



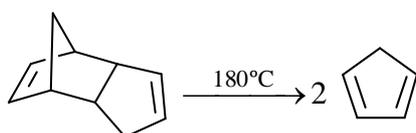
Organometallics (2)

FERROCENE [Bis (cyclopentadienyl)iron(II)]

Ferrocene is the first sandwich compound and was first synthesised by P. L. Pauson and T.J. Kealy in 1951.

Synthesis

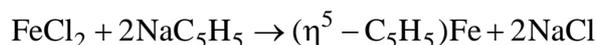
The general synthesis of metallocenes begins with the preparation of parent molecule, cyclopentadiene C_5H_6 which is obtained by thermal cracking of dicyclopentadiene.



Hydrogen atoms on the cyclopentadiene are slightly acidic, therefore, metallic sodium reacts with a solution of cyclopentadiene in tetrahydrofuran (THF) to form sodium cyclopentadienide and liberate hydrogen.



The reaction of sodium cyclopentadienide with FeCl_2 in ethereal solvent, especially THF gives ferrocene.

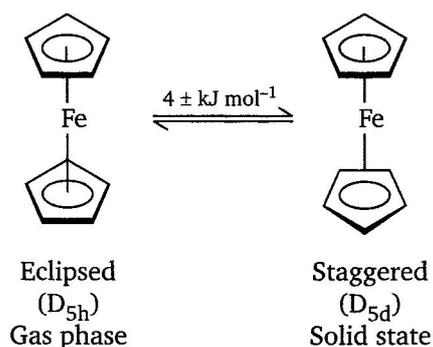


The other metallocenes can also be prepared by this reaction.

Physical Properties

1. Ferrocene is a diamagnetic crystalline solid with an odour like camphor and has a m.p. 174°C , boiling point 249°C and it sublimates at 100°C .
2. Ferrocene is the most stable of all the metallocenes and it is exceptionally stable and does not decompose upto 500°C .
3. It is insoluble in water but dissolves in most organic solvents.
4. It is unaffected by air i.e., not easily oxidized by air. It is also stable towards hydrolysis due to absence of ionic bonding.
5. It is readily oxidized by, for example, aqueous silver ion or I_2 or FeCl_3 or dil. HNO_3 to give paramagnetic blue ferrocenium ion, Cp_2Fe^+ . This large size cation is precipitated by large size anions like I_3^- , Br_3^- , SbCl_6^- , BF_4^- etc.

6.



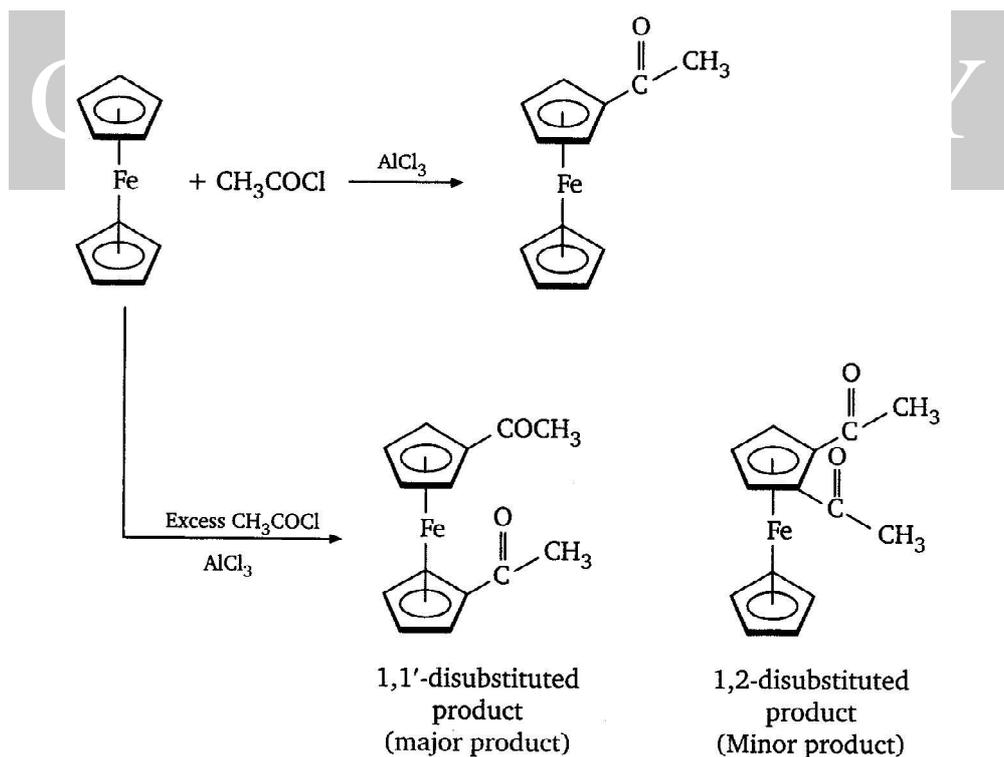
7. Ferrocene gives one ^1H NMR signal because all hydrogens are in the same environment and are equivalent. Ferrocene is not a fluxional molecule.



