Learning Objectives

In this lecture you will learn the following

- The cyclopentadienyl ligands.
- The synthesis and reactivity of metal–cyclopentadienyl complexes.
- The metal–cyclopentadienyl interaction.

Cyclopentadienyl moiety acts as an important “spectator” ligand and is quite ubiquitous in organometallic chemistry. It remains inert to most nucleophiles and electrophiles and solely engages in stabilizing organometallic complexes. The cyclopentadienyl ligands form a wide array of organometallic compounds exhibiting different formulations that begin with the so-called “piano stool” CpML\(_n\) (\(n = 2, 3\) or \(4\)) type ones and extends to the most commonly observed “metallocene” Cp\(_2\)M type ones to even go beyond further to the “bent metallocene” Cp\(_2\)MX\(_n\) (\(n = 1, 2\) or \(3\)) type ones. In the “piano stool” CpML\(_n\) structure, the cyclopentadienyl (Cp) ligand is regarded as the “seat” of the piano stool while the remaining L ligands are referred to as the “legs” of the piano stool. Though the cyclopentadienyl ligand often binds to metal in a \(\eta^5\) (pentahapto) fashion, e. g. as in ferrocene, the other form of binding to metal at lower hapticities, like that of the \(\eta^3\) (trihapto) binding e. g. as in \((\eta^5–\text{Cp})(\eta^3–\text{Cp})\text{W(CO)}_2\) and that of the \(\eta^1\) (monohapto) binding e. g. as in \((\eta^5–\text{Cp})(\eta^1–\text{Cp})\text{Fe(CO)}_2\), are also seen on certain rare occasions.

The binding modes of the cyclopentadienyl ligand in metal complexes can be ascertained to a certain degree by \(^1\text{H NMR}\) in the diamagnetic metal complexes, in which the Cp–protons appear as a singlet between 5.5–3.5 ppm while the \(\beta\) and \(\gamma\) hydrogens come at 7–5 ppm.

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**Cyclopentadienyl–metal interaction**

The frontier molecular orbital of the cyclopentadienyl ligand contains 5 orbitals (\(\Psi_1–\Psi_5\)) residing in three energy levels (Figure \(\langle\text{PageIndex}(1)\rangle\)). The lowest energy orbital \(\Psi_1\) does not contain any node and is represented by an \(a_1\) state, followed by a doubly degenerate \(e_1\) states that comprise of the \(\Psi_2\) and \(\Psi_3\)orbitals, which precede another doubly degenerate \(e_2\) states consisting of \(\Psi_4\) and \(\Psi_5\) orbitals.

![Molecular orbital diagram of cyclopentadienyl ligand](image)
The above frontier molecular orbital diagram becomes more intriguing on moving over to the metallocenes that contain two such cyclopentadienyl ligands. Specifically, in the Cp₂M system, (e. g. ferrocene) each of these above five molecular orbital of the two cyclopentadienyl ligands combines to give ten ligand molecular orbitals in three energy levels (Figure \(\PageIndex{2}\)). Of these, the orbitals that subsequently interact with the metal orbitals to generate the overall molecular orbital correlation diagram for the Cp₂M type of complexes are shown below (Figure \(\PageIndex{3}\)).
Generic metallocene Cp₂M type complexes are formed for many from across the 1st row transition metal series along Sc to Zn. The number of unpaired electrons thus correlates with the number unpaired electrons present in the valence orbital of the metal (Figure 4). Of the complexes of the 1st row transition metal series, the manganocene exists in two distinct forms, one in a high-spin form with five unpaired electrons, e.g. as in Cp₂Mn and the other in a low-spin form with one unpaired electron, e.g. as in Cp*₂Mn owing to the higher ligand field strength of the Cp* ligand. Cobaltocene, Cp₂Co, has 19 valence electrons (VE) and thus gets easily oxidized to the diamagnetic 18 VE valence electron species, Cp₂Co⁺. Of these metallocenes, the much-renowned ferrocene, Cp₂Fe is a diamagnetic 18 VE complex, whose molecular orbital diagram is shown above (Figure \(\PageIndex{3}\)).

Bent metallocenes

Bent metallocenes are Cp₂MXₙ type complexes formed of group 4 and the heavier elements of groups 5–7. In these complexes the frontier doubly degenerate e₂g orbitals of Cp₂M fragment interacts with the filled lone pair orbitals of the ligand (Figure \(\PageIndex{5}\)).
Synthesis of cyclopentadienyl-metal complexes

The metal–cyclopentadienyl complexes are synthesized by the following methods.

i. from Cp−

\[
\text{NaCp} + \text{FeCl}_2 \rightarrow \text{Fe(Cp)}
\]

ii. from Cp+

\[
\text{Fe(CO)}_2 \text{Cp} + \text{C}_5\text{H}_4\text{Br} \rightarrow \text{Fe(CO)}_2\text{Cp(CpH)}
\]

\[\Delta \rightarrow \text{Fe(Cp)}\]
Reactivity of cyclopentadienyl-metal complexes

The reactivity of cyclopentadienyl−metal complexes of the type Cp₂M is shown for a representative nickelocene complex.

i. reaction with NO

ii. reaction with PR₃

iii. reaction with CO

iv. reaction with H⁺
Problems

1. Comment on the p-acceptor property of the cyclopentadienyl ligand.
   Ans: The ligand being anionic shows very little π-acceptor properties.

2. Give the total valence electron count at the metal in a nickelloocene complex.
   Ans: 20 electrons.

3. Explain why the metal center in cobalticene gets easily oxidized.
   Ans: 19 electrons cobalticene gets easily oxidized to 18 electron Cp₂Co⁺.

4. Specify the number unpaired electrons present in chromocene.
   Ans: 2

Self Assessment test

1. Specify the number of unpaired electron present in vanadocene.
   Ans: The ligand being anionic shows very little π-acceptor properties.

2. What different hapticities are exhibited by cyclopentadienyl ligand?
   Ans: 1, 3, and 5.

3. Specify the hapticities of the cyclopentadienyl ligands in Cp₂W(CO)₂.
   Ans: 5 and 3.

4. Specify the hapticity of the cyclopentadienyl ligands in CpRh(CO)₂(PMe₃).
   Ans: 3.

Summary

Cyclopentadienyl moiety is almost synonymous with the transition metal organometallic complexes as the ligand played a pivotal role at the early developmental stages of the field of organometallic chemistry in the 1960s and 1970s. An important quality of the cyclopentadienyl ligand is that it behaves as an extremely good “spectator” ligand being inert to nucleophiles and electrophiles and displays uncanny ability towards stabilizing metal complexes of elements from across the different parts of the periodic table. Cyclopentadienyl moiety thus forms several types of complexes of different formulations like that of the “piano stool” CpMLₙ (n = 2, 3 or 4) types, the metallocene Cp₂M types and the bent metallocene Cp₂MXₙ (n = 1, 2 or 3) types. Cyclopentadienyl metal complexes make valuable catalysts for many
chemical transformations of interest to academia and industries alike. The cyclopentadienyl moiety participates in a complex interaction with the metal involving ligand frontier molecular orbitals and the metal valence orbitals. Cyclopentadienyl metal complexes can be accessed by many methods.