What are Organometllic Compoounds?

Organometallic compounds (also called organometallics) are the compounds in which the central metal atom is linked directly with the C-atom of the organic ligand. Thus these compounds contain one or more metal-to-carbon bonds. The metal atom may be a transition metal or a lanthanide or an actinide or a main group element. The organic ligand may be alkyl, aryl etc. group or alkene, alkyne etc.

Although B, Si, Ge, As, Sb, Se and Te are borderline metals, organoboron, organosilicon, organoarsenic etc. compounds are also classified as organometallic compounds.

Although carbides and cyanides contain metal-carbon bonds, these compounds are not put in the category of organometallic compounds by convention.

Organometallic Compounds of Lithium: Organolithium Compounds

Organolithium compounds are those compounds which contain Li–C bond. For example:

CH_3-Li	CH_3-CH_2-Li	CH_3-CH_2-CH_2-Li	C_6H_5-Li
Methyllithium	Ethyllithium	n-propyllithium	Phenyllithium

Preparation.

(*i*) By alkyl halide-lithium reaction in ether

$$RX + 2Li \rightleftharpoons RLi + LiX$$

For example:

$$CH_3I + 2Li \xrightarrow[-10°C]{Ether} CH_3Li + LiI$$

$$C_2H_5\,Br + 2Li \longrightarrow C_2H_5Li + Li\,Br$$

$$\underset{\text{n-butyl bromide}}{n\text{-}C_4H_9\,Br} + 2Li \longrightarrow \underset{\text{n-butyl lithium}}{n\text{-}C_4H_9\,Li} + Li\,Br$$

(*ii*) **By metal-halogen exchange reactions**

$$R'X + RLi \longrightarrow R'Li + RX$$

R=n-butyl and R′X = an aryl bromide or iodide.

(*iii*) **By metal-metal displacement reactions**

$$R_2Hg + 2Li \longrightarrow 2RLi + Hg$$

(*iv*) **By metallation reactions**

$$RH + n\text{-BuLi} \longrightarrow RLi + \underset{n\text{-butane}}{n\text{-BuH}}$$

Properties

(*i*) The monomeric organometallic compounds of alkali metals are not very stable thermodynamically. However, polymeric compounds are comparatively stable. For example, some polymeric lithium alkyls do not decompose even up to 100°C.

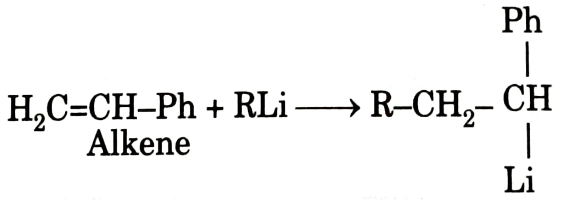
(ii) Organolithium derivatives undergo reactions similar to those of Grignard reagents.

(*iii*) Hydrolysis (to hydrocarbon) with water is rapid.

(*iv*) With halogen compounds, R groups are replaced by halogen. For example:

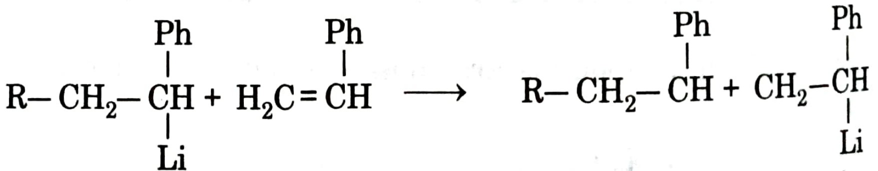
$$R'_3SiCl + RLi \longrightarrow R'_3SiR + LiCl$$

(*v*) Unlike Grignard reagents, organolithium compounds add to the double bonds in alkenes. For example:



$$\underset{\text{Alkene}}{H_2C{=}CH{-}Ph} + RLi \longrightarrow R{-}CH_2{-}\underset{\underset{Li}{|}}{\overset{\overset{Ph}{|}}{CH}}$$

The product formed above reacts with more quantity of alkene and gives a polymer.



$$R{-}CH_2{-}\underset{\underset{Li}{|}}{\overset{\overset{Ph}{|}}{CH}} + H_2C{=}\overset{\overset{Ph}{|}}{CH} \longrightarrow R{-}CH_2{-}\overset{\overset{Ph}{|}}{CH} + CH_2{-}\underset{\underset{Li}{|}}{\overset{\overset{Ph}{|}}{CH}}$$

Polymeric compound

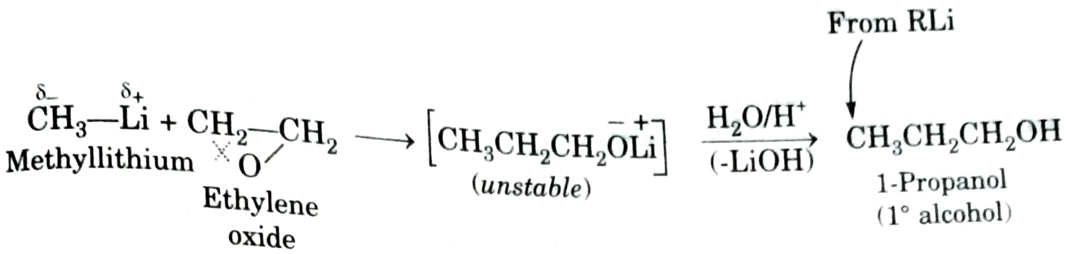
Properties of Alkyl Lithium (RLi)

The increased reactivity of organolithium compounds over Grignard reagents is due to the greater polar character of C-Li bond in comparison to C-Mg bond. Organolithium compounds are particularly sensitive towards air and moisture. They react with compounds containing active hydrogens, aldehydes, ketones, carbon dioxide, and ethylene oxide in the same way as do Grignard reagents.

(*i*) **Reaction with water.** Organolithium compounds react with water to form alkanes.

$$\underset{\text{Methyllithium}}{CH_3-Li} + H-OH \longrightarrow \underset{\text{Methane}}{CH_4} + LiOH$$

(*ii*) **Reaction with ethylene oxide.** They react with ethylene oxide to give an addition product which on hydrolysis forms primary alcohols.

