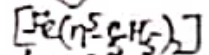
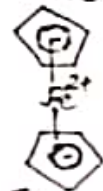


⇒ Ferrocene? Cyclopentadienyl ion ( $C_5H_5^-$ ) behaves as a  $5e^-$  donor  $\pi$ -ligand. It is represented as  $(\eta^5 \text{ or } \pi-C_5H_5)$ . Cyclopentadienyl complex of iron(II) is known as Ferrocene. It is made up of  $Fe^{2+}$  &  $C_5H_5^-$  ( $2 \text{ moles}$ ). It has formula  $Fe(\pi-C_5H_5)_2$ , and also called di( $\pi$ -cyclopentadienyl)iron. It is typical example of metallocenes,  $M(\pi-C_5H_5)_2$ . It has 'sandwich' structure shown as:  
It is first cyclopentadienyl compound/metallocene discovered by Kealy & Pauson in 1951.



⇒ Methods of Preparation of Ferrocene: Ferrocene can be prepared in laboratory/commercially by different methods:

1. By action of Grignard reagent of cyclopentadiene,  $(C_5H_5)MgBr$  on  $FeCl_2$  (Kealy & Pauson, 1951)  
 $FeCl_2 + 2(C_5H_5)MgBr \rightarrow Fe(C_5H_5)_2 + MgCl_2 + 2MgBr_2$   
(Cyclopentadiene mag. bromide) (Ferrocene)

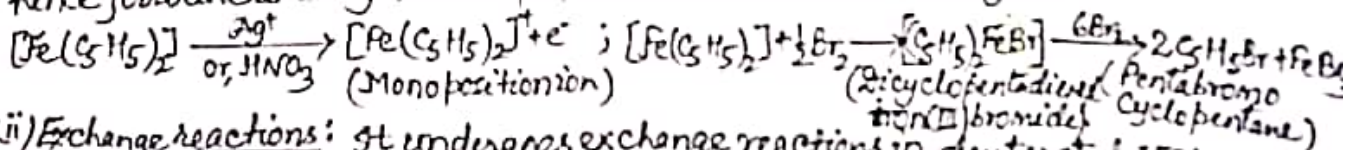
2. By the action of anhydrous iron(II) halide on cyclopentadiene ( $C_5H_6$ ) in presence of strong base, diethylamine.  $FeCl_2 + 2C_5H_6 + 2NH(C_2H_5)_2 \rightarrow (C_5H_5)_2Fe + 2(C_2H_5)_2NH.HCl$ .  
(Iron(II) chloride) (Diethylamine) (Ferrocene)

3. By the action of iron(II) halide on sodium cyclopentadiene ( $NaC_5H_5$ ). Sodium cyclopentadiene is prepared by treating cyclopentadiene ( $C_5H_6$ ) with finely divided dispersed sodium metal in tetrahydrofuran (THF).  $C_5H_6 + Na \xrightarrow{THF} C_5H_5Na + \frac{1}{2}H_2$   
 $2C_5H_5Na + FeCl_2 \rightarrow Fe(C_5H_5)_2 + 2NaCl$   
(Ferrocene)

4. Commercial prep<sup>n</sup>: Commercially (large scale) ferrocene can be prepared by the action of cyclopentadiene ( $C_5H_6$ ) on Fe or  $FeO$  at  $250-300^\circ C$ .  
 $2C_5H_6 + Fe \xrightarrow{300^\circ C} (C_5H_5)_2Fe + H_2$ ;  $2C_5H_6 + FeO \xrightarrow{250^\circ C} (C_5H_5)_2Fe + H_2O$

⇒ Properties: Physical (i) It is an orange crystalline solid, melting point  $173^\circ C$  and sublimates with decomposition. (ii) It is soluble in organic solvents. (iii) It has high thermal stability up to  $\approx 500^\circ C$ . (iv) It is stable to air and water. It does not undergo hydrolysis.

Chemical: (i) Oxidation or Redox reaction: Cyclopentadiene stabilises the positive charge, ferrocene is easily oxidised in acidic solution as well as by  $Br_2$ .