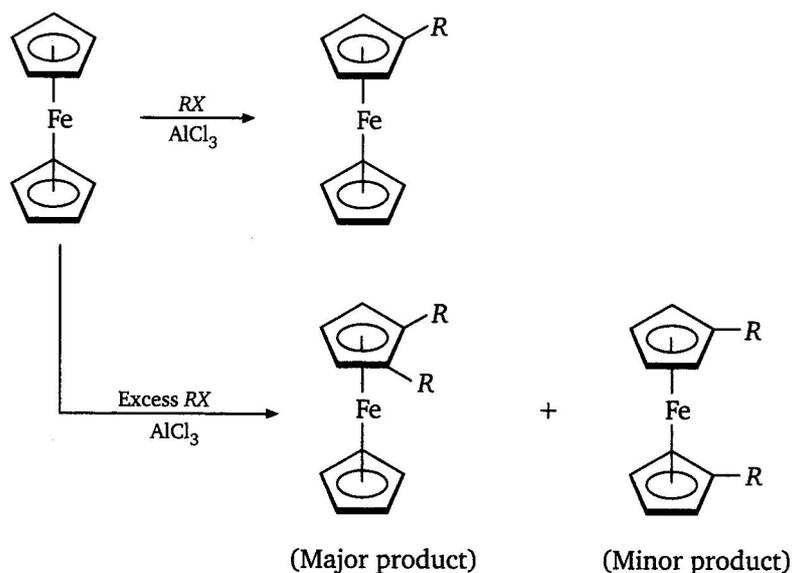
Reactions of Ferrocene

The rings in ferrocene are aromatic and undergo electrophilic substitution reactions. Ferrocene undergoes electrophilic substitution reactions more faster than benzene.