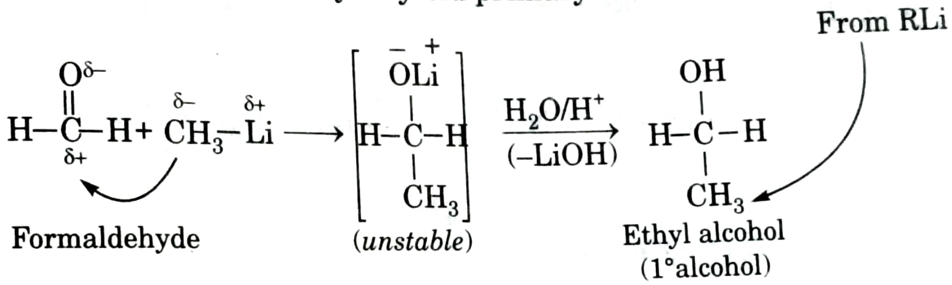


$$\underset{\text{Methyllithium}}{\overset{\delta-}{CH_3}-\overset{\delta+}{Li}} + \underset{\text{Ethylene oxide}}{\underset{O}{CH_2-CH_2}} \longrightarrow \underset{(unstable)}{\left[CH_3CH_2CH_2\overset{-}{O}\overset{+}{Li}\right]} \xrightarrow[\text{(-LiOH)}]{H_2O/H^+} \underset{\substack{\text{1-Propanol}\\ \text{(1° alcohol)}}}{CH_3CH_2CH_2OH}$$

From RLi

(*iii*) **Reaction with aldehydes.** Primary or secondary alcohols are obtained.

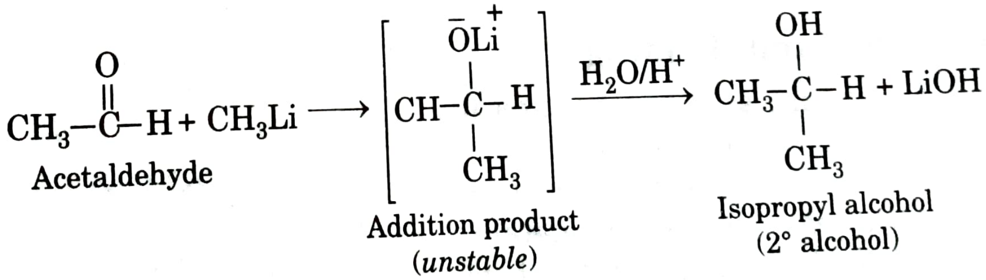
(*a*) Formaldehyde reacts with organolithium compounds to give addition products which on hydrolysis yield primary alcohols.



$$\underset{\text{Formaldehyde}}{H-\overset{\overset{O^{\delta-}}{\|}}{\underset{\delta+}{C}}-H} + \overset{\delta-}{CH_3}-\overset{\delta+}{Li} \longrightarrow \underset{(unstable)}{\left[H-\overset{\overset{\overset{-}{O}\overset{+}{Li}}{|}}{\underset{\underset{CH_3}{|}}{C}}-H\right]} \xrightarrow[(-LiOH)]{H_2O/H^+} \underset{\substack{\text{Ethyl alcohol}\\ \text{(1°alcohol)}}}{H-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H}$$

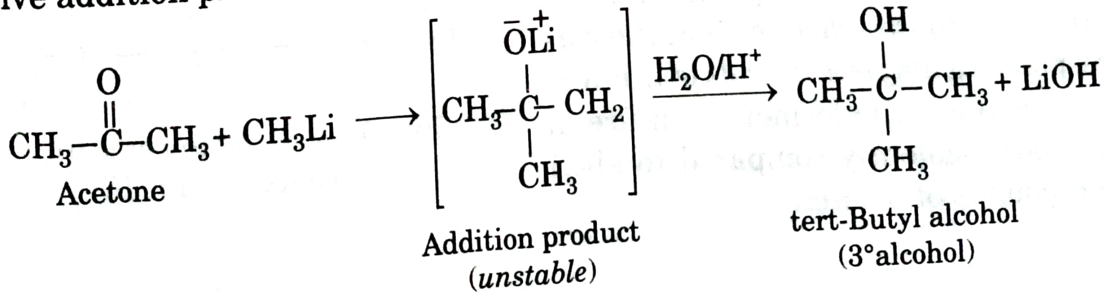
From RLi

(*b*) Other aldehydes react with organolithium compounds to give addition products which on hydrolysis yield secondary alcohols.



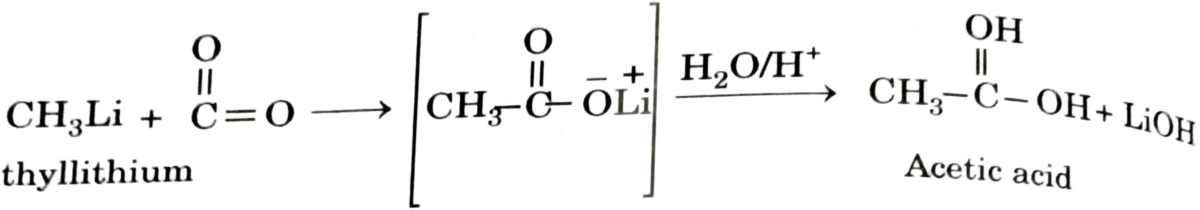
$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + CH_3Li \longrightarrow \underset{\substack{\text{Addition product}\\ (unstable)}}{\left[CH-\overset{\overset{\overset{-}{O}\overset{+}{Li}}{|}}{\underset{\underset{CH_3}{|}}{C}}-H\right]} \xrightarrow{H_2O/H^+} \underset{\substack{\text{Isopropyl alcohol}\\ \text{(2° alcohol)}}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H} + LiOH$$

(*iv*) **Reaction with ketones.** Organolithium compounds react with ketones to give addition products which on hydrolysis form tertiary alcohols.



