

9.2: Metal Allyl and Diene Complexes

Learning Objectives

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 η^1 (monohapto) form and a η^3 (trihapto) form (Figure 9.2.1). (i). In its monohapto (η^1) form, it behaves as an anionic $1e$ -donor X type of a ligand analogous to that of a methyl moiety while (ii) in a trihapto (η^3) form, it acts as an anionic $3e$ -donor LX type of a ligand.

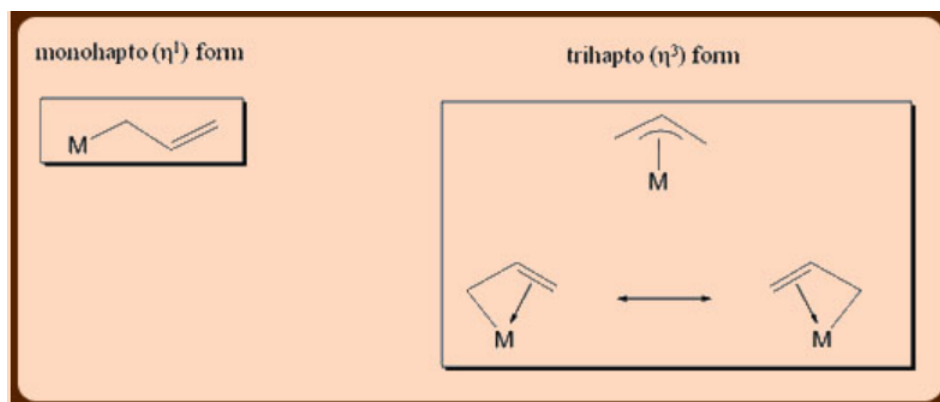


Figure 9.2.1: Metal–allyl interaction.

Metal–allyl interaction

Of particular interest are the molecular orbitals namely Ψ_1 , Ψ_2 and Ψ_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 Ψ_1 and Ψ_2 orbitals usually engage in ligand to metal σ -donation, with Ψ_1 involving in a dative L-type bonding and Ψ_2 participating in a covalent X-type bonding with the metal d orbitals (Figure 9.2.2).

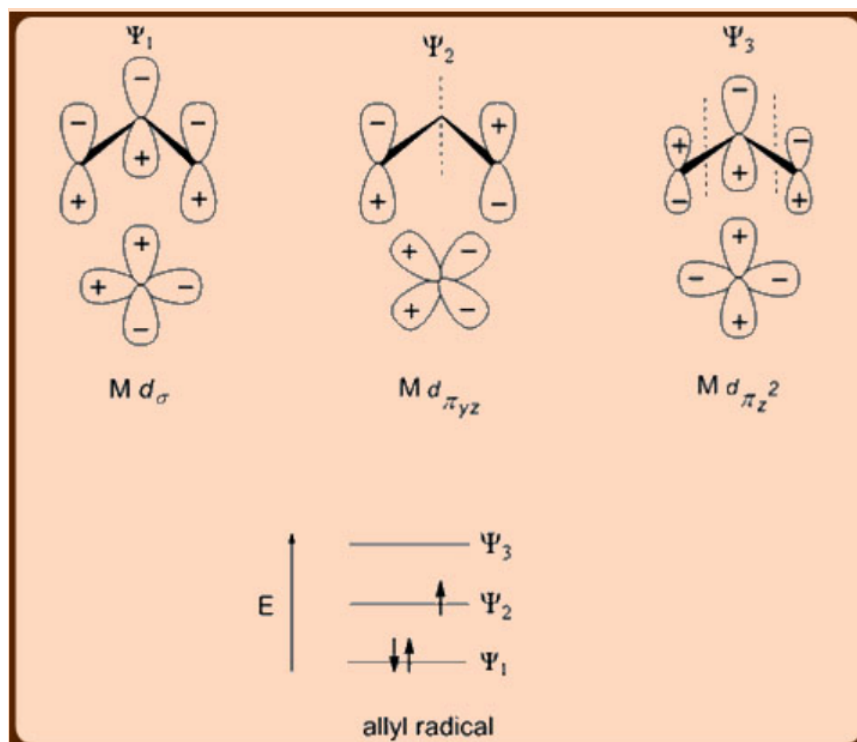
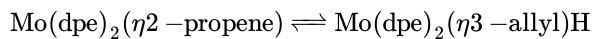


Figure 9.2.2: Metal-allyl interactions.

