

# Nucleophilic addition and abstraction

- In the case of *reductive elimination* and *migratory insertion* we have seen how reaction can occur between two ligands of the coordination sphere, therefore causing reaction between two organic fragments resulting in an independent organic product once eliminated.
- In contrast, a metal can also activate a ligand so that direct attack of an external reagent can take place on the ligand without prior binding of that reagent to the metal.
- The attacking reagent can be either an electrophile or a nucleophile.

## ➤ ***Nucleophilic attack***

**Favored when the metal fragment  $L_nM$  is a poor  $\pi$  base but a good  $\sigma$  acid.**

e.g. if  $L_nM$  bears a net positive charge or has electron-withdrawing ligands, one of the ligands L may be depleted of electron density to such an extent that a nucleophile,  $Nu^-$  (e.g.,  $LiMe$ ,  $OH^-$ , etc.), can attack L.

## ➤ ***Electrophilic attack***

**Favored when the metal is a weak  $\sigma$  acid but a strong  $\pi$  base.**

e.g. if  $L_nM$  has a net anionic charge, a low oxidation state, and ligands L that are good donors. The electron density of one of the ligands is enhanced by back donation so that it now becomes susceptible to attack by electrophiles,  $E^+$  ( $H^+$ ,  $MeI$ , etc.).

***Two possible modes of nucleophilic or electrophilic attack are found:***

**1) *Addition***

- The reagent can become covalently attached to the ligand L so that a bond is formed between the reagent and L.
- In this case, the newly modified ligand stays on the metal and we have an *addition*.

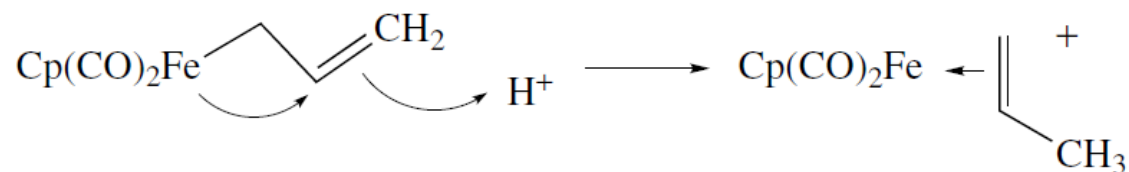
**2) *Abstraction***

- Alternatively, the reagent can detach a fragment from the ligand L or even detach the entire ligand, in which case the modified reagent leaves the coordination sphere of the metal and we have an *abstraction*.
- *A nucleophile abstracts a cationic fragment, such as H<sup>+</sup> or Me<sup>+</sup>, while an electrophile abstracts an anionic fragment, such as H<sup>-</sup> or Cl<sup>-</sup>.*

*Note: Often, reaction with an electrophile generates a positive charge on the complex and prepares it for subsequent attack by a nucleophile.*

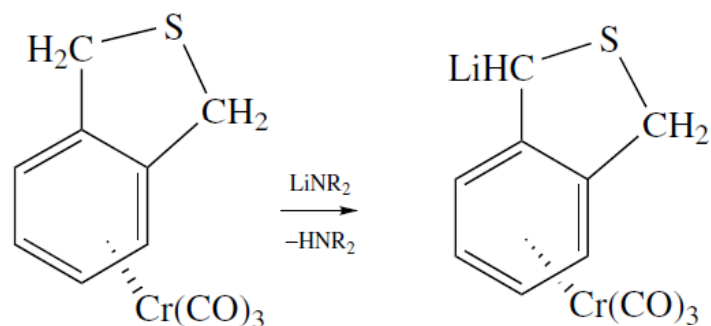
### ***Electrophilic addition of a proton (protonation)***

- When the added electrophile is a proton, the reaction is normally considered as a protonation by an acid.