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + CH_3Li \longrightarrow \underset{\substack{\text{Addition product}\\ (unstable)}}{\left[CH_3-\overset{\overset{\overset{-}{O}\overset{+}{Li}}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2\right]} \xrightarrow{H_2O/H^+} \underset{\substack{\text{tert-Butyl alcohol}\\ \text{(3°alcohol)}}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3} + LiOH$$

(*v*) **Reaction with carbon dioxide.** Organolithium compounds react with carbon dioxide (O=C=O) to give addition products which on hydrolysis yield carboxylic acids.



$$CH_3Li + \overset{O}{\overset{\|}{C}}=O \longrightarrow \left[CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Li}\right] \xrightarrow{H_2O/H^+} CH_3-\overset{OH}{\overset{\|}{C}}-OH + LiOH$$

Methyllithium

Addition product (*unstable*)

Acetic acid

Uses

Lithium alkyls and organometallic compounds of other alkali metals are frequently employed in the synthesis of a number of organic compounds. These uses are evident from the following reactions:

$$3LiR + BCl_3 \longrightarrow 3LiCl + BR_3$$

$$Li(C_6H_5) + (CH_3C_6H_4)_2CO \longrightarrow (CH_3C_6H_4)_2C(C_6H_5)OLi$$

$$\xrightarrow{H_2O} (CH_3C_6H_4)_2C(OH)C_6H_5 + LiOH$$

Tertiary carbinols

Organometallic Compounds of Magnesium

Magnesium forms main three types of organometallic compounds: (*i*) Compounds of MgR_2 type (R=alkyl or aryl group), (*ii*) Grignard reagents, RMgX and (*iii*) Organometallic compounds containing one alkyl (R) and one alkoxy group (OR′), R—Mg—OR′.

The dialkyl and diaryl magnesium compounds can be prepared in the following manner:

$$\text{LiR} + \text{R—Mg—X} \xrightarrow[\text{ether}]{\text{Solvent}} \text{MgR}_2 + \text{LiX}$$

$$\text{HgR}_2 + \text{Mg} \xrightarrow[\text{ether}]{\text{Solvent}} \text{MgR}_2 + \text{Hg}$$

Magnesium dimethyl, $Mg(CH_3)_2$ can be made from reaction of magnesium with mercury dimethyl.

$$\text{Hg(CH}_3)_2 + \text{Mg} \longrightarrow \text{Mg (CH}_3)_2 + \text{Hg}$$

or by the action of methyl iodide on a calcium-magnesium alloy in ether:

$$2\text{CH}_3\text{I} + \text{Ca} - \text{Mg} \longrightarrow \text{Mg (CH}_3)_2 + \text{Cal}_2$$

Magnesium dimethyl is a white, infusible solid, having vapour pressure of about 0.2 mm at 190°C. Apparently it is highly associated, presumably through methyl bridging. It is spontaneously inflammable in air and reacts very vigorously wi water. It undergoes many reactions of a Grignard reagent. $Mg(CH_3)_2$ is polymeric. It contains Mg—CH_3—Mg bridges in its structure.

Magnesium diphenyl, $Mg(C_6H_5)_2$ is formed by heating of magnesium with mercury diphenyl in a sealed tube:

$$Hg(C_6H_5)_2 + Mg \longrightarrow Mg\,(C_6H_5)_2 + Hg$$

It is a stable solid, decomposing at 280°C with the formation of diphenyl and magnesium. It is insoluble in benzene but has some solubility in ether, forming addition compounds. It reacts with lithium phenyl in ether solution forming lithium magnesium phenyl, $LiMg(C_6H_5)_3$.

$$LiC_6H_5 + Mg(C_6H_5)_2 \xrightarrow{\text{Ether}} LiMg(C_6H_5)_3$$

Another class of organometallic compounds of magnesium, called *Grignard reagents*, can be synthesised by refluxing alkyl or aryl halides with magnesium in dry solvent ether:

$$RBr + Mg \xrightarrow[\text{ether (dry)}]{\text{Solvent}} RMgBR$$

Grignard reagents are of great synthetic value in organic chemistry.

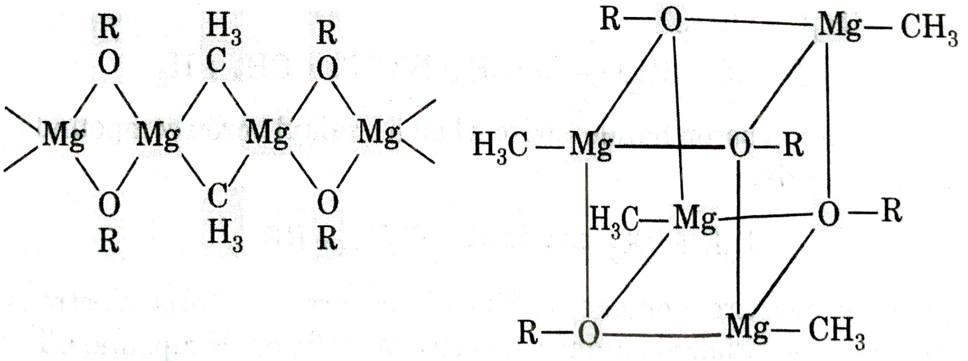
Organometallic compounds containing one alkyl and the other alkoxy group attached with Mg can be easily synthesised by reacting dialkyl magnesium compounds with alcohols in the following manner:

$$MgR_2 + R'OH \longrightarrow R\text{—}Mg\text{—}OR' + ROH$$

These compounds are polymeric and contain alkyl and alkoxy bridges between Mg atoms. The degree of polymerisation depends upon the bulk of the alkyl and alkoxy groups.

CH_3—Mg—OR (R is CH_3 or C_2H_5) exists in two polymeric forms whose structures are given below in Fig. 31.6 (a) and (b).

It should be noted that the lines shown between Mg and alkyl (CH_3) or alkoxy (OR) do not depict the exact bond order.



