B. Sc. (Semester - VI)
Subject: Inorganic Chemistry
Subject Code: US06CCHE22
UNIT: II (A) : Organo-Metallic Chemistry

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Introduction

The term organometallic or metallo-organic is used nowadays for compounds containing metal-to-carbon bond. Organo-metallic compounds thus include various hydrocarbon derivatives, carbonyls, certain chelate complexes, carbides and related compounds, but do not include carbonates of the metals, complexes of the metals with organic amines and metallic salts of organic acids.

General Methods of Preparation

Following three methods have been used:

Substitution methods: These methods can be any of the following types:

1. A type reactions: $RX + M \rightarrow RM + X$. These reactions involve those compounds containing an acidic hydrogen or a metal less electropositive than the substituting metal. Some examples of the organo-metallic syntheses involving A type reactions with compounds containing an acidic hydrogen are:

$$RC \equiv CH + Na \longrightarrow RC \equiv C^{-}Na^{+} + 1/2H_2$$

$$C_6H_5 + K \longrightarrow C_5H_5^{-}K^{+} + 1/2H_2$$

$$Ph_3CH + Na \xrightarrow{NH_3\,(l)} Ph_3C^{-}Na^{+} + 1/2H_2$$

The preparative value of A type reactions in which X is less electropositive than M is quite limited, but it is probably the best method of preparing alkyls of the more reactive metals such as alkali and alkaline earth metals and zinc.

$$2Na + (CH)_2Hg \longrightarrow 2CH_3Na + Hg$$

$$Mg + (CH)_2Hg \longrightarrow (CH)_2Mg + Hg$$

$$Zn + (CH)_2Hg \longrightarrow (CH)_2Zn + Hg$$

2. B type reactions: $RY + 2M \rightarrow RM + MY$. These reactions can be illustrated by the following examples:

$$2Mg + 2RBr \xrightarrow{Ether} 2RMgBr \longrightarrow MgBr_2 + R_2Mg$$

$$2Li + EtI \longrightarrow EtLi + LiI$$

$$2Na + C_6H_5Cl \xrightarrow{Pentane} C_6H_5Na + NaCl$$

$$2Zn + 2EtI \longrightarrow 2EtZnI \longrightarrow Et_2Zn + ZnI_2$$

$$Hg + 2MeBr + 2Na \longrightarrow Me_2Hg + 2NaBr$$

3. C type reactions: RY + MZ → RM + YZ. These reactions may be of the following types:

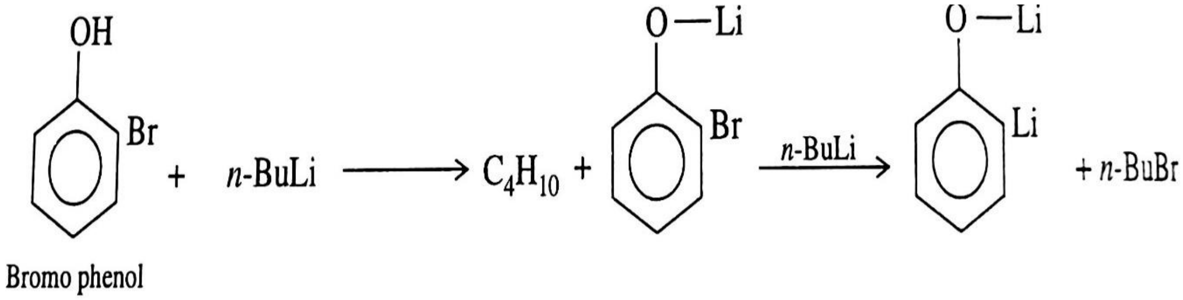
(i) Metallation: This term is usually restricted to metal-hydrogen exchange reactions. Illustrative examples of the organometallic syntheses carried out by this type of reaction are:

$$C_5H_6 + RONa \longrightarrow C_5H_5^-Na^+ + ROH$$

$$RC \equiv CH + NaH \longrightarrow RC \equiv CNa + H_2$$

$$RC \equiv CH + NaNH_2 \xrightarrow{NH_3(l)} RC \equiv CNa + NH_3$$

(ii) Metal-halogen exchange reactions: These reactions are best illustrated by reaction of halogenated phenol with n-butyl-lithium (*n*-BuLi).



(iii) Reactions of organo-metallic compounds with metal salts: They are generally the most useful preparative methods for those organo-metallic compounds which cannot be obtained by the direct reaction of the metal with hydrocarbons or halocarbons. The most convenient and easily available starting materials for such reactions are the Grignard reagents and organolithium compounds. Thus, the alkyls of cadmium, mercury, beryllium and aluminium are best prepared in this way:

$$\begin{aligned}
2RMgBr + ZnBr_2 &\longrightarrow R_2Zn + 2MgBr_2\\
2RMgCl + CdCl_2 &\longrightarrow R_2Cd + 2MgCl_2\\
2RMgCl + HgCl_2 &\longrightarrow R_2Hg + 2MgCl_2\\
2RMgCl + BeCl_2 &\longrightarrow R_2Be + 2MgCl_2\\
3RMgCl + AlCl_3 &\longrightarrow R_3Al + 3MgCl_2
\end{aligned}$$

(iv) Reactions of bimetallic compounds with halides: Many derivatives of group IVB metals and metal carbonyls are best prepared by this method. For example,

$$Ph_3PbLi + PhCH_2Cl \rightarrow Ph_3PbCH_2Ph$$

$$NaMn(CO)_5 + MeI \rightarrow MeMn(CO)_5 + NaI$$

4. D type reactions: A + MY → AM + Y. These reactions may be of the following types:

(i) Displacement of one neutral ligand by another: The extent of displacement depends upon metal type of ligand and nature of solvent. Thus, isonitriles displace carbon monoxide from metal carbonyls to different degrees depending on the nature of the metal.

$$Ni(CO)_4 + 4PhNC \longrightarrow Ni(CNPh)_4 + 4CO$$

$$Cr(CO)_6 + 3PhNC \longrightarrow Cr(CO)_3(CNPh)_3 + 3CO$$

In contrast to PhNC, EtNC displaces only three CO groups from $Ni(CO)_4$.

$$Ni(CO)_4 + 3EtNC \longrightarrow Ni(CO)(EtNC)_3 + 3CO$$

In reaction of $BrMn(CO)_5$ with PhNC in boiling THF as solvent, all the five carbonyl groups are displaced; but in ethanol solution only two such groups are displaced.

$$BrMn(CO)_5 + 5PhNC \xrightarrow{THF} BrMn(CNPh)_5 + 5CO$$

$$BrMn(CO)_5 + 2PhNC \xrightarrow{ethanol} BrMn(CO)_3(CNPh)_2 + 2CO$$

(ii) *Displacement of neutral ligands by negative ligands.* These reactions are exemplified by

$$K_2[PtCl_4] + 2CO \longrightarrow Pt(CO)_2Cl_2 + 2KCl$$

and $$Mn(CO)_5Br + C_2H_4 + AlBr_3 \longrightarrow [Mn(CO)_5(C_2H_4) + AlBr_4$$

(iii) Displacement of negative ligands by neutral ligands: Some examples of this type of reaction are:

$$[Fe(CN)_5(H_2O)]^{3-} + CN^- \rightarrow [Fe(CN)_6]^{4-} + H_2O$$

$$[Fe(o\text{-}phen_3]^{2+} + 2KCN \rightarrow Fe(o\text{-}phen)_2 (CN_2) + 2K^+ + o\text{-}phen$$

