mercury-carbon bond is stable to water and to alcohols, but mineral acids such as (Scheme 3)HCl cleave Hg-C bonds in R_2Hg compounds. The carboxylic acids, such as acetic acid, cleave only one Hg-C bond. It may be significant to note that the mercury-aryl bond undergoes protonlysis more readily than does the mercury-alkyl bond (equation 54). The order of cleavage of Hg-R bond has been observed to be Me < p-chlorophenyl < phenyl < p-tolyl < p-anisyl. The organomercurials R_2Hg and RHgX both react with halogens (Cl_2, Br_2 and I_2) to form RX and HgX_2 as the final products (Scheme 4).

$$\text{R-Hg-R} + HCl \longrightarrow \text{R-Hg-Cl} + RH$$

$$\text{R-Hg-Cl} + HCl \longrightarrow \text{Cl-Hg-Cl} + RH$$

Scheme 3

$$\text{R-Hg-R} + AcOH \longrightarrow \text{R-Hg-OAc} + RH \qquad \text{Eq 54}$$

$$\text{R-Hg-R} + \text{Cl-Cl} \longrightarrow \text{R-Hg-Cl} + RCl$$

$$\text{R-Hg-Cl} + \text{Cl-Cl} \longrightarrow \text{Cl-Hg-Cl} + RCl$$

Scheme 4

The organic groups bonded to mercury are labile and can be transferred to other metals and this process is known as transmetallation. This method is a classical synthetic route and has been used conveniently for the synthesis of organometallic compounds of other metals. The organometallic compounds of transition, main group metals including sulfur, selenium and tellurium have been prepared. The equations 55 and 56 have been used for metals of group IA, IIA, IIIA, or transition metals usually a complex, such as $Pt(PPh_3)_n$; while equation 57 is used for the group III, IV and V metals, and transition metals. In equation 56, M is replaced by M/Hg alloy for M = Sn and Bi.

$$R_2Hg + R'–M \longrightarrow RHgR' + R\text{-}M \qquad \text{Eq. 55}$$

$$R_2Hg + 2M \longrightarrow Hg + 2R\text{-}M \qquad \text{Eq. 56}$$

$$R_2Hg + MX \longrightarrow R\text{-}M + RHgX \qquad \text{Eq. 57a}$$

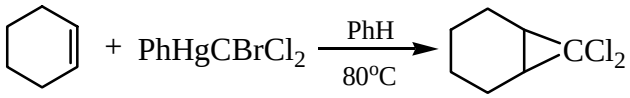
$$\longrightarrow R\text{-}M + Hg + RX \qquad \text{Eq. 57b}$$

Photolysis of Ph_2Hg with CCl_4 at 100°C yielded, PhHgCl, PhCl and C_2Cl_6 (hexachloroethane). The nature of products may depend on the organomercurial used. Reaction of Bu_2Hg with CCl_4 at 100°C in presence of benzoyl peroxide as initiator, can lead to the formation of alkylmercury chloride and other products including β-elimination product, an alkene (equations 58 and 59). Trihalomethylmercury derivatives ($PhHgCBrCl_2$) can be readily made from reaction of PhHgBr with $CHCl_3$ in presence of $KOBu^t$ in benzene solvent (equation 60). Further reaction with an alkene formed a cyclopropane (equation 61). The insertion of CH_2 in Hg-I bond formed $PhCH_2HgCH_2I$, which reacted with an alkene to form cyclopropane (equation 62).

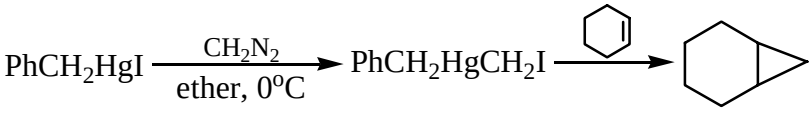
$$Bu_2Hg + CCl_4 + (PhCO_2)_2 \xrightarrow{100^oC} BuCl + EtCH{=}CH_2 + Hg + CHCl_3 \qquad \text{Eq. 58}$$
$$+ BuHgX \qquad X = Cl, PhCO_2$$

$$(PhCO_2)_2 \xrightarrow{\Delta} 2PhCO_2^{\bullet} \xrightarrow{Bu_2Hg} BuHgO_2CPh + B\dot{u} \qquad \text{Eq. 59}$$

$$PhHgBr + HCCl_3 \xrightarrow[PhH]{KOBu^t} PhHgCBrCl_2 \qquad \text{Eq.60}$$

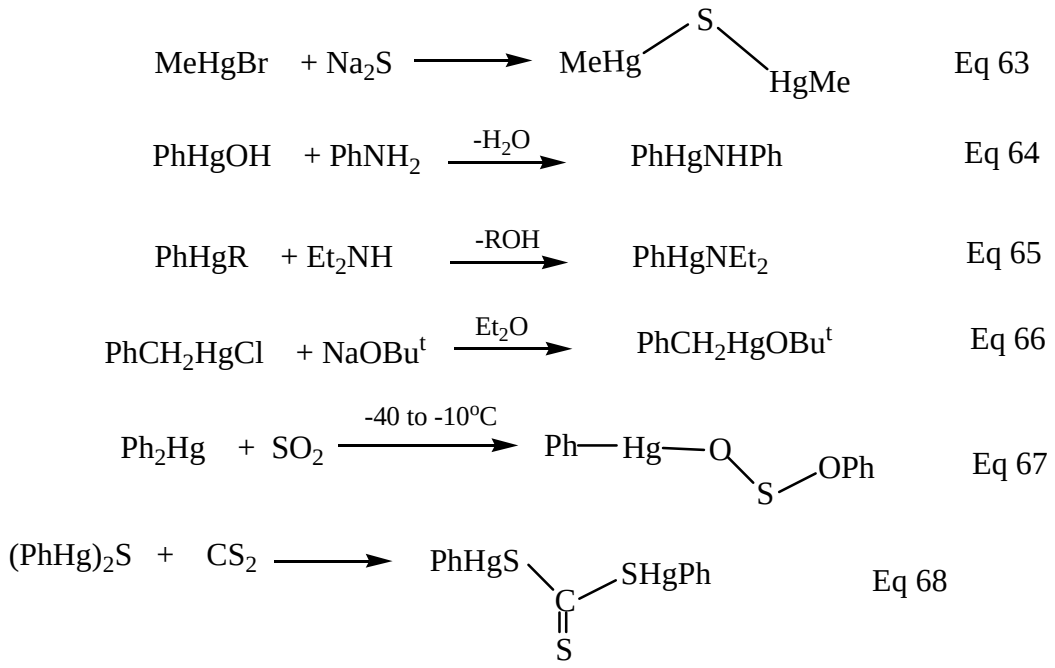


Eq. 61



Eq. 62

Some other reactions of organomercury compounds are shown in equations 63-68, such as reactions of RHgBr with Na_2S, PhHgOH with $PhNH_2$, PhHgOR with Et_2NH, $PhCH_2HgCl$ with $NaOBu^t$, R_2Hg with SO_2, $(PhHg)_2S$ with CS_2.



Structure and Bonding : The geometry around Hg center in its R_2Hg compounds is linear or bent. For example, C-Hg-C angles in CF_3-Hg-CF_3, Ph-Hg-Ph, p-MeC_6H_4-Hg-C_6H_4Me-p, and o-MeC_6H_4-Hg-C_6H_4Me-o are 180, 176.9, 180, and 178.0° respectively. In Ph-Hg-Ph, mercury atom is out of plane of Ph rings; the p-tolyl rings are planar in p-MeC_6H_4-Hg-C_6H_4Me-p and in o-MeC_6H_4-Hg-C_6H_4Me-o the angle between planes is 58.9°. The structure of Me_2Hg is expected to be linear similar to CF_3-Hg-CF_3. Similarly, RHgX compounds, where X is a halide or pseudo halide , are linear or bent. In compounds in which X is like acetate, then C-Hg-X angle varies according to how strongly X is binding to Hg. In Ph-Hg-OAc, the angle C-Hg-O is 170° . The geometry is not trigonal planar for RHgX with chelating X, such as 8-hydroxyquinoline (oxine), rather it is usually labelled as distorted T-shaped. In PhHg(oxine), structure 6g (angles C-Hg-O, 142°, C-Hg-N, 144°) resulted when compounds was crystallized from methanol and structure 6h resulted (angles C-Hg-O, 175°, C-Hg-N, 113°) when it was crystallized from CCl_4. Fig. 6.1 depicts structures of some organomercury compounds. The two coordinate linear or bent structures can be easily understood that Hg is sp hybridized involving 6s-6p orbitals. Each sp-hybridized orbital of Hg with one electron forms covalent bond with sp^3, sp^2 or sp hybrid orbitals of C of alkyl or aryl group or unsaturated organic group as the case may be group, (R), having Hg-C bonds. In RHgX compounds an halogen will use its sp^3 hybrid orbital in forming covalent bond with Hg sp-hybrid orbital. Fig. 6.2 depicts overlap of orbitals in Hg-C bonds.

