

9.1: Metal Alkene Complexes

Learning Objectives

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 K_2PtCl_4 with EtOH in 1827, the Danish chemist Zeise synthesized the famous **Zeise's salt** $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ containing a Pt bound ethylene moiety and which incidentally represented the first metal–olefin complex (Figure 9.1.1).

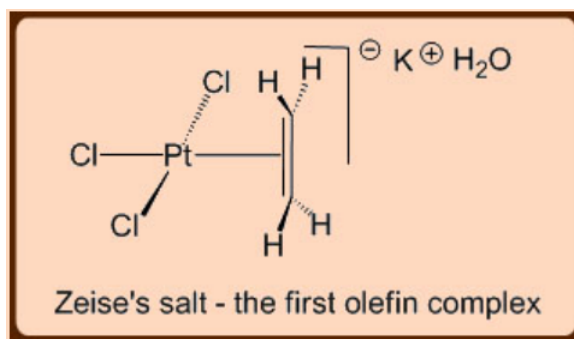


Figure 9.1.1: Zeise's salt

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 $\text{C}=\text{C}$ π -electrons to an empty d_π metal orbital followed by π -back donation from a filled metal d_π orbital into the unoccupied $\text{C}=\text{C}$ π^* orbital. Quite understandably so, for the d^0 systems, the formations of metal–olefin complexes are not observed. The extent of the $\text{C}=\text{C}$ forward π -donation to the metal and the subsequent π -back donation from the filled d_π orbital to the olefinic $\text{C}=\text{C}$ π^* orbital have a direct bearing on the $\text{C}=\text{C}$ bond of the metal bound olefinic moiety in form of bringing about a change in hybridization as well as in the $\text{C}-\text{C}$ bond distance (Figure 9.1.2).

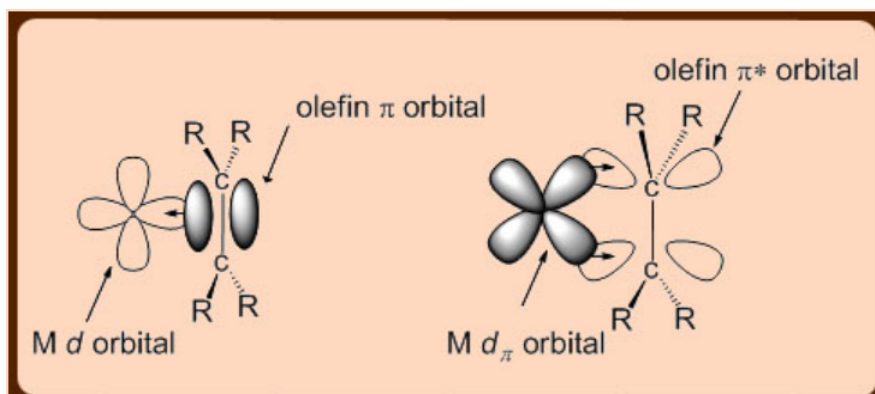


Figure 9.1.2: Metal olefin bonding interactions.

If the metal to ligand π -back donation component is smaller than the ligand to metal σ -donation, then the lengthening of the $\text{C}-\text{C}$ 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 $\text{C}=\text{C}$ π -electrons away from the $\text{C}-\text{C}$ bond of the olefin moiety and towards the metal center, thus, decreasing its bond order and increasing the $\text{C}-\text{C}$ 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 $\text{C}-\text{C}$ bond length. The lengthening of the $\text{C}-\text{C}$ 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 9.1.3). 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.

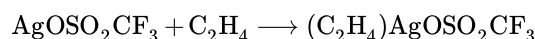


Figure 9.1.3: Metalacyclopropane system and Dewar-Chatt model

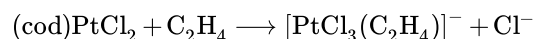
Synthesis

Metal alkene complexes are synthesized by the following methods.

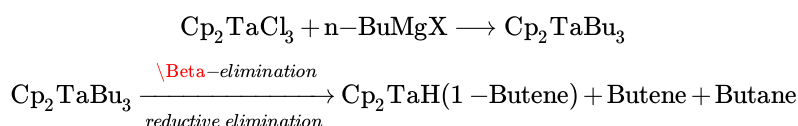
i. Substitution in low valent metals



ii. Reduction of high valent metal in presence of an alkene



iii. From alkyls and related species

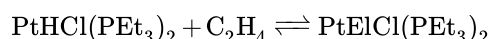


Reaction of alkenes

The metal alkene complexes show the following reactivities.

i. 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 $\text{X} = \text{H}$, whereas for other elements ($\text{X} = \text{other atoms}$), such insertions become rare. Also, the strained alkenes and alkynes undergo such insertion readily.



ii. Umpolung reactions

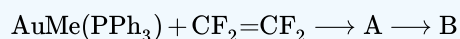
Umpolung reactions are observed only for those metal-alkene complexes for which the metal center is a poor π -base and as a result of which the olefin undergoes a nucleophilic attack.

iii. Oxidative addition

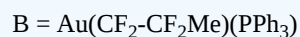
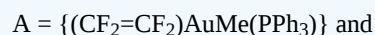
Alkenes containing allylic hydrogens undergo oxidative addition to give a allyl hydride complex.

? Exercise 9.1.1

Predict the product of the reaction.



Answer



? Exercise 9.1.2

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?

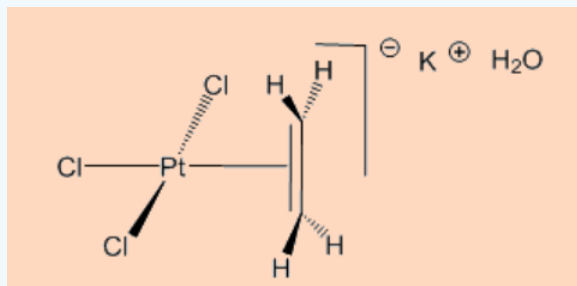
Answer

Lengthening

? Exercise 9.1.3

Draw the structure of Zeise's salt.

Answer



? Exercise 9.1.4

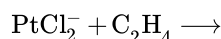
The change in hybridization at the olefinic C from sp^2 to sp^3 primarily arise due to?

Answer

Metal-ligand π -back donation.

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}

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 ^1H , ^{13}C NMR and IR spectroscopic methods.

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