(iv) Displacement of one negative ligand by another: An illustrative example of this type of reaction is

$$K_2[Pt(SCN)_4] + 4KC{\equiv}CR \xrightarrow{NH_3\ (l)} K_2Pt(C{\equiv}CR)_4 + 4KSCN$$

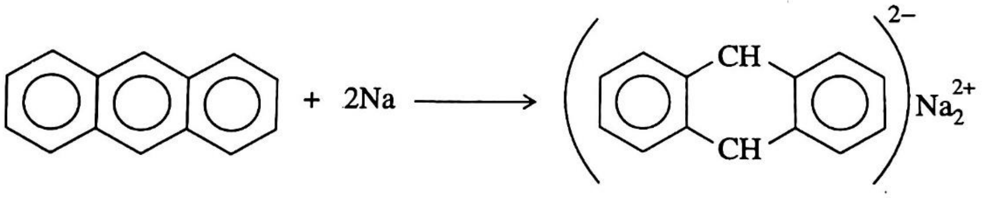
II. Addition methods :

These reactions may be of the following types:

1. Reaction of metals with CO, unsaturated hydrocarbons or radicals: These reactions are illustrated by the following examples:

$$Ni + 4CO \longrightarrow Ni(CO)_4 \ ; \qquad Fe + 5CO \longrightarrow Fe(CO)_5$$

$$Ph_3C{=}CH_2 + Na \longrightarrow (Ph_2C{-}CH_2)^- Na^+ \longrightarrow [Ph_2C{-}CH_2{-}CH_2{-}CPh_2]^{2-}\ Na_2^{2+}$$



$$Ph_3C + Na \longrightarrow Ph_3C^-Na^+$$

2. Ionisation reactions: Some examples of this type of reactions are as follows:

$$B_2H_6 + 6H_2C{=}CH_2 \longrightarrow 2(C_2H_5)_3B$$

$$Et_2AlH + H_2C{=}CH_2 \longrightarrow Et_2Al$$

$$HSiCl_3 + HC{\equiv}CH \longrightarrow H_2C{=}CHSiCl_3$$

$$H_2C{=}CHSiCl_3 + HSiCl_2 \longrightarrow Cl_2SiCH_2CH_2SiCl_3$$

$$Ph_3SnH + HC{=}CPh \xrightarrow{90°C} Ph_3SnCH{=}CHPh$$

3. Oxidation addition reactions. An interesting oxidation addition reaction is that in which oxidation of the metal is accompanied by an increase in its coordination number. Some examples of these reactions involve five-coordinate (d^7), four-coordinate (d^8) and two-coordinate (d^{10}) complexes.

$$2[Co^{II}(CN)_5]^{3-} + X{-}Y \longrightarrow [Co^{III}(CN)_5X]^{3-} + [Co(CN)_5Y]$$

where X—Y = H, Br_2, HOH, CH_3I, ICN, etc.

$$[Ir^{I}(CO)(PPh_3)_2Cl] + X{-}Y \longrightarrow [Ir^{III}(X)(Y)(CO)(PPh_3)_2Cl]$$

where X—Y = H_2, Cl_2, HCl, CH_3I etc., and

$$Pt^0(PPh_3)_2 \xrightarrow{X-Y} Pt^{II}(PPh_3)_2(X)(Y) \xrightarrow{X-Y} Pt^{IV}(PPh_3)_3X_2Y_2$$

III. Reduction reactions:

More important reduction reactions are:

1. Chemical reduction: For the preparation of a number of metal carbonyls and carbonyl halides, carbon monoxide is the most commonly used reducing agent.

$$NiS + 5CO + 4OH^- \longrightarrow Ni(CO)_4 + CO_3^{2-} + S^{2-} + 2$$

$$Tc_2O_7 + CO \xrightarrow{275°C} Tc_2(CO)_{10}$$

$$2RuCl_3 + 5CO \xrightarrow{400\ atm.} 2Ru(CO)_2Cl_2 + COCl_2$$

2. Electrolytic reduction: Some illustrative examples of organo-metallic synthesis carried out employing electrolytic reduction are as follows:

$$CH_2CHCN + NaOH \xrightarrow[\text{Sn–cathode}]{\text{electrolysis}} Sn(CH_2CH_2CN)_4$$

$$[(C_2H_5)_3Al]_2.NaF \xrightarrow[\text{Sn–cathode}]{\text{electrolysis}} Pb(C_2H_5)_4 + Al + NaF$$

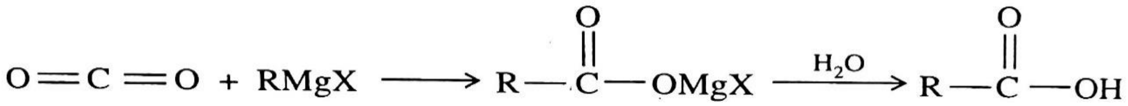
General Properties

1. Physical properties and covalent character: The primary covalent character of most organo-metallic compounds is reflected in their physical properties. They are typically low-melting solids, liquids or gases at ordinary temperatures and are usually soluble in non-polar or weekly polar organic solvents such as alkanes, toluene, ether or even alcohols. Their chemical properties, (especially their thermal stability) vary widely. For example, Me_4Si is unchanged even after many days at 500°C, whereas Me_4Ti decomposes rapidly at room temperature. Reaction rates of these compounds also vary widely; e.g., dimethyl mercury is not attacked at room temperature by oxygen in the air, whereas dimethyl zinc is spontaneously inflammable.

2. Stability to oxidation: All organo-metallic-compounds are thermodynamically unstable to oxidation. Many are also kinetically unstable to oxidation at room temperature. Although Me_2Hg and Group IVB derivatives are inert, most derivatives of Group IVA elements are rapidly oxidised. Kinetic instability to oxidation may be associated with the stability of either empty low-lying orbitals, e.g., *4p* in Me_3Ga or of a lone pair of electrons, e.g., in Me_3Bi. In contrast, the Group IVB alkyls possess neither of these features and behave as saturated compounds.

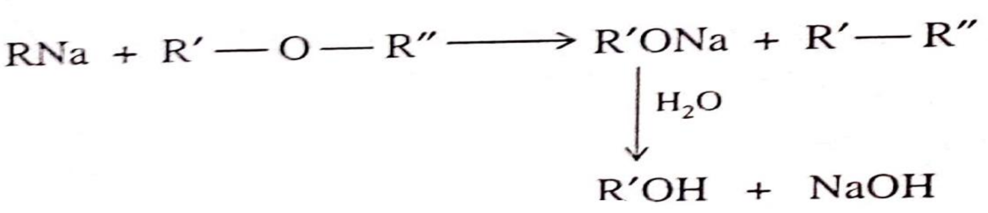
3. Stability to hydrolysis: Organo-derivatives of Groups IVB and VB are kinetically stable to attack by water, whereas those of the Group IA and IIA elements and of zinc, cadmium, Al, Ga and In are readily hydrolysed. These hydrolysis reactions usually involve the nucleophilic attack by water and are thus facilitated by the presence of empty low-lying orbitals on the metal atom (e.g., Al) which attract the electron pair of the nucleophile. In the tetra-akyls of group IVB and tri-alkyls of Group VB elements, metal contains filled low-energy orbitals and nucleophilic attack is not favoured. The rate of hydrolysis is dependent on the polarity of the metal-carbon bond and where this is high (e.g., Me_3Al), rapid hydrolysis occurs. Me_3B is unaffected by water at room temperature inspite of the empty *2p*-orbitals on the boron atom.