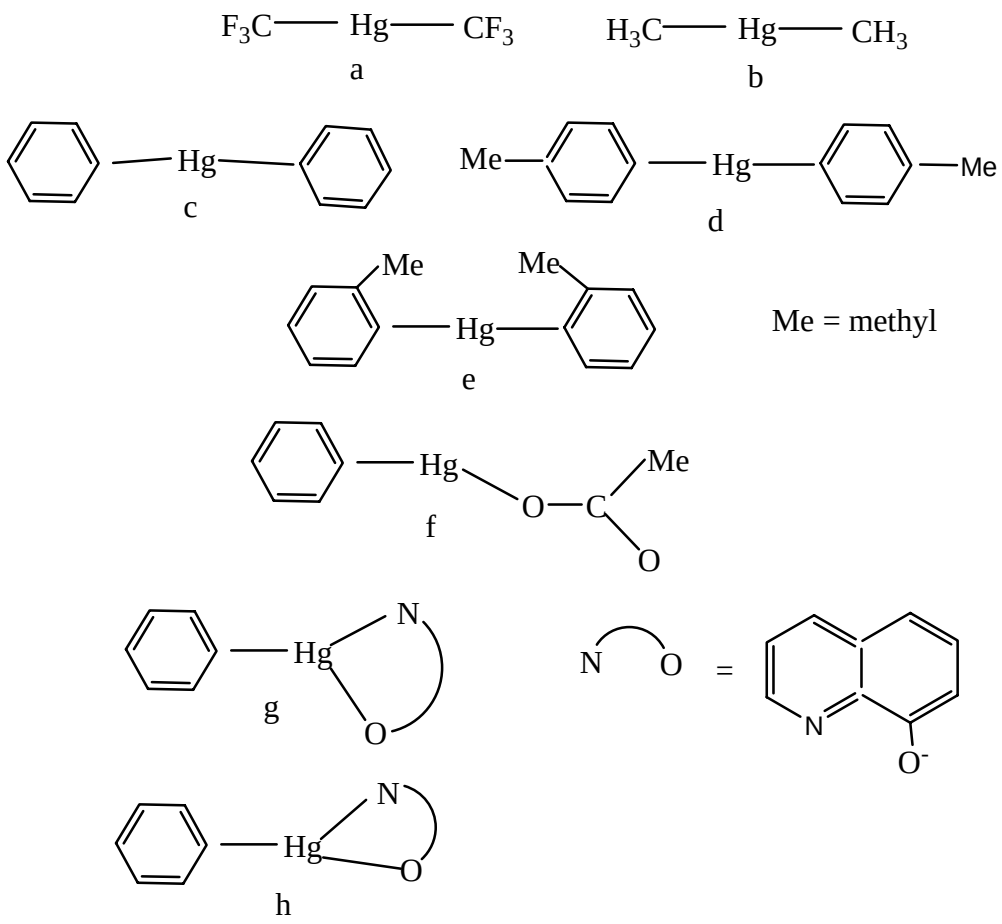


Fig. 6.1. Structures of some organomercury compounds

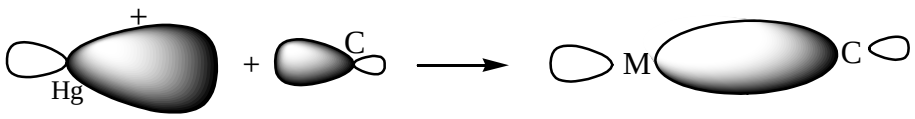
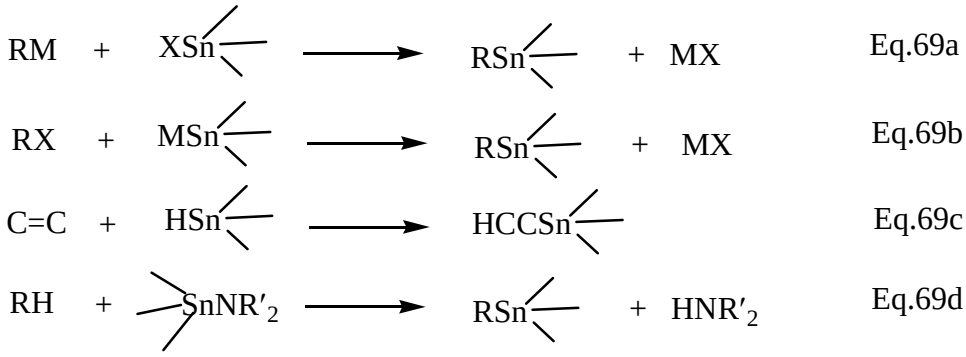


Fig. 6.2. Bonding in linear molecules

Organometallic Compounds of Tin

Preparation: Mono-, di-, tri-, and tetra-organo derivatives of tin(IV), viz. $R_{4-n}Sn$ (n = 3, 2, 1, 0) are known, while tin(II) has formed only R_2Sn(II). A brief account of methods of preparation is described below. In general tin-carbon bonds can be formed by four different methods, as shown in equations 69a-d.



The alkylation of $SnCl_4$ using a Grignard reagent in 1: 4 molar ratio in THF at 80°C, or toluene (containing a small amount of diethyl ether to solvate Grignard reagent) leads to nearly complete alkylation yielding R_4Sn (equation 70). If diethyl ether is solvent, and Grignard reagent is not in excess, some alkyltin chlorides also accompany the tetraakyltins, which, however, can be removed by precipitating them using dry NH_3 , as insoluble complexes, $R_nSnCl_{4-n}(NH_3)_m$ (n = 1-3; m = 1-2).

$$4RMgX + SnCl_4 \longrightarrow R_4Sn + 4MgXCl \qquad \text{Eq. 70.}$$

$$4PhMgBr + SnCl_4 \longrightarrow Ph_4Sn + 4MgBrCl \qquad \text{Eq. 71.}$$

$$4CH_2{=}CHMgBr + SnCl_4 \longrightarrow (CH_2{=}CH)_4Sn + 4MgBrCl \qquad \text{Eq. 72}$$

Phenyl-, and vinyl- tin compounds can be prepared in the same way (equations 71 and 72) . Organoaluminium compounds can also be used for alkylation of $SnCl_4$ and no solvent is needed in this method (equation 73). Both Bu_4Sn and Oct_4Sn are industrially prepared by this method in the absence of any solvent. The only limitation is that resulting $AlCl_3$ complexes with di- and tri-alkyltinchlorides formed in the reaction, which inhibit further alkylation to tetraalkyltins. This can be readily avoided if a solvent such as ether or amine are added to the reaction mixture which form strong complexes with alkyltin chlorides and thus alkylation goes to completion.

$$4R_3Al + 3SnCl_4 + 4R'_2O \longrightarrow 3R_4Sn + 4AlCl_3{\cdot}OR'_2 \qquad \text{Eq. 73}$$

Tetraorganotin(IV) compounds are the sources for preparing organotin halides (X = Cl, Br). R_3SnCl is formed when R_4Sn and $SnCl_4$ are heated in 3:1 molar ratio; similarly, R_2SnCl_2 is prepared from R_4Sn and $SnCl_4$ in 1:1 molar ratio. The use of excess $SnCl_4$ forms $RSnCl_3$ (equations 74-76). Direct reaction of methyl chloride with tin metal at 315°C catalyzed by Cu metal, also forms predominantly, Me_2SnCl_2 (75%), along with other organotin halides. Several other organotin compounds can be prepared from $R_nSnCl_{4-n,}$ by reaction with a suitable nucleophilic reagent, the description of some will be given in section on reactions.

$$3R_4Sn + SnCl_4 \longrightarrow 4R_3SnCl \qquad \text{Eq. 74}$$

$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2 \qquad \text{Eq. 75}$$

$$R_4Sn + 3SnCl_4 \longrightarrow 4RSnCl_3 \qquad \text{Eq. 76}$$

Organotin halides can be made by direct methods, and this method was originally used by Frankland for the synthesis of diethyltin diiodide (equation 77). Reaction of tin metal with alkyl halides forms organotin halides. However, this method has limited industrial application owing

to the fact that most commonly diorganotin dihalides are formed in direct method. . The order of reactivity of alkyl halides is RCl < RBr < RI. A catalyst such as quaternary halide, R_4MX (M = N, P, or Sb) is also required. In some cases no catalyst is needed, such as reaction of benzyl chloride with tin metal in toluene or water under boiling conditions yields di- or tri-benzyltin chloride respectively (equations 78 and 79).

$$2EtI + Sn \longrightarrow Et_2SnCl_2 \qquad \text{Eq. 77}$$

$$2RX + Sn \xrightarrow{R_4MX} RSnX_2 \qquad \text{Eq. 78}$$

$$3BzCl + 2Sn \xrightarrow[\text{reflux}]{H_2O} Bz_3SnCl + SnCl_2 \qquad \text{Eq. 79}$$

In summary, two main approaches are used. According to first approach, SnX_4 is used for the preparation of R_4Sn, from which other organotin halides are prepared. The second approach involves use of tin metal with an alkyl halide.

Properties: Tetraalkyl- and tetraaryl-organotin compounds are usually liquids, or solids and are thermally stable up to 200^{o}C. They do not react with air or water rapidly, rather very slowly they are degraded to inorganic tin compounds. Their melting points vary over a wide range depending on the type organic group bonded to Sn atom. Organotin halides, R_nSnX_{4-n} are generally soluble in organic solvents for X = Cl to I and are insoluble for X = F. Again they are insoluble in water except some methyltin halides for X = Cl to I. In solution and gas states, organotin halides exist as monomers.

