B. Sc. Part-III (Hons), Paper-VI, Gr-C, Unit-1 Organometallic Compds (Contd)

⟹ **Organometallic compounds of Magnesium:** Magnesium form different types of organometallic compounds: 1. Dialkyl or diaryl of Mg. 2. Grignard reagent (R-Mg-X)/Alkyl or aryl magnesium halides 3. Alkyl-alkoxy magnesium (R-Mg-OR')

1. **Dialkyl/aryl magnesium Compds:** Magnesium form compounds of MgR_2 type (R = alkyl or aryl group), called dialkyl or diaryl magnesium. e.g. $Mg(CH_3)_2$, $Mg(C_2H_5)_2$ etc.

* **Methods of Preparation:** (i) when alkyl lithium is treated with Grignard reagent in dry ethers, magnesium dialkyl or diaryl is formed.

$$LiR + R\text{-}Mg\text{-}X \xrightarrow[(solvent)]{Ether} MgR_2 + LiX \quad (R = alkyl\ or\ aryl\ group)$$

(ii) When mercury dialkyl/aryl is heated with magnesium, magnesium dialkyl/aryl is formed. e.g. $Hg(CH_3)_2 + Mg \xrightarrow{\Delta} Mg(CH_3)_2 + Hg$; $Hg(C_2H_5)_2 + Mg \longrightarrow Mg(C_2H_5)_2 + Hg$.
(Mercury dimethyl) (Dimethyl magnesium / Magnesium dimethyl).

(iii) Methyl iodide reacts with Ca-Mg alloy in ether to form dimethyl magnesium (Specific method)

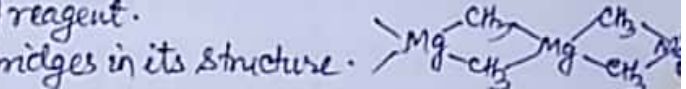
$$2CH_3I + Ca\text{-}Mg \longrightarrow Mg(CH_3)_2 + CaI_2$$

* **Properties:** (i) Magnesium dimethyl (Dimethyl magnesium) is a white, infusible solid. (ii) It is spontaneously inflammable in air. (iii) It reacts very vigorously with water to form methane (CH_4).

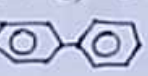
$$Mg(CH_3)_2 + 2H_2O \longrightarrow \underset{(Methane)}{2CH_4} + Mg(OH)_2$$

(iv) It undergoes many reactions of Grignard reagent.

(v) It is polymeric and contains Mg-CH_3-Mg bridges in its structure.



Magnesium diphenyl: (i) It is a white stable solid. (ii) It decomposes at 280°C into diphenyl & magnesium. $Mg(C_6H_5)_2 \xrightarrow{\Delta} H_5C_6\text{-}C_6H_5$ (Diphenyl) $+ Mg$



(iii) It is insoluble in benzene but little soluble in ether forming addition compounds.

(iv) It reacts with lithium phenyl in ether solution forming lithium magnesium phenyl.

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

⟹ **Organometallic compounds of Group-13 elements (B & Al):**

Organo boron Compounds: Boron forms alkyl or aryl borons of type R_3B (R = alkyl or aryl group). They are also called alkyl or aryl boranes. e.g. $(C_2H_5)_3B$, $(C_6H_5)_3B$ etc.

* **Methods of Preparation:** (i) **From Boron trihalide:** When boron trihalide is treated with alkyl or aryl lithium, trialkyl or aryl borane is formed.

$$BX_3 + \underset{(Excess)}{3LiR} \longrightarrow R_3B + LiX \quad (Where\ R = alkyl\ or\ aryl\ group,\ X = Cl, Br\ or\ I)$$

(ii) **From boron hydride:** When boron hydride (BH_3) is treated with alkene (e.g. ethene) in THF (solvent), trialkyl borane is formed.

$$e.g.;\ BH_3 + \underset{(Ethene)}{H_2C=CH_2} \xrightarrow[(3\ steps)]{THF} \underset{(Triethyl\ borane)}{(H_5C\text{-}CH_2)_3B}$$

(iii) **From diborane:** When diborane is reacted with alkene (e.g. butene), trialkyl borane is formed.

$$\underset{(1\text{-}Butene)}{H_3C\text{-}CH_2\text{-}CH=CH_2} + \underset{(Diborane)}{B_2H_6} \longrightarrow \underset{(Tributyl\ borane)}{2(CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2)_3B}$$

*Properties: (i) Trimethylborane is a gas, triethyl & tripropyl boranes are liquids, and triphenylborane is a solid. (ii) Lower trialkyl boranes catch fire spontaneously in air. (iii) Trialkylboranes undergo oxidation with H_2O_2 cautiously to yield trialkyl borate.

$$R_3B + 3H_2O_2 \longrightarrow B(OR)_3 + 3H_2O.$$
(Trialkyl borate)

Triphenyl borane is not spontaneously inflammable, but very easily oxidized by air.