4. Reaction with carbon dioxide: Grignard reagents react with excess CO_2 to yield acids.



$$O{=}C{=}O + RMgX \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OMgX \xrightarrow{H_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

5. Reaction with ethers: Alkyls of metals with electronegativities less than 0.9 generally react with ethers, producing a hydrocarbon and an alkoxide; the later is converted to an alcohol by hydrolysis.

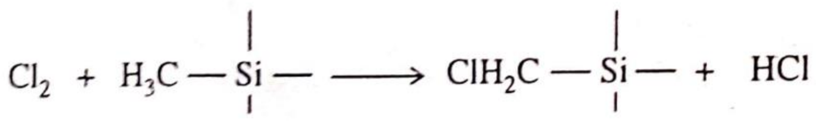


$$RNa + R'-O-R'' \longrightarrow R'ONa + R'-R''$$
$$R'ONa \xrightarrow{H_2O} R'OH + NaOH$$

6. Reaction with non-metallic elements (other than oxygen) and their inorganic Compounds:

Halogens decompose all reactive organo-metallic compounds to form hydrocarbon halides.

$$C_2H_5Li + Br_2 \longrightarrow C_2H_5Br + LiBr$$



$$Cl_2 + H_3C-\overset{|}{\underset{|}{Si}}- \longrightarrow ClH_2C-\overset{|}{\underset{|}{Si}}- + HCl$$

Organo-metallic Compounds of Alkali Metals

Alkali metals, especially Li, form many organo-metallic compounds.

Preparation:

Organo-metallic compounds of Li are generally obtained as follows:

$$Li(n\text{–}C_3H_7) + C_4H_5I \xrightarrow[\text{ether}]{\text{Solvent}} Li(C_6H_5) + n\text{–}C_2H_7I$$

$$4Li(C_6H_5) + Sn(CH_2\text{—}CH{=}CH_2)_4 \xrightarrow[\text{ether}]{\text{Solvent}} 4Li(CH_2\text{—}CH{=}CH_2) + Sn(C_6H_5)_4$$

$$2Li + C_2H_5I \xrightarrow[\text{ether}]{\text{Solvent}} LiI + Li(C_2H_5)$$

Organo-metallic compounds of other alkali metals such as $Na(C_6H_6)$, $Ph_2C(Na)C(Na)Ph_2$, $CsCH_2CH_2Cs$, are also known. These are generally prepared from the corresponding mercury compounds, as for example,

$$2K + HgR_2 \rightarrow Hg + 2KR$$

Properties:

The monomeric organo-metallic 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 upto 100°C.

Structure:

Alkyl and aryl compounds of lithium are polymeric having considerable covalent character in their Li-C bonds whereas such organo-metallic compounds of other alkali metals have predominantly ionic character so that these can be represented as M^+R^-. The alkyl and aryl sodium, potassium, etc. are much more reactive than the corresponding alkyls and aryls of lithium. For instance, the former catch fire in air more violently compared to alkyl compounds of lithium.

Uses:

Lithium alkyls and organo-metallic 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:

$$3LiR + BCl_3 \longrightarrow 3LiCl + Br_2$$

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

$$\xrightarrow{H_2O} \underset{\text{Tertiary carbinols}}{(CH_3C_6H_4)_2C(OH)C_6H_5} + LiOH$$

$$Li(C_6H_5) + CO_2 \xrightarrow[\text{solvent}]{\text{Nonpolar}} [C_6H_5CO_2Li] \xrightarrow{H_2O} \underset{\text{Carboxylic acid}}{C_6H_5COOH} + LiOH$$

$$LiR + R'CON(CH_3)_2 \longrightarrow LiN(CH_3)_2 + \underset{\text{Ketones}}{R'COR}$$

Organo-metallic Compounds of Beryllium

Beryllium forms a large number of organo-metallic compounds like BeR_2 ($R=CH_3$, C_2H_5 etc), $Be(C_5H_5)X$ ($X =$ Cl, Br, I) etc.

Preparation:

Dialkyls of beryllium (BeR_2) can be obtained as follows:

$$2LiR + BeCl_2 \xrightarrow[\text{ether}]{\text{Solvent}} BeR_2 + 2LiCl$$

$$Be + HgR_2 \xrightarrow{\Delta} BeR_2 + Hg$$

Properties and structure:

Compounds of BeR_2 type are colourless solids or viscous liquids. Dimethyl beryllium is Polymeric and contains Be-CH_3-Be bridges in its structure. The extent of polymerisation of other dialkyl beryllium compounds decreases with increase in the bulk of the alkyl group, so much so that di-t-butyl beryllium is monomeric.

The beryllium also forms complexes with cyclopentadiene. The cyclo-pentadienyl group is linked with the metal through a sigma or a pi bond as in $[Be(\eta^5 - C_5H_5)X]$ (where X is Cl, Br or I) and in $[Be(\eta^1 - C_5H_5)(\eta^5 - C_5H_5)$ respectively.

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$$Be + HgR_2 \xrightarrow{\Delta} BeR_2 + Hg$$

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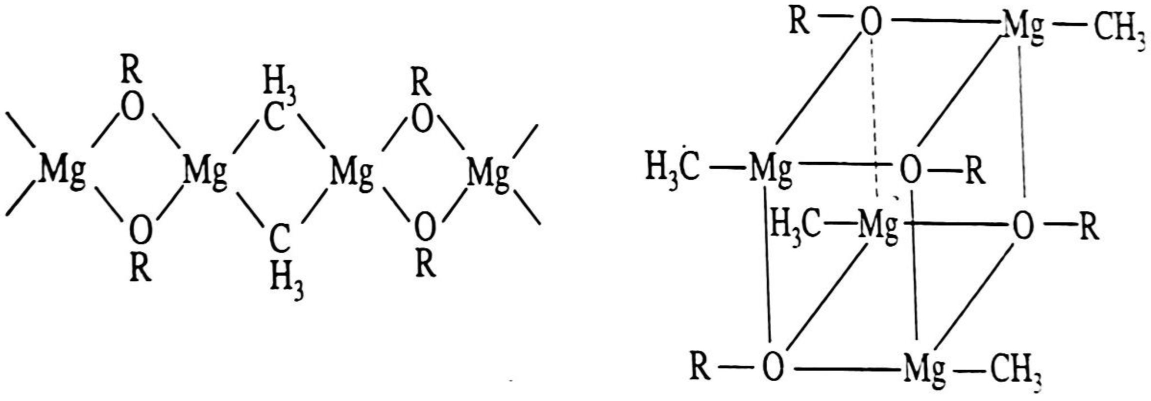
Grignard reagents are of great synthetic value in organic chemistry. .

Organo-metallic 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.

$$MgR_2 + R'OH \rightarrow R\text{-}Mg\text{-}OR' + ROH$$

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.