Reactions: The Sn-C bond cleavage of tetraorganotin compounds occurs with protic acids such as carboxylic acids, halogens etc. The rupture involves nucleophilic attack at tin center and electrophilic attack at carbon. The reaction of alkyltin compounds with carboxylic acids forms alkyltin carboxylates and the replacement of one R group occurs easily (equation 80). For R =Me, R′ = CF_3, the corresponding products are $Me_3Sn(OCOCF_3)$ and MeH. It may be noted that tetravinyltin and tetrallytin $\{(CH_2{=}CHCH_2)_4Sn\}$ react with carboxylic acids by replacing all the four vinyl or ally groups by carboxylates (equations 81 and 82). Reaction of R_4Sn with halogens form R_3SnX and RX. (R = Ph, Me, $PhCH_2$ etc.; X = Br, I). This reaction occurs via homolytic cleavage of Sn-R bond (equation 83).

$$R_4Sn + R'CO_2H \longrightarrow R_3Sn(OCOR') + RH \qquad \text{Eq. 80}$$

$$(CH_2{=}CH)_4Sn + 4RCO_2H \longrightarrow 4(CH_2{=}CH_2) + Sn(OCOR)_4 \qquad \text{Eq. 81}$$

$$(CH_2{=}CHCH_2)_4Sn + 4RCO_2H \longrightarrow 4(CH_2{=}CHCH_3) + Sn(OCOR)_4 \qquad \text{Eq. 82}$$

$$R_4Sn + X_2 \longrightarrow R_3SnX + RX \qquad \text{Eq. 83}$$

The organotin chlorides are used for the preparation of a number other organotin derivatives. The chloride of R_3SnCl can be readily replaced by a number of nucelophilic reagents such a, OH^-, H^-, N_3^-, $R'S^-$, S_2^-, CN^-, NCS^-, NCO^-, $R_2'N^-$, $R'COO^-$, OR′ etc as shown in equations 84 -86. Similarly, chlorides of R_2SnCl_2 and $RSnCl_3$ can be replaced by a number similar nucleophilic

reagents. Some specific reactions are delineated in equations equations 87a-f. One can easily grasp the potential of preparing a large number of organotin derivatives.

$$R_3SnCl + X^- \longrightarrow R_3SnX + Cl^- \qquad \text{Eq. 84}$$

X^- = CN, NCS, NCO, R′O, R′CO_2, R′$_2$N, R′S, N_3, F, Br, I

$$R_3SnCl + OH^- \longrightarrow R_3SnOH + Cl^- \qquad \text{Eq. 85a}$$

$$2R_3SnOH \xrightarrow[-H_2O]{} R_3SnOSnR_3 \qquad 85b$$

$$2R_3SnCl + S^{2-} \longrightarrow R_3SnSSnR_3 + 2Cl^- \qquad \text{Eq. 86}$$

$$Bu_3SnCl + AgNO_3 \xrightarrow{CCl_4} R_3SnNO_3 + AgCl \qquad \text{Eq. 87a}$$

$$BuSnCl_3 + 3AgOCOMe \xrightarrow{CCl_4} BuSn(OCOMe)_3 + 3AgCl \qquad \text{Eq. 87b}$$

$$BuSnCl_3 + NaOMe \xrightarrow{MeOH} BuSn(OMe)Cl_2 + NaCl \qquad \text{Eq. 87c}$$

$$Bu_3SnCl + NaOMe \xrightarrow{MeOH} Bu_3Sn(OMe) + NaCl \qquad \text{Eq. 87d}$$

$$Ph_3SnOH + HNO_3 \longrightarrow Ph_3Sn(NO_3) + H_2O \qquad \text{Eq. 87e}$$

$$Ph_2Sn{=}O + 2HNO_3 \longrightarrow Ph_2Sn(NO_3)_2 + H_2O \qquad \text{Eq. 87f}$$

Structure and Bonding : Organotin(IV) compounds of type, $RSnX_3$, R_2SnX_2, R_3SnX, and R_4Sn (X = halide /pseudo halide) generally have simple tetrahedral geometry, or some distortions in geometry due to unequal bond lengths and angles, which may be due to packing effect in the solid state. Steric effect within the molecule may also alter bond parameters. However, polymerization can occur particularly with R_2SnF_2 type compounds where in fluoride acts as a bridging group, and R groups stay non –bridging terminal. If the anion such as NO_3 is present, then the geometry may change from tetrahedral to trigonal bipyramid, or octahedral depending on whether one or two O atoms are coordinating. If the organotin compounds form adducts with Lewis bases, then the geometry will be either trigonal bipyramid (e. g. $R_3SnX{\cdot}L$) or octahedral (e. g. $R_2SnX_2{\cdot}L_2$). Further, bonding is a simple matter, and here tin atom can be considered sp^3 hybridized and each sp^3 hybrid orbital interacts with sp^3 orbitals of R group, or X group as the case may be. R groups may have sp^2 or sp - hybridized carbon atoms and bonding arguments can be similarly taken into account. Fig. 7 shows structures of some organotin compounds. Dimers like $R_3Sn\text{-}X\text{-}SnR_3$ have bridging O ro S atoms, with tetrahedral geometry around each Sn atom, as shown Fig. 7.

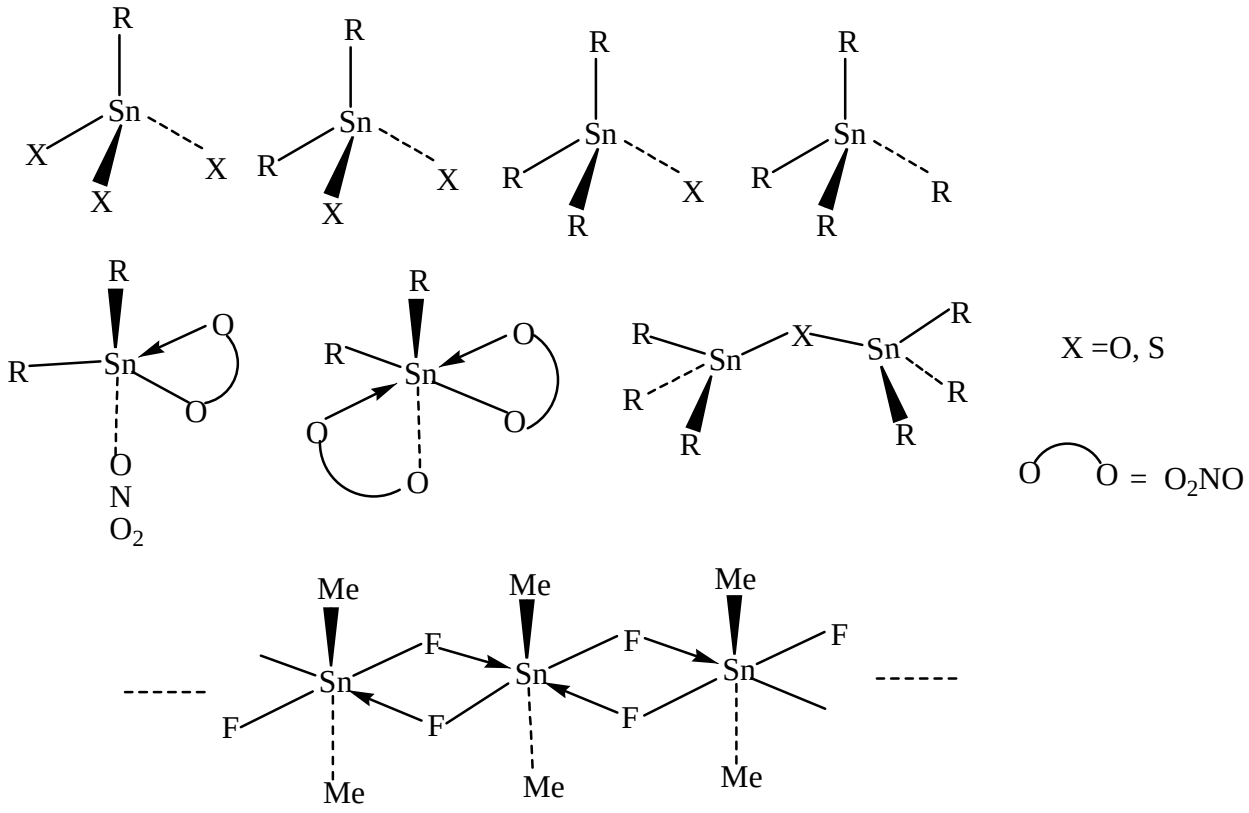


Fig. 7. Strcutures of some organotin compounds

Organometallic Compounds of Titanium

Organometallic compounds of titanium(IV) metal can be broadly classified into three main categories : (a) compounds with Ti-C σ-bonds, (b) compounds with Ti-C π-bonds and (c) compounds with both σ- and π- bonds . Several of organotitanium compounds contain σ- and π-bonded cyclopentadienyl ligand, C_5H_5, probably due to their higher thermal and kinetic stability and ease in their preparation. Organometallic compounds of titanium in oxidation states III, II, and 0 are also known. A major interest in organotitanium compounds is due to their importance in Ziegler-Natta alkene polymerization reactions. A brief account of the organotitanium(IV) compounds is given below.

Preparation:`

Compounds with Ti-C σ-bonds : In this section a brief account of preparation , properties and reactions of σ-hydrocarbyl compounds of titanium(IV), that is, organotitanium compounds with Ti-C σ-bonds of the type, $TiRX_3$, TiR_2X_2 and TiR_4 (R = alkyl-, aryl-, or alkyl-aryl- group; X = halide, other anions such as NR_2^- etc.) are described.