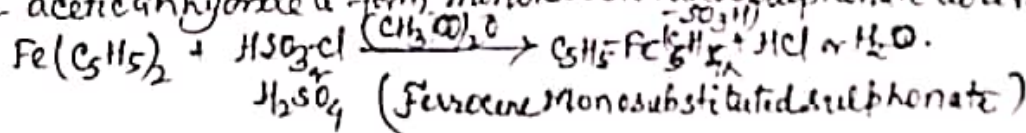


(ii) Exchange reactions: It undergoes exchange reactions in deuterated  $FeCl_3$  or deuterated trifluoroacetic acid.

(iii) Nitration & halogenation: It does not undergo direct nitration and halogenations but gets oxidised to ferricinium ion,  $[Fe(C_5H_5)_2]^+$ , though it has aromatic character.

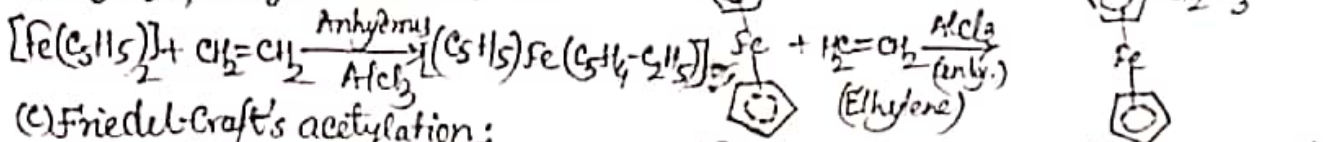
(iv) Aromatic character: It has two  $C_5H_5^-$  (cyclopentadienyl ion), which obeys  $(4n+2)$  rule, Huckel's rule. So it is aromatic nature. It undergoes sulphonation, Friedel-Craft alkylation/acetylation, Mannich condensation etc.

(v) Sulphonation: It reacts with chlorosulphuric acid ( $ClSO_3H$ ) or  $H_2SO_4$  in presence of acetic anhydride to form monosubstituted sulphate derivative.



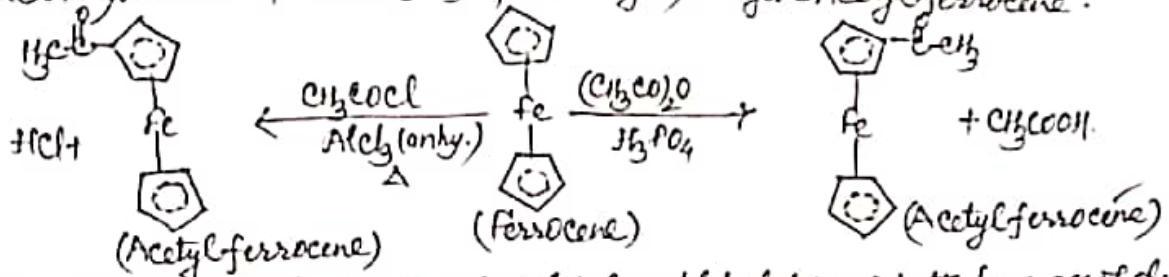


(b) Friedel-Craft's alkylation: It reacts with ethylene ( $\text{CH}_2=\text{CH}_2$ ) in presence of anhydrous  $\text{AlCl}_3$  to form ethyl derivative of ferrocene.

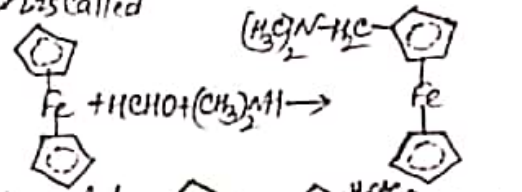


(c) Friedel-Craft's acetylation:

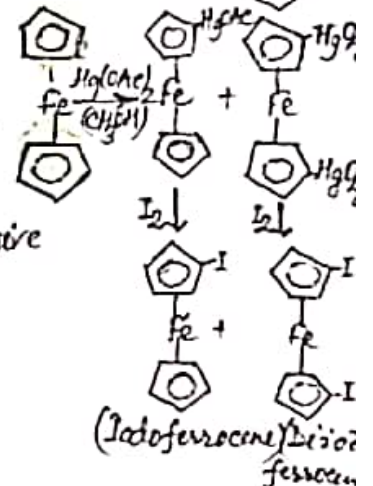
It undergoes acetylation with  $\text{CH}_3\text{COCl}$  (acetyl chloride) in presence of anhydrous  $\text{AlCl}_3$  or acetic anhydride in presence of  $\text{H}_3\text{PO}_4$  (as catalyst) to give acetyl ferrocene.



