Skills to Develop

In this lecture you will learn the following

- The metal alkene complexes.
- The metal–olefin bonding interactions.
- The synthesis and reactivities of the metal–olefin complexes.
- The umpolung reactivities of olefins in the metal alkene complexes.

Though the first metal olefin complex dates back a long time to the beginning of 19th century, its formulation was established only a century later in the 1950s. While reacting K₂PtCl₄ with EtOH in 1827, the Danish chemist Zeise synthesized the famous Zeise’s salt K[PtCl₃(C₂H₄)]•H₂O containing a Pt bound ethylene moiety and which incidentally represented the first metal–olefin complex (Figure 1).

Figure 1. Zeise’s salt.

The metal–olefin bonding interaction is best explained by the Dewar–Chatt model, that takes into account two mutually opposing electron donation involving σ–donation of the olefinic C=C π–electrons to an empty dπ metal orbital followed by π–back donation from a filled metal dπ orbital into the unoccupied C=C π* orbital. Quite understandably so, for the d⁰ systems, the formations of metal–olefin complexes are not observed. The extent of the C=C forward π–donation to the metal and the subsequent π–back donation from the filled dπ orbital to the olefinic C=C π* orbital have a direct bearing on the C=C bond of the metal bound olefinic moiety in form of bringing about a change in hybridization as well as in the C–C bond distance (Figure 2).
If the metal to ligand π−back donation component is smaller than the ligand to metal σ−donation, then the lengthening of the C–C bond in the metal bound olefin moiety is observed. This happens primarily because of the fact that the alkene to metal σ−donation removes the C=C π−electrons away from the C–C bond of the olefin moiety and towards the metal center, thus, decreasing its bond order and increasing the C–C bond length. Additionally, as the metal to ligand π−back donation increases, the electron donation of the filled metal $d_π$ orbital on to the $π^*$ orbital of the metal bound olefin moiety is enhanced. This results in an increase in the C–C bond length. The lengthening of the C–C bond in metal bound olefin complex can be correlated to the π−basicity of the metal. For example, for a weak π−basic metal, the C–C bond lengthening is anticipated to be small while for a strong π−basic metal, the C–C lengthening would be significant.

Another implication of ligand−metal π−back donation is in the observed change of hybridization at the olefinic C atoms from pure $sp^2$, in complexes with no metal to ligand π−back donation, to $sp^3$, in complexes with significant metal to ligand π−back donation, is observed. The change in hybridization from $sp^2$ to $sp^3$ centers of the olefinic carbon is accompanied by the substituents being slightly bent away from the metal center in the final metalacyclopropane form (Figure 3). This change in hybridization can be conveniently detected by $^1H$ and $^{13}C$ NMR spectroscopy. For example, in case of the metalacyclopropane systems, which have strong metal to ligand π−back donation, the vinyl protons appear 5 ppm (in the $^1H$ NMR) and 100 ppm (in the $^{13}C$ NMR) high field with respect to the respective position of the free ligands.

An interesting fallout of the metal to ligand π−back bonding is the tighter binding of the strained olefins to the metal center as observed in the case of cyclopropene and norbornene. The strong binding of these cyclopropene and norbornene moieties to the metal center arise out of the relief of ring strain upon binding to the metal. Lastly, in the metal−olefin complexes having very little π−back bonding component, the chemical reactivities of the metal bound olefin appear opposite to that of a free olefin. For example, a free olefin is considered electron rich by virtue of the presence of π−electrons in its outermost valence orbital and hence it undergoes an electrophilic attack. However, the metal bound olefin complexes having predominantly σ−donation of the olefinic π−electrons and negligible metal to ligand π−back donation, the olefinic C becomes positively charged and hence undergoes a nucleophilic attack. This nature of reversal of olefin reactivity is called umpolung character.
**Synthesis**

Metal alkene complexes are synthesized by the following methods.

1. Substitution in low valent metals \[
\text{AgOSO}_2\text{CF}_3 + \text{C}_2\text{H}_4 \rightarrow (\text{C}_2\text{H}_4)\text{AgOSO}_2\text{CF}_3
\]

2. Reduction of high valent metal in presence of an alkene \[
(\text{cod})\text{PtCl}_2 + \text{C}_2\text{H}_4 \rightarrow [\text{PtCl}_3(\text{C}_2\text{H}_4)]^+ + \text{Cl}^-
\]

3. From alkyls and related species \[
\text{Cp}_2\text{TaCl}_3 + \text{n-BuMgX} \rightarrow \{\text{Cp}_2\text{TaBu}_3\}
\]

**Reaction of alkenes**

The metal alkene complexes show the following reactivities.

1. Insertion reaction
   These reactions are commonly displayed by alkenes as they insert into metal−X bonds yielding metal alkyls. The reaction occurs readily at room temperature for X = H, whereas for other elements (X = other atoms), such insertions become rare. Also, the strained alkenes and alkynes undergo such insertion readily.

2. *Umpolung* reactions
   *Umpolung* reactions are observed only for those metal−alkene complexes for which the metal center is a poor π−base and as a result of which the olefin undergoes a nuclophilic attack.