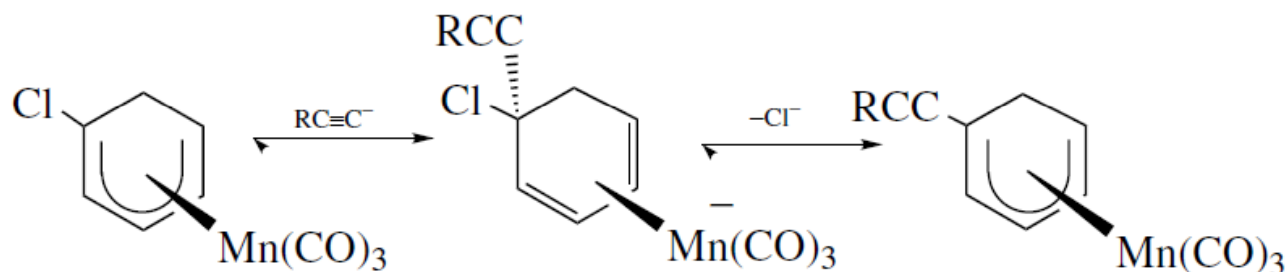
### ***Nucleophilic abstraction of a proton (deprotonation)***

- When a nucleophile abstracts H<sup>+</sup>, we normally consider the reaction as deprotonation by a base.

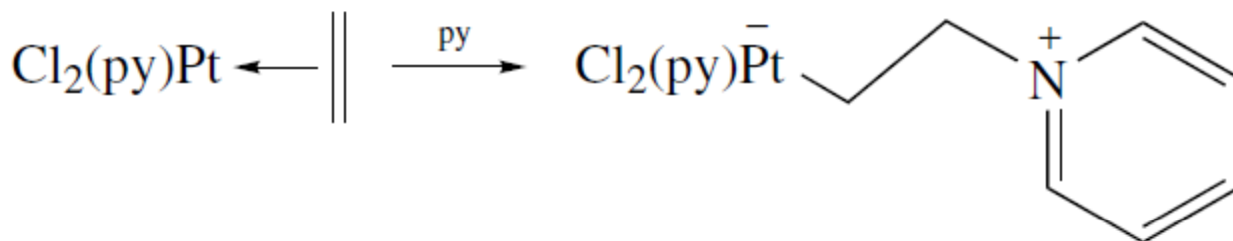


**For nucleophilic addition reactions, in general:**

- Nucleophiles tend to **reduce the hapticity of the ligands** to which they add because they displace the metal from the atom to which the addition takes place.
- **an  $L_m X_n$  ligand is converted to an  $L_m X_{(n-1)}$  ligand.**
- **an  $L_m$  ligand is converted to an  $L_{(m-1)} X$  ligand.**



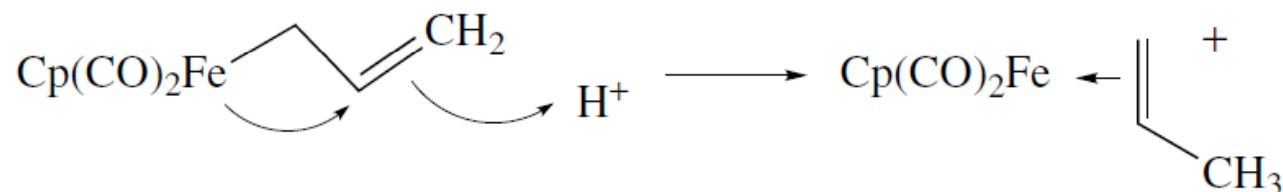
- $\eta^5-L_2X \rightarrow \eta^4-L_2$  ligand .....the net ionic charge on the complex is one unit more negative, and the overall electron count at the metal is unchanged.



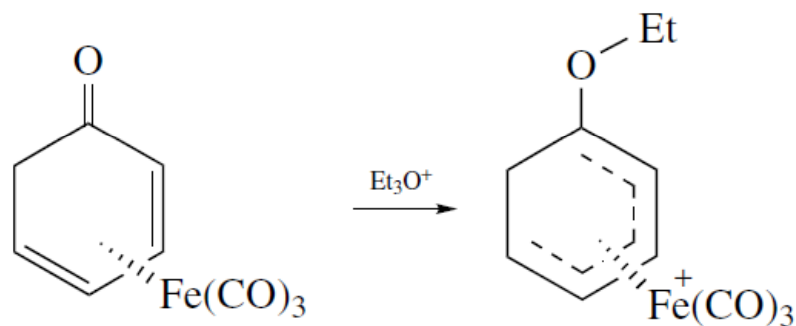
- $\eta^2-L \rightarrow \eta^1-X$  ligand .....again, the net ionic charge on the complex is one unit more negative, and the overall electron count at the metal is unchanged.

