Types of organometallic compounds ÷

four types.

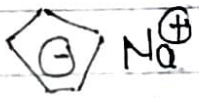
- Ionic
- covalent (Bicentric bielectronic)
- Electron deficient
- Trans.

I. Ionic organometallic compounds ÷ primarily formed by the electro +ve metals of Gp I & II.

→ The metal is present in the cationic form M^{n+} and the group is carbanion.

→ The -ve charge of carbanion can either be localized a particular carbon atom or can be delocalized over carbon atoms.

$CH_3CH_2^{\ominus}Na^{\oplus}$ — Localised -ve charge



Delocalised -ve charge.

→ Ionic organometallic compounds are typically ionic and insoluble in non-polar solvents.

→ These occur in crystalline form when pure & their stru depend upon the ~~stability of the anion~~ nature of it in the crystal.

→ Ionic organometallic compounds are readily hydrolysed

$C_4H_9Na + H_2O \longrightarrow C_4H_{10} + NaOH$

Butyl sodium. Butane.

→ The reactivity of ionic organometallic compounds depends stability of the anion.

2. Covalent organometallic compounds (Bicentric bielectronic)

→ Most simplest & most studied, that contain a classical covalent bond, shared by metal & organic gp each contributing a single electron.

→ These compounds are readily formed by representative elem of gp 13, 14 & 15 in addition to elements of gp 12 i.e Zn, Cd & Hg.

→ Covalent organometallic compounds are insoluble in water bu are readily soluble in organic solvents.

→ These compounds display the properties of typical organi. compounds. e.g. These are volatile & soluble in organic solvents.

e.g $(C_2H_5)_4Pb$, $(CH_3)_2Hg$ $(C_2H_5)_2Zn$, $(CH_4)_4Si$ $(CH_3)_3Al$ etc.

→ Presence of electron attracting substituents in organic group ↑s the stability of M-C bond in covalent organometallic compounds.

→ Thus compounds, containing $M-CF_3$ & $M-C_6H_5$ bonds are more stable thermally than their non-flourinated analo

3. Electron deficient Organometallic Organometallic Compound

→ formed by Be, Li, Mg & Al.

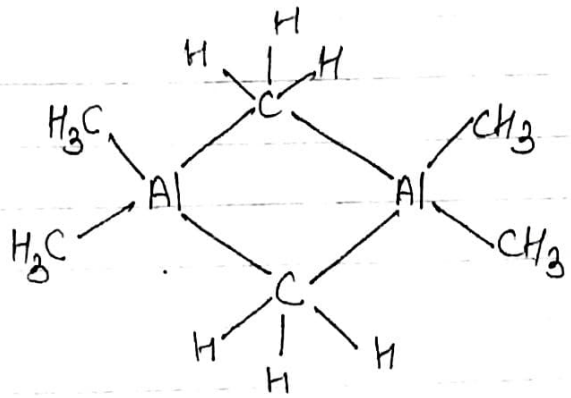
→ All these metals form very strongly polarizing cations cations with a very high charge to radius ratio) and the electron density away from the anion i.e. it polariz the anion.)

→ As a result, the charge seperation in the compound $M^+CH_3^-$ ↑ses & a polar covalent bonds results.

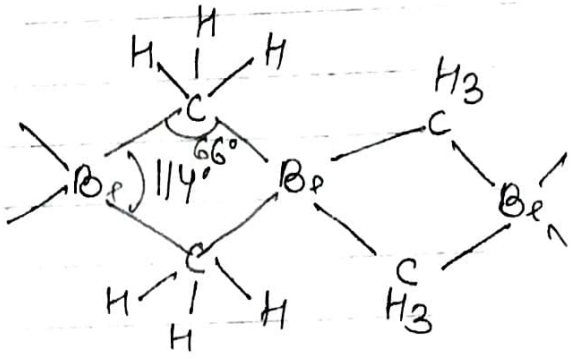
M^+CH_3 changes to $M^{\delta+}-CH_3^{\delta-}$

→ Such covalent but polar structures have a tendency to associate strongly that lead to the formation of polymeric structures.

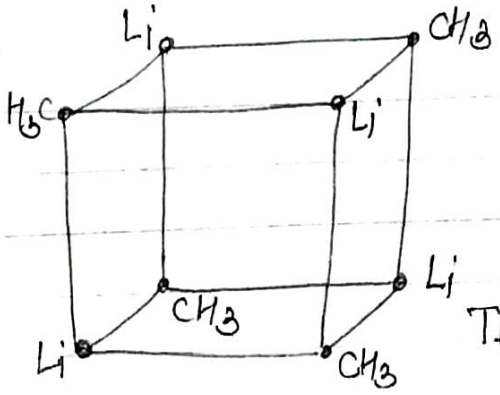
e.g.