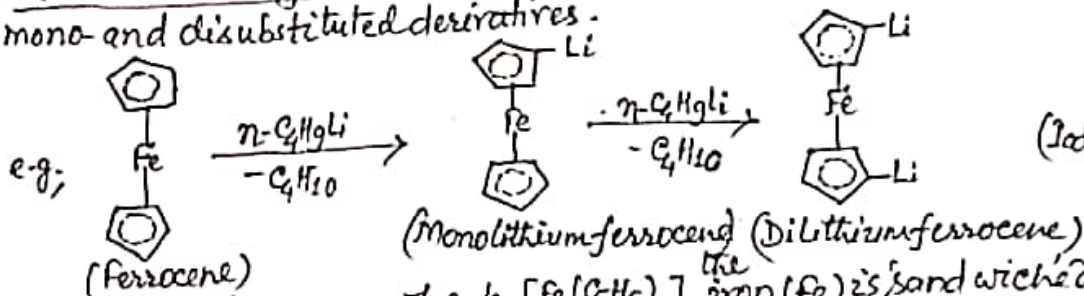
(d) Mannich Condensation: It reacts with formaldehyde ( $\text{HCHO}$ ) in the presence of dimethyl amine to give mono-substituted ferrocene. This reaction is called Mannich condensation or Amino methylation reaction. This reaction shows higher reactivity of ferrocene/cyclopentadienyl rings than benzene.



(e) Mercuriation/Iodination: It reacts with mercuric acetate ( $\text{HgOAc}$ ) to give mono & disubstituted products. These products react with  $\text{I}_2$  to give iodo derivatives. This reaction is indirect method for iodination of ferrocene.



(f) Reaction with alkyl Lithium: It reacts with alkyl lithium to give mono- and disubstituted derivatives.



$\Rightarrow$  Structure: In ferrocene molecule,  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ , the iron (Fe) is sandwiched between two parallel cyclopentadienyl rings ( $\text{C}_5\text{H}_5^-$ ) equidistance from Fe atom. In the solid state, these two rings ( $\text{C}_5\text{H}_5^-$ ) of ferrocene have staggered configuration, as shown in the figure.

In  $\text{C}_5\text{H}_5^-$  (Cyclopentadienyl) group or ion, each C-atom is  $\text{sp}^2$  hybridised.  $\text{C}_6: 2s^1 2p_x^1 2p_y^1 2p_z^1$  or  $\uparrow \uparrow \uparrow \uparrow$  (Excited state) in  $\text{C}_5\text{H}_5^-$  ion/group.

Each C-atom forms three  $\sigma$  bonds using its singly filled  $\text{sp}^2$  hybrid orbitals. A singly filled  $2p_z$  atomic orbital left unhybridised on each C-atom perpendicular to the molecular plane of  $\text{C}_5\text{H}_5^-$  ring. These 5 parallel singly filled atomic orbitals on each C-atom overlap together to form 5  $\pi$ -molecular orbitals. In  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ ,  $\text{Fe}^{2+}$  ion present which shows  $d^2\text{sp}^3$  hybridisation. Each  $\text{C}_5\text{H}_5^-$  ion donates 3 electron pairs which are accommodated in 2 vacant  $d^2\text{sp}^3$  hybrid orbitals of  $\text{Fe}^{2+}$  ion. Thus, 6  $d^2\text{sp}^3$  hybrid orbitals accept 6 e-pairs from  $\text{C}_5\text{H}_5^-$ .