**For electrophilic addition reactions, in general:**

- Electrophilic reagents, in contrast, tend to **increase the hapticity of the ligand** to which they add. Electrophilic attack on a ligand gives rise to a deficiency of electron density on that ligand, which is compensated by the attack of a metal lone pair on the ligand.
- **an  $L_m X_n$  ligand is converted to an  $L_{(m+1)} X_{(n-1)}$  ligand**
- **an  $L_m$  ligand is converted to an  $L_m X_{(n+1)}$  ligand.**

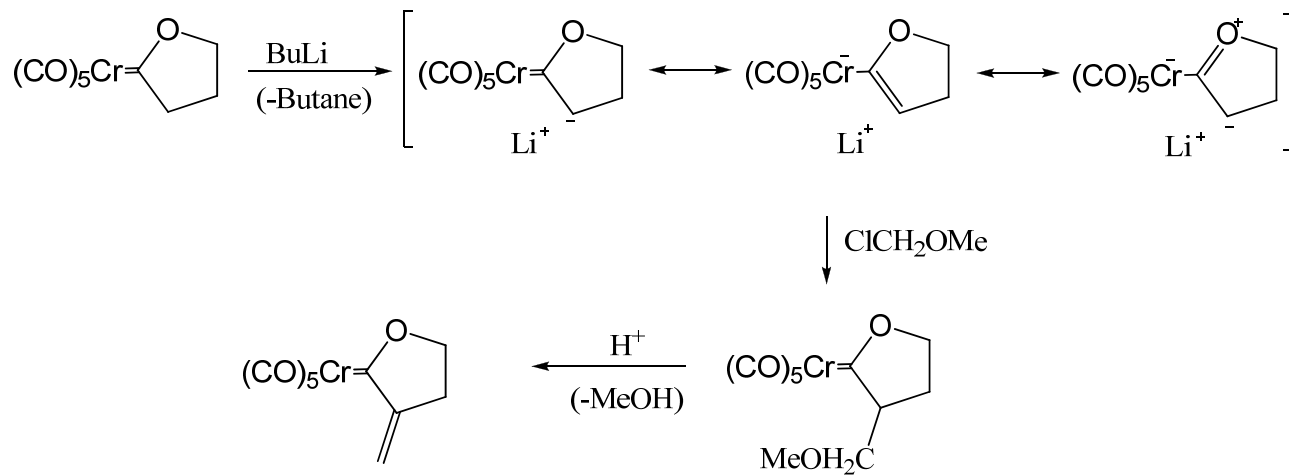
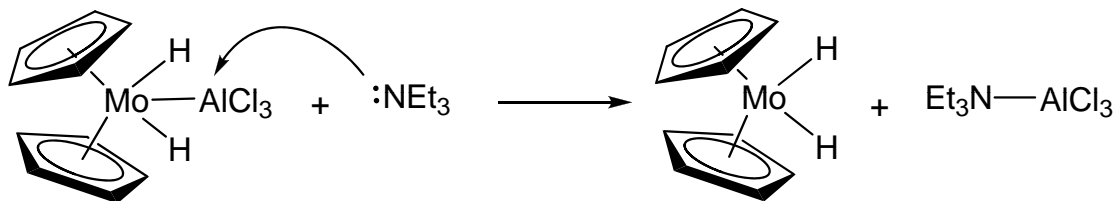
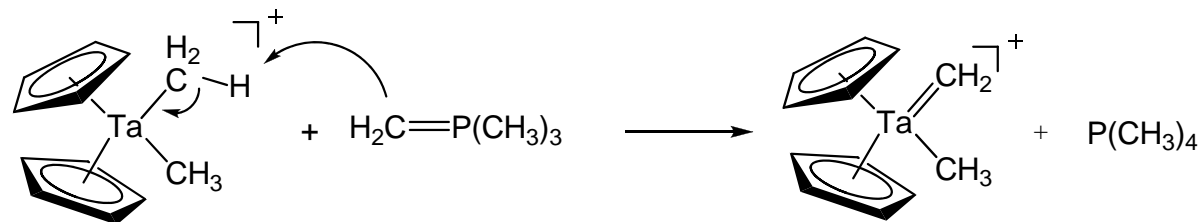


- $\eta^1\text{-X} \rightarrow \eta^2\text{-L}$  .....a net positive charge is added to the complex, and the overall electron count at the metal is unchanged.