Dimeric $[Al(CH_3)_3]_2$



Polymeric $[BeCH_3)_2]_n$



Tetrameric methyl lithium $(CH_3Li)_4$

4. Transition metal Organometallic Compounds :-

In these compounds, the transition metal forms bonds ~~between~~ to more than one carbon atoms of the same organic compou

→ This type of bonding is of considerable importance in transition metal chemistry.

→ The interaction primarily occurs between the π- orbitals of th organic ligand and the appropriate p or d- orbitals of t transition metal atom.

Bonding in Organometallic compounds ÷

1. Ionic Bonding	2. σ- Covalent Bonding	3. Multiple Covalent Bond.
→ Observed in organometallic compounds of alkali & alkaline earth metals. → Ionic Organometallic compounds are highly reactive & undergo easy hydrolysis as well as oxidation in air.	· Observed in organometallic compounds of main gp as well as some transition metals e.g. $Ti(CH_3)_4$, $(CH_3)_5Nb$. $W(CH_3)_2$ etc. → But these are highly unstable.	

6. Covalent Bonding ÷

Organometallic compounds containing σ- covalent bonds are thermodynamically stable

→ The compounds with weak M-C bonds (e.g. CdR_2, HgR_2, $PbBiR_3$) readily pyrolyse with the deposition of the metal. These compounds are thermodynamically unstable w.r.t. their decomposition to metals & hydrocarbons.

→ Most of the transition metal carbon σ- bonded organome. compounds are kinetically unstable.

→ This basically arises on account of the availability of the empty lower energy inner d- orbitals on the metals. This explains why Me_4Si is stable upto 500°C where Me_4Ti undergoes spontaneous decomposition at room temperature.

→ The instability of these compounds arise from the incomplete occupation of d- orbitals.

→ when electron pairs donated by π- acceptor ligand (eg. CO PR_3, C_5H_5) fill the d- orbitals, the kinetic stability of the

compounds is considerably increased. Thus $Ti(CH_3)_4$ is unstable at R.T., but $(\pi\text{-}C_5H_5)_2TiR_2$ alkyls are stable.

In brief organometallic compounds of transition elements are kinetically unstable but thermodynamically stable.

ctors Responsible for kinetic instability of transition metal σ- bonded organometallic compounds.

formation of Reactive species due to M-C bond cleavage:
The reactive species can combine either with each other or with a solvent to give chain Rx^n's resulting in exothermic Rx^n's.

In contrast other metal inorganic compounds containing $M\text{-}OH_2$, $M\text{-}NR_2$ & M-X (X= halogen) upon cleavage of M-L bond provide less reactive species such as H_2O, $NR_2^{\ominus}$ or $X^{\ominus}$ respectively.

÷ Cleavage products form strong bonds ÷ Cleavage of M-C bond in organometallic compounds result in reactive species which combine among themselves and form strong bonds such as C-C, C-O, C-N & C-X etc depending upon the nature of the organometallic compounds.
The formation of strong bonds is always accompanied with the release of energy & consequently thermodynamically favoured.

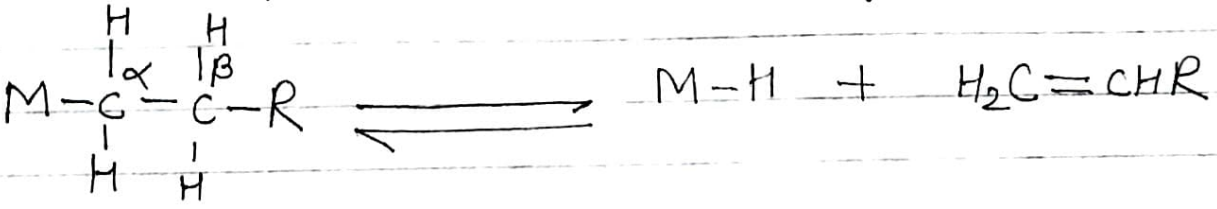
$$M\text{-}R \xrightarrow{\text{cleavage}} M\text{- derivatives} + R\text{-}R + \text{Heat}$$

The main factor affecting the kinetic stability of organometallic alkyl compound is the activation energy required for the cleavage Rx^n.