(*a*) (*b*)

Fig. 31.6. Two polymeric forms of CH_3–Mg –OR (R = CH_3 or C_2H_5) (*a*) Chain polymer (*b*) Three-dimensional polymer.

Organometallic Compounds of Boron: Organoboron Compounds

Boron forms the following types of organometallic compounds:

I. Alkyl or Aryl Borons, R_3B.

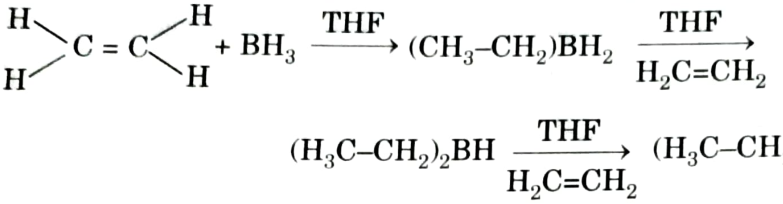
These compounds are also called *alkyl* or *aryl boranes*.

Preparation. Trialkyl or triaryl boranes are prepared as follows:

(*i*) $BX_3 + 3LiR \longrightarrow BR_3 + 3LiX$ (R = alkyl or aryl group).

Actually, in this reaction we get a mixture of BRX_2, BR_2X and BR_3.

(*ii*)



$$H_2C=CH_2 + BH_3 \xrightarrow{THF} (CH_3\text{–}CH_2)BH_2 \xrightarrow[H_2C=CH_2]{THF}$$

$$(H_3C\text{–}CH_2)_2BH \xrightarrow[H_2C=CH_2]{THF} (H_3C\text{–}CH_2)_3B$$

(*iii*) Trialkyl boranes can also be prepared, for example, from reaction of 1-butene with diborane.

$$\underset{\text{1-butene}}{6CH_3CH_2CH = CH_2} + \underset{\text{diborane}}{B_2H_6} \longrightarrow 2(CH_3CH_2CH_2CH_3)_3B$$

Properties. Trimethyl borane is a gas while triethyl and tri-*n*-propyl boranes are liquids and triphenyl borane is a solid. The lower trialkyl boranes take fire spontaneously in air, the cautious oxidation of trialkyl boranes yields borate esters. Thus, oxidation with hydrogen peroxide yields a triakyl borate:

$$R_3B\ ^{(Na^+\ \bar{C}\equiv H)}\ B(OR)_3$$

Triphenyl borane $(C_6H_5)_3B$ is not spontaneously inflammable, but is very easily oxidised and must be protected from air. Trialkyl and triaryl boranes are very reluctant to react with water and only at high temperatures they are partially de-alkylated. At about 200°C, trimethyl borane is hydrolysed to dimethyl borinic acid, $(CH_3)_2B(OH)_3$:

$$(CH_3)_3B + 3H_2O \longrightarrow (CH_3)_2B(OH)_3 + CH_4 + H_2$$

Mixtures of alkyl boron halides arise when a trialkyl boron compound is mixed with a boron trihalide:

$$R_3B + BX_3 \rightleftharpoons R_2BX + RBX_2$$

Trialkyl boranes are monomeric. Since there are only three clectrons in the valency shell of boron, trialkyl boranes are electron-deficient compounds. They form addition compounds with ammonia, amines and hydrazine.

Uses Alkyl and aryl borons are of great synthetic value. These are employed in the synthesis of hydrocarbons, alcohols, phenols, carbonyl compounds and carboxylic acids.

$$\begin{tikzcd}
 & RH \\
R_3B \arrow[ur, "H+"] \arrow[r, "H_2O"] \arrow[dr, "\text{(i) } CO", "\text{(ii) } H_2O_2"'] & ROH \\
 & R_3COH
\end{tikzcd}$$

$$R_2BH \xrightarrow[\text{(ii) } H_2O_2]{\text{(i) } CO} R_2CO$$

$$RBH_2 \xrightarrow[\text{(ii) } H_2O_2]{\text{(i) } CO} RCOOH$$

II. Boronic and Boronous Acids.

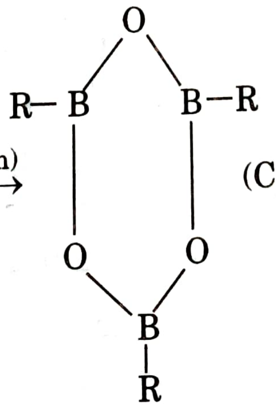
Boronic acid is $B(OH)_2R$ and boronous acid is $B(OH)R$. These are prepared as follows:

$$\begin{tikzcd}
BF_3 + RMgBr \arrow[r, "\text{Ether}", "-MgFBr"'] & RBF_2 \arrow[r, "2H_2O", "-2HF"'] \arrow[d, "\text{RMg Br (ether)}", "-MgFBr"'] & \begin{array}{l} RB(OH)_2 \\ \text{Boronic acid} \end{array} \\
 & R_4BF \arrow[r, "H_2O", "-HF"'] & \begin{array}{c} RBOH \\ \text{Boronous acid} \end{array}
\end{tikzcd}$$

The strength of these acids depends upon the nature of R group.

Boronic acid is stable in water but on warming it polymerises into a cyclic trimer

$3RB(OH)_2 \xrightarrow[(-3H_2O)]{\Delta(\text{Dehydration})}$



(Cyclic trimer) + $3H_2O$

$$\text{or } \underset{\text{Boronic acid}}{3RB(OH)_2} \xrightarrow[(-3H_2O)]{\Delta(\text{Dehydration})} \underset{\substack{\text{Boranic} \\ \text{anhydride} \\ \text{or boroxine}}}{(RBO)_3} + 3H_2O$$

III. Salts of $M^+ [BR_4]^-$ Type.

Preparation. (*i*) Trialkyl borons (R_3B) react with alkyl lithium (RLi) to form the salts of $M^+ [BR_4]^-$ type.

$$\underset{\text{Trialkyl boron}}{R_3B} + \underset{\text{Alkyl lithium}}{RLi} \longrightarrow Li^+[BR_4]^-$$