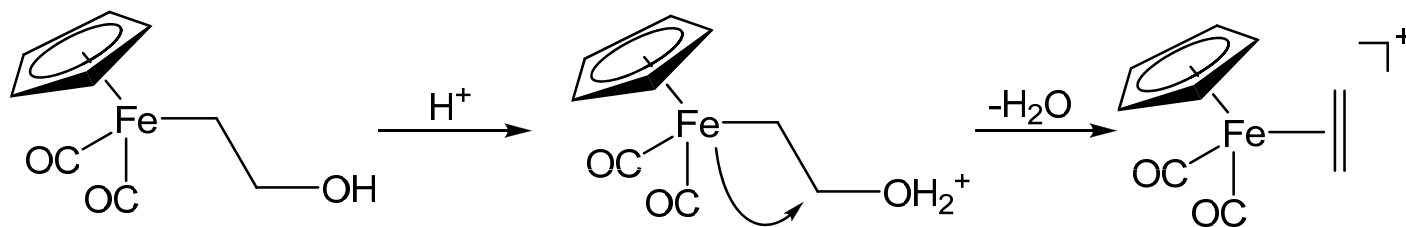
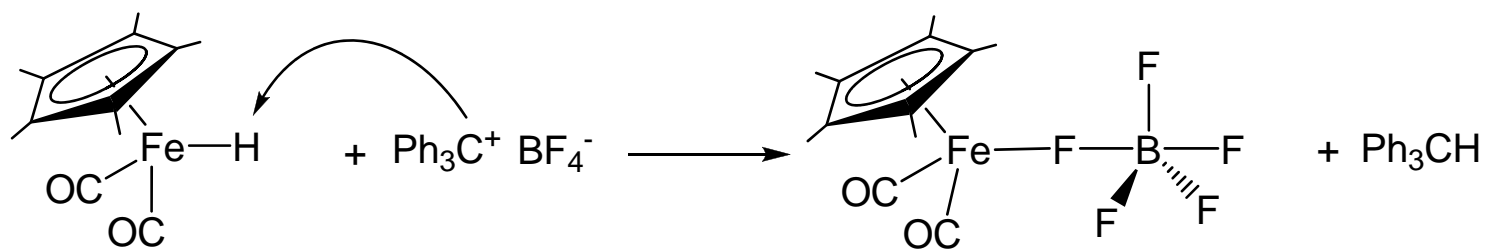


- $\eta^4\text{-L}_2 \rightarrow \eta^5\text{-L}_2\text{X}$  .....a net positive charge is added to the complex, and the overall electron count at the metal is unchanged.

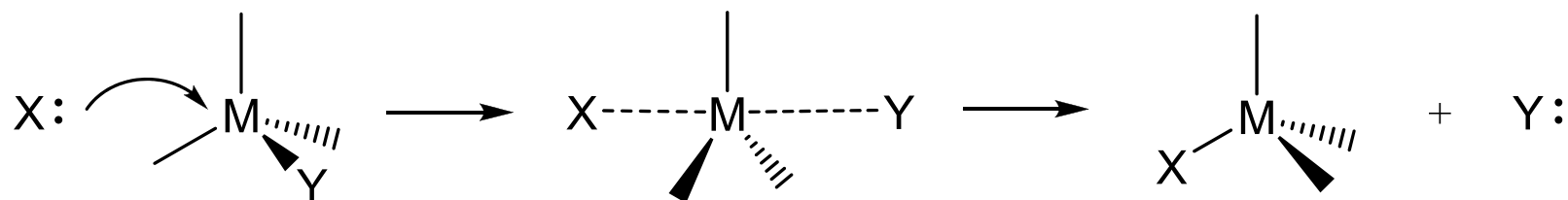
## Nucleophilic Abstraction (examples)