Reaction of $TiCl_4$ with $AlMe_2Cl$ in n-hexane formed methyltitanium(IV) trichloride ($TiMeCl_3$), a simplest member of the series (equation 88). The addition of excess NaCl is necessary to

complex $AlMeCl_2$ as insoluble salt {e.g. $Na[AlMeCl_3]$ etc. }. Various other alkylating agents such as Grignard reagent (MeMgCl), $ZnMe_2$, Me_4Pb, $AlMe_3$, and $CdMe_2$ react with $TiCl_4$ to yield $TiMeCl_3$. It is found that on a smaller scale (laboratory level) $ZnMe_2$ is very convenient and provides relatively pure compound. The prepared $TiMeCl_3$ compound contains occluded hydrocarbon and should be stored at low temperature (-78^oC). For preparing solvent free compound, vacuum distillation should be carried out, but thermal decomposition occurs and products are difficult to identify.

$$TiCl_4 + AlMe_2Cl \overset{\text{hexane}}{\rightleftharpoons} TiMeCl_3 + AlMeCl_2 \qquad \text{Eq. 88}$$

Further alkylation of $TiMeCl_3$ with $ZnMe_2$ or $AlMe_3$ yields $TiMe_2Cl_2$; however this compound is thermally less stable than $TiMeCl_3$. Other alkyl derivatives such as $TiMe_3Cl$ are less stable and can be isolated only as adducts of Lewis bases such as 2, 2'-bipyridine, $TiMe_3Cl.(bipy)$. Other alkyltitanium halides such as $TiEtCl_3$, $TiEtBr_3$, and $TiPrCl_3$ can be similarly prepared : $TiEtCl_3$ from $TiCl_4$ and $AlEt_2Cl$ (or $PbEt_4$ or EtMgBr); $TiEtBr_3$ from $TiBr_4$ and $PbEt_4$; $TiPrCl_3$ from $TiCl_4$ and $ZnPr_2$.

$$2TiX_4 + ZnPh_2 \xrightarrow[\text{hexane/pentane}]{-30^oC} 2TiPhX_3 + ZnX_2 \qquad \text{Eq. 89}$$

$$Ti(OPr^i)_4 + LiPh/LiBr \xrightarrow[\text{ether}]{8\text{-}15^oC} TiPh(OPr^i)_3 + Li(OPr^i) + LiBr \xrightarrow{TiCl_4} TiPh(OPr^i)_3 \qquad \text{Eq. 90}$$

$$TiCl(OPr^i)_3 + LiPh \xrightarrow[\text{ether}]{-10^oC} TiPh(OPr^i)_3 + LiCl \qquad \text{Eq. 91}$$

Aryltitanium trihalides, $TiRX_3$ can be prepared from TiX_4 and an appropriate arylating reagent, such as $ZnPh_2$, PhLi, PhMgBr, $Hg(C_6F_5)_2$ or LiC_6F_5. Reaction of TiX_4 with $ZnPh_2$ gave, $TiPhX_3$ (X = Cl, Br) compounds (equation 89). Pentafluorphenyltitanium(IV) trichloride, $Ti(C_6F_5)Cl_3$ is prepared from $TiCl_4$ and $Hg(C_6F_5)_2$ or LiC_6F_5. Aryltitanium trihalides are thermally more stable than the alkyltitanium trihalides. Phenyltris(isopropoxo)titanium(IV), $TiPh(OPr^i)_3$, can be prepared from $Ti(OPr^i)_4$ and PhLi in diethyl ether at low temperature ($8\text{-}10^oC$) followed by treatment with $TiCl_4$ (equation 90). Reaction of $TiCl(OPr^i)_3$ with LiPh gave good yield of $TiPh(OPr^i)_3$ (equation 91) This solid is stable in the dark below 10^oC but decomposes above its melting point around 90^oC. Other derivatives such as $TiMe(OPr^i)_3$, $Ti(C_6F_5)(OPr^i)_3$ are made from $TiCl(OPr^i)_3$ and MeLi or LiC_6F_5. Compounds such as $TiMe_2(OPr^i)_2$ can be prepared from $TiMe(OPr^i)_3$ and MeLi. The group OPr^i can be replaced by OMe and OBu groups for preparing $TiR(OR)_3$ compounds.

The σ-hydrocarbyltris(dialkylamido) $TiR(NR'_2)_3$ derivatives (R and R' may be same or different), can be prepared in ether or ether-hexane mixture, from $TiBr(NR'_2)_3$ and RLi or RMgX (equation 92). Thus compounds such as $TiR(NR'_2)_3$ with R, R' = Me, Me; Me, Et; Ph, Et and CH_2Ph, Et have been reported. Tetralkyl-, aryl-, or alkyl-aryl- derivatives of Ti(IV) are also known. $TiMe_4$ (yellow crystals) can be made from $TiCl_4$ and MeLi (or MeMgBr) in diethyl ether at -78^oC and is stored in this solvent. It can be separated from lithium salts by distillation in vacuo at -30^oC. Ether solutions decompose between –20 to 0^oC. $Ti(CH_2Ph)_4$ (red), $TiPh_4$ (yellow) and $Ti(C_6F_5)_4$ (brown) were prepared from $TiCl_4$ and $LiCH_2Ph$, PhLi and $Li(C_6F_5)$ respectively.

$$TiBr(NR'_2)_3 + RMgX / RLi \longrightarrow TiR(NR'_2)_3 + MgBrX / LiBr \qquad \text{Eq.92}$$

Compounds with Ti-C π-bonds: A large number of the organotitanium(IV) compounds with Ti-C π-bonds are essentially formed by cyclopentadienyl ($C_5H_5^-$) anion, or its derivatives, and are thus focus of discussion in this chapter. Further, Cp_2TiX_2 compounds (X = halides or other anions; Cp = $C_5H_5^-$) among $Cp_{4-n}TiX_n$ (n = 0, 1, 2, 3) are most widely studied. Cp_2TiCl_2 was first reported in 1952 by the reaction of $TiCl_4$ with C_5H_5MgBr and now a number of routes are available for its synthesis. It has been synthesized using reaction of $TiCl_4$ with LiCp, TlCp, $PbCp_2$, NaCp or CpMgCl in xylene –petroleum ether mixture, and the preferred method is that using NaCp (equation 93). Cp_2TiCl_2 is a red solid with high melting point (289-291^oC) and can be crystallized from acetone, chloroform etc, and is a commercial product. Similarly, Cp_2TiX_2 (X = Br, I) can be prepared using LiCp, TlCp, $MgCp_2$, or CpMgX (X = Br, I). TiF_2Cp_2 can be prepared by treatment of Cp_2TiX_2 with hydrofluoric acid (HF) (X = Cl, Br, I) ,or from Cp_2TiCl_2 and AgF in water (or using alkali metal fluoride). The ring-susbtituted derivatives can be similarly prepared. Usually, LiCp' or MgCp' , LiCp'' or MgCp''$_2$ are used to prepare Cp'$_2$TiCl$_2$ and Cp''$_2$TiCl$_2$ (Cp' = C_5H_4Me; Cp'' = C_5Me_5). Several related compounds have been prepared.

$$TiCl_4 + 2NaCp \longrightarrow Cp_2TiCl_2 + 2NaCl \qquad \text{Eq. 93}$$

Monocyclopentadienyltitanium(IV) compounds of type $CpTiX_3$ are also known. These can be easily prepared by reaction of TiX_4 with NaCp, oxidation of Cp_2TiX_2 with halogens (Cl_2, Br_2), and redistribution method involving $TiCl_4$ and Cp_2TiCl_2. The ring-substituted derivatives (Cp' for Cp) can be similarly prepared. The oxidation of Cp_2TiCl_2 with Cl_2 and that with Br_2 gave orange solids $CpTiCl_3$ and $CpTiCl_2Br$ respectively.

Compounds with Ti-C σ- and π-Bonds: Here the organotitanium compounds of Ti(IV) with both σ- and π-bonds are briefly discussed. Reaction of Cp_2TiCl_2 with MeMgI in thf gave $TiCp_2Me_2$ in poor yield in 1956. However, it can be conveniently prepared in good yield with high purity using $TiCl_2Cp_2$ and MeLi (equation 94) $TiMe_2Cp_2$ is orange-yellow solid, stable in air, unreactive towards cold water, possesses moderate thermal stability, should be stored in a refrigerator and is light sensitive. It is the first most widely studied σ-hydrocarbylderivative of bis(π-cyclopentadienyl)-titanium(IV). The ethyl derivative, $TiEt_2Cp_2$ can be similarly made, but it is less stable thermally than methyl analogue. The butyl derivative, $TiBu_2Cp_2$ is difficult to isolate and is stable in solution state below –50^oC. The presence of bulky trimethylsilyl groups stabilize the complex (at 20^oC) by stopping β-hydrogen elimination reaction (equation 95). Other derivatives, $TiPh_2Cp_2$, $Ti(C_6F_5)_2Cp_2$, $TiMe_2Cp'_2$ and $TiMe_2Cp''_2$ (Cp' = C_5H_4Me; Cp'' = C_5Me_5) are also known and can be similarly prepared using lithium salts. Compounds $TiMe_2Cp'_2$ and $TiMe_2Cp''_2$ are more stable thermally at RT and upto 90^oC in solution state.

$$TiCl_2Cp_2 + 2\,MeLi \longrightarrow TiMe_2Cp_2 + 2LiCl \qquad \text{Eq. 94}$$

$$TiCl_2Cp_2 + 2\,LiCH_2SiMe_3 \xrightarrow{\text{ether}} Ti(CH_2SiMe_3)_2Cp_2 + 2LiCl \qquad \text{Eq. 95}$$

Another well established compound with both σ- and π-bonds is tetrakis -(cyclopentadienyl)titanium(IV), Ti(σ-Cp_2)(π-Cp_2) prepared from $TiCl_2Cp_2$ and two moles of NaCp. It is a air and moisture sensitive violet-black solid (m. p. 128^oC). It has two sigma bonded Cp rings and two pi-bonded rings. It shows fluxional behavior in solution in temperature range -140 to 80^oC involving interchange of σ- and π-bonded rings. At room temperature it shows one broad signal in its ^1H NMR spectroscopy due to coalescence of peaks due to two types of rings.