3. Oxidative addition
   Alkenes containing allylic hydrogens undergo oxidative addition to give a allyl hydride complex.

**Problems**

1. Predict the product of the reaction.
Ans: \( A = \{(\text{CF}_2=\text{CF}_2)\text{AuMe}(\text{PPh}_3)\} \) and \( B = \text{Au(CF}_2-\text{CF}_2\text{Me})(\text{PPh}_3) \). 2. Specify whether the lengthening/shortening of the C–C bond distance in the metal bound olefin moiety is observed as a result of metal to ligand π–back donation? Ans: Lengthening. 3. Draw the structure of Zeise’s salt. Ans:

4. The change in hybridization at the olefinic C from \( sp^2 \) to \( sp^3 \) primarily arise due to? Ans: Metal-ligand π-back donation.

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**Self Assessment test**

1. Predict the product of the reaction.

Ans: \([\text{PtCl}_3(\text{C}_2\text{H}_4)]^+ \) and Cl\(^-\). 2. Specify whether the lengthening/shortening of the C–C bond distance in the metal bound olefin moiety is observed as a result of ligand to metal σ– donation? Ans: Lengthening. 3. Metalacyclopropane intermediate in a metal bound olefin complex is primarily formed due to which kind of interaction? Ans: Metal–ligand π–back donation 4. The oxidation state of Pt in Zeise’s salt is? Ans: Pt\(^{II}\)

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**Summary**

Alkenes are an important class of unsaturated ligands that bind to a metal by σ–donating its C=C π–electrons and also accepts electrons from the metal in its π* orbital of C=C bond. These symbiotic σ–donation and π–back donation in metal bound olefin complexes have a significant impact on their structure and reactivity properties. Quite importantly, the structural manifestations arising out of these forward σ–donation and π–back donation can be characterized by using \(^1\text{H}, \text{ }^{13}\text{C} \) NMR and IR spectroscopic methods.

Pi-ligands are those that bond to a metal via donating electron density to the metal from their σ-orbitals and their π-orbitals and by the metal center’s donation of electron density into the π* orbitals of the ligands. The degree of π* back-donation from the metal depends upon the energy level of the ligand’s π* orbitals, the lower the energy, the easier it is for the metal to donate electron density. According to molecular orbital theory, it is the metal’s d-electrons that share common symmetry with ligands’ p-orbitals that lead to direct bonding with the metal while those that lie in between the axes of the ligands, including \( d_{xz} \) and \( d_{yz} \) can donate electron density into the empty π* orbitals[1]. The metal orbitals that the ligand participates in backbonding with will help determine the orientation of the ligands in space around the molecule, for example, ethylene blinded to iron will lie in the equatorial plane of the Oh (Octahedral) complex due to the
π* orbital being closer in energy to the dx2-y2 metal orbital than the dxz orbital[2]. The energy of these orbitals and thus the degree of backbonding that occurs can be changed by altering the substituents of the pi-lignads. substituents. The more electronegative the substituents on an alkene ligand, the lower in energy the π* orbitals and the greater the degree of backbonding. \( \pi \) bonding is not limited to a metal's d-orbitals, but can also occur between f-orbitals and pi-electron density as in more exotic organometallic compounds including uranocene, where δ-bonds play an important role[4]. In addition to alkenes, alkynes can also act as pi-ligands and are more stable than alkenes and thus are better π* acceptors in-part because they have 2 additional π and π* orbitals that can participate in bonding.

Bonding and Pi-Backbonding in a generic metal-ethylene system. Image adapted from Pfenning, Brian W., Principles of Inorganic Chemistry (2015) p. 642. Image used with permission (CC BY-SA 4.0; Macbaband).

These type of ligand are anionic and thus act to increase the oxidation state of the metal center. When determining the likely stability of a metal complex using an ionic method of electron counting, each “double-bond” that participates in bonding donates two electrons to the metal center. In an olefin ligand, especially conjugated arenes, not all of the carbons participate directly in bonding[5]. The number of carbon atoms that participate in bonding in an arene ring is referred to as the hapticity symbolized \( \eta_n \) where \( n \) is the number of carbon atoms that are directly bonded to the metal center. This allows ligands of this type to play unique roles in organic mechanisms such as what's referred to as "ring slippage" where, in a ligand substitution, the hapticity of a ligand is reduced followed by the addition of a new ligand to the metal center which is then followed by an increase in the hapticity and the rejection of a different ligand.

Hapticity of greater than 1 in a pi-ligand is not limited to cyclic alkenes or aromatic alkenes corresponding to double bonds but whenever the electron density is spread out over multiple carbons. For example, CH2=CH-CH2- (Allyl Anion) can act as a ligand with \( \eta_3 \) because its delocalized pi-MO's can share symmetry with the metal center's d-orbitals.

Examples of pi-ligands are cyclopentadiene (as in the famous ferrocene sandwich compound), ethylene, benzene and many other alkenes and alkynes.
Contributors

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