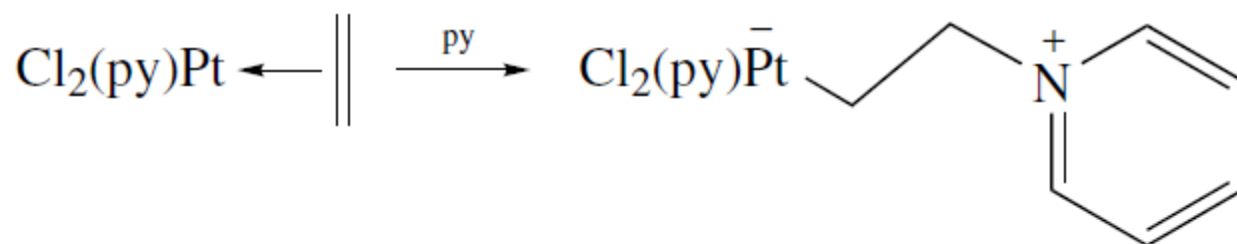
## Electrophilic Abstraction (examples)



- Nucleophilic or electrophilic **attack at the metal**, rather than at the ligands, can also be observed.
- Nucleophilic attack at the metal is simply associative substitution and can lead to the displacement of the polyene.



- If the original metal complex is 16e, attack may take place directly on the metal, if 18e, a ligand must usually dissociate first. A nucleophile is therefore more likely to attack a ligand, rather than the metal, if the complex is 18e.
- The pyridine here is a potential 2e ligand, but it does not attack the metal because an 18e configuration is not a favorable situation for Pt(II).

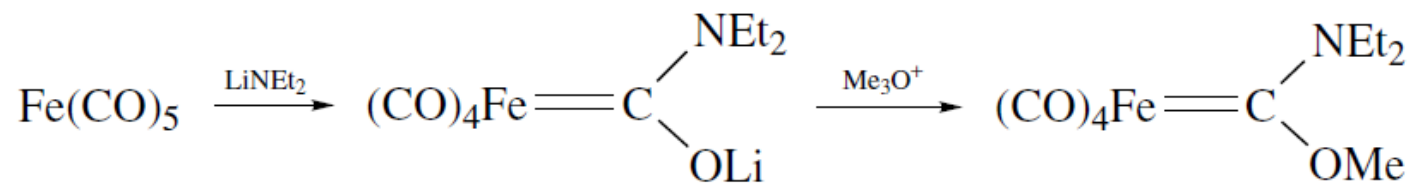




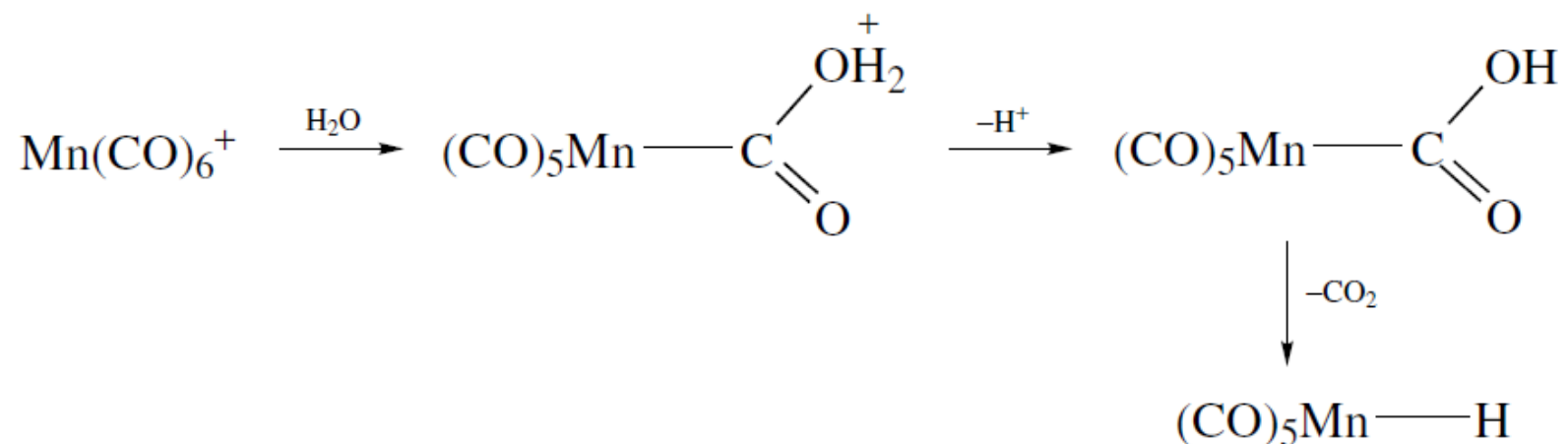
- As a 0e reagent, electrophilic attack at the metal does not increase the electron count of the metal (similar to electrophilic addition at the ligand).
- Electrophilic attack at the metal is always a possible alternative pathway even for an 18e complex (*except for d0 complexes that have no metal-based lone pairs*).
- However, large electrophiles such as trityl ( $\text{Ph}_3\text{C}^+$ ) may have steric problems in attacking the metal directly.
- As 1e reagents, organic free radicals can also give addition and abstraction reactions, but these reactions are less well understood.
- Radical addition and abstraction also tends to occur only as part of a larger reaction scheme in which radicals are formed and quickly react.
- We briefly looked at the attack of radicals at the metal in connection with oxidative addition.

