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**E-Content Title:** Transition Metal $\pi$-Complexes: Metal-Cyclopentadienyl Complexes

**Stream:** M. Sc. (4th Semester)
**Metal-Cyclopentadienyl Complexes (η⁵-complexes):** Ligands contributing five electrons formally, upon bonding with a transition metal are called dienyl ligands. For example: cyclopentadienyl group, C₅H₅: Ferrocene, [Fe(η⁵-C₅H₅)₂] and other 'Metallocenes', where metal atoms are sandwiched between two cyclopentadienyl rings.

Large numbers of π-cyclopentadienyl derivatives are known so far. They generally possess high kinetic stability towards thermal decomposition and oxidation. All the metals of first row transition series from titanium to nickel are now known to form neutral bis-(π-cyclopentadienyl) complexes. Vanadium, chromium, cobalt and nickel complexes are isomorphous with ferrocene. Bis-(π-cyclopentadienyl) derivatives of zirconium, technetium, ruthenium, osmium, rhodium and iridium have been prepared. Ruthenium and osmium complexes have structures similar to ferrocene, but with the rings in the eclipsed conformation. They are less stable than ferrocene. Order of reactivity found is:

\[
[(\text{Cp})_2\text{Fe}] < [(\text{Cp})_2\text{Ni}] < [(\text{Cp})_2\text{Co}] < [(\text{Cp})_2\text{V}] < [(\text{Cp})_2\text{Cr}] < [(\text{Cp})_2\text{Ti}]
\]

**Methods of Preparation:** First reported syntheses of ferrocene were nearly simultaneous. Pauson and Kealy synthesised ferrocene using iron (III) chloride and a Grignard reagent, cyclopentadienyl magnesium bromide. Iron (III) chloride is suspended in anhydrous diethyl ether and added to the Grignard reagent. A redox reaction occurs, forming the cyclopentadienyl radical and iron (II) ions. Dihydrofulvalene is produced by radical-radical recombination while the iron (II) reacts with the Grignard reagent to form ferrocene.

Ferrocene undergoes many of the conventional electrophilic substitution reactions of organic chemistry, notably acylation, alkylation, halogenation and metallation; but is more resistant than benzene to hydrogenation.

General method for the preparation of metallocenes is by the action of freshly prepared sodium cyclopentadienide on a halide or other soluble salt of the desired metal in tetrahydrofuran, 1, 2-dimethoxyethane or other ethers.

\[
\text{MX}_2 + 2 \text{[Na(C₅H₅)]} \rightarrow \text{[M(η⁵-C₅H₅)₂]} + 2 \text{NaX}
\]
Complexes of other metals (Cr, Fe, Co, Ni) are also prepared using similar method. However, now-a-days thallium cyclopentadienide is preferred than sodium cyclopentadienide, because sodium being strongly electropositive reduces the product to give hydride complex. Use of thallium salt considerably reduces this possibility.

\[
\text{ReCl}_2 + \text{Na}^+\text{C}_5\text{H}_5^- \rightarrow [\text{ReH(\eta^5-C}_5\text{H}_5)_2]\]

Other important methods of preparation are:

(i) Reaction of metal halides with cyclopentadiene in presence of base (pyridine, diethylamine etc).

\[
\text{MCl}_2 + 2\text{C}_5\text{H}_6 + 2\text{NH(C}_2\text{H}_5)_2 \rightarrow [(\eta^5-\text{C}_5\text{H}_5)_2\text{M}] + 2\text{NH}_2(\text{C}_2\text{H}_5)_2^+\text{Cl}^-; (\text{M}=\text{Fe, Co, Ni})
\]

(ii) Reaction of cyclopentadiene with metal or metal carbonyl:

\[
\begin{align*}
2\text{C}_5\text{H}_6 + \text{Fe (atom)} & \rightarrow [\text{Fe(\eta^5-C}_5\text{H}_5)_2] + \text{H}_2 \\
[\text{Fe(CO)}_5] + 2\text{C}_5\text{H}_6 & \rightarrow [\text{Fe(\eta^5-C}_5\text{H}_5)_2] + 5\text{CO}
\end{align*}
\]

**Structure and Bonding:** Structure of ferrocene in the solid state, as seen by X-ray diffraction is a sandwich in which two cyclopentadienyl groups are staggered with respect to one another. Whereas, electron diffraction study of the vapour shows that in this phase the rings are eclipsed. With reference to ferrous iron, structure of ferrocene is pentagonal anti-prismatic. All C–C distances inside the ring are 1.40 ± 0.02 Å, almost exactly the same as in benzene. Inter–ring distance is 3.22 Å, and iron-carbon distance 2.04 Å. The compound is diamagnetic. Pentagonal ring of Cp (C\(_5\)H\(_5\)), analogous to hexagonal ring of benzene, is obtained by Sp\(^2\) hybridization of carbon atoms.