(a) (b)

Fig.: Two polymeric forms of CH_3- Mg-OR (R = CH_3 or C_2H_5)

(a) Chain polymer (b) three dimensional polymer

Organo-metallic Compounds of Aluminium

Organometallic compounds of Al of $(R_3Al)_2$, $(C_6H_6)_3Al$ etc type can be prepared as follows

$$2Al + 3R_2Hg \longrightarrow (R_3Al)_2 + 3Hg$$

$$AlCl_3 + RMgCl \xrightarrow{-MgCl_2} \underbrace{RAlCl_2,\ R_2AlCl \text{ and } R_3Al}_{\text{(mixture)}}$$

$$AlH_3 + 3C_2H_4 \longrightarrow Al(C_2H_5)_3$$

The trialkyl aluminium compounds are generally dimeric and contain Al-R-Al bridges and R-Al bonds in their structures, the terminal alkyl and the bridging allyl groups in such dimeric compounds are in a process of very fast exchange at room temperature

The trialkyl aluminium compounds are efficient Lewis acids and combine with Lewis acids and combine with Lewis bases such as amines, phosphines, etc., to form adducts of the type R_3Al Lewis base.

The trialkyl aluminium compounds react with alkyl lithium to produce derivatives of $LiAlH_4$.

$$R_3Al + RLi \rightarrow Li[AlR_4]$$

Triphenyl aluminium and of dimethyl phenyl aluminium are dimeric containing Al-phenyl-Al bridges.

The alkyl chlorides, bromides and iodides of aluminium are also dimeric but they contain Al-halogen-Al bridges instead of Al- alkyl bridges in their structures. Alkyls fluorides of aluminium have cyclic tetrameric structures having Al – F - Al bridges. The structure of $(CH_3)_2AlF$ is as shown in Fig.

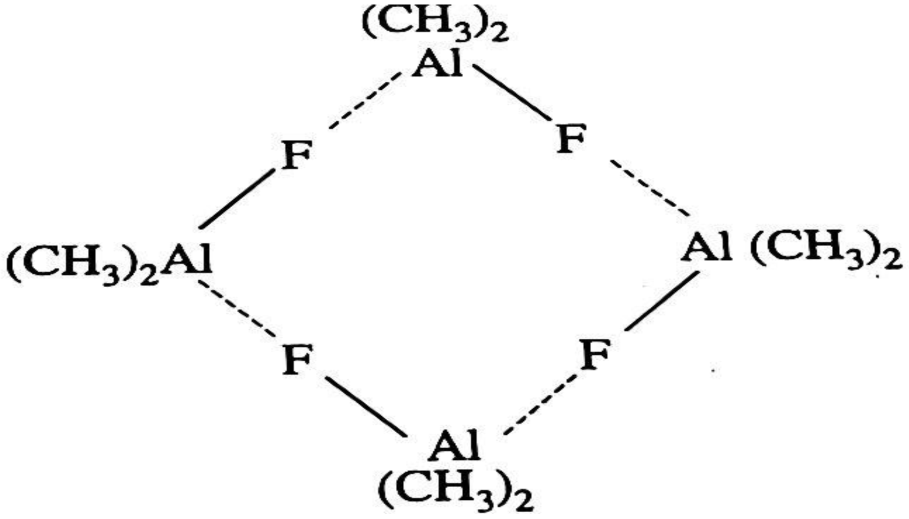


Fig.: Cyclic tetrameric structure of $(CH_3)_2AlF$

Metal-olefine (alkene) Complexes

These are π-bonded organo-metallic complexes. Olefins are two-electron ligands. Ethylene, propylene and a number of other olefins form well-defined complexes with Pd(II), Pt(II), Hg(II),Cu(I) and Ag(I) salts.

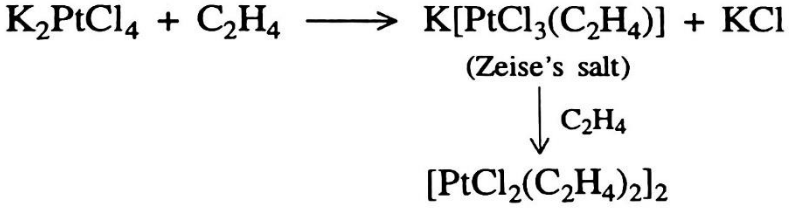
Preparation:

(i) Olefin complexes are generally prepared by the displacement of:

(a) loosely-held ligand such as solvent molecules.

$$2RhCl_3 + 2H_2O + 6C_2H_4 \rightarrow [RhCl(C_2H_2)]2 + 2CH_3CHO + 4HCl$$

(b) ionic ligand



$$K_2PtCl_4 + C_2H_4 \longrightarrow \underset{\text{(Zeise's salt)}}{K[PtCl_3(C_2H_4)]} + KCl$$
$$K[PtCl_3(C_2H_4)] \xrightarrow{C_2H_4} [PtCl_2(C_2H_4)_2]_2$$

(c) neutral ligand

$$[Rh(CO)_2Cl]_2 + 2C_8H_{12} \longrightarrow [RhCl(C_8H_{12})]_2 + 4CO$$

(ii) They can also be prepared by the direct reaction of a metal salt with the olefin.

$$2PdCl_2 + 2C_2H_4 \longrightarrow [PdCl_2(C_2R_4)]_2$$

Properties:

The chemical stabilities of the metal-olefin complexes vary widely. The complexes are usually labile; olefins being easily displaced by ligands such as phosphines. The complexed olefins are more susceptible to nucleophilic attack than the complexes species.

Structure and bonding:

The platinum complex $PtCl_2.C_2H_4$ is a dimer as shown by freezing point depression measurements in benzene and has a bridged structure with trans-arrangement of two ethylene molecules.

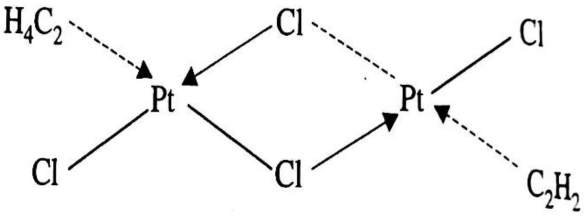
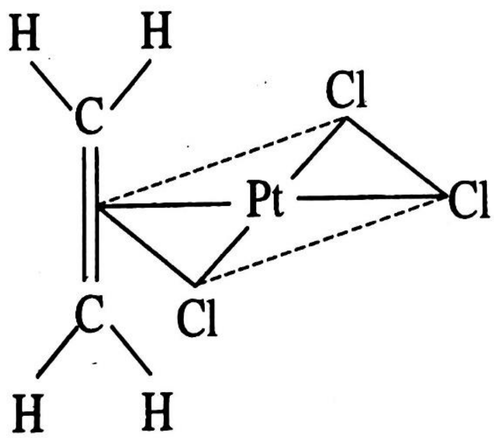