# Nucleophilic addition to CO

- CO is very sensitive to nucleophilic attack when coordinated to metal sites of *low  $\pi$  basicity*.
- On such a site, the CO carbon is positively charged ( $\delta^+$ ) because  $L \rightarrow M$   $\sigma$  donation is not compensated by  $M \rightarrow L$  back donation, and the CO  $\pi^*$  orbitals are open to attack by the nucleophile.
- Nucleophilic attack converts a number of metal carbonyls to their corresponding anionic acyls. The net negative charge now makes the acyl liable to electrophilic addition producing the Fischer carbene complex.

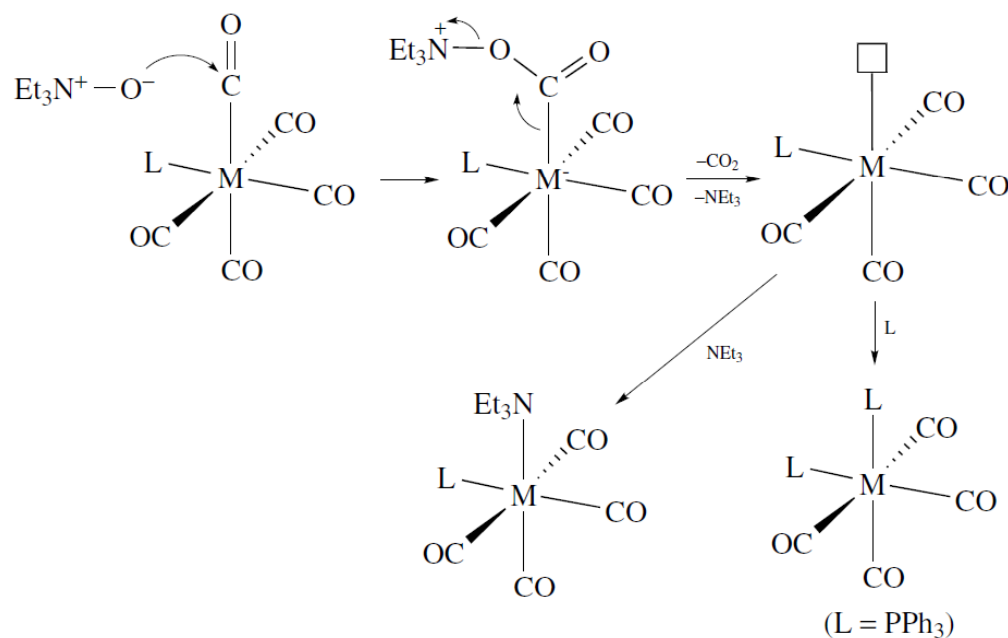


- $[\text{Mn}(\text{CO})_6]^+$  is more sensitive to nucleophilic attack than the neutral  $[\text{Mo}(\text{CO})_6]$  complex. In this case, hydroxide, or even water, can attack coordinated CO to give an unstable metalacarboxylic acid intermediate, which decomposes to  $\text{CO}_2$  and the metal hydride by  $\beta$  elimination.