![Structure of ferrocene](image)

Each p\(_z\) orbital of each carbon atom having one electron is used for formation of mobile (delocalized) \(\pi\)-bond. In this way, five electrons from five carbon atoms and an additional electron (obtained during Cp-formation) give total six electrons, which are placed in three of the five \(\pi\)-bonding orbitals (as electron pair); while remaining two \(\pi\)-bonding molecular orbitals remain vacant. During combination with central Fe (II) [d\(^2\)sp\(^3\)-hybridised], each Cp coordinates giving three electron pairs. Filled orbitals (t\(_{2g}\)) of Fe (II) form back \(\pi\)-bond with vacant antibonding orbitals (\(\pi^*\) MOs) of Cp\(^-\). Thus, each Cp\(^-\) links as \(\pi\)-donor and \(\pi\)-acceptor, with Fe (II).
Linear combinations of five available p orbitals (one on each carbon atom) give rise to three bonding and two anti-bonding molecular orbitals. The most strongly bonding overlap (when all the wave functions on one side of the ring, have the same sign) is designated as 'A2'. At slightly higher energy, there is a doubly degenerate set of molecular orbitals (E1), each of which has one nodal plane. This is followed by another doubly degenerate set of molecular orbitals (E2) with two nodal planes and yet some higher energy. A schematic representation of the π-molecular orbitals of cyclopentadienide anion is given below with their energy increasing from bottom to top. The A2 and E1 orbitals are both fully occupied in the electronic configuration of the Cp− anion whereas the E2 orbitals are net anti-bonding and are unfilled.

For constructing the ten ligand group orbitals of ferrocene from two cyclopentadienide anion, the five group molecular orbitals of one cyclopentadienide anion are combined in pairs with a similar set from the second C5H5 in symmetric and antisymmetric manner [i.e. sum and difference of corresponding molecular orbitals must be taken, e.g. (ψ1+ψ1, ψ1-ψ1, ψ2+ψ2, ψ2-ψ2) etc.] to form the symmetry-adapted linear combination of molecular orbitals (SALC’s). For
example, 'ψ_1+ψ_1' gives rise to a molecular orbital of \(a_{1g}\) symmetry. Overall this gives rise to three sets of ligand molecular orbitals of gerade (g) and ungerade (u) symmetry with respect to the centre of inversion:

1. A low-lying filled bonding pair of \(a_{1g}\) and \(a_{2u}\) symmetry.
2. A filled weakly bonding pair of \(e_{1g}\) and \(e_{1u}\) symmetry.
3. An unfilled anti-bonding pair of \(e_{2g}\) and \(e_{2u}\) symmetry.

Therefore, SARC orbitals for a \([\eta^5-Cp]_2M\) complex; \(\Gamma_\pi = A_{1g} + A_{2u} + E_{1g} + E_{1u} + E_{2g} + E_{2u}\).

By considering the SARC orbitals and how overlap with metal atomic orbitals can be affected, the molecular orbital bonding picture of ferrocene can be constructed. For example, the \(a_{1g}\) SARC orbital can in theory overlap with the Fe 4s and 3d\(^z^2\) orbitals as they are also of \(a_{1g}\) symmetry. This interaction gives rise to the bonding and anti-bonding molecular orbitals of the complex \(a_{1g}\) and \(a_{1g}^*\), respectively. Each combination of ligand molecular orbitals and metal molecular orbitals leads to a bonding molecular orbital \([\psi_{\text{ligand molecular orbital}} + \psi_{\text{metal atomic orbital}}]\)
and a corresponding anti-bonding molecular orbital \([\psi_{\text{ligand molecular orbital}} - \psi_{\text{metal atomic orbital}}]\), providing that the energies of the two component sets are sufficiently close for overlap. Metal orbitals transform as \([A_{1g} (d_z^2, s) + A_{2u} (p_z) + E_{1u} (p_x, p_y) + E_{1g} (d_yz, d_xz) + E_{2g} (d_{x^2-y^2}, d_{xy})]\). Matching atomic orbitals of iron in ferrocene are shown below.