Finally, compounds of type $TiMe_3Cp$ (from $TiCl_3Cp$ and MeLi), $TiPh_3Cp$ (from $TiCl_3Cp$ and PhLi), are also reported, but are not very stable and decompose to form different products. Methyl and phenyls are σ-bonded and Cp ring is π-bonded.

Compounds of Titanium in low Valent states (III, II, 0): The stable organometallic compounds of titanium(III) are those having at least one π-bonded Cp ring. The reduction of compounds TiX_3Cp with zinc powder in dry THF forms paramagnetic $TiX_2Cp(THF)$, and coordinated THF can be removed by heating the complexes under vacuum at 120°C (X = Cl, Br, I) (equation 96). The iodo complex has lower thermal stability at this temperature, and a pure sample free from THF could not be made. The Bu^i_2AlCl reagent removes one Cp from $TiCl_2Cp_2$ in toluene/heptane at 50°C (equation 97).

$$2TiX_3Cp + Zn \xrightarrow{THF} 2TiX_2(Cp)(THF) + ZnCl_2 \xrightarrow{120^oC} 2TiX_2(Cp) \qquad \text{Eq. 96}$$

$$TiCl_2Cp_2 + Bu^i_2AlCl \xrightarrow{toluene} TiCl_2Cp \qquad \text{Eq. 97}$$

Paramagnetic bis(cyclopentadienyl)titanium(III) chloride, $TiClCp_2$, can be prepared by various methods as shown in equations, 98-102. The bromide or iodide analogues can be made either by reduction with Al method or by halide exchange using boron trihalides (equations 103 and 104). The compounds with substituted Cp rings are also similarly prepared. Paramagnetic monomeric $TiRCp_2$ compounds for R = $CHPh_2$, CH_2SiMe_3, Ph, o-, m-, p-MeC_6H_4, etc. have been prepared by reacting lithium alkyls- or aryls, or Grignard reagent using dimeric $TiClCp_2$.

$$TiCl_3 + 2NaCp \xrightarrow{THF} 0.5(TiClCp_2)_2 + 2NaCl \qquad \text{Eq. 98}$$

$$TiCl_3 + MgCp_2 \xrightarrow{THF} 0.5(TiClCp_2)_2 + MgCl_2 \qquad \text{Eq. 99}$$

$$TiCl_3 + 2TlCp \xrightarrow{THF} 0.5(TiClCp_2)_2 + 2TlCl \qquad \text{Eq. 100}$$

$$2TiCl_2Cp_2 + Zn \xrightarrow{THF} 0.5(TiClCp_2)_2 + ZnCl_2 \qquad \text{Eq. 101}$$

$$6TiCl_2Cp_2 + 2Al \xrightarrow{THF} 3(TiClCp_2)_2 + 2AlCl_3 \qquad \text{Eq. 102}$$

$$6TiBr_2Cp_2 + 2Al \xrightarrow{THF} 3(TiBrCp_2)_2 + 2AlBr_3 \qquad \text{Eq. 103}$$

$$3[(TiClCp_2)_2] + 2BBr_3 \xrightarrow{THF} 3(TiBrCp_2)_2 + 2BCl_3 \qquad \text{Eq. 104}$$

Reaction of $(TiClCp_2)_2$ with NaCp gave green $TiCp_3$. The monomeric alkyl complexes of Ti(III), TiR_3 with non-cyclopentadienyl ligand are stable only with bulky ligands such as for R = CH_2SiMe_3, $CH(SiMe_3)_2$, CH_2Ph. For R = Me, Ph, coordination to Ti by solvent used is necessary to isolate $TiCl_2R(S)_3$ (S = py, Et_2O etc.) complexes.

Organotitanium(II) compounds such as $Ti(CO)_2Cp_2$, $TiPh_2(S)$ (S = NH_3, Et_2O etc.), $Ti(CH_2Ph)_2(S)_3$ (S = dioxane, $C_4H_8O_2$) ; $Ti(Ph(Cp)(S)_2$ (S= Et_2O), Ti(butadiene)$_2$(dmpe),(dmpe = $Me_2PCH_2CH_2PMe_2$), $Ti(Cp)(C_7H_7)$ (C_7H_7 = cycloheptatrienyl), $Ti(C_8H_8)_2$ (C_8H_8 = cyclooctatetraene) as well as organotitanium(0) compounds, Ti(π-arene)$_2$ have been reported.

Properties: Organotitanium compounds are soluble in various organic solvents, such as ether, THF, benzene, etc. The compounds are liquids, low melting solids, and some are high melting solids. The air, moisture and thermal stability also vary from compound to compound depending on the nature of organic group and other groups bonded to titanium. Every compound requires a specific handling and some are explosive also. Some of the general properties are discussed in preparation section of organotitanium compounds.

Reactions: Organotitanium compounds undergo a variety of reactions involving either Ti-C or Ti-X bonds, and only some are briefly delineated below. Compound $MeTiCl_3$ exchanges halogen or other anion on reaction with metal halides or other compounds as shown in equations 105-110. With protic substrates evolution of methane occurs. Reaction of $MeTiCl_3$ with isobutene $Me_2C=CH_2$, gave neopentyl derivative as shown in equation 111 and that with ethylene, it forms similar product which however goes on adding ethylene molecules to form long chain with C31 carbon atoms (equation 112). $PrTiCl_3$ undergoes another side reaction with ethylene to form $EtTiCl_3$ and C_3H_6 and reaction continues to form $BuTiCl_3$ and so on upto C30 carbon atoms. $TiMe_4$ reacts with MeLi to form addition product, $LiTiMe_5$, and with CH_3COOH to form titanium(IV tetracetate, $Ti(O_2CCH_3)_4$, alongwith evolution of methane. It may be pointed out that direct reaction of $TiCl_4$ with acetic acid did not form similar product. It reacts with $AlMe_3$ to form ionic salt, $[TiMe_3]^+[AlMe_4]^-$.

$$TiMeCl_3 + HgCl_2 \longrightarrow TiCl_4 + MeHgCl \qquad \text{Eq. 105}$$

$$TiMeCl_3 + SnCl_4 \longrightarrow TiCl_4 + MeSnCl_3 \qquad \text{Eq. 106}$$

$$TiMeCl_3 + H_2O \longrightarrow Ti(OH)Cl_3 + CH_4 \qquad \text{Eq. 107}$$

$$TiMeCl_3 + ROH \longrightarrow Ti(OR)Cl_3 + CH_4 \qquad \text{Eq. 108}$$

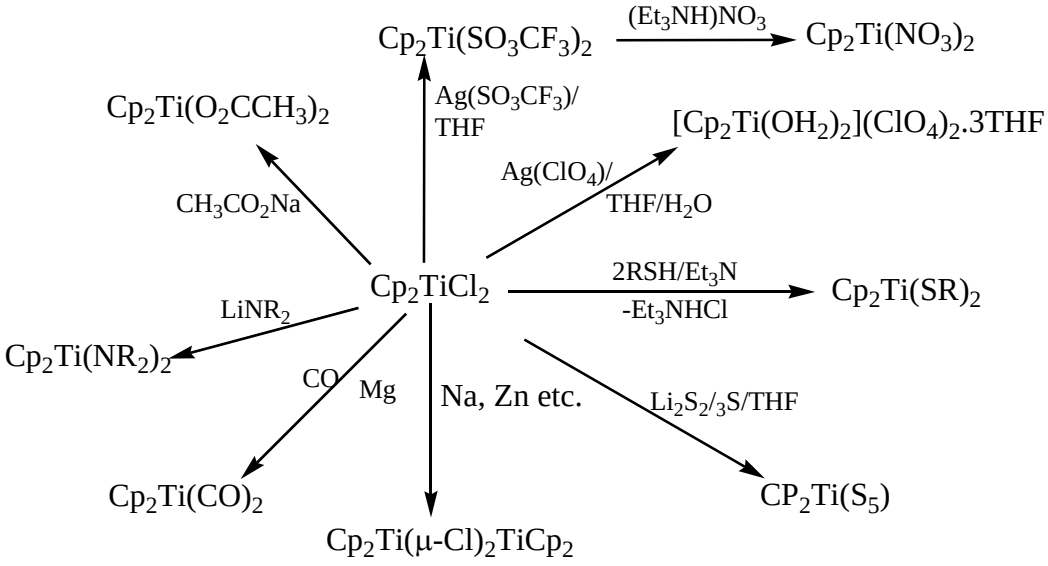
$$TiMeCl_3 + HX \longrightarrow Ti(X)Cl_3 + CH_4 \qquad \text{Eq. 109}$$

$$TiMeCl_3 + I_2 \longrightarrow TiICl_3 + CH_3I \qquad \text{Eq. 110}$$

$$TiMeCl_3 + Me_2C=CH_2 \xrightarrow[\text{heptane}]{20^oC} Ti(CH_2CMe_3)Cl_3 \qquad \text{Eq. 111}$$

$$TiMeCl_3 + H_2C=CH_2 \longrightarrow Ti(Pr)Cl_3 \xrightarrow{H_2C=CH_2} Ti(C_5H_{11})Cl_3 \qquad \text{Eq. 112}$$

Cp_2TiCl_2 is the starting material of many organotitanium compounds and thus some important reaction trends of this substrate are given below. It reacts with a series of alkali metal pseudohalides in aqueous or non-aqueous medium, or with silver salt of the psuedohalide in non-aqueous medium to form Cp_2TiX_2 (X = NCS, NCSe, CN, NCO, N_3). Titanium is bonded to N donor atoms of NCS, NCSe, NCO and N_3 and to C end of CN group.The susbstituted rings, Cp' and Cp" gave similar products. Scheme 5 depicts some other reactions of Cp_2TiCl_2.