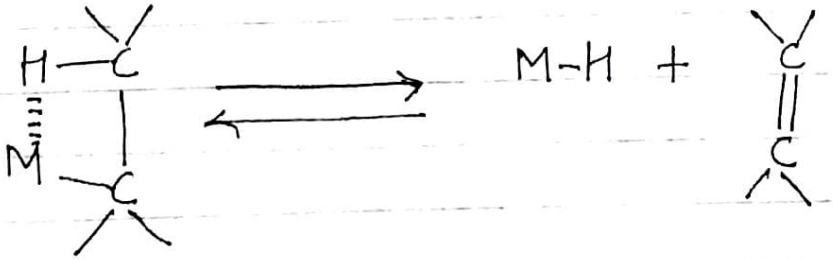
If the activation energy is low, the organometallic compound will be unstable.
However, if the activation energy is large, the organometallic compound will be stable even if the overall decomposition has a strongly favourable free energy change. i.e. $-\Delta G$.

(iii) :- Hydrogen transfer from alkyl to metal :-

Alkyl organometallic compounds with higher alkyl gp are now unstable in case these contain H at the β-carbon. In fact, the presence of H at the β-carbon provides an additional pathway for the decomposition of metal-alkyls into metal hydride & olefin according as.



This Rxn occurs becoz the metal atom & the β carbon position themselves in such a way that leads to the elimination of β-hydrogen as.



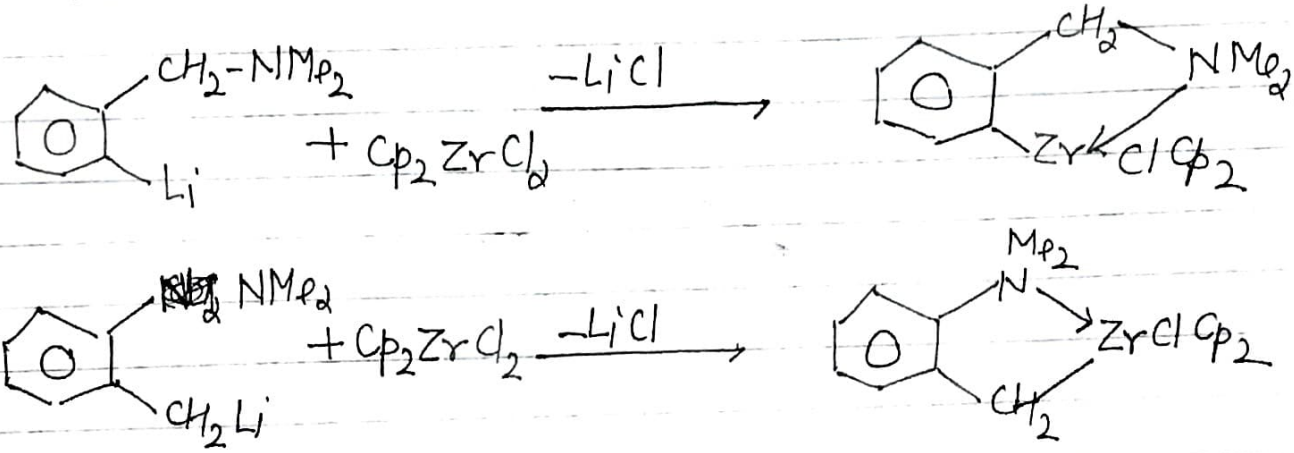
In fact, β-elimination provides a low energy pathway for the organic group to be eliminated as an olefin with the formation of metal hydride.

- When β-elimination is not possible becoz of the structure of organic group as in case of $M-CH_3$, $M-CH_2-C_6H_5$ or $M-CH_2-SiMe_3$ the 6-covalent compounds of transition metals are stabilized.

factor which Increase the stability of metal-alkyl complex:

1. Absence of β-elimination.
2. Increase in the coordination number.
   → stability of metal alkyls is significantly increased by incorporating π-acid ligands such as CO, R_3P, cyclopentadi

3. Chelation :-



4:- Delocalization of -ve charge on carbon :- In most of the M-C bond there is a polarity ($M^{\delta+}-C^{\delta-}$) due to the difference in the electro-vity value b/w metal atom & the carbon atom.

The compounds can be stabilized be delocalizing the -ve charge of the carbon. As a result poly halogenated especially perfluorinated gps (CF_3) are more stable than the analogo non-halogenated gps. It means $M-CF_3$ bonds are mor stable than $M-CH_3$ bonds.

→ similarly, aromatic gps should form more stable compounds the aliphatic compounds.

3. Metal Carbon Multiple Bonding :-