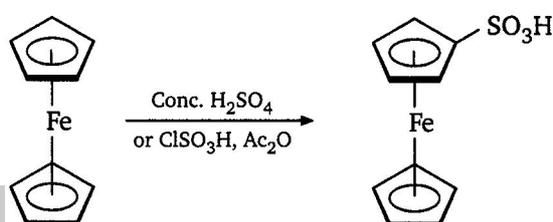
(1) Friedal-Craft Acylation



(2) Friedel-Craft Alkylation

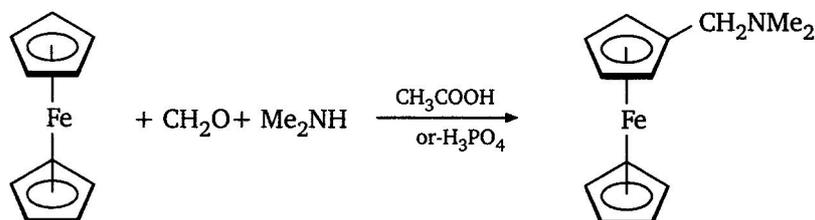


Sulphonation



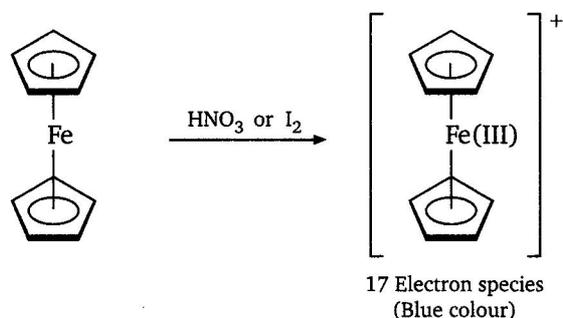
Mannich Reaction

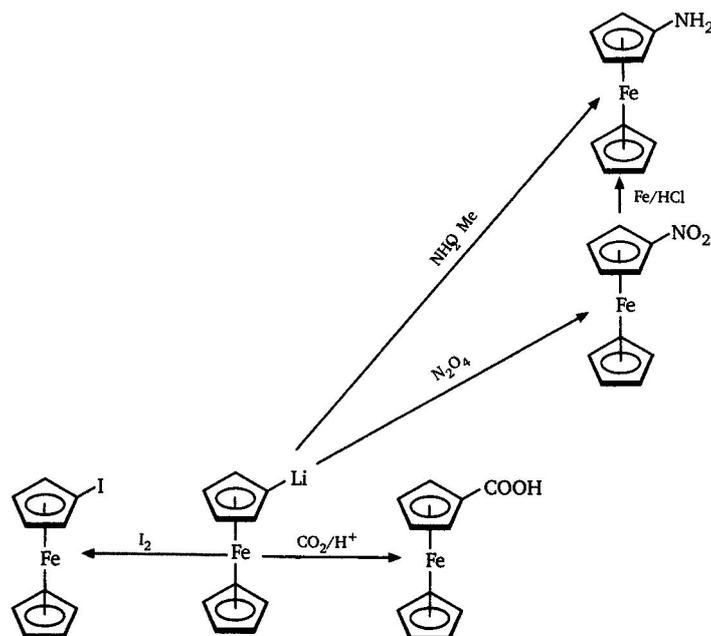
Dimethylamine and formaldehyde undergo a Mannich reaction with ferrocene to give dimethylaminomethylferrocene.



Nitration and Halogenation

The direct introduction of -NO₂ or -X group into ferrocene is not possible because ferrocene is readily oxidized to ferrocenium ion by the oxidizing electrophile and makes it inactive.

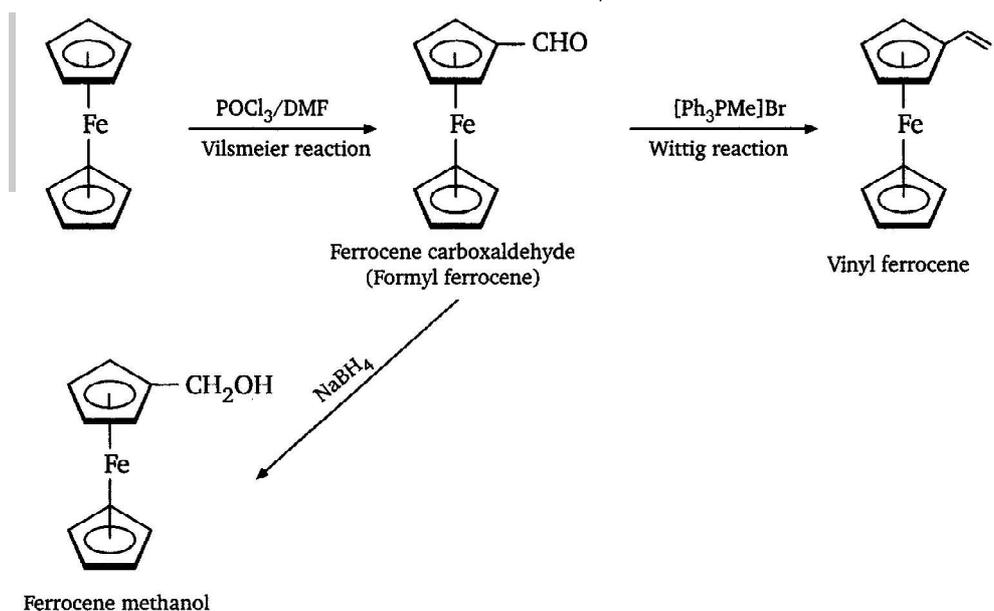




Vilsmeier Reaction

Ferrocene reacts with $POCl_3$ in presence of DMF to give ferrocene carboxaldehyde (Vilsmeier reaction) which on reaction with $[Ph_3PMe]Br$ gives Vinyl ferrocene (Wittig reaction).

Ferrocene carboxaldehyde on reduction with $NaBH_4$ gives ferrocene methanol.



Application of Ferrocene

Ferrocene and its derivatives have many applications because of the redox properties of the iron and the fact that the Cp rings can be derivatized. Some important applications of ferrocene and its derivatives are:

1. as a liquid hydrocarbon fuel additive. Its addition to diesel fuel reduces smoke emissions and increases fuel economy.
2. as electron transfer catalysts.
3. as biosensor.
4. as UV absorber.