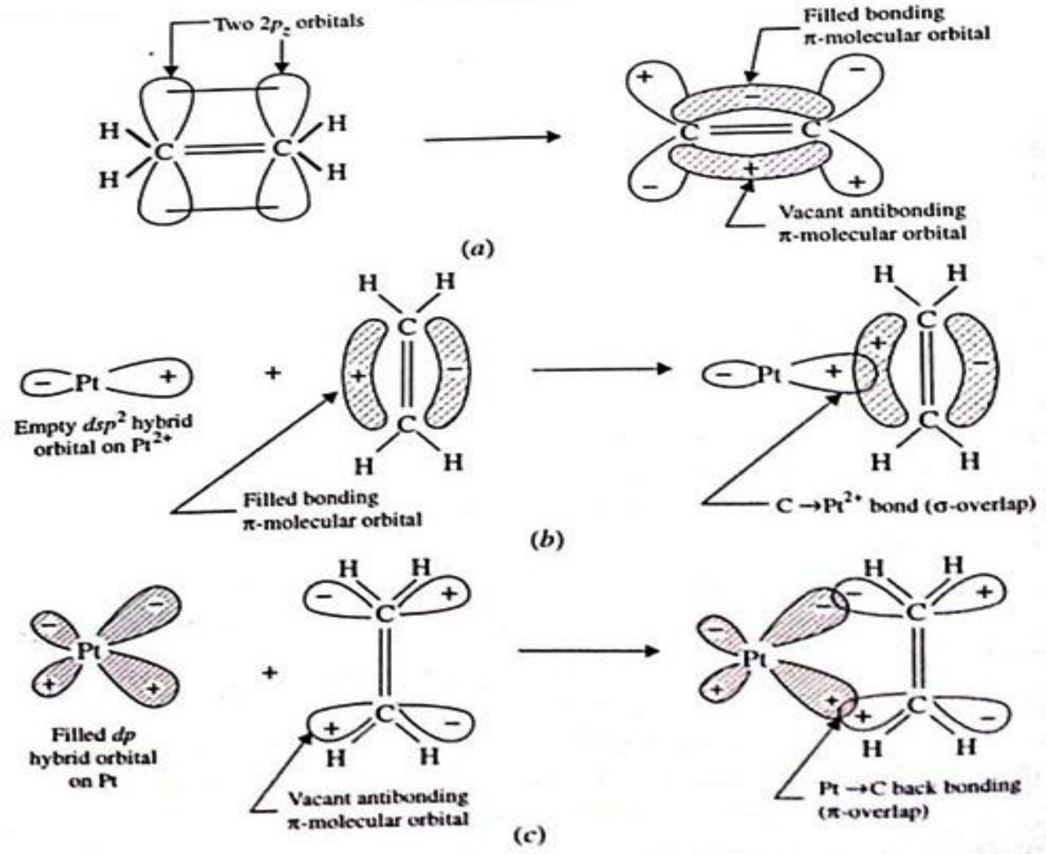
Fig.: Bridged structure of dimer, $[PtCl_2.C_2H_4]_2$



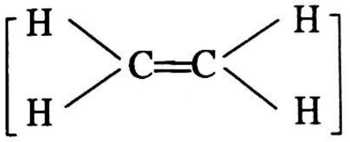
X-ray examination of anion of Zeise's salt shows that the platinum atom is at the centre of a square plane with chlorine atoms at each of the three corners. The ethylene is at the fourth corner but perpendicular to the plane, with the centre of the double bond in the plane. Indeed, the C=C bond of ethylene is perpendicular to the expected normal metal-ligand bond axis. The two carbon atoms are equidistant from the metal.

Fig.: Structure of the anion, $[PtCl_3(C_2H_4)]^-$

The bonding in olefine complexes can be explained by considering the bond formation in ethylene complex with Pt^{2+} ion.



Bonding in ethylene complex with Pt^{2+} ion.

We know that in ethylene molecule,  , $2P_z$ orbitals on two C-atoms overlap to form π - bonding and π^*- antibonding molecular orbitals. π-bonding molecular orbital is filled while π^*- antibonding molecular orbital is vacant. The filled π-bonding molecular orbital or C_2H_4 molecule overlaps with the empty *dsp²* hybrid orbital (which is a σ-type orbital) of Pt^{2+} ion and forms ethylene→ Pt^{2+} bond (σ-overlap). The empty π^*-antibonding molecular orbital of ethylene molecule overlaps with the filled *dp* hybrid orbital (which is a dπ orbital) on Pt^{2+} ion. This type of overlap gives dπ -pπ back bonding. All the three steps have been shown in above given Fig.

The two processes, viz, the donation of π-bonding electrons of the olefin to the metal σ-orbital and back donation of electrons from the metal to the antibonding orbitals of the olefin are synergically related and weaken the π-bonding in the olefin, and in all cases, except the anion of Zeise's salt, there is a marked increase in the C-C bond length. Owing to the lengthening of C-C bond, ν(C=C) decreases in metal-olefin complexes as compared with the free ligand by 60-150 cm^{-1}.

(B): Cyclopentadienyl Complexes: Metallocenes

Cyclopentadienyl group, C_5H_5 is the most important and familiar five-electron ligand. Complexes formed by this group with transition elements are called **metallocenes.** Examples of metallocence are $(C_5H_5)_2M$ (M = Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cr^{2+}, V^{2+}, Ti^{2+} etc.). Out of these, **ferrocene,** $(C_5H_5)_2Fe$ is the most important. For the first time it was reported in 1951. Cyclopentadienyl derivatives like $(C_5H_5)Mn(CO)_3$, $(C_5H_5)M(NO)$ (M=Pt, Pd, Ni) etc., are also known.

Preparation of metallocenes and their derivatives:

(i) by the reaction of alkali metal cyclopentadienides with transition elements.

$$2NaC_5H_5 + MCl_2 \xrightarrow[\text{Reflux}]{\text{THF}} (\pi\text{-}C_5H_5)_2M + 2NaCl$$

$$2NaC_5H_5 + [Co(NH_3)_6](SCN)_2 \longrightarrow \underset{\text{Unstable}}{[Co(NH_3)_6][C_5H_5]_2} + 2NaSCN$$

$$\longrightarrow 6NH_3 + (\pi\text{-}C_5H_5)_2Co$$

Complexes of Fe, Ni, Cr are also obtained by this method.

Alkali metal cyclopentadienides react with salts in solvents such as liquid ammonia.

$$Cd(SCN)_2 \xrightarrow{4NH_3} Co(NH_3)_4(SCN)_2$$

$$Co(NH_3)_4(SCN)_2 + 2C_5H_5Li \longrightarrow Co(NH_3)_4(C_5H_5)_2 + 2LiSCN$$

$$\xrightarrow{\text{At reduced pressure}} 4NH_3 + (\pi\text{-}C_5H_5)_2Co$$

(ii) by the action of anhydrous metal (II) halides on cyclopentadiene in an amine.

$$2Cr(CO)_6 + 2C_5H_6 \rightarrow [(C_5H_5)Cr(CO)_3]_3 + 6CO + H_2$$

[(C_5H_5) Co can also be prepared in a similar way.

(iv) by the action of cyclopentadiene on metal or metal oxide [Commercial preparation of $(C_5H_5)_2Fe$]

$$2C_5H_6 + Fe \xrightarrow{300°C} (\pi\text{-}C_5H_5)_2Fe + H_2$$

$$2C_5H_6 + FeO \xrightarrow{250°C} (\pi\text{-}C_5H_5)_2Fe + H_2O$$

(v) from Grignard reagent by reacting with the metal halides (Laboratory method).

$$2C_5H_5MgBr + FeCl_2 \longrightarrow (\pi\text{-}C_5H_5)_2Fe + 2MgClBr$$

Cr and V complexes can also be prepared.

Properties:

(1) All the 3*d* transition metal complexes are neutral soluble in organic hydrocarbon solvents and are sublimable at 100°C, and do not pyrolyse even at 470°C. All the 3*d* complexes possess the melting point between 172-174°C while the heavier metal complexes melt at higher temperatures. These complexes very very much in their stabilities. Ferrocene only is stable in air but V, Cr, Ti, Ni, Co complexes should be handled in vacuum.

Stability order is Fe > Ni > Co > V > Cr > Ti

Thus (π -C_5H_5)$_2$ Ni is moderately stable, i.e., decomposes in air in two days in solid phase, but decomposes faster in solution.

(2) All these are stable towards the hydrolysis.