Symmetry matching of SALC orbitals with the metal atomic orbitals

A perusal of the MO diagram for ferrocene indicates that ligand group orbitals can be categorized in three sets: a filled pair of \(a_{1g}\) and \(a_{2u}\) symmetry; a higher energy filled set of \(e_{1g}\) and \(e_{1u}\) symmetry; and even a higher energy unfilled set of \(e_{2g}\) and \(e_{2u}\) symmetry. It can be noticed that the metal \(d_{xz}\) and \(d_{yz}\) orbitals have been found to interact more effectively with the cyclopentadienyl ligand group orbitals than the metal \(s(a_{1g}); p_x, p_y(e_{1u});\) and \(p_z (a_{2u})\) orbitals. These bonds are believed to provide most of the stabilization that holds the ferrocene molecule together. The antibonding \(e_{2g}\) ligand orbitals interact with the metal \(3d_{x^2-y^2}\) and \(3d_{xy}\) orbitals producing slightly bonding molecular orbitals which comprise mostly of metal orbitals. Based on the above simple molecular orbitals picture, it is not surprising that the ferrocene in which all the nine molecular orbitals of the lowest energy are occupied by electrons, is the most stable...
metallocene. These nine electron pairs (total 18 electrons) necessary for stabilization of ferrocene further strengthens EAN rule, but, it is not universal.

Qualitative molecular orbital diagram for ferrocene

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Unpaired Electrons</th>
<th>Electronic Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂V</td>
<td>Pink</td>
<td>3</td>
<td>e²g₁, d¹g₁</td>
</tr>
<tr>
<td>Cp₂Cr</td>
<td>Red</td>
<td>2</td>
<td>e³g₂, d¹g₁</td>
</tr>
<tr>
<td>Cp₂Mn</td>
<td>Amber</td>
<td>5</td>
<td>e²g₂, d¹g₁, e¹g₂</td>
</tr>
<tr>
<td>Cp₂Fe</td>
<td>Orange</td>
<td>0</td>
<td>e⁴g₂, a¹g₁</td>
</tr>
<tr>
<td>Cp₂Co</td>
<td>Pink</td>
<td>1</td>
<td>e⁴g₂, d¹g₁, e¹g₁</td>
</tr>
<tr>
<td>Cp₂Ni</td>
<td>Green</td>
<td>2</td>
<td>e⁴g₂, d¹g₁, e¹g₂</td>
</tr>
</tbody>
</table>
Due to a difference in energies the lowest energy a_{1g} molecular orbital is mainly ligand based with a slight mixture of the Fe 4s and 3d_{x^2} orbitals. Similarly the a_{2u} level has little if any metal character due to higher lying Fe 4p_{z} orbital with which it is formally able to combine. The e_{1g} molecular orbital arises from the bonding combination of the ligand e_{1g} orbitals with the Fe 3d_{xz} and 3d_{yz} orbitals. This is the only symmetry combination of orbitals in the two Cp rings that has appreciable overlap with the metal 3d orbitals to act as an efficient donor and it is thus this interaction which is mainly responsible for the stability of the complex. The corresponding anti-bonding orbitals, e_{1g}^{*} [LUMO], are unfilled in the ground state of ferrocene but they are involved in excited state transitions. The e_{1u} bonding molecular orbitals are again mainly ligand based but with a small contribution from the higher energy Fe 3p_{x}, p_{y} orbitals. The a_{1g} [HOMO] mostly consists of the Fe 3d_{x^2} orbital as the a_{1g} SALC and the metal d_{z^2} orbital result in little or no overlap. The e_{2g} (d_{x^2} + \epsilon_{y}, d_{xy}) metal orbitals are considered weakly-bonding due to poor overlap with the e_{2g} SALC orbitals. Since the occupied orbitals are either of a_{1g}, e_{1g} or e_{2g} type symmetry, no intrinsic barrier to internal rotation is predicted as each of these molecular orbitals are symmetric about the axis of rotation.

**Characteristic Properties:** On the basis of structures η⁵-cyclopentadienyl complexes can be classified in several categories.

1. [M(Cp)₂]: Symmetrical "sandwich" type derivatives represented by [Fe(η⁵-C₅H₅)₂] (ferrocene), [Co(η⁵-C₅H₅)₂], [Mn(η⁵-C₅H₅)₂] etc., often called 'metallocenes'.

2. [(Cp)₂MLₓ]: "Bent metallocene" derivatives, in which the plane of two cyclopentadienyl rings are at an angle and L represents some other ligand such as hydride, alkyl(aryl), halide, alkene, carbon monoxide or even η¹-cyclopentadienyl groups and 'x' may have values generally from one to three. Important examples are [Cp₂ReH], [Cp₂TiCl₂] and [Cp₂TaH₃].

3. [(Cp)₃M₂]: Triple deckers, e.g. [Cp₃Ni₂]. In this complex there is layered structure involving cyclo-pentadienyl rings and nickel atoms.
4. [(Cp)MLx]: 'Half-sandwich" compounds, where L = ligands like H, halide, CO, PR₃ etc. and x ranges from one to four. Most important compounds in this category are cyclopentadienyl carbonyl complexes, e.g. [(η⁵-C₅H₅)V(CO)₄], [(η⁵-C₅H₅)Cr(CO)₃]₂, [(η⁵-C₅H₅)Mn(CO)₃], [(η⁵-C₅H₅)Fe(CO)₂]₂, [(η⁵-C₅H₅)Co(CO)₂], [(η⁵-C₅H₅)Ni(CO)₂] etc. Important fact about these compounds is that the elements with even number of atomic number form dimer, while the elements with odd number of atomic number (V, Mn and Co) form monomer. This behavior is quite opposite to that of normal carbonyls. All these compounds follow EAN rule.

Cyclopentadienyl carbonyl complexes are generally prepared by the action of cyclopentadiene on metal carbonyls or action of carbon monoxide on cyclopentadienyl complexes. Example:

\[ 2 \text{C}_5\text{H}_6 + [\text{Co}_2(\text{CO})_8] \rightarrow 2 [(\eta^5-\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2] + 4 \text{CO} + \text{H}_2 \]

Beryllium and magnesium complexes have special importance with reference to ionic bonding, opposite to covalent bonding. Though, magnosine, [Cp₂Mg], has structure similar to ferrocene, but it is considered mainly ionic. According to \(^1\text{H}-\text{NMR},\) it is fluxional molecule, while x-ray and electron diffraction studies show it a slipped sandwich complex. In which one Cp ring is pentahapto and the other is \(\pi\)- or probably \(\sigma\)-bonded.

Metallocene gives aromatic reactions, compared to benzene metalloccenes are more reactive with electrophilic reagents. Cyclopentadienyl complexes are covalent compounds. These are stable not only against oxidation, but also thermodynamically. Some specific reactions are given below:
- **Aromatic Properties:**

- **Reduction Reaction:** Metal atom or/and cyclopentadienyl group is reduced.
  
  \[
  \text{[Co(\eta^5-C_5H_5)_2] + NaBH}_4 \rightarrow \text{[Co(\eta^5-C_5H_5)(\eta^4-C_4H_6)]} \\
  \text{[Fe(\eta^5-C_5H_5)_2] + Li} \rightarrow \text{Fe} + 2 \text{C}_5\text{H}_5^-
  \]
Transfer of \( \eta^5\text{-C}_5\text{H}_5 \) to other metal:

\[
[M(\eta^5\text{-C}_5\text{H}_5)_2] + \text{FeCl}_2 \rightarrow [\text{Fe}(\eta^5\text{-C}_5\text{H}_5)] + \text{MCl}_2 \quad (\text{M=Cr, Mo, V, Mn})
\]

\[
[Ni(\eta^5\text{-C}_5\text{H}_5)_2] + \text{Ni(CO)}_4 \rightarrow 2[\text{Ni(CO)}(\eta^5\text{-C}_5\text{H}_5)_2] + 2\text{CO}
\]

Addition reaction:

\[
\text{Co (}\eta^5\text{-C}_5\text{H}_5)_2 + \text{CF}_2 = \text{CF}_2 \rightarrow \text{Co}\]

\[
\text{Ni (}\eta^5\text{-C}_5\text{H}_5)_2 + \text{CF}_2 = \text{CF}_2 \rightarrow \text{Ni}\]