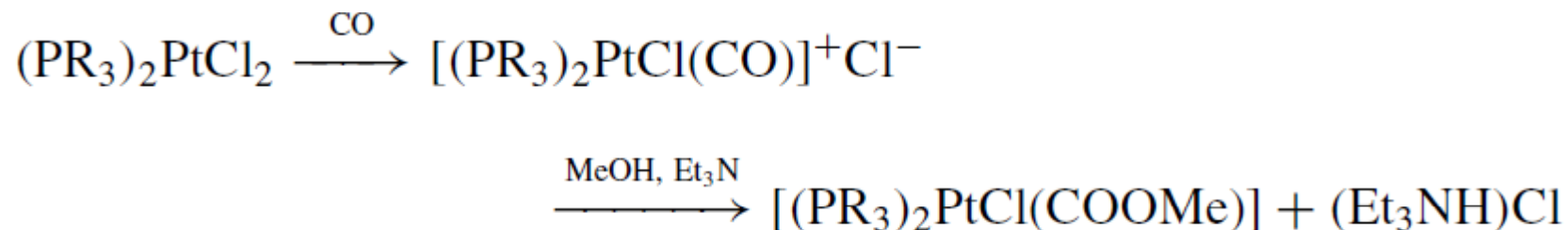
- The nucleophilic attack of MeOH instead of  $\text{H}_2\text{O}$  can give a metalaester,  $\text{L}_n\text{M}(\text{COOR})$ , which is stable because it has no  $\beta$ -H.

- Nucleophilic oxygen ( $\text{Et}_3\text{N}^+\text{-O}^-$ ) is capable of attacking the CO carbon to give a species that can break down to  $\text{Et}_3\text{N}$ ,  $\text{CO}_2$ , and the corresponding 16e metal fragment:



- Note how the *cis*-disubstituted product is obtained selectively because a CO *trans* to another CO has less back donation from the metal and hence is more activated toward nucleophilic attack at carbon than is the CO *trans* to the weak  $\pi$ -acid  $\text{PPh}_3$ .
- Unfortunately, the amine formed can sometimes coordinate to the metal.
- A second problem with the method is that successive carbonyls become harder and harder to remove as the back bonding to the remaining CO groups increases and so we are usually unable to remove more than one CO.

- Note how the displacement of Cl<sup>-</sup> is favored here in the first step over displacement of PPh<sub>3</sub>.



- This is a consequence of the polar solvent used and sets the stage for the subsequent nucleophilic attack by putting a positive charge on the complex ion, which activates the CO.
- Acid can reverse the addition reaction by protonating the methoxy group, which leads to loss of methanol. This is, of course, a methoxide abstraction reaction and is an example of a nucleophilic addition being reversed by a subsequent electrophilic abstraction.
- This is common and means that the product of an addition reaction may even decompose via its inverse reaction if unsuitable workup conditions are used.
- For example, the product of a nucleophilic addition may revert to the starting material if excess acid is added to the reaction mixture with the object of neutralizing the excess nucleophile.

# Nucleophilic addition to polyene and polyenyl ligands

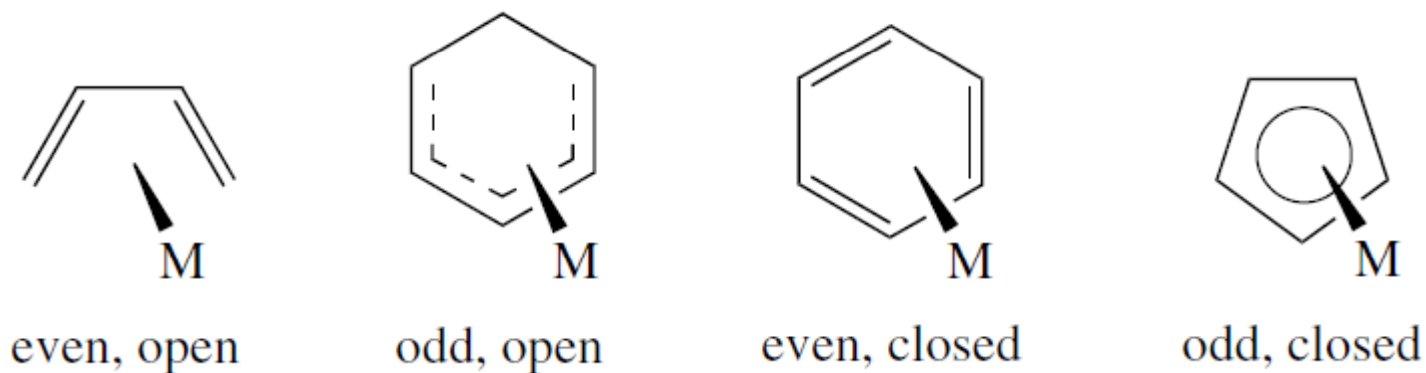
- Simple polyenes in the free state, such as benzene and ethylene, normally undergo electrophilic attack.
- ***Both benzene and ethylene become sensitive to nucleophilic, and inert to electrophilic, attack when complexed to a metal centre (umpolung).***
- If we are interested in inhibiting electrophilic attack, we would regard the metal as a protecting group.
- On the other hand, if we are interested in promoting nucleophilic attack, we would regard the same metal fragment as an activating group.
- In the vast majority of cases, ***the nucleophile adds to the face of the polyene opposite to the metal.***
- Since the metal is likely to have bound to the least hindered face of the free polyene, we may therefore see a selective attack of the nucleophile on what was the more hindered face in the free polyene; this is often useful in organic synthetic applications.