(3) All these are easily oxidised in the acid solution to give cations (oxidations generally are reversible).

$$\pi(C_5H_5)_2Fe \xrightleftharpoons{\text{acid}} \underset{\text{Blue green}}{(\pi\text{-}C_5H_5)_2Fe^+} \; \textit{(Ferrocenium ion)}$$

$$Cr(\pi\text{-}C_5H_5)_2 \rightleftharpoons (\pi\text{-}C_5H_5)_2Cr^+ \; \textit{(Chromocenium)}$$

$$V(\pi\text{-}C_5H)_2 \rightleftharpoons \underset{\text{Purple}}{(\pi\text{-}C_5H_5)_2V^+} \; \textit{(Vanadocenum)}$$

$$\cdot\pi\text{-}(C_5H_5)_2Co \rightleftharpoons \underset{\text{Yellow-green}}{(\pi\text{-}C_5H_5)_2\ Co^+} \; \textit{(Cobaltocenium)}$$

(4) Hydrogenation: Ferrocene is more resistant to catalytic hydrogenation than benzene because of the co-ordination of π-electron density of the ring to the metal atom.

Some properties of ferrocene

(1) Ferrocene is orange yellow solid, m.p., 178°C, sublimable and soluble in organic solvents.

(2) Stable in air and towards hydrolysis.

(3) Oxidised by bromine as well as in acid solution.

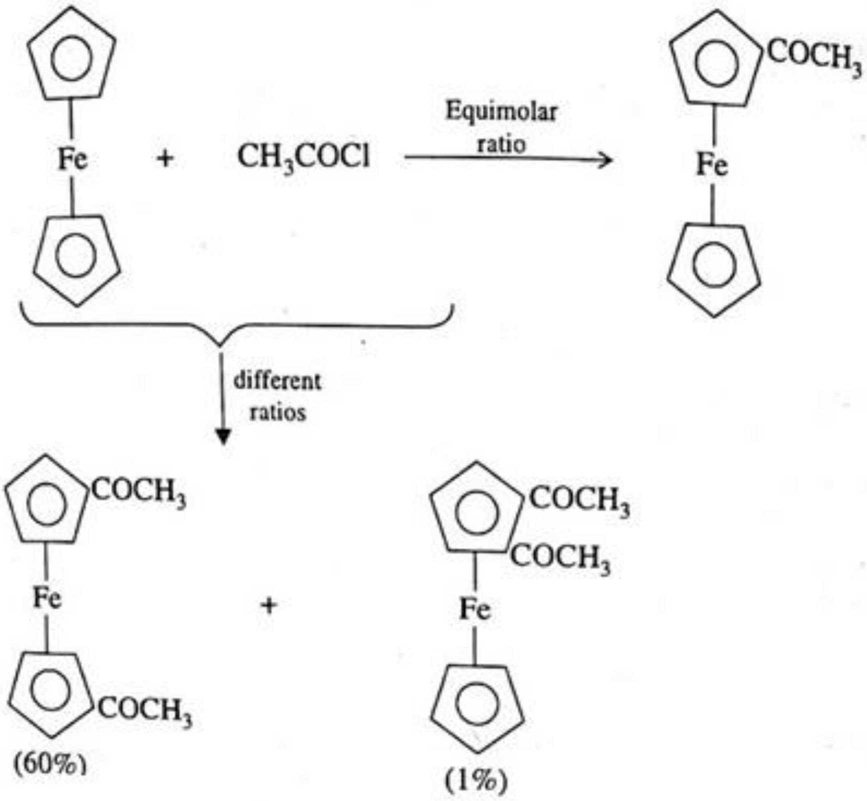
$$Fe(\pi\text{-}C_5H_5)_2 \xrightleftharpoons{\text{acid}} Fe^+(\pi\text{-}C_5H_5)_2$$

$$C_{10}H_{10}Fe + \frac{1}{2}Br_2 \longrightarrow C_{10}H_{10}FeBr \xrightarrow{6Br_2} FeBr_3 + \underset{\substack{\text{Pentabromo}\\ \text{cyclopentane}}}{2C_5H_5Br_5}$$

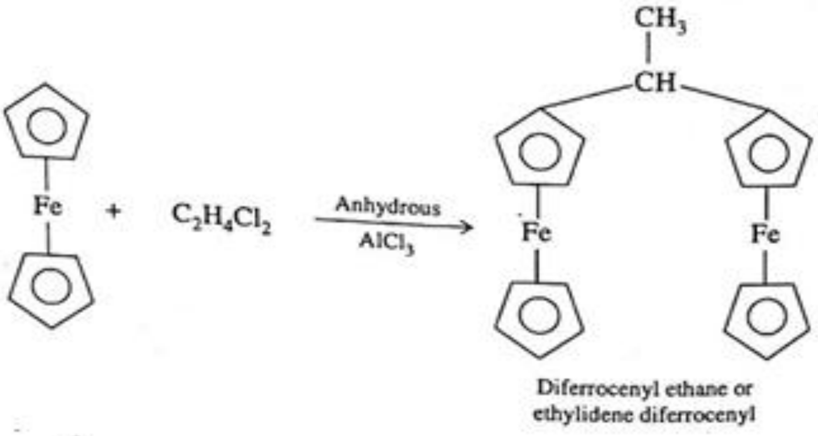
(4) No Diels-Alder reaction possible.

(5) **Organic reactions**: As cyclopentadienyl rings in the molecule of ferrocene are aromatic in nature, they can undergo aromatic substitution.

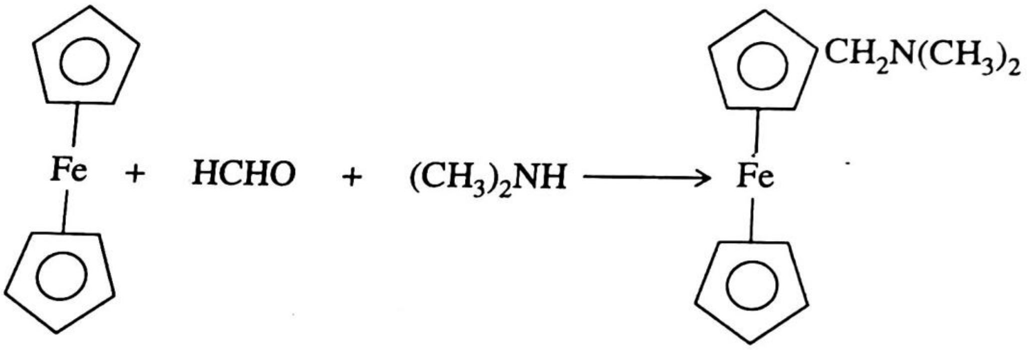
(a) **Friedel crafts acylation**: Ferrocene and acetyl chloride in the equimolar quantities give the mono substituted derivative while in the double quantities disubstituted derivative is formed.



(b**) Friedel crafts alkylation**:



c) Amino methylation:

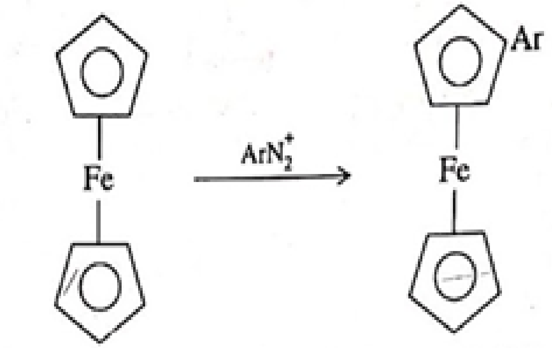


(d) Sulphonation: It can undergo sulphonation with H_2SO_4 or chlorosulphuric acid in the presence of acetic anhydride giving monosubstituted and heterosubstituted derivatives.