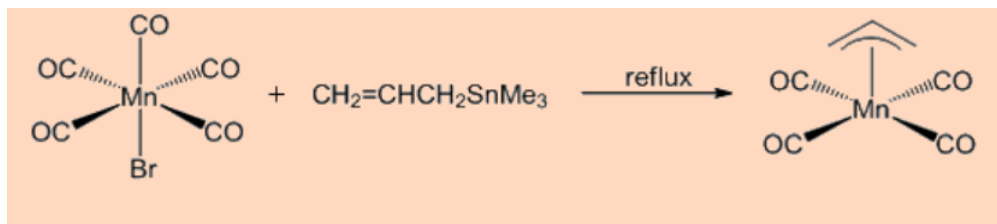
Synthesis of the metal allyl complexes

The metal allyl complexes are synthesized by the following methods.

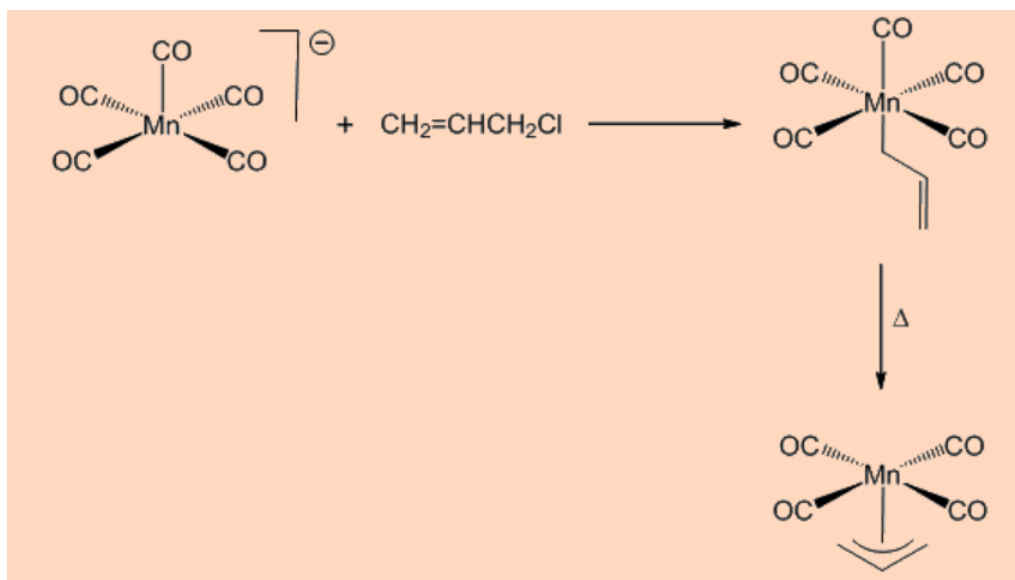
i. From an alkene complex as shown below.



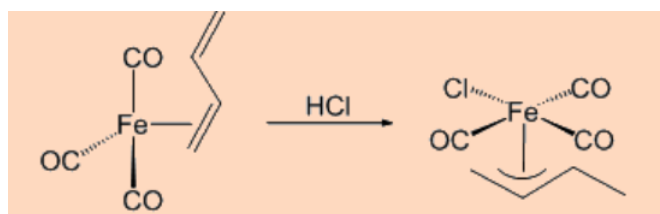
ii. By a nucleophilic attack of an allyl compound as shown below.



iii. By an electrophilic attack of an allyl compound as shown below.



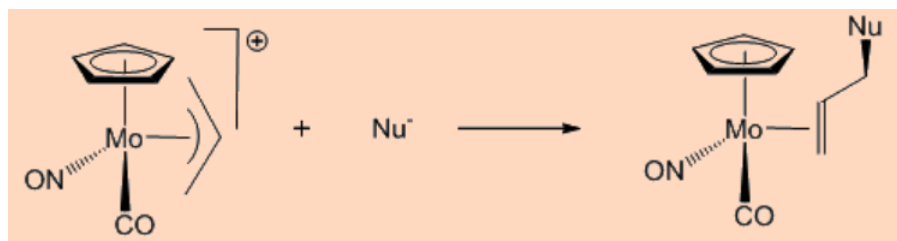
iv. From a diene complex as shown below.