(*ii*) $Li^+ [B(C_6H_5)_4]^-$ is prepared as follows:

$$\underset{\text{Triphenyl boron}}{(C_6H_5)_3B} + \underset{\text{Lithium phenyl}}{Li\ C_6H_5} \xrightarrow{\text{Ether}} Li^+ [B(C_6H_5)_4]^-$$

Properties. (*i*) $Li^+[B(C_6H_5)_4]^-$ is insoluble in non-polar solvents but soluble in alcohol and water. The sodium salt, $Na^+[B(C_6H_5)]^-$ is used as an analytical reagent for the gravimetic estimation of heavy alkali metal ions (K^+, Rb^+ and Cs^+) and a number of other cations. $NaB(C_6H_5)_4$ can cause complete precipitation of K^+, Rb^+ and Cs^+ from aqueous solutions of their salts:

$$NaB(C_6H_5)_4 + KCl \longrightarrow NaCl + KB(C_6H_5)_4$$

Structure. The $[R_4B]^-$ anion is tetrahedral in shape, with a complete octet around boron. It is isoelectronic with R_4N^+ and R_4C.

Organometallic Compounds of Lead.

Preparation. The tetraalkyl or tetraaryl lead can be prepared by any one of the following reactions:

$$LiR + 2PbCl_2 \longrightarrow PbR_4 + Pb + 4LiCl$$

$$4AlR_3 + 6PbCl_2 \longrightarrow 3PbR_4 + 4AlCl_3 + 3Pb$$

$$4RMgX + 2PbCl_2 \longrightarrow PbR_4 + 4Mg(X)Cl + 3Pb$$

$$4RX \xrightarrow[\text{alloy}]{\text{Pb-Na}} PbR_4 + 4NaX$$

Among these compounds, tetraethyl lead, $(C_2H_5)_2Pb$ is an important organolead, since it finds use in industry under the name TEL. It is prepared:

(*i*) By the action of ethylmagnesium iodide on lead chloride.

$$\underset{\substack{\text{Ethylmagnesium}\\ \text{iodide}}}{4C_2H_5MgI} + 2PbCl_2 \longrightarrow \underset{\text{Tetraethyllead}}{(C_2H_5)_4Pb} + Pb + 4MgICl$$

(*ii*) By heating ethyl chloride with a sodium-lead alloy.

$$\underset{\text{Ethyl chloride}}{4C_2H_5Cl} + (4Na + Pb)\ \text{alloy} \longrightarrow \underset{\text{Tetraethyllead}}{(C_2H_5)_4Pb} + 4NaCl$$

It is pertinent to add here that no matter whether we take Pb(II) or Pb(IV) compounds, for the preparation of organolead compounds, we almost always end up with organolead compounds of Pb(IV).

Although the extent of catenation between Pb atoms in organolead compounds is very small as compared to the compounds of Si and Sn, yet there are few dimeric organo compounds of Pb which contain Pb—Pb bonds. Pb_2R_6 is an example of such compounds.

Properties Tetraalkyl and tetraaryl compounds of lead are monomeric volatile liquids which are quite stable. Tetraethyl lead is the most widely used organolead compound. It is mixed in petrol and serves as an excellent anti-knock in automobile engines.

Tetraethyllead is a colourless liquid, bp 202°C. Like other lead compounds, it is a highly toxic substance. It is soluble in organic liquids like gasoline but is insoluble in water. Being largely covalent in nature, tetraethyllead has low reactivity.

Use of $(C_2H_5)_4Pb$ as an anti-knock Tetraethyllead is an important *anti-knock* additive in gasoline (petrol) used in automobile engines. It improves its *Octane Number*. One disadvantage in using this gasoline additive is that its combustion product, lead oxide, gets reduced to metallic lead. This is deposited inside the cylinders of the engine, causing clogging of the cylinder valves. To avoid accumulation of metallic lead in engine cylinders, ethylene bromide ($BrCH_2CH_2Br$) is added along with tetraethyllead into gasoline. The ethylene bromide reacts with the lead in the engine and converts it into gaseous lead bromide ($PbBr_2$). The lead bromide is discharged through the exhaust pipe, However, lead compounds are very poisonous and automobile exhaust poses a big health hazard in large cities.

Organometallic Compounds of Zn, Cd and Hg

These metals form dialkyls and diaryls of R_2M type. These metals also form alkyl metal halides (RMX).

Preparation (*i*) Dialkyls and diaryls of zinc, cadmium and mercury can be best prepared from the action of the appropriate Grignard reagent on metal halide:

$$2RMgCl + MCl_2 \longrightarrow R_2M + 2MgCl_2$$

where R = alkyl or aryl and M = Zn, Cd or Hg.

(*ii*) These compounds can also be prepared from reactions such as the following:

$$2CH_3I + Zn\text{-}Mg \longrightarrow (CH_3)_2Zn + MgI_2$$

$$2C_2H_5ZnI \xrightarrow{\text{Heat}} (C_2H_5)_2Zn + ZnI_2$$

$$(CH_3)_2Hg + Zn \longrightarrow (CH_3)_2\,Zn + Hg$$

$$2CH_3Li + CdCl_2 \longrightarrow (CH_3)_2Cd + 2LiCl$$

$$(C_6H_5)_2Hg + Cd \longrightarrow [(C_5H_5)_2Cd + Hg$$

$$2RNa + HgCl_2 \longrightarrow R_2Hg + 2NaCl$$

$$Hg + 2CH_3Br + 2Na \longrightarrow (CH_3)_2Hg + 2NaBr$$

(*iii*) Zinc, cadmium and mercury also form alkyl metal halides, RMX and these can be obtained from the dialkyl metals by the reaction with metal dihalides:

$$R_2M + MX_2 \longrightarrow 2RMX$$

(*iv*) Alkyl metal halides can also be prepared from reactions of alkyl halides with metal:

$$RX + M \longrightarrow RMX$$

or Grignard reagent with metal halides:

$$RMgCl + MCl_2 \longrightarrow RMCl + MgCl_2$$

Properties. Dialkyls of zinc, cadmium and mercury are colourless liquids while the diaryls of these metals are colourless solids. Dialkyls and diaryls of zinc take fire immediately on exposure to air and burn with an intense flame, yielding a white smoke of zinc oxide. The corresponding alkyls of cadmium do not ignite spontaneously in air unless favoured by a large surface area; those of mercury do not ignite at all. Yet the thermal stability of zinc alkyls is considerably higher than that of the cadmium or the mercury compounds showing that there is no direct relationship between stability and reactivity. Mercury alkyls are exceedingly poisonous. Many mercury compounds are very toxic and this biological activity has led to the synthesis of a large number of compounds in search for materials which may be of medicinal value. The alkyls of Group IIB metals are monomeric and linear. The reactivity of organometallic compounds of Group IIB metals decreases down the group. The zinc and cadmium compounds both form adducts with donor molecules such as ethers and amines. Cadmium is readily complexed than zinc and mercury compounds form no adducts at all with ethers and amines.