(e) Formylation: It can be formylated with N-methyl formaldehyde in presence of $POCl_3$.

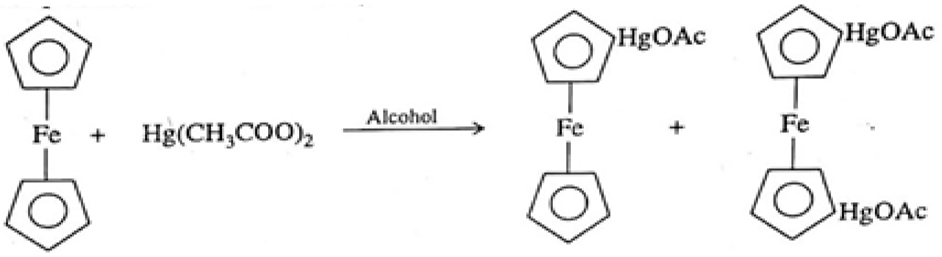
(f) Condensation: On condensation with HCHO in presence of H_2SO_4 or liquid HF followed by reduction, it gives 1, 2 diferrocenyl ethane.

(g) Arylation:



(h) Exchange reactions: Ferrocene undergoes exchange reactions, in deuterated HCl or deuterated trifluoro acetic acid.

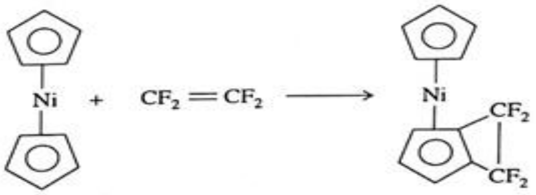
(i) Metallation: With mercuric acetate in alcohol at room temperature, it gives mono and disubstituted products (Ac = CH_3COO).

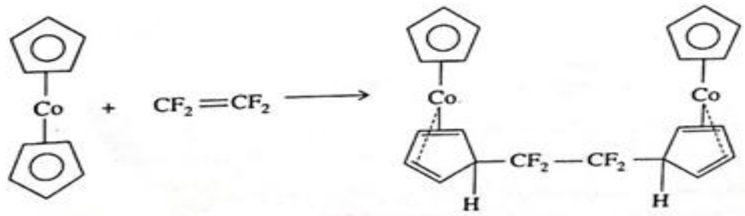


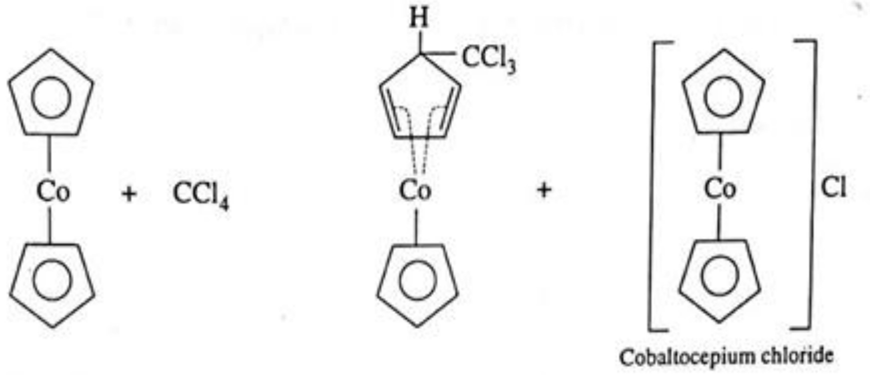
Other cyclopentadienyl complexes which undergo substitution reactions are $Os(\pi\text{-}C_5H_5)_2$, $(\pi\text{-}C_5H_5)_2Mn$, $(\pi\text{-}C_5H_5)_2$ Ru and $(\pi\text{-}C_5H_5)_2V(CO)_4$.

Reactions of other cyclopentadienyl complexes:

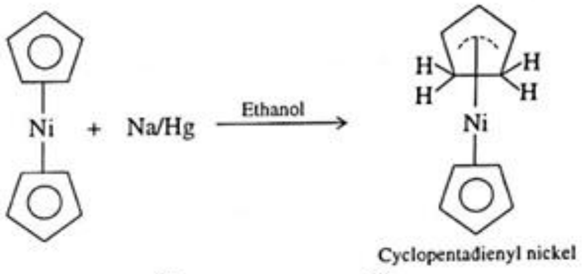
(1) Addition reactions :

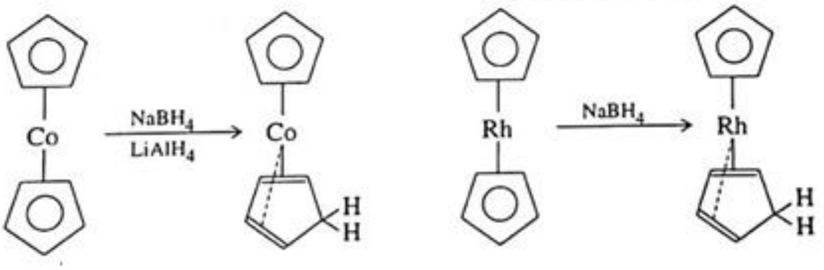






(2) Reduction:





Structure and bonding in $(C_5H_5)_2Fe$ molecule:

X-ray studies as well as a variety of physical and chemical evidence show that ferrocene has a sandwich structure; the iron atom being placed between two cyclopentadiene rings in a pentagonal antiprismatical arrangement. The other binary covalent cyclopentadienyl compounds have sandwich structures similar to ferrocene. In the solid state, the two rings in ferrocene have a staggered configuration with respects to each other, but an eclipsed configuration is observed for ruthenocene.

Ferrocene (Staggered) Ruthenocene (Eclipsed)

Fig.: Structure of ferrocene, $(C_5H_5)_2Fe$ and ruthenocene, $(C_5H_5)_2Ru$ molecule

A number of theories have been advanced regarding the bonding in ferrocene and related cyclopentadienyl compounds.

According to German workers, such as **Fischer and Fritz (1959)**, the bonding in ferrocene is similar to that in a low spin octahedral complex of iron (II), such as $Fe(CN)_6^{4-}$. Each $C_5H_5^-$ ion donates its three pairs of π-electrons to the vacant d^2sp^3 hybrid orbitals of Fe^{2+} as shown below in Fig.