Scheme 5

Bonding and Structure: Organotitanium compounds have both σ-bonded, π-bonded or both σ- and π-bonded R groups. The structures of σ-bonded compounds of type, $RTiX_3$, R_2TiX_2, R_3TiX and R_4Ti (X = halide or other anion having single Ti-X bond), are expected to be tetrahedral or distorted tetrahedral, similar to tin compounds. The structure determination using x-ray crystallography are known only for limited number of compounds. For example, tetrabenzyltitanium(IV), $(PhCH_2)_4Ti$, has distorted structure as shown by x-ray crystallography. Here benzyl groups are bent with one C of each phenyl ring is close to Ti ($Ti\text{-}C_{CH2}$ = 2.61 Å and $Ti\text{-}C_{Ph}$ = 2.81 Å)(Fig. 8). If X group is like OR, then geometry might change to a dimer. For example, $Ti(CH_2Ph)_2(OEt)_2$ is alkoxy-bridged dimmer (8a) The geometry around each Ti center can be considered as trigonal bipyramidal. Compounds such as $Cp_4Ti_2Cl_2$ have π-bonded cyclopentadienyl rings with chloride anions bridges. The structures of $(\pi\text{-}Cp_2)TiX_2$ (X = Cl, ONO_2, OSO_2CF_3), $[Cp_2Ti(OH_2)_2](ClO_4)_2$, and $(\sigma\text{-}Cp_2)(\pi\text{-}Cp_2)Ti$ are also shown in Fig. 8b.

The bonding in organotitanium compounds may be understood as follows. For all σ-bonded organotitanium compounds, Ti can be considered as sd^3 hybridized, thus each sd^3 orbital (4s, $3d_{xy}$, $3d_{yz}$, $3d_{xz}$) overlaps with sp^3 orbital of C atom of R or X group as the case may be, leading to a tetrahedral geometry. In case of π-bonded cyclopentadienyl, each Cp ring donates, or shares 6 electrons with metal orbitals (ring is treated as anionic). Thus in $(\sigma\text{-}Cp_2)(\pi\text{-}Cp_2)Ti$ two Cp rings are σ- bonded and two are π-bonded.

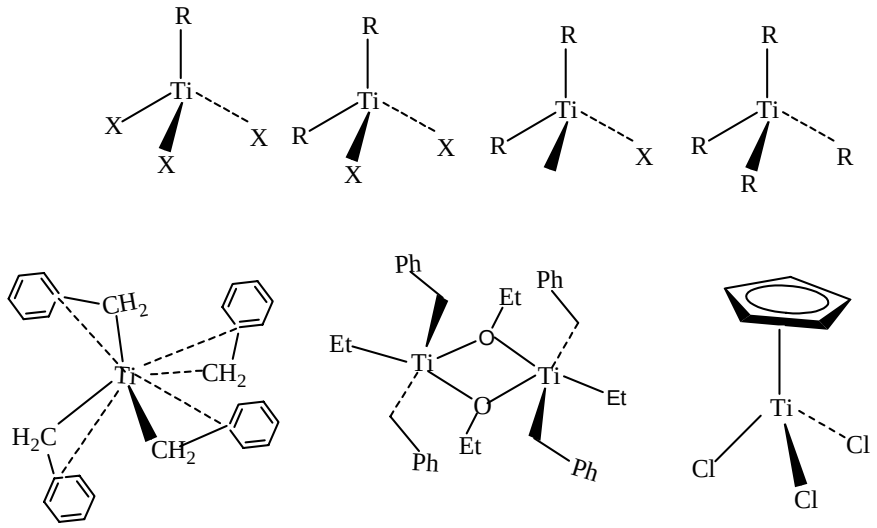


Fig. 8a. Strcutures of some organotin compounds

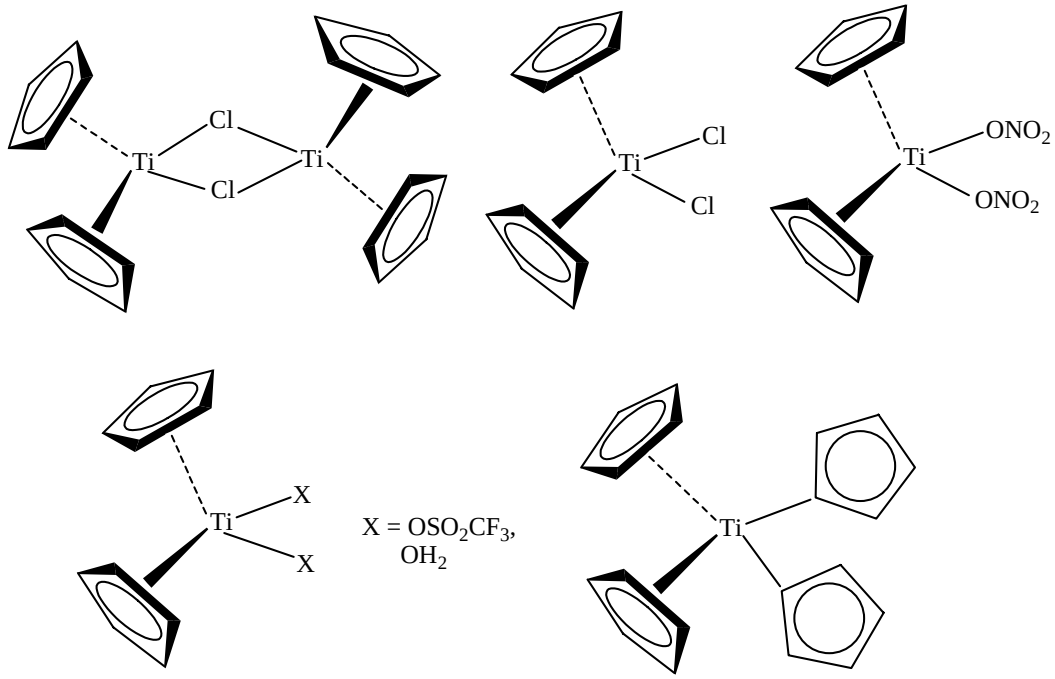


Fig. 8b. Strcutures of some organotin compounds

Applications

A brief account of applications of organometallic compounds of Li, Al, Sn, Hg, and Ti is given in this section.

Lithium-Organolithium compounds are used in the synthesis of organic and inorganic compounds. In organic reactions, they are used for generating carbanions (R^-) necessary for organic reactions as described in lithium section. In some reactions, organolithium compounds are considered as radicals, $R^{\cdot}$.

Aluminium- Organoaluminium compounds such as Et_3Al are very important commercially as activators for olefin polymerization catalysts. They are also widely used as reducing and alkylating agents for transition metal complexes. Trialkylaluminium compounds are better alkylating agents than dialkylaluminium halides. Dialkylaluminium hydrides, R_2AlH, are used for C–H bond formation by cleaving C–O, C–X, C–N and C–S bonds.

Mercury- Organomercury compounds are very useful for the preparation of other organometallic compounds of other metals by transmetallation process. Perhalogeno alkyl derivatives, $Hg(CF_3)_2$, $Hg(CCl_3)_2$ are useful reagents for transferring CX_3, CX_2 and CX groups to other elements. Organomercury compounds are also used in organic synthesis, in seed dressings, and as fungicides.

Tin- Organotin compounds are used in organic synthesis, as stabilizers for poly(vinylchloride), as fungicides, biocides, in agrochemicals, wood preservation, marine paints, disinfectant. They are also used as precursors for forming SnO_2-films on glass, as homogeneous catalysts and as water repellant chemicals.

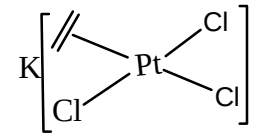
Titanium- Initially, it was discovered that ethylene and propylene can be polymerised using $TiCl_3$- aluminium alkyl mixtures in hydrocarbons at room temperature and 1 atm pressure. Later it was found that $TiMeCl_3$ also polymerized ethylene in the absence of aluminium alkyls as cocatalysts. This led to interest in organotitanium chemistry. Now, a number of organotitanium compounds are useful as catalysts (Ziegler-Natta catalysts) in a number of organic reactions, particularly for the polymerization of alkenes.

Metal –Alkene Complexes

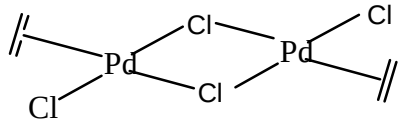
In this section some complexes of metals with alkenes, such as ethylene, are briefly discussed. A double bond made, up of σ- and π-bonds, is known to act as a donor ligand via π-electrons (Lewis base), similar to other Lewis bases such as NH_3, H_2O, thf, Et_2O, etc. which form bonds via σ-electrons. Metal –alkene complexes are known for nearly all the d-block elements, however, the most stable complexes are formed by the elements late in the transition series. For metal-alkene bonds to be strong, and hence for the formation of a stable complex, a metal should form a π-bond with the empty π*- orbitals over a double bond.