Alkyl and aryl mercury halides are monomeric linear molecules; conversion into hydroxides, cyanides and other derivatives is easily accomplished by ion-exchange or by the use of silver salts:

$$CH_3HgI + AgCN \longrightarrow CH_3HgCN + AgI.$$

The compounds ranging from salt-like (RHg^+X^-) (where X is highly electronegative such as F^-, NO_3^-, $\frac{1}{3}(SO_4^{2-})$ to non-polar compounds, soluble in organic solvents when X is less electronegative (*e.g.*, I^-) are known. Alkyl zinc halides are associated compounds.

Applications. Many alkyls of zinc have been found useful in many syntheses of zinc complexes. Cadmium compounds have proved very useful for converting carboxylic chlorides to ketones and they have essentially replaced zinc compounds for this purpose. Mercury compounds are useful in the synthesis of other organometallic compounds particularly when pure products are required. We have already mentioned about their use in the preparation of sodium and lithium compounds Organomercury compounds may also be used as prime reagent to attach any organi group to silicon or arsenic or boron by action on their chlorides.

Ferrocene, $Fe(C_5H_5)_2$

Preparation of Ferrocene, $Fe(C_5H_5)_2$

Ferrocene, can be prepared:

(i) By the action of anhydrous iron (II) halides on cyclopentadiene (C_5H_6) *in presene of a strong base like diethyl amine,* $NH(C_2H_5)_2$

$$FeCl_2 + 2C_5H_6 + 2NH\,(C_2H_5)_2 \longrightarrow (C_5H_5)_2\,Fe + 2(C_2H_5)_2\,NH_2Cl$$

$$\textit{or}\ 2(C_2H_5)_2\,NH.\,HCl$$

(ii) By the action of Fe (II) halide on sodium cyclopentadiene (NaC_5H_5). In this method cyclopentadiene (C_6H_5) is first converted into sodium cyclopentadienide (C_5H_5 Na) by treating it with finely-divided dispersed Na in tetrahydrofuran (THF).

$$\underset{\text{Cyclopentadiene}}{C_5H_5 + Na} \rightleftharpoons \underset{\text{Sodium cyclopentadienide}}{C_5H_5Na + \frac{1}{2} H_2}$$

C_5H_5 Na is then treated with $FeCl_2$.

$2C_5H_5Na + FeCl_2 \rightarrow Fe(C_5H_5)_2 + 2NaCl$.

(iii) By the action of Grignard reagent of cyclopentadiene, (C_5H_5)MgBr on $FeCl_2$.

$$FeCl_2 + 2(C_5H_5)MgBr \longrightarrow Fe(C_5H_5)_2 + MgCl_2 + MgBr_2.$$

Commercial Preparation of $Fe(C_5H_5)_2$

On large scale, $Fe(C_5H_5)_2$ can be obtained by the action of cyclopentadien (C_5H_6) on Fe or FeO.

$$2C_5H_6 + Fe \xrightarrow{300°C} (C_5H_5)_2\,Fe + H_2$$

$$2C_5H_6 + FeO \xrightarrow{250°} (C_5H_5)_2\,Fe + H_2O$$

Physical Properties of Ferrocene

Some important physical properties of ferrocene are:

(*i*) It is an orange crystalline solid.

(*ii*) It is soluble in organic solvents.

(*iii*) Its melting point is 174°C.

(*iv*) It sublimes without decomposition.

(*v*) It has high thermal stability, up to about 500°C

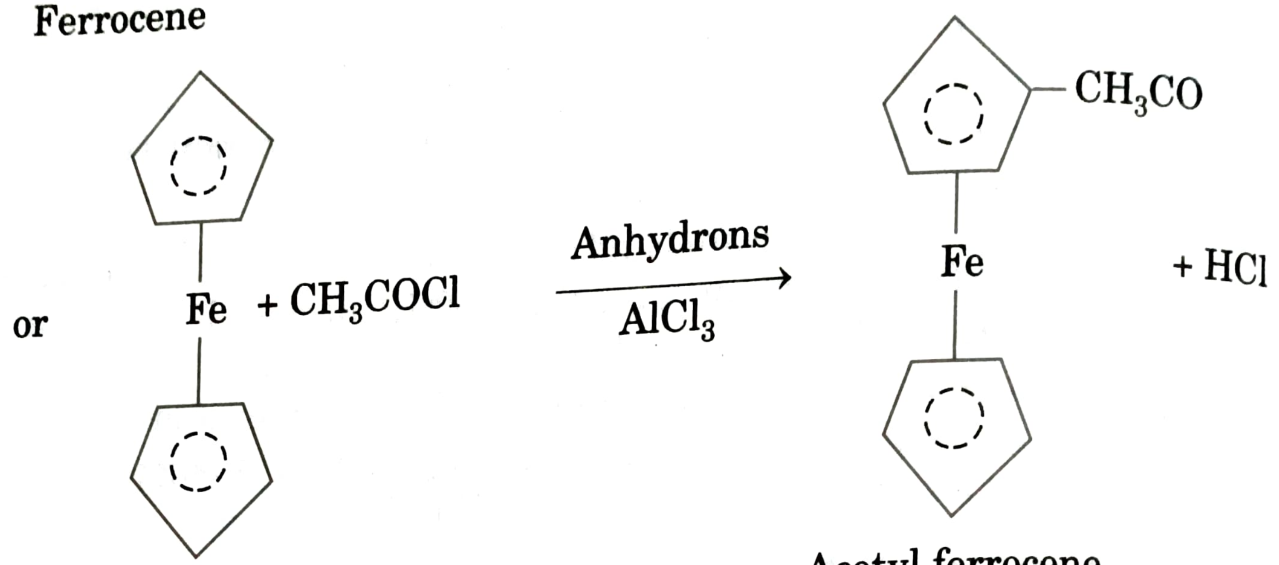
(*vi*) Unlike other organometallic compounds, ferrocene is stable to air and water.