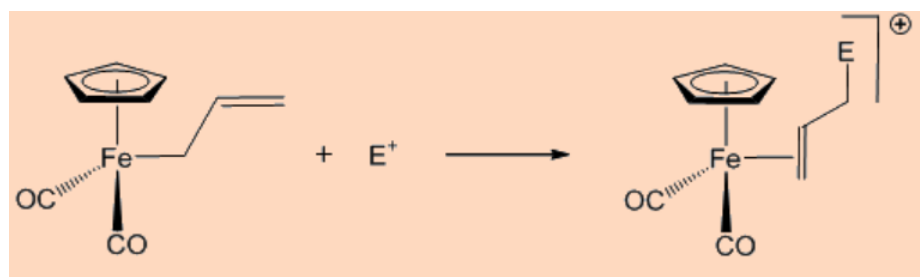
Reactions of metal allyl complexes

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

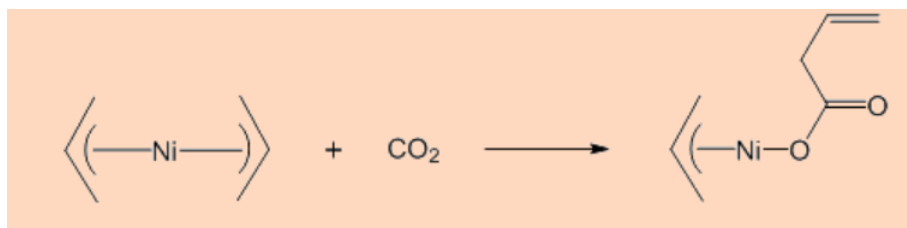
i. Reaction with nucleophiles



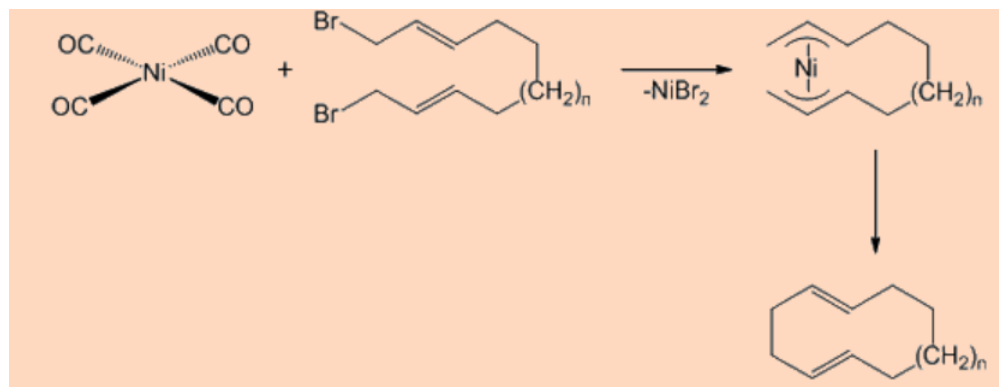
ii. Reaction with electrophiles



iii. Insertion reaction



iv. Reductive elimination



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 an L_2 (π_2) donor type, similar to that of an alkene, or as an LX_2 ($\sigma_2\pi$) donor type, similar to that of a metalacyclopropane form. The L_2 binding of 1,3-butadiene is rare, *e.g.* as in $(\text{butadiene})\text{Fe(CO)}_3$, while the LX_2 type binding is more common, *e.g.* as in $\text{Hf(PMe}_3)_2\text{Cl}_2$. An implication of the LX_2 type binding is in the observed shortening of the $\text{C}_2\text{--C}_3$ (1.40 Å) distance alongside the lengthening of the $\text{C}_1\text{--C}_2$ (1.46 Å) and $\text{C}_3\text{--C}_4$ (1.46 Å) distances (Figure 9.2.3).

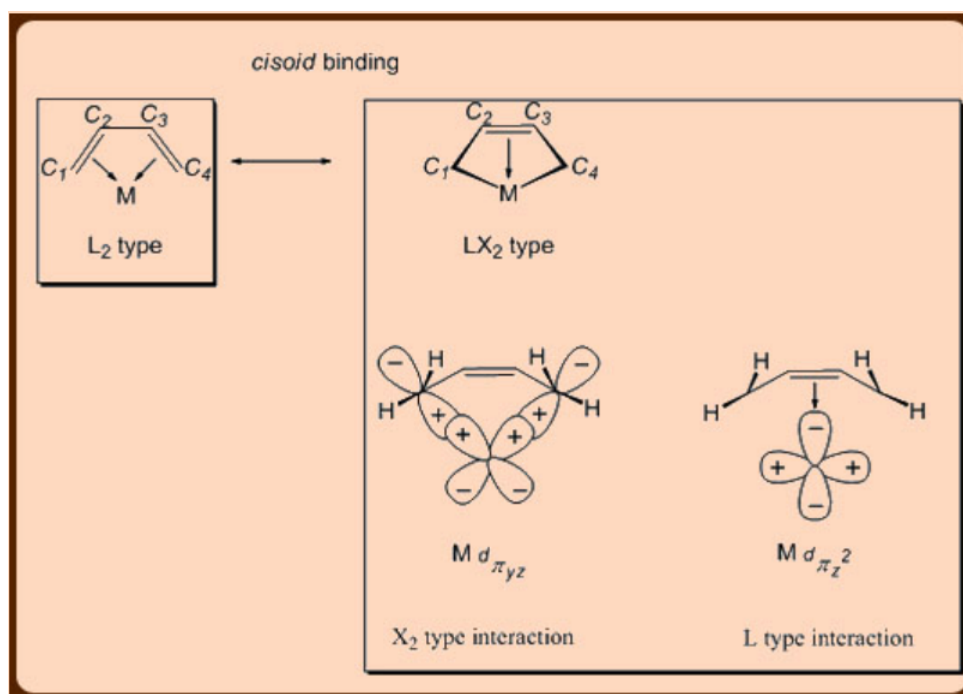


Figure 9.2.3: Metal–diene interaction in *cisoid* binding.

The molecular orbitals of the 1,3-butadiene ligand comprises of two filled Ψ_1 (HOMO–1) and Ψ_2 (HOMO) orbitals and two empty Ψ_3 (LUMO) and Ψ_4 (LUMO+1) orbitals. In a metal–butadiene interaction the ligand to metal σ -donation occurs from the filled Ψ_2

orbital of the 1,3-butadiene ligand while the metal to ligand π -back donation occurs on to the empty Ψ_3 orbital of the 1,3-butadiene ligand (Figure 9.2.4).

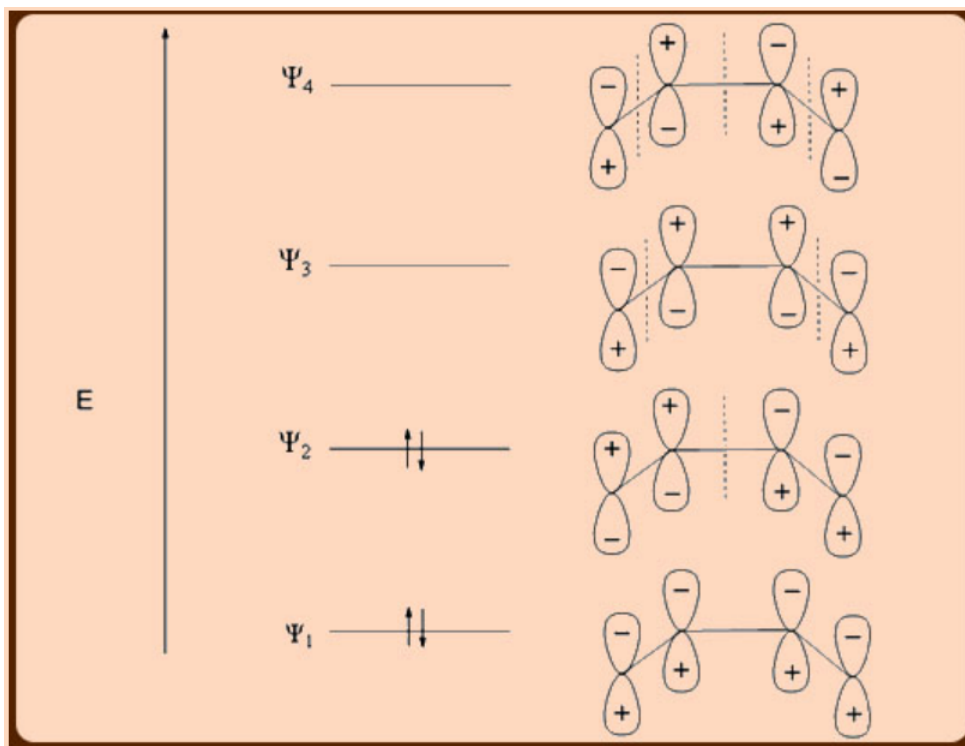


Figure 9.2.4: Metal-diene interaction.

Though *cisoid* binding is often observed in metal butadiene complexes, a few instances of *transoid* binding is seen in dinuclear, *e.g.* as in $\text{Os}_3(\text{CO})_{10}(\text{C}_4\text{H}_6)$, and in mononuclear complexes *e.g.* as in $\text{Cp}_2\text{Zr}(\text{C}_4\text{H}_6)$ (Figure 9.2.5).

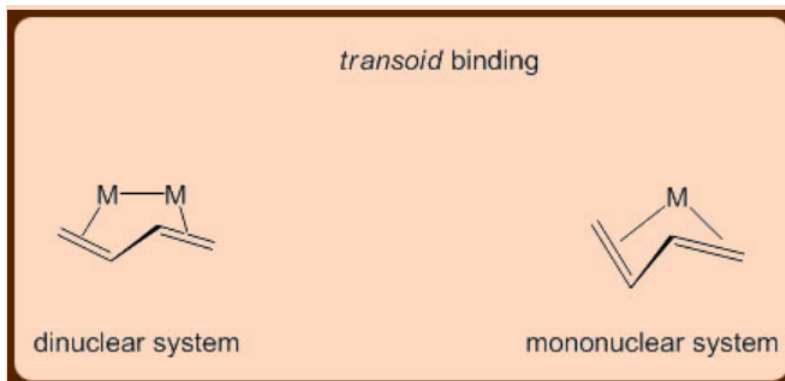
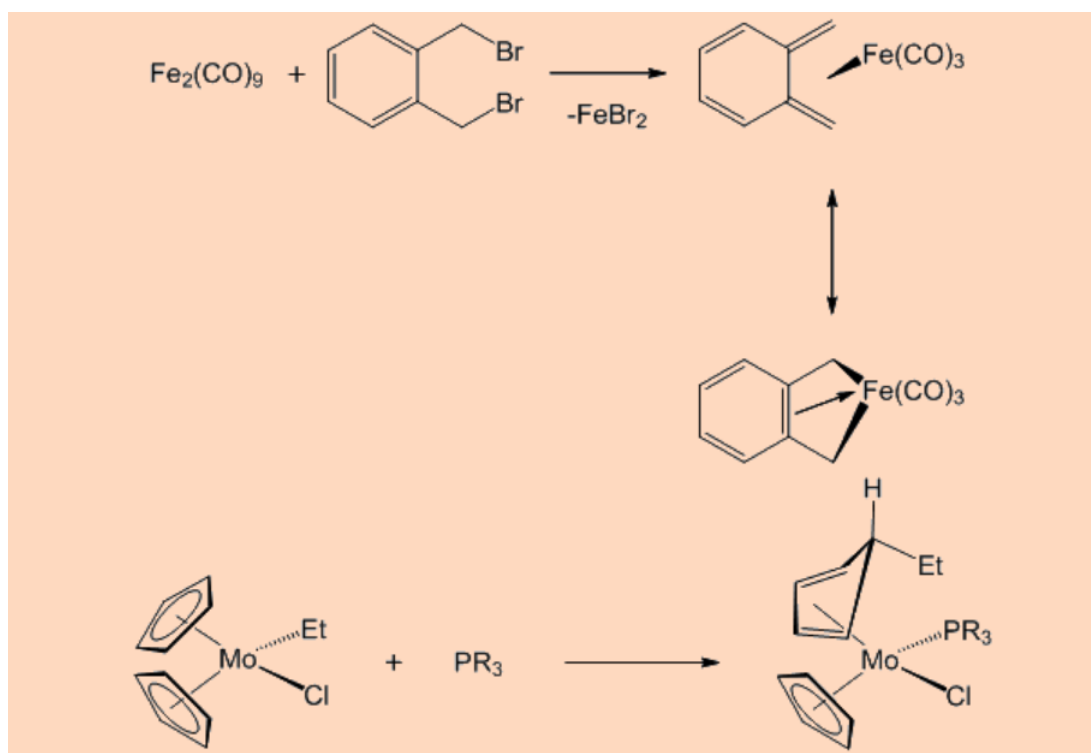


Figure 9.2.5: Metal-diene interaction in *transoid* binding.

Synthesis of metal butadiene complex

Metal butadiene complexes are usually prepared by the same methods used for synthesizing metal alkene complexes. 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 9.2.6), 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.

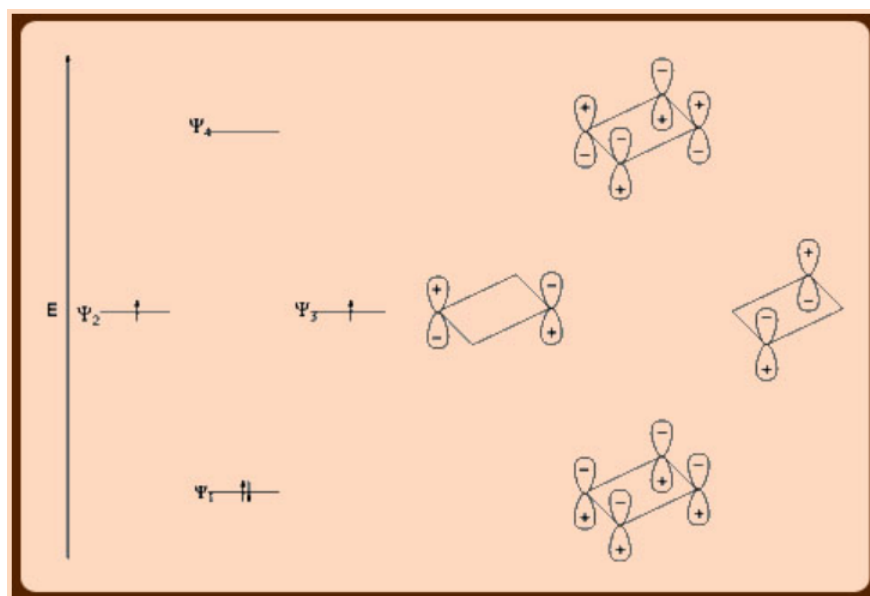
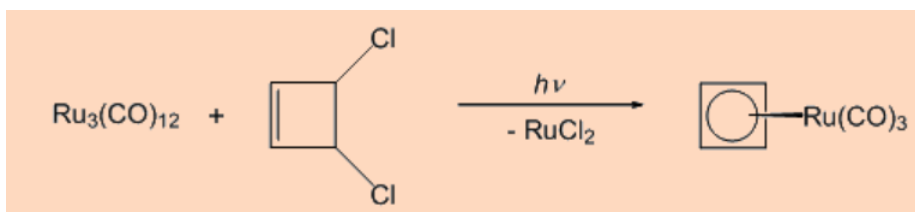


Figure 9.2.6: Electronic structure of cyclobutadiene ligand.

A synthetic route to metal cyclobutadiene complex is shown below.



Problems

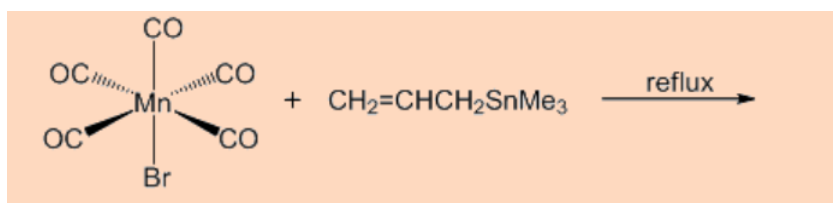
1. The hapticities displayed by an allyl moiety in binding to metals are?

Ans: 1 and 3.

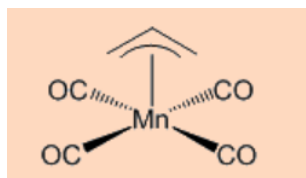
2. Identify which molecular orbitals of an allyl moiety engage in σ -interaction with a suitable d orbital of a metal in a η^3 -metal allyl complex?

Ans: Ψ_1 and Ψ_2 .

3. Predict the product of the reaction.



Ans:

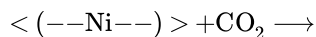


4. Identify which molecular orbitals of a butadiene moiety engage in σ -interaction with a suitable d orbital of a metal in a η^4 -metal butadiene complex?

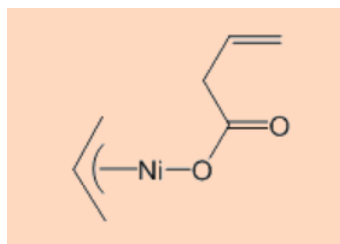
Ans: Ψ_2 .

Self Assessment test

1. Predict the product of the reaction.



Ans:



2. Identify which molecular orbitals of a butadiene moiety engage in π -interaction with a suitable d orbital of a metal in a η^4 -metal allyl complex?

Ans: Ψ_3 .

3. Mention the type of orientations displayed by butadiene ligands for binding to metal.

Ans: Cisoid (common) and transoid (rare).

4. Comment on the number of π -electrons present in the cyclobutadiene moiety of a metal cyclobutadiene complex.

Ans: 6 π -electrons.

Summary

Allyl, 1,3-butadiene and cyclobutadiene together constitute an important class of σ -donor/ π -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.

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