(iv) Trialkyl & triaryl boranes very reluctant against water at ordinary temp. However, they are partially dealkylated at higher temperature. Trimethyl borane is hydrolysed at 200°C into dimethyl borinic acid.

$$(H_3C)_3B + 3H_2O \xrightarrow{200°C} (H_3C)_2B(OH)_3 + CH_4 + H_2.$$
(Trimethylborane) (Dimethyl borinic acid)

(v) Trialkyl boranes are electron deficient compounds. They are monomeric. They form addition compounds with NH_3, $R-NH_2$, H_2N-NH_2 (Hydrazine) etc.

e.g. $R_3B + :NH_3 \longrightarrow [R_3B \leftarrow :NH_3]$
(Addition compd.)

*Structure: They are monomeric. They have three B–C bonds at 120°, giving triangular planar structure.

(R = alkyl or aryl gr.)

*Uses: The alkyl and aryl boranes have great synthetic value. They used in synthesis of different classes of organic compds, e.g. Alkanes, alcohols, phenols, aldehydes, ketones etc.

⟹ Organoaluminium compounds: Aluminium forms alkyl aluminium of type R_3Al.

*Methods of preparation: (i) From alkenes: When alkene is treated with aluminium metal and hydrogen, alkyl aluminium is formed.

e.g. $H_2C=CH_2 + 2Al + 3H_2 \longrightarrow 2(H_3C-CH_2)_3Al$
(Ethene) (Triethylaluminium)

(ii) From alkyl halides: When alkyl halide is treated with Al-metal, alkyl aluminium halide is formed, which converted into trialkyl aluminium by reduction with Mg.

e.g. $3CH_3I + 2Al \longrightarrow (CH_3)_2AlI + CH_3AlI_2$; $(CH_3)_2AlI + CH_3AlI_2 \xrightarrow{Mg} (CH_3)_3Al + MgI_2$
(Methyliodide) (Trimethylaluminium)

(iii) From Grignard reagent or Organolithium compds: When Grignard reagent or organolithium compound is treated with aluminium chloride, trialkyl or triaryl aluminium is formed. e.g. $3C_6H_5Mg-Cl + AlCl_3 \longrightarrow (C_6H_5)_3Al + 3MgCl_2$
(Phenyl magnesium chloride Grignard reagent) (Triphenylaluminium)

$3H_3C-Li + AlCl_3 \longrightarrow Al(CH_3)_3 + 3LiCl$
(methyl Lithium) (Trimethyl aluminium)

*Properties: (i) Lower trialkyl aluminium compds. are reactive liquids. (ii) They are catch fire/inflaming in air or O_2. (iii) They are react explosively with water/moisture. Reactivity with air (O_2) and water decrease with the increase of mol. wt/size of alkyl or aryl groups.

$R_3Al + 3H_2O \longrightarrow 3RH + Al(OH)_3$ (R = alkyl or aryl group.)

(iv) Trialkyl aluminium compds undergo controlled oxidation to give aluminium alkoxides.

$2R_3Al + 3O_2 \longrightarrow 2Al(OR)_3$ (R = alkyl group)

e.g. $2(C_2H_5)_3Al + 3O_2 \longrightarrow 2Al(OC_2H_5)_3$
(Aluminium ethoxide)

(v) Aluminium alkyls or Trialkyl aluminium compds. also react with alkyl lithium in benzene to form lithium aluminium alkyls.

e.g. $(C_2H_5)Al + LiC_2H_5 \xrightarrow{(Benzene)} LiAl(C_2H_5)_4$

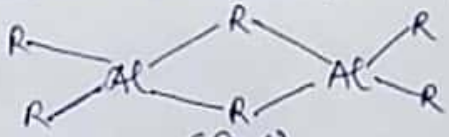
(Triethyl aluminium) (ethyl Lithium) (Lithium aluminium methyl)

* **Uses:** (i) Trimethyl & triethyl aluminium have used as jet fuels.

(ii) Trialkyl aluminium & alkyl hydrides together with transition metal halides / alkoxides are used as catalysts (e.g., Ziegler catalysts) for polymerisation of C_2H_4, C_3H_6 etc. (iii) They are also used widely as reducing and alkylating agents for transition metal complexes

(iv) Alkyl aluminium compds. are used as reagents for the synthesis of other organometallic or organic compounds.

* **Structure & Bonding:** Trialkyl or aryl aluminium compounds are generally dimeric. They contain two bridged Al-R-Al bonds and four terminal R-Al bonds in their structures. The bridging alkyl C-atoms are involved in three centred two electrons bonds. These bonds involve sp^3-hybrid orbitals from the two Al-atoms as well as from bridging C-atom (fig. 1)



(R = alkyl or aryl group)

(fig. 1)