Chemical Reactions of Ferrocene

2. Friedel-Craft's acetylation. (1) Fe$(C_5H_5)_2$ undergoes acetylation reactions with acetyl chloride (CH_3COCl) in presence of anhydrous $AlCl_3$.

$$(a)\ \underset{\text{Ferrocene}}{Fe(C_5H_5)_2} + CH_3COCl \xrightarrow[AlCl_3]{\text{Anhydrous}} \underset{\text{Acetyl ferrocene}}{(C_6H_4CH_3CO) — Fe(C_5H_5)} + HCl$$

or

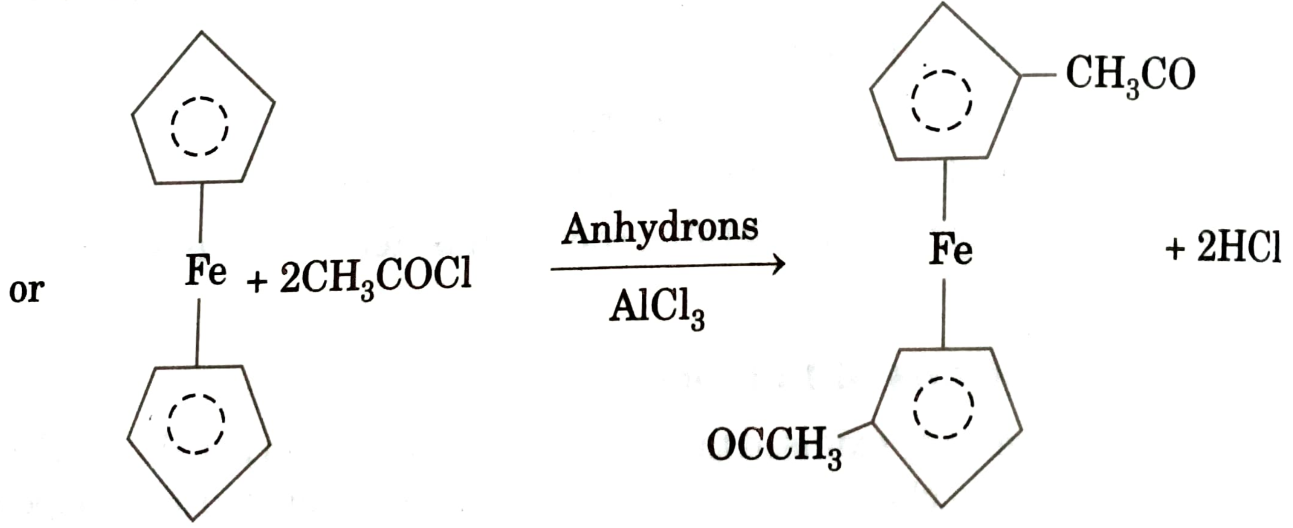


Ferrocene

Acetyl ferrocene

$$(b)\ \underset{\text{Ferrocene}}{Fe(C_5H_5)_2} + 2CH_3COCl \xrightarrow[AlCl_3]{\text{Anhydrous}} \underset{\text{1, 1′–diacetyl ferrocene}}{(C_5H_4CH_3CO)–Fe–(C_5H_4CH_3CO)} + 2HCl$$

or



Ferrocene

1, 1′ - diacetyl ferrocene

This reaction occurs *more readily with ferrocene than with benzene*. Since this reaction involves electrophilic attack by the CH_3CO^+ cation, this indicates that *there is a greater availability of negative charge on the π-cyclopentadienyl rings than on benzene.*

The intimate mechanism of electrophilic attack on ferrocene is given in Fig. 31.48. The electrophile (E^+) first coordinates to the iron, oxidising it from iron (II) to iron (III) before being transferred to the π-cyclopentadienyl ring. The final step involves expulsion of a proton with simultaneous reduction of Fe (III) back to Fe (II).