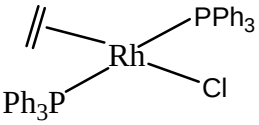
When ethene ($H_2C=CH_2$) is passed through an acidic solution of K_2PtCl_4, Zeise's salt, $K[Pt(\eta^2\text{-}C_2H_4)Cl_3]\cdot H_2O$ is formed (equation 113, η-refers to number of bonds a ligand makes; in ethene case Pt is interacting with both C atoms). This reaction is very slow and needs high pressure, and long time (many days), however, an addition of stannous chloride ($SnCl_2$) catalyzes the reaction and is complete in 4 h at ambient temperature and pressure. Palladium(II) chloride can be dissolved in benzonitrile (PhCN) on heating, and $PdCl_2(NCPh)_2$ is formed which is the staring material. Reaction of $PdCl_2(NCPh)_2$ with ethylene ($H_2C=CH_2$) displaces PhCN forming chloride-bridged dimer, $[Cl(\eta^2\text{-}C_2H_4)Pd(\mu\text{-}Cl)_2Pd(\eta^2\text{-}C_2H_4)Cl]$ (equation 114). Reaction of

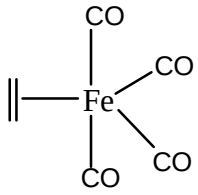
Wilkinsons's catalyst $RhCl(PPh_3)_3$ with ethene displaces one PPh_3 forming ethene complex, $RhCl(PPh_3)_2(\eta^2\text{-}C_2H_4)$ (equation 115).

$K_2PtCl_4 + H_2C{=}CH_2 \longrightarrow$  Eq. 113

$PdCl_2 + PhCN \longrightarrow PdCl_2(PhCN)_2$ 114a

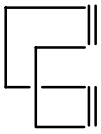
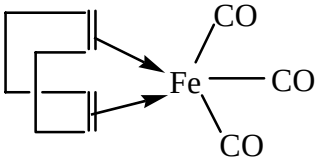
$2\ PdCl_2(PhCN)_2 \xrightarrow{H_2C=CH_2}$  Eq. 114b

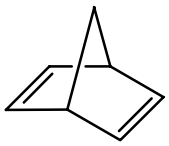
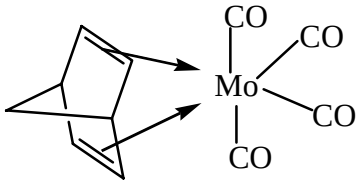
$RhCl(PPh_3)_3 + H_2C{=}CH_2 \longrightarrow$  Eq. 115

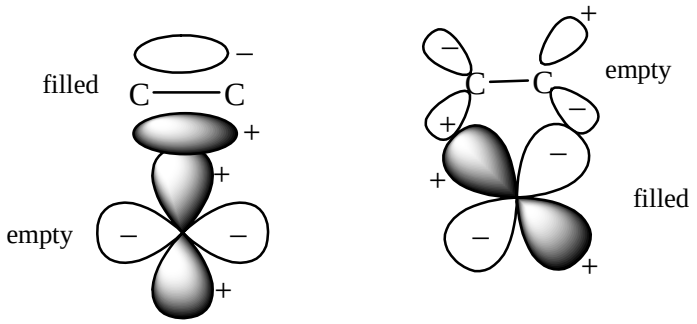
$Fe_2(CO)_9 + H_2C{=}CH_2 \xrightarrow[2d]{50\ atm}$  $+ Fe(CO)_5$ Eq. 116

Iron dicarbonyl, $Fe_2(CO)_9$ readily reacts with ethene forming ethene complex, $(\eta^2\text{-}C_2H_4)Fe(CO)_4$ (equation 116). The complexes formed by mono-olefins are generally unstable. Thus tetracarbonyl(ethene)iron(0) slowly decomposes forming a trinuclear complex, $Fe_3(CO)_{12}$. $Mo(CO)_6$ with ethene under UV radiations forms stepwise monosubstitution, $Mo(CO)_5(\eta^2\text{-}C_2H_4)$ and disubstitution $Mo(CO)_4(\eta^2\text{-}C_2H_4)_2$ products.

Diolefins such as 1, 5-cyclooctadiene (1, 5-COD) or norbornadiene (nbd) can chelate to a metal and thus complexes are more stable than those obtained with monoolefins. Reaction of $Fe(CO)_5$ with 1, 5-COD under photolysis forms tricarbonyl(η^2: η^2 -1, 5-cyclooctadiene)iron(0) , (1,5-COD)$Fe(CO)_3$ (equation 117). The ligand nbd with $Mo(CO)_6$ in octane under reflux gave yellow compound, tetracarbonyl(η^2: η^2 - norbornadiene)molybdenum (equation 118).

 $+ Fe(CO)_5 \xrightarrow{h\nu}$  Eq 117

$Mo(CO)_6 +$  $\xrightarrow[reflux]{octane}$  Eq 118



a, ligand to metal bond b, metal ligand bond

Fig. 9. Metal-olefin bonding (a) ligand to metal σ–bond

(b) metal to ligand bond π–bond

Fig. 9 shows bonding in metal-alkene complexes represented in simplistic manner. The π-electrons from double bond donate electrons to empty metal d-orbital forming σ-bond (Fig. 9a), and metal filled d-orbital forms π-bond with empty π*-orbitals of double bond(Fig. 9b). This mode of σ-π bond formation is synergic, according to which a σ-bond is strengthened by π-bond formation due to greater flow of electron density form metal to ligand and π-bond formation is strengthened by σ-bond formation due to greater flow of electron density form ligand to metal.

Metal Carbonyls

Carbon monoxide (CO) is a two electron donor, and usually forms a σ-bond to a metal center via its lone pair of electrons on carbon atom, which is obviously due to low electronegativity of C versus that of O atom. It is a weak Lewis base and thus forms a weak M-CO σ-bond and this bond can sustain only if filled metal d-orbitals are engaged in π-bond formation with the empty π* orbitals on CO ligand. Metal carbonyls of several elements of d-block elements have been reported, but most stable metal carbonyls are formed only by the transition elements in low oxidation states.

The range of transition metal carbonyls is wide spread from mononuclear, dinuclear, trinuclear, oligomer to polymers. The discussion here is mainly limited to mononuclear carbonyls. A few most common mononuclear carbonyls are, $V(CO)_6$, $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, $Mo(CO)_6$, $W(CO)_6$, $Ru(CO)_5$, and $Os(CO)_5$. Vanadium carbonyl $V(CO)_6$, is pyrophoric, while chromium and iron group carbonyls, $M(CO)_6$ (M = Cr, Mo, W), and $M(CO)_5$ (M = Fe, Ru, Os) are air stable, and $Ni(CO)_4$ is air sensitive. Metal carbonyls generally follow 18-electron rule, or nine orbital rule. According to this rule metals have tendency to use all the (n-1)d, ns and np metal orbitals in bonding in order to attain configuration of nearest inert gas-which is the most stable configuration known. Thus metals bind to different number of CO ligands so as to follow 18-electron rule. The resulting metal carbonyls may be paramagnetic, or diamagnetic depending on the atomic number of the metal. Let us count the electrons in the following metal carbonyls (Table 1) and note if all these follow 18-electron rule or not.

Table 1

$V(CO)_6$	23	5	6 x 2	17
$Cr(CO)_6$	24	6	6 x 2	18
$Mo(CO)_6$	42	6	6 x 2	18
$W(CO)_6$	74	6	6 x 2	18
$Fe(CO)_5$	26	8	5 x 2	18
$Ni(CO)_4$	28	10	4 x 2	18
$Ru(CO)_5$	44	10	5 x 2	18

Tetracarbonylnickel(0), $Ni(CO)_4$, is the first metal carbonyl reported in 1890 by Mond, Langer and Quincke. This is a volatile carbonyl and can be prepared by direct method by passing CO gas over metallic Ni at or just above the room temperature (equation 119). Iron does not react at the room temperature, but only at higher temperature and pressure

$$Ni + 4CO \longrightarrow Ni(CO)_4 \qquad \text{Eq. 119}$$

Metal carbonyls such as $Ti(CO)_6$, $Nb(CO)_6$, $Ta(CO)_6$, $Pd(CO)_4$, $Pt(CO)_4$ are very unstable and are prepared by cocondensation of metal vapours and CO in frozen noble gas matrices at very low temperature 4 –20 K and are stable only at this temperature.

Binary metal carbonyls $\{M(CO)_x\}$ are usually prepared by reacting a metal halide or metal complex such as $M(acac)_n$ (Hacac = acetylacetone, $CH_3COCH_2COCH_3$) with CO in the presence of a reducing agent. The reaction of VCl_3 with Na metal under high pressure of CO gas in diglyme solvent (diglyme = diethyleneglycol dimethyl ether) formed initially carbonyl anion, which is acidified to get neutral compound. It is thermally unstable and readily yields $V(CO)_6$ with the evolution of hydrogen (equation 120). Similarly, $Cr(CO)_6$, can be prepared as shown in equation 121.