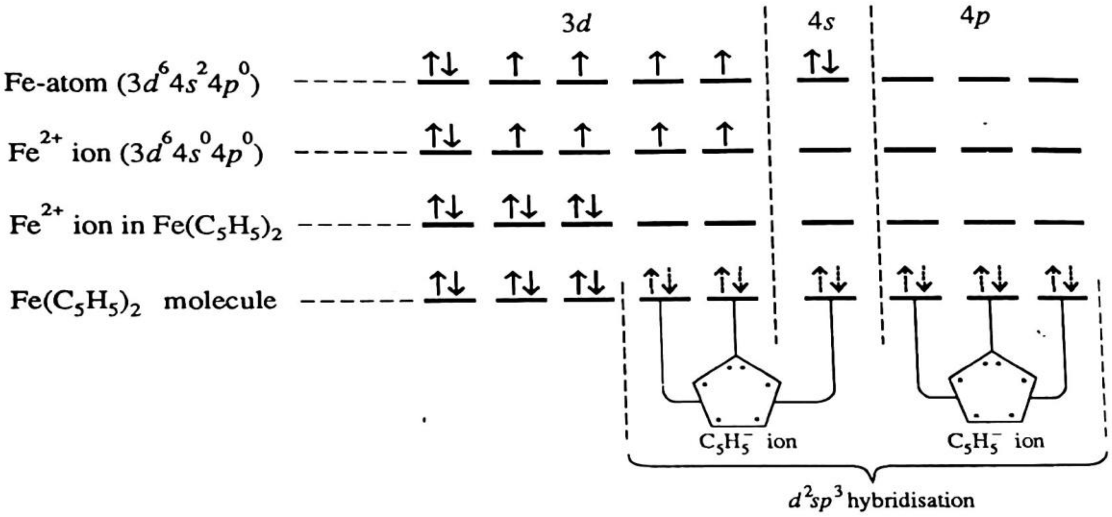


Fig.: d^2sp^3 hybridization of Fe^{2+} ion in the formation of ferrocene, $Fe(C_5H_5)_2$

However, the aromaticity of ferrocene implies a ready availability of π-electrons in each ring and this is inconsistent with the involvement of six electrons in bonding with the metal.

Dunitz and Orgel, however, are of the view that iron in the zero-oxidation state is joined to two cyclopentadienyl rings by essentially two covalent σ-bonds.

The π-bonded structure H_5C_5 – Fe - C_5H_5 is, however, compatible with the properties of ferrocene. The metal atom is not attached to any particular carbon atoms in the cyclopentadienyl ring but is equidistant from all the five carbon atoms and lies on the axis which passes at right angles through the centre of the ring.

The molecular orbital description of bonding in ferrocene as given by **Moffit (1954)** is not appealing. There are five atomic π-orbitals in each cyclopentadienyl ring, one on each carbon atom and five molecular orbitals are compounded from them. These are designated as $\Psi 1, \Psi 2, \Psi 3, \Psi 4, \Psi 5$. $\Psi 2$ *and* $\Psi 3$ are degenerate and so are $\Psi 4$ and $\Psi 5$. $\Psi 1$ has the lowest energy. The energy order of five π-M.Os is $\Psi 1 < \Psi 2 = \Psi 3 < \Psi 4 = \Psi 5$. The arrangement of five π-electrons of each cyclopentadiene ring in the above π-M.Os is as follows :

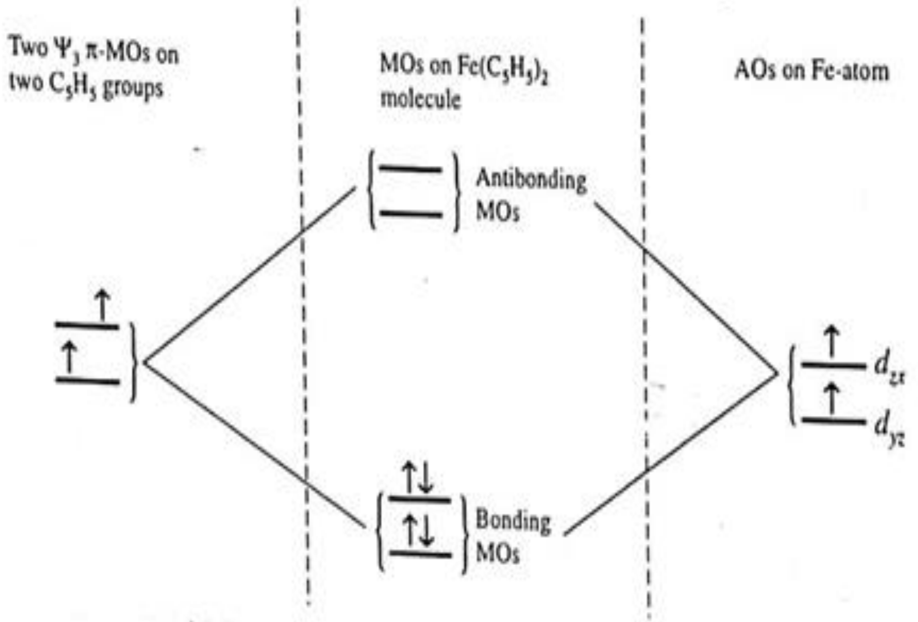
$(\Psi 4)^2\ (\Psi 2)^2\ (\Psi 3)^1$.

The valence-shell electronic configuration of Fe-atom ($4s^2 3d^6 4p^0$) in its ground state is: $(3d_{xy})^2 (3d_{yz})^1\ (3d_{zx})^1\ (3d_{x^2-y^2})^2 (3d_{z^2})^0\ 4S^2\ 4p_x^0\ 4p_y^0\ 4p_z^0$.

According to **Moffit**, the $4s$ and $3d_{z^2}$ orbitals of iron atom hybridize under the influence of the approaching cyclopentadienyl radicals yielding two non-equivalent *sd*-hybrid orbitals. One of these hybrid orbitals designated as $(sd)_1$ has a lower energy than the $3d_{z^2}$ -orbital, the other orbital. $(sd)_2$ has a higher energy, close to that of the $4p$-orbitals. The valence-shell configuration of iron atom in the excited state is:

$(3d_{xy})^2 (3d_{yz})^1\ (3d_{zx})^1\ (3dx^2 - y^2)^2 (sd)^2_1 (sd)_2^0\ 4p_x^0\ 4p_y^0\ 4p_z^0$.

Ferrocene has 18-electron configuration with 5 electrons on π-M.Os of each cyclopentadienyl radical and 10 electrons on orbitals of iron atom. Five π-M.Os of each cyclopentadienyl radicals and 9 orbitals of iron atom combine to yield 9 bonding or non-bonding M.Os and 10 antibonding M.Os. The electrons are accommodated in the bonding and non-bonding M.Os; bonding M.Os accommodating 4 electrons and non-bonding M.Os the remaining 14 electrons. The bonding in ferrocene results effectively from the overlap of singly occupied d_{xy} and d_{yz} metal orbitals with singly occupied π-M.Os ($\Psi 2$ or $\Psi 3$) of cyclopentadienyl radicals of similar symmetry. The relevant molecular orbital energy level for $Fe(C_5H_5)_2$, molecule is shown below in Fig.



Molecular orbital energy level diagram from ferrocene molecule. $Fe(C_5H_5)_2$. (After Moffit).

Ionic Cyclopentadienyl Compounds

Cyclopentadiene is a weak acid ($pK_a \sim 20$), dissociating to give H^+ and $C_5H_5^-$ ions. $C_5H_5^-$ forms ionic compounds- cyclopentadienides with strongly electropositive metal ions. The more important cyclopentadienides are formed by the alkali metals, MC_5H_5, the alkaline earth metals, $M(C_5H_5)_2$, the lanthanides and actinides, $M(C_5H_5)_2$, $Mn(C_5H_5)_2$ closely resembles the corresponding magnesium compounds and evidently has an ionic structure containing $C_5H_5^-$ and Mn^{2+} ions. The magnetic moment (5.9 B.M.) of $Mn(C_5H_5)_2$, is in conformity with the ionic bonding for the above compound. The ionic cyclopentadienides are very reactive towards air and water and react with ferrous chloride in tetrahydrofuran to yield ferrocene. Some of the ionic compounds of the type $M(C_5H_5)_2$, have, like ferrocene, sandwich structures. Thus, the Structure of a cyclopentadienyl complex appears to be independent of the bond type.

The End