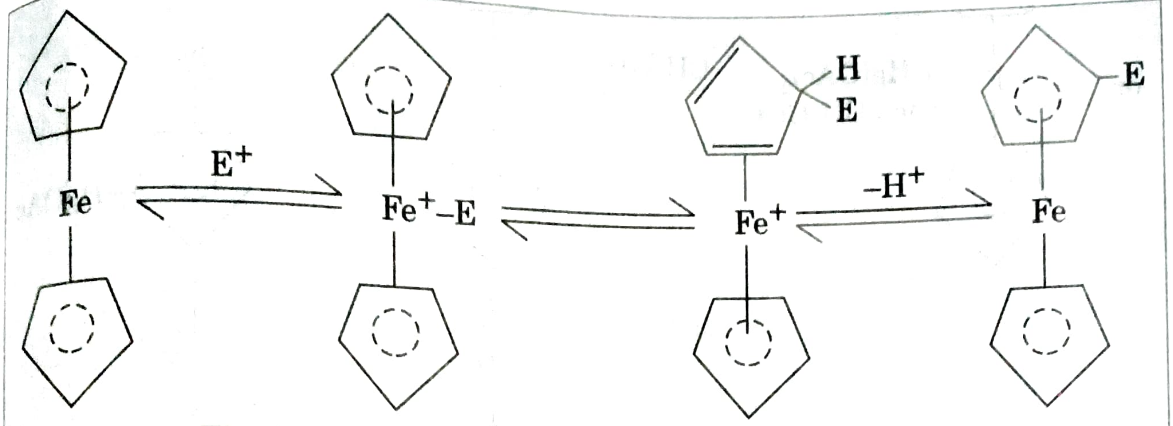
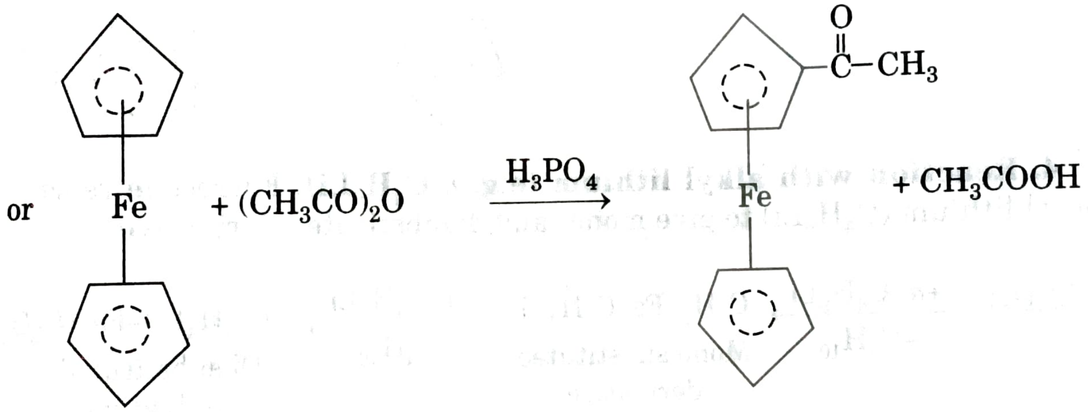


Fig. 31.48. Mechanism of electrophilic attack on ferrocene

(*ii*) Acetylation of a ring in ferrocene is also brought about by acetic anhydride in the presence of phosphoric acid as a catalyst.

$$Fe(C_5H_5)_2 + (CH_3CO)_2O \xrightarrow{H_3PO_4} (CH_3COC_5H_4)\,Fe(C_5H_5) + CH_3COOH$$



3. Reaction with mercuric acetate, Hg(OAc)$_2$: Metallation. Ferrocene reacts with mercuric acetate (HgOAc) to give mono and disubstituted products.

The substituted derivatives of mercuric acetate react with iodide to give iodine derivatives. *This provides an indirect method for carrying out iodination of ferrocene.*

$$Fe(C_5H_5)_2 + Hg(OAc)_2 \xrightarrow{CH_3OH}$$

$$C_5H_4\,HgOAc–Fe–C_5H_5 + C_5H_4\,Hg\,OAc\,–Fe–C_5H_4\,HgOAc$$

$$\downarrow I_2 \qquad\qquad \downarrow I_2$$

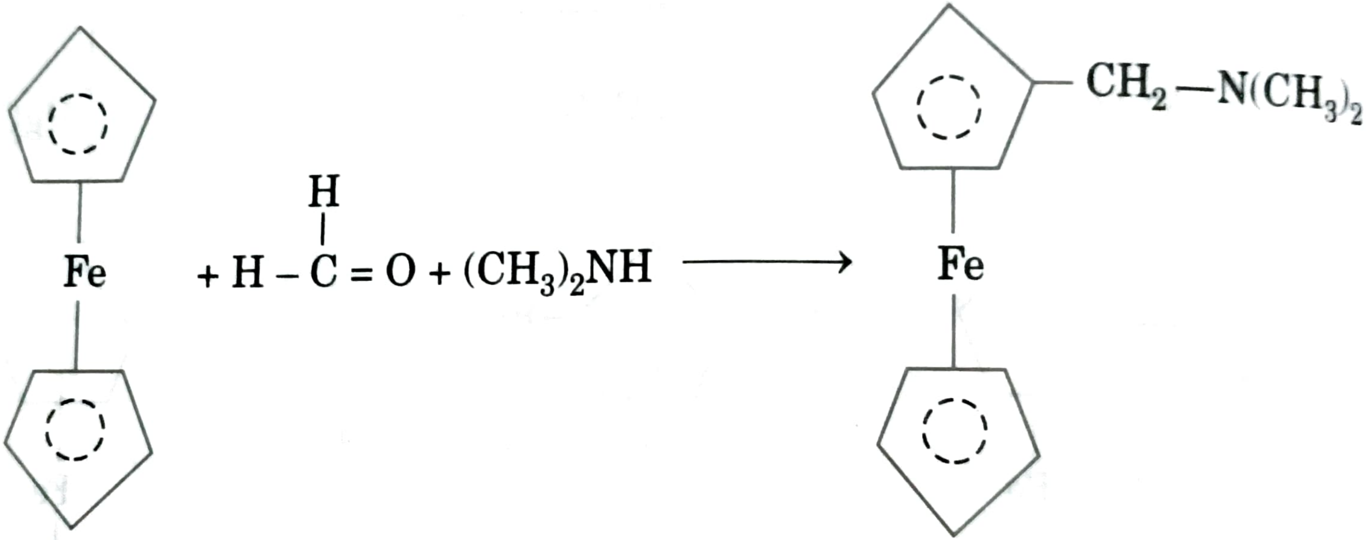
$C_5H_4I–Fe–C_5H_5$
Monosubstituted product

$C_5H_4I–Fe–C_5H_4I$
Disubstituted product

5. Mannich condensation: Amino methylation. Ferrocene reacts with formaldehyde in the presence of dimethylamine to give mono-substituted ferrocene. This reaction is called **Mannich condensation reaction**.

$$Fe\,(C_5H_5)_2 + HCHO + HN(CH_3)_2 \xrightarrow[H_3PO_4]{CH_3COOH} (C_5H_5)\,Fe[C_5H_4{-}CH_2{-}N(CH_3)_2] + H_2O$$

or



This reaction shows higher reactivity of ferrocene rings than benzene which does not undergo Mannich condensation. Other reactive rings which undergo this condensation are thiophene and phenol.