Allyl Complexes

An allyl ligand can functions as a monohapto η^1 (one electron donor) as Me ligand or a trihapto η^3 (three electron donor) as enyl ligand. As a monohapto η^1 ligand it binds the metal with a σ bond with a free C = C bond as shown in Fig. 5.21. Intermediate cases between Figure 5.21 (a) and 5.21 (b) are also known :

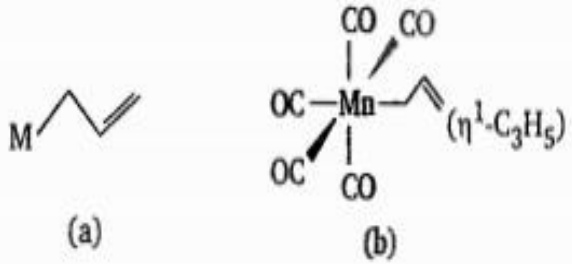


Fig. 5.21

As a trihapto η^3-ligand, it has delocalized π-electrons over the three π-orbitals and has all the three carbon atoms at the same bonding distance from the metal (Figure 5.22)

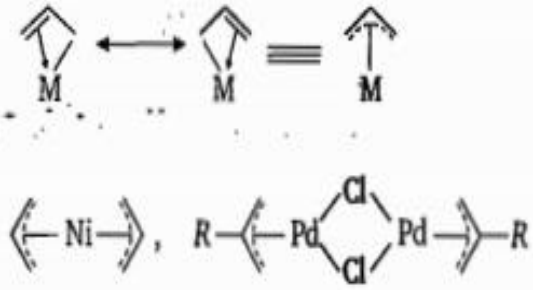


Fig. 5.22

Bonding between metal and $\eta^3 - C_3H_5$ ligand is shown in Figure 5.23. The three π-molecular orbitals of the allyl radical can overlap with σ and π orbitals of the metal. The lowest energy π orbital of η^3-allyl ligand can donate its electron density to a suitable orbital on the metal to form a σ-bond.

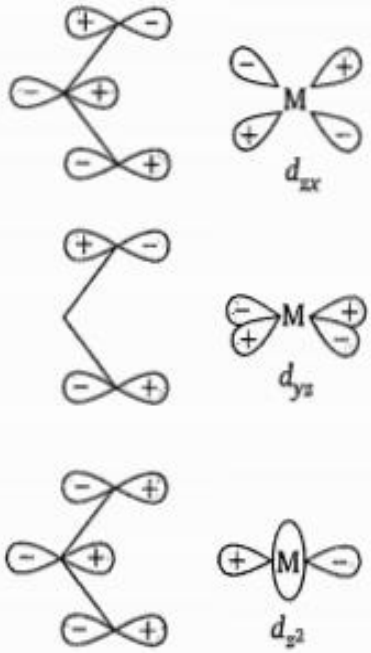
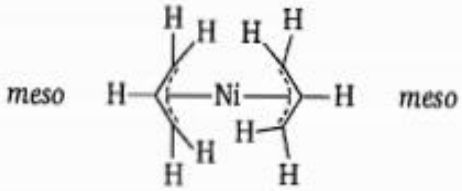
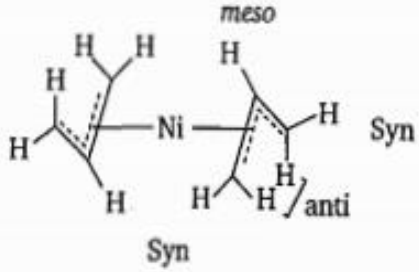


Fig. 5.23 Bonding interactions between metal *d*-orbitals and the π-orbitals of an allyl ligand

The next π-orbital, non-bonding in free allyl can act as a π-donor or π-acceptor depending upon the electron distribution between the metal and the η^3-allyl ligand. The highest energy empty π-orbital acts as a π-acceptor. Therefore, these can be synergistic σ-and π-interactions between metal and η^3-allyl ligand. The C—C—C bond angle within the η^3-allyl ligand is about 120° which is consistent with sp^2-hybridization. The π-interaction between a π-orbital of allyl ligand and the metal d_{xz} orbital is not very significant.

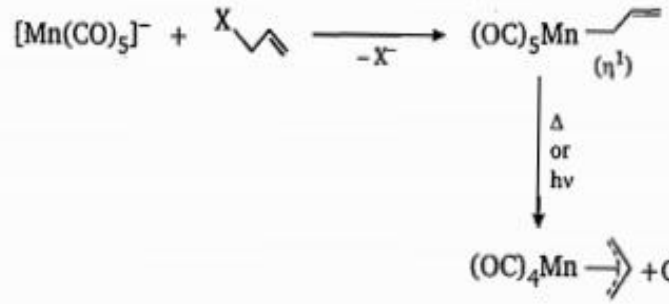
The anti (*trans* to *meso*) hydrogen atoms bent away from the metal and the syn (*cis* to *meso*) and *meso* hydrogen atoms bent towards the metal.





Synthesis of Allyl complexes

1. By the reaction of organometallic anion and allyl halides.



where X = Cl, Br

In this reaction loss of one CO ligand results in conversion of η^1- to η^3-allyl.

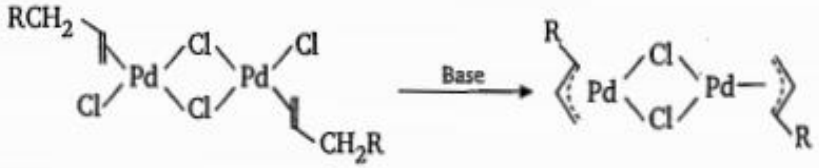
The $[Mn(CO)_5]^-$ ion displace X^- from allyl halide to give an 18-electron product containing η^1-allyl ligand. The allyl ligand switches to η^3-allyl when a CO ligand is lost.

2. By the reaction of metal halide with the Grignard reagent.

$$NiX_2 + 2CH_2 = CHCH_2MgX \longrightarrow Ni(\eta^3 - C_3H_5)_2 + MgX_2,\ X = Cl, Br$$

$$ZrX_4 + 4CH_2 = CHCH_2MgX \longrightarrow Zr(\eta^3 - C_3H_5)_4 + 4MgX_2$$

3. From alkenes



The coordinated allyl group is susceptible to nucleophilic attack and very useful in organic synthesis.

Buta-1,3-diene complexes

Buta-1, 3-diene usually acts as a 4e donor in its *cisoid* conformation. The two possible bonding interactions between metal and butadiene ligand are shown below:

(I) (II)

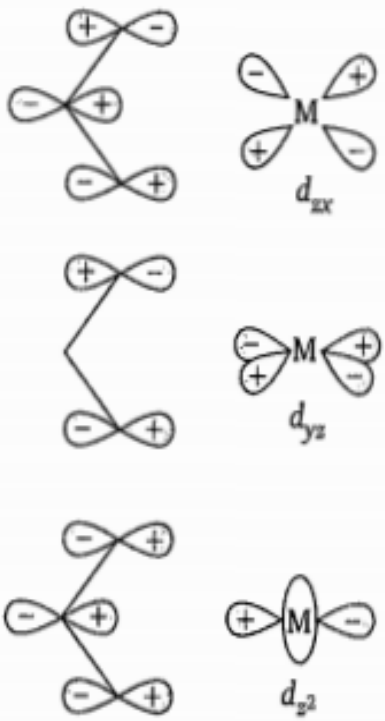


Fig. 5.23 Bonding interactions between metal *d*-orbitals and the π-orbitals of an allyl ligand

The next π-orbital, non-bonding in free allyl can act as a π-donor or π-acceptor depending upon the electron distribution between the metal and the η^3-allyl ligand. The highest energy empty π-orbital acts as a π-acceptor. Therefore, these can be synergistic σ-and π-interactions between metal and η^3-allyl ligand. The C—C—C bond angle within the η^3-allyl ligand is about 120° which is consistent with sp^2-hybridization. The π-interaction between a π-orbital of allyl ligand and the metal d_{xz} orbital is not very significant.

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