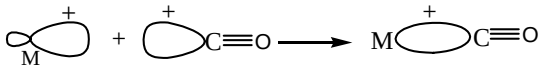
$$VCl_3 + 4Na + 6CO \xrightarrow[160^oC/200\ atm]{diglyme} [Na(diglyme)_2]^+[V(CO)_6]^- + 3NaCl$$

$$[Na(diglyme)_2]^+[V(CO)_6]^- \xrightarrow{acidification} HV(CO)_6 \longrightarrow 2V(CO)_6 + H_2 \qquad \text{Eq. 120}$$

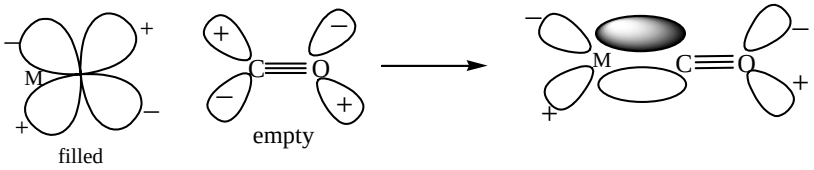
$$CrCl_3 + 5Na + 5CO \xrightarrow[0\text{-}25^oC\ /150\ atm]{diglyme} [Na(diglyme)_2]^+ [Cr(CO)_5]^- + 3NaCl$$

$$[Na(diglyme)_2]^+ [Cr(CO)_5]^- \xrightarrow[0^oC/50\ atm]{CO/H_2SO_4} Cr(CO)_6 \qquad \text{Eq. 121}$$

Metal carbonyls undergo substitution reactions with the replacement of CO by other ligands such as phosphines. For example, $Fe(CO)_5$ gave both monosubstituted and disubstituted products namely, $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$. NO can also replace CO groups readily. Three CO groups are replaced by two NO ligands (three elelctron donors) to form, $Fe(CO)_2(NO)_2$ while all CO of $Cr(CO)_6$ are replaced by four NO ligands to form, $Cr(NO)_4$.



a, ligand to metal bond



b, metal to_ ligand bond

Fig. 10. Metal-carbonyl bonding (a) ligand to metal σ–bond

(b) metal to ligand π–bond

Ligand to metal σ - bonding and metal to ligand π - bonding are depicted in Fig. 10 and is similar to that shown in metal-olefin bonding. This mode of σ-π bond formation is synergic, according to which a σ-bond is strengthened by π-bond formation due to greater flow of electron density form metal to ligand and π-bond formation is strengthened by σ-bond formation due to greater flow of electron density form ligand to metal. The structure of $Ni(CO)_4$ is tetrahedral, while $M(CO)_5$ and $M(CO)_6$ have trigonal bipyramid and octahedral structures respectively as shown inn Fig. 11.

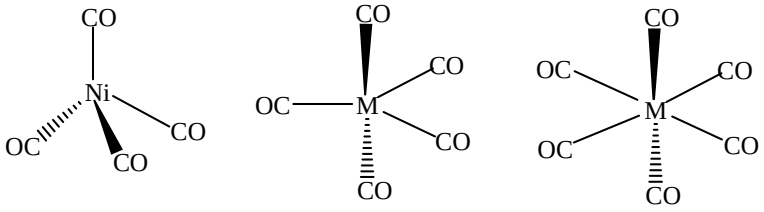
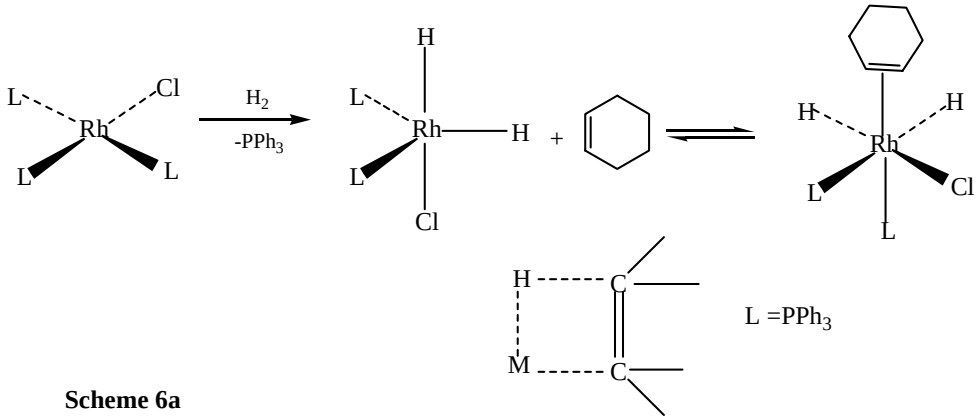


Fig. 11. Structures of $Ni(CO)_4$, $M(CO)_5$ (M = Fe, Ru, Os)and $M(CO)_6$

(M =V, Cr, Mo, W) carbonyls

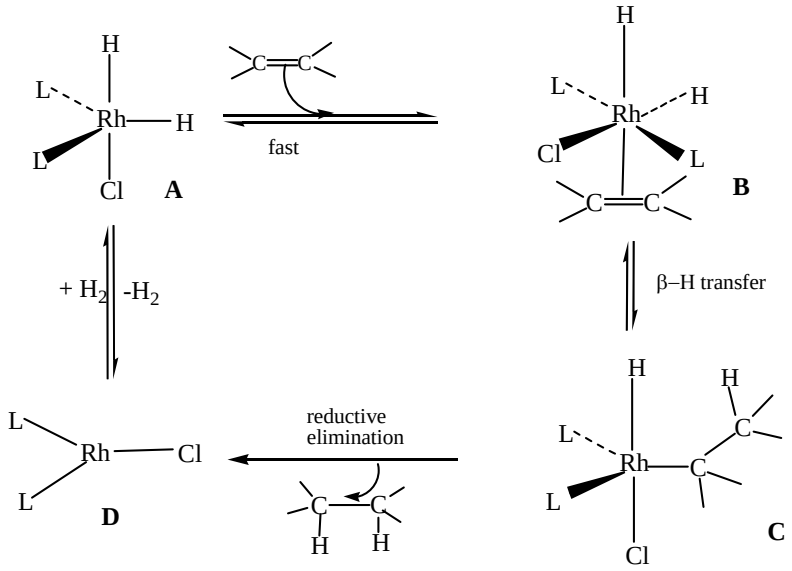
Homogeneous Hydrogenation

Homogeneous hydrogenation deals with hydrogenation of organic compounds using a metal complex as catalyst in the solution state; while heterogeneous catalysis involves hydrogenation when the catalyst used is in the solid state. In this section only homogeneous hydrogenation is briefly discussed.



Scheme 6a

Homogeneous hydrogenation of organic compounds, such as alkenes, alkynes, and other unsaturated compounds, is readily carried out with $RhCl(PPh_3)_3$ catalyst at low pressure and room temperature. This catalyst known as Wilkinson's catalyst can be prepared by reacting $RhCl_3{\cdot}3H_2O$ with excess PPh_3 in ethanol solvent. There are several other catalysts, namely, $RuHCl(PPh_3)_3$, $[RuH(PMe_2Ph)_5]^+$ etc. which are used for hydrogenation purpose. Hydrogen reacts with $RhCl(PPh_3)_3$ in benzene to give a yellow solution, forming six- coordinated cis-$RhH_2Cl(PPh_3)_3$. The strong trans effect of hydride, H^-, labilizes one PPh_3 trans to it and five coordinated species, $\{RhH_2Cl(PPh_3)_2$, is generated, which binds to unsaturated substrates such as cyclohexene. M-H and C = C bonds are coplanar, in a four center arrangement, and lead to transfer of H to double bond (Scheme 6a). This is followed by transfer of second hydrogen. A complete catalytic cycle is shown in Scheme 6b for hydrogenation of ethylene. As mentioned above five coordinated species, $\{RhH_2Cl(PPh_3)_2$ (**A**), obtained from cis-$RhH_2Cl(PPh_3)_3$ is the active species engage in the hydrogenation process. Ethylene binds to vacant site of the species in a fast step (**B**), and then transfer of β-hydrogen occurs forming again 5-five coordinated species (**C**), which undergoes reductive elimination to generate three coordinate species (**D**) This species again involves oxidative addition of H_2 to regenerate 5-coordinated species (**A**). This catalytic cycle goes on to hydrogenate other ethylene molecules.



Scheme 6b

Suggested Readings:

1. P. Powell, **Principles of Organometallic Chemistry**, Second edition, London, Chapman and Hall, 1988 (General Book).
2. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, **Advanced Inorganic Chemistry,** Sixth Edition, John Wiley and Sons, New York, 1999.
3. G. Wilkinson, F. G. A. Stone, and E. W. Abel (eds), **Comprehensive Organometallic Chemistry,** Vols. 1, Pergamon Press, Oxford, U. K. 1982 (Lithium and Aluminium)
4. G. Wilkinson, F. G. A. Stone, and E. W. Abel (eds), **Comprehensive Organometallic Chemistry,** Vols. 2, Pergamon Press, Oxford, U. K. 1982 (Mercury and Tin).
5. G. Wilkinson, F. G. A. Stone, and E. W. Abel (eds), **Comprehensive Organometallic Chemistry,** Vols. 3, Pergamon Press, Oxford, U. K. 1982 (Titanium).
6. John J. Eisch, **The Chemistry of Organometallic Compounds** - *The main Group Elements*. The Macmillan Company, New York, 1967.
7. M. Tsutsui, M. N. Levy, A. Nakamura, M. Ichikawa, K. Mori, **Introduction to Metal-π-Complex Chemistry**, Plenum Press, New York, 1970.