# Green–Davies–Mingos Rules for Nucleophilic addition

- It is not unusual for a single complex to have several polyene or polyenyl ligands, in which case we often see selective attack at one site of one ligand only.
- Green, Davies, and Mingos noticed certain patterns in these reactions and from them devised a set of rules that usually allow us to predict the site of addition:
  - 1) **Polyenes (even or  $L_m$  ligands) react before polyenyls (odd or  $L_mX$  ligands).**
  - 2) **Open ligands react before closed.**
  - 3) **Open polyenes: terminal addition in all cases. Open polyenyls: usually terminal attack, but non-terminal if  $L_nM$  is electron donating.**

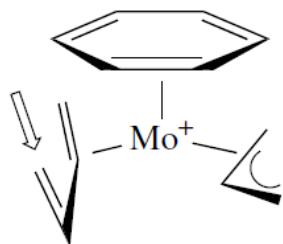
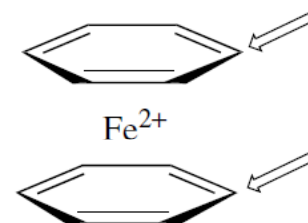
*(rule 1 takes precedence over rule 2 whenever they conflict)*

- **Polyenes** or even ligands are simply ones having an ***even electron count on the covalent model*** (e.g.,  $\eta^2\text{-C}_2\text{H}_4$ ,  $\eta^6\text{-C}_6\text{H}_6$ )
- **Polyenyls** or odd ligands have an ***odd electron count on the covalent model*** (e.g.,  $\eta^3\text{-C}_3\text{H}_5$ ,  $\eta^5\text{-C}_5\text{H}_5$ ).
- Closed ligands are ones like benzene, Cp in which the coordinated  $\pi$  system of the polyene or -enyl is ***fully conjugated*** in a ring.
- In open ligands like allyl, ***the conjugation is interrupted***.
- Some ligands and their classification according to these rules are illustrated below:



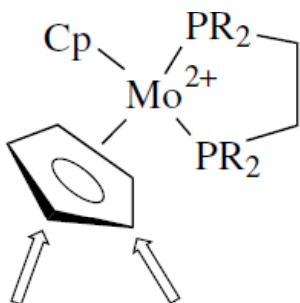
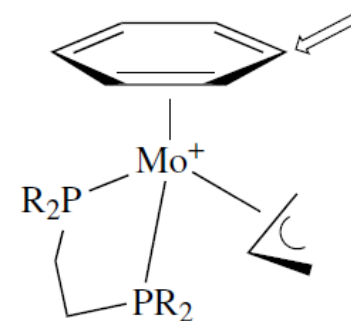


Addition of a variety of nucleophiles takes place at the arene ring, [rule 1]. A second nucleophile can also add, but to the other ring, [rule 1].



Addition takes place to the even, open butadiene ligand, rather than to the even, closed arene [rule 2] and at the terminal position [rule 3].

The even, closed arene is attacked rather than the odd open allyl; we must be careful in a case such as this [apply rule 1 before rule 2].



