Study Notes on Ferrocene

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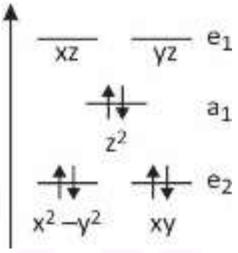
Ferrocene

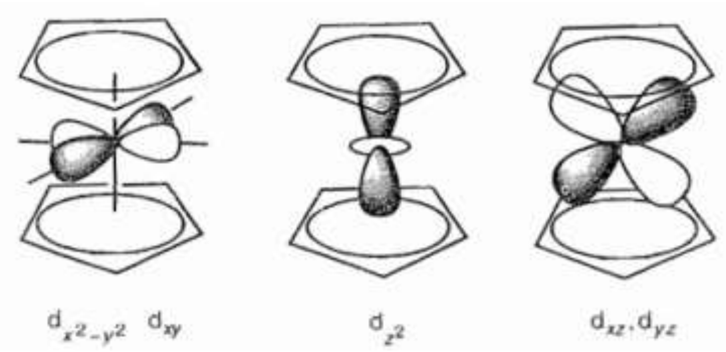
Ferrocene is an orange, crystalline solid which exists in monoclinic form at room temperature. Between 110 K and 164 K, it is triclinic, while below 110 K, it exists in orthorhombic form. It melts at 446 K, sublimes at 673 K and decomposes above 743 K. It is diamagnetic in nature, dissolves in the most organic solvents but is insoluble in water. It remains stable in air.

Structure: In ferrocene, the iron atom is sandwiched between the two cyclopentadienyl rings. The π electron cloud of each ring is delocalized over all five carbon atoms. The two cyclopentadienyl rings have staggered configuration relative to each other. In gaseous state, the two cyclopentadienyl groups acquire eclipsed configuration with respect to each other. The energy barrier to ring rotation is very small.

Bonding: With the help of an electrostatic model, the sequence of the chemically relevant frontier orbitals of metallocenes with axial symmetry can be easily obtained. According to this model, the crystal field generated by two negatively charged Cp rings splits the energy levels of the metal d orbitals. The reason behind the splitting is due to the presence of unequal electrostatic repulsions between the metal d electrons and the charge loops. Refer to the figure given below:

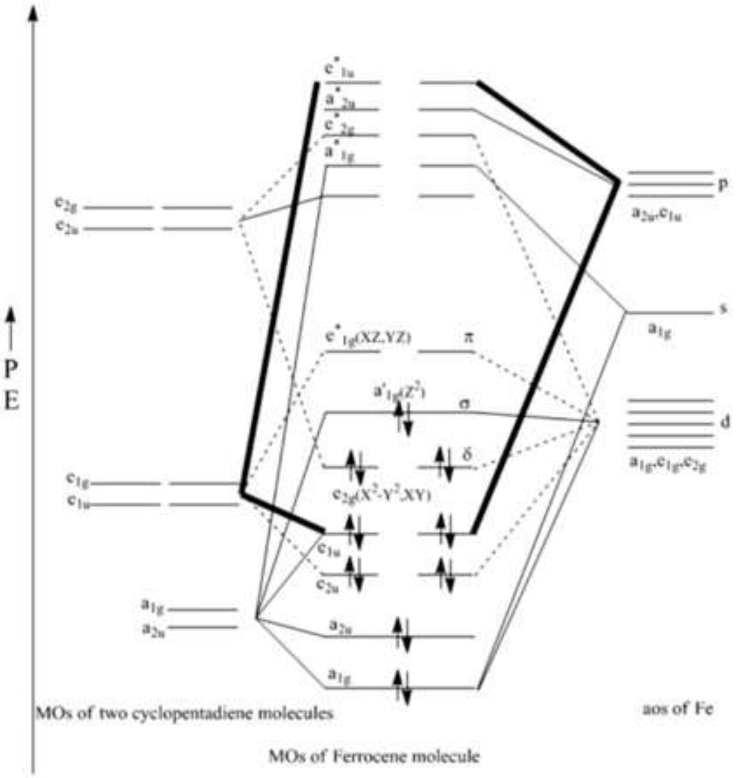


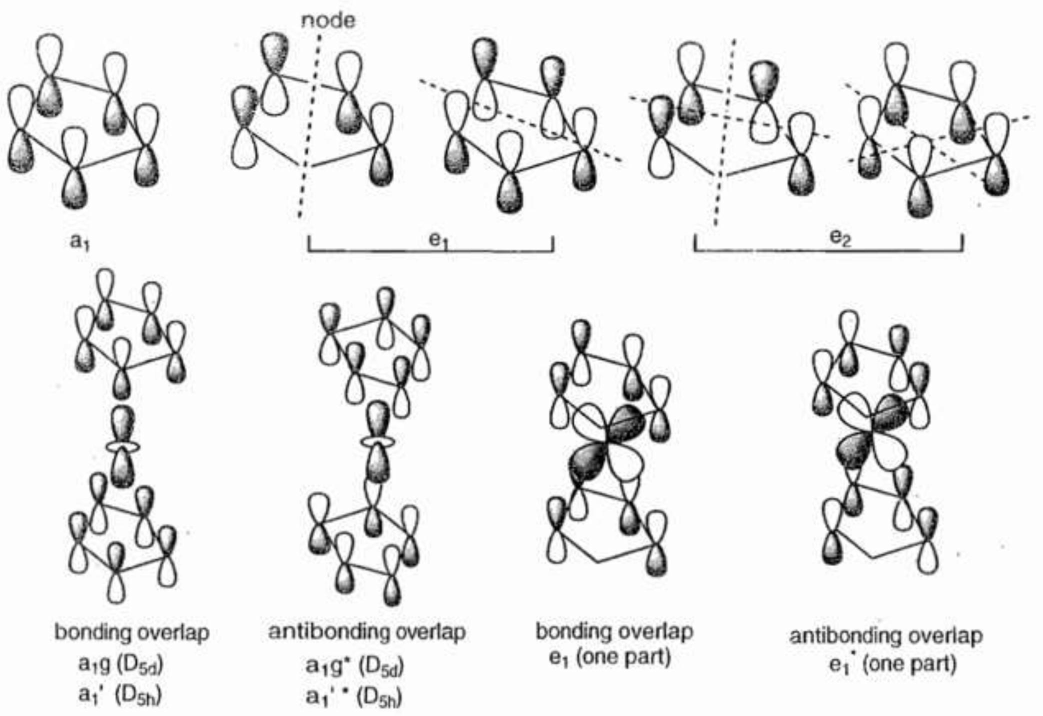
The minimum electron-electron repulsion present between the metal orbitals and r electron density on Cp ring will be for $d_{x^2-y^2}$ and d_{xy} because lobes of these orbitals will not direct towards the Cp ring. The d_{z^2} orbital has one and the d_{xz}/d_{yz} orbitals have two lobes directed towards the Cp ring. So, the correct electronic configuration of the frontier orbital region in the ferrocene is $(e_2)^4(a_1)^2(e_1)^0$. In the chemically relevant frontier orbital region, the order is $e_2 < a_1 < e_1$. This order is the same as obtained from the crystal field model. The energies of these frontier orbitals with reference to the basic orbitals can be regarded as bonding (e_2), nonbonding (a_1) and antibonding (e_1). When oxidation of ferrocene to ferrocenium ion takes place, no significant change will be observed in bond length as the frontier orbitals are neither strongly bonding nor strongly antibonding. Also, the proximity of the frontier orbitals among themselves indicates that metallocenes with 17, 19 or 20 electrons can also exist with stabilities not too far off from the 18 electron metallocenes. By considering the chemical structure of ferrocene, its redox property can be understood; ferrocene can be understood in terms of its chemical structure and from the orbital point of view; oxidation corresponds to the removal of an electron from a nonbonding a_1 orbital. So, due to this, bond lengths can be correlated with the electronic occupancy in the bonding and antibonding orbitals. Ferrocene gets readily oxidized to the ferrocenium ion even by I_2, so the electrophile reacting with ferrocene should not be an oxidizing agent.



The Reactions of Ferrocene and its Derivatives:

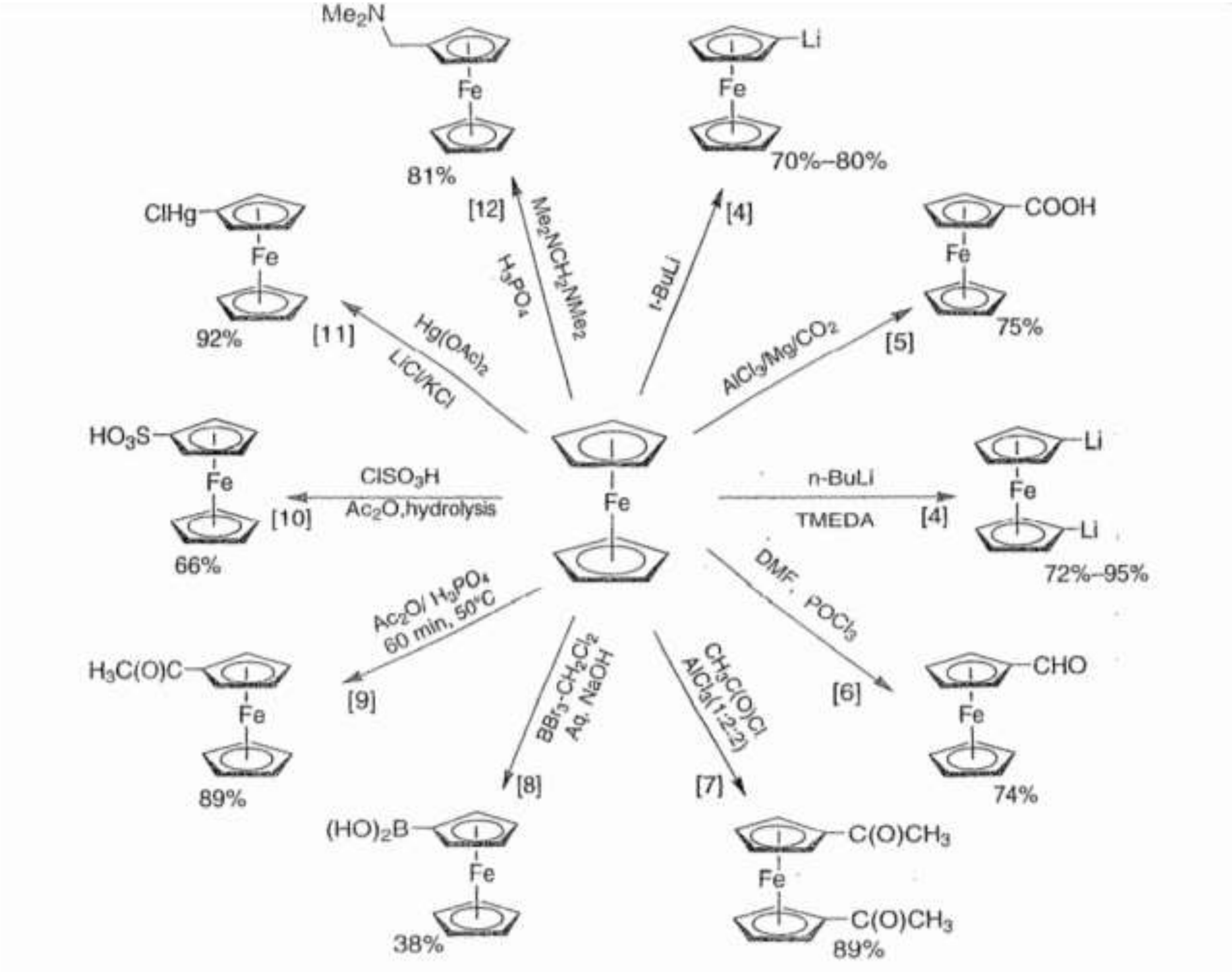
As compared to other organometallic compounds, ferrocene is inexpensive, has high thermal stability and high tolerance to oxygen as well as moisture. In reactions, it behaves like an electron rich compound. Also, it can stabilise stabilize carbocations at its benzylic-like position are properties which pave the way to prepare functionalized substituted ferrocenes. A major interest in ferrocene chemistry is centred around developing chiral chelating ligands with planar and lateral chirality and their use as prochiral ligands in asymmetric catalysis. The use of ferrocenophanes as precursors for ferrocene-based polymers is another important application.



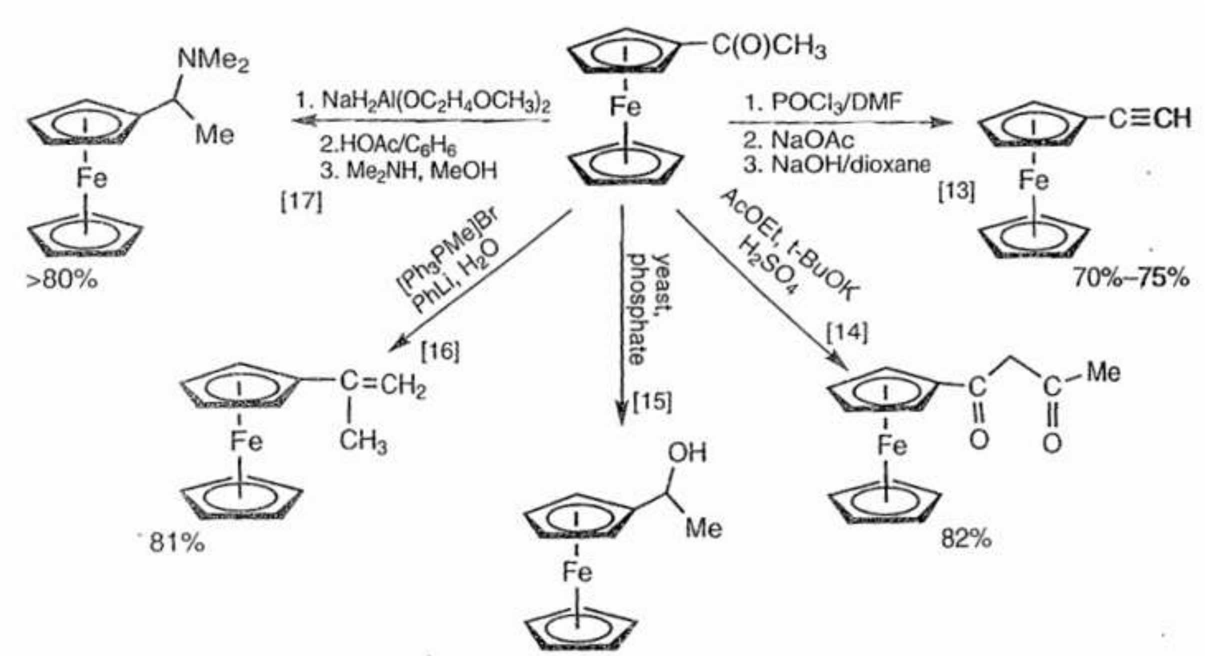


Reactions of Acetyl Ferrocene and Formyl Ferrocene:

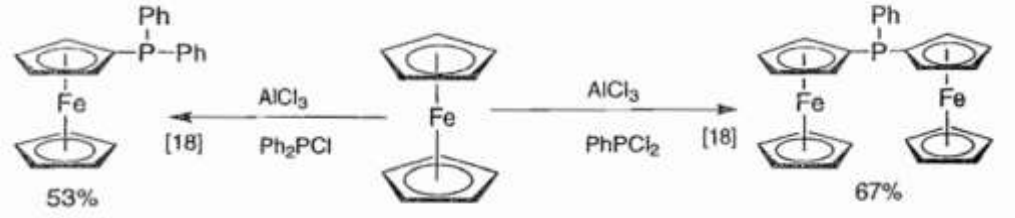
As compared to benzene, toluene, or phenol, the 6π electron system of ferrocene is more electron rich due to which it can undergo aromatic substitution reactions rather easily. In the Friedel-Crafts acetylation, ferrocene is 3.3×10^6 times more reactive than benzene and about 1×10^3 times more reactive than mesitylene. Friedel-Crafts acetylation which uses acetyl chloride and aluminium chloride results in the formation of 1,1′-diacetyl compound. Only one isomer will be formed which points to free rotation of the Cp rings around Fe. In the presence of an excess acetylating agent, 1,1′ and 1,2-derivatives (same ring substitution) are formed in a 60: 1 ratio. This is because deactivation of the Cp ring will take place once an acetyl group is substituted. Mono acetylation of ferrocene will take place under mild conditions or when acetic anhydride and phosphoric acid are used.



The most widely used derivatives are alkynyl ferrocene and N,N-dimethyl-1-ferrocenylethylamine (Ugi's amine). This compound was first prepared by Ivar Ugi, opening diverse synthetic routes for introducing both planar and central chirality on ferrocene derivatives.



When ferrocene undergoes Friedel crafts type reactions with $AlCl_3$ and phenylphosphorus chlorides result in the formation of air stable ferrocene derived tertiary phosphines. Ferrocene undergoes a wide variety of electrophilic substitution reactions. Electrophile should not be oxidizing in nature as ferrocene is prone to oxidation and the oxidized Cp_2Fe^+ (ferrocenium cation) will repel the electrophile. Therefore, nitration, halogenation and similar reactions cannot be carried out directly on ferrocene. The 17-electron ferrocenium ion complex is an excellent radical trap. This unique property enables the ferrocene to stabilize an adjacent carbocation centre. It is mostly prepared in situ by reagents such as I_2 or H_2SO_4, air stable ferrocenium salts with an intense blue colour can readily be isolated by the reaction of ferrocene with oxidants such as p-benzoquinone or $FeCl_3$.



Scheme: Preparation of mono-and di-ferrocenyl phenyl phosphines

$$FeCp_2 + HBF_4.OEt_2 \xrightarrow[Et_2O]{p\text{–benzoquinone}} [FeCp_2][BF_4]$$

$$FeCp_2 + NH_4PF_6 \xrightarrow[H_2O/Acetone]{FeCl_3} [FeCp_2][PF_6]$$