Skills to Develop

In this lecture you will learn the following

- The metal–allyl complexes.
- The metal–diene complexes.
- The metal–cyclobutadiene complexes.
- The respective metal–ligand interactions.

The allyl ligand is often referred to as an “actor” ligand rather than a “spectator” ligand. It binds to metals in two ways *i.e.* in a $\eta^1$ (monohapto) form and a $\eta^3$ (trihapto) form (Figure 1). (i). In its monohapto ($\eta^1$) form, it behaves as an anionic $1e^{-}\text{donor } X$ type of a ligand analogous to that of a methyl moiety while (ii) in a trihapto ($\eta^3$) form, it acts as an anionic $3e^{-}\text{donor } LX$ type of a ligand.

**Figure 1.** Metal–allyl interaction.

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**Metal–allyl interaction**

Of particular interest are the molecular orbitals namely $\Psi_1$, $\Psi_2$ and $\Psi_3$ of the allyl ligand that interact with the metal in a metal allyl complex. The energy of these molecular orbitals increase with the increase in the number of nodes. Of the three, the $\Psi_1$ and $\Psi_2$ orbitals usually engage in ligand to metal $\sigma$–donation, with $\Psi_1$ involving in a dative $L$–type bonding and $\Psi_2$ participating in a covalent $X$–type bonding with the metal $d$ orbitals (Figure 2).
Figure 2. Metal–allyl interactions.

Synthesis of the metal allyl complexes

The metal allyl complexes are synthesized by the following methods.

1. From an alkene complex as shown below.

2. By a nucleophilic attack of an allyl compound as shown below.

3. By an electrophilic attack of an allyl compound as shown below.
Reactions of metal allyl complexes

The reactivities of the metal allyl complexes toward various species are illustrated below.

1. Reaction with nucleophiles

2. Reaction with electrophiles
3. Insertion reaction

4. Reductive elimination

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**Diene complexes**

1,3-Butadiene is a 4e-donor ligand that binds to a metal in a cisoid conformation. The *Dewar–Chatt* model, when applied to 1,3-butadiene, predicts that the ligand may bind to metal either as a L$_2$ (π2) donor type, similar to that of an alkene, or as an LX$_2$ (σ2π) donor type, similar to that of a metalacyclopropane form. The L$_2$ binding of 1,3-butadiene is rare, e.g. as in (butadiene)Fe(CO)$_3$, while the LX$_2$ type binding is more common, e.g. as in Hf(PMe$_3$)$_2$Cl$_2$. An implication of the LX$_2$ type binding is in the observed shortening of the C$_2$–C$_3$ (1.40 Å) distance alongside the lengthening of the C$_1$–C$_2$ (1.46 Å) and C$_3$–C$_4$ (1.46 Å) distances (Figure 3).
Figure 3. Metal−diene interaction in cisoid binding.

The molecular orbitals of the 1,3-butadiene ligand comprises of two filled Ψ₁ (HOMO−1) and Ψ₂ (HOMO) orbitals and two empty Ψ₃ (LUMO) and Ψ₄ (LUMO+1) orbitals. In a metal−butadiene interaction the ligand to metal σ−donation occurs from the filled Ψ₂ orbital of the 1,3-butadiene ligand while the metal to ligand π−back donation occurs on to the empty Ψ₃ orbital of the 1,3-butadiene ligand (Figure 4).
Though cisoid binding is often observed in metal butadiene complexes, a few instances of transoid binding is seen in dinuclear, e.g. as in Os₃(CO)₁₀(C₄H₆), and in mononuclear complexes e.g. as in Cp₂Zr(C₄H₆) (Figure 5).
Two noteworthy synthetic routes are shown below.

**Metal cyclobutadiene complexes**

Cyclobutadiene is an interesting ligand because of the fact that its neutral form, being anti-aromatic (4π-electrons), is unstable as a free molecule (Figure 6), but its dianionic form is stable because of being aromatic (6π-electrons). Consequently, the cyclobutadiene ligand is stabilized by significant metal to ligand π-back donation to the vacant ligand orbitals.
Figure 6. Electronic structure of cyclobutadiene ligand.

A synthetic route to metal cyclobutadiene complex is shown below.

Problems

1. The hapticities displayed by an allyl moiety in binding to metals are? Ans: 1 and 3.
2. Identify which molecular orbitals of an allyl moiety engage in $\sigma$–interaction with a suitable $d$ orbital of a metal in a $\eta^3$–metal allyl complex? Ans: $\Psi_1$ and $\Psi_2$.
3. Predict the product of the reaction.

Ans:
4. Identify which molecular orbitals of a butadiene moiety engage in $\sigma$–interaction with a suitable $d$ orbital of a metal in a $\eta^4$–metal butadiene complex? Ans: $\Psi_2$.

**Self Assessment test**

1. Predict the product of the reaction.

Ans:

2. Identify which molecular orbitals of a butadiene moiety engage in $\pi$–interaction with a suitable $d$ orbital of a metal in a $\eta^4$–metal allyl complex? Ans: $\Psi_3$.

3. Mention the type of orientations displayed by butadiene ligands for binding to metal. Ans: Cisoid (common) and transoid (rare).


**Summary**

Allyl, 1,3–butadiene and cyclobutadiene together constitute an important class of $\sigma$–donor/$\pi$–acceptor ligands that occupy a special place in organometallic chemistry. The complexes of these ligands with metals are important intermediates in many catalytic cycles and hence an understanding of their interaction with metal is of significant importance. In this context, the synthesis, characterization and the reactivities of the organometallic complexes of these ligands are described alongside the respective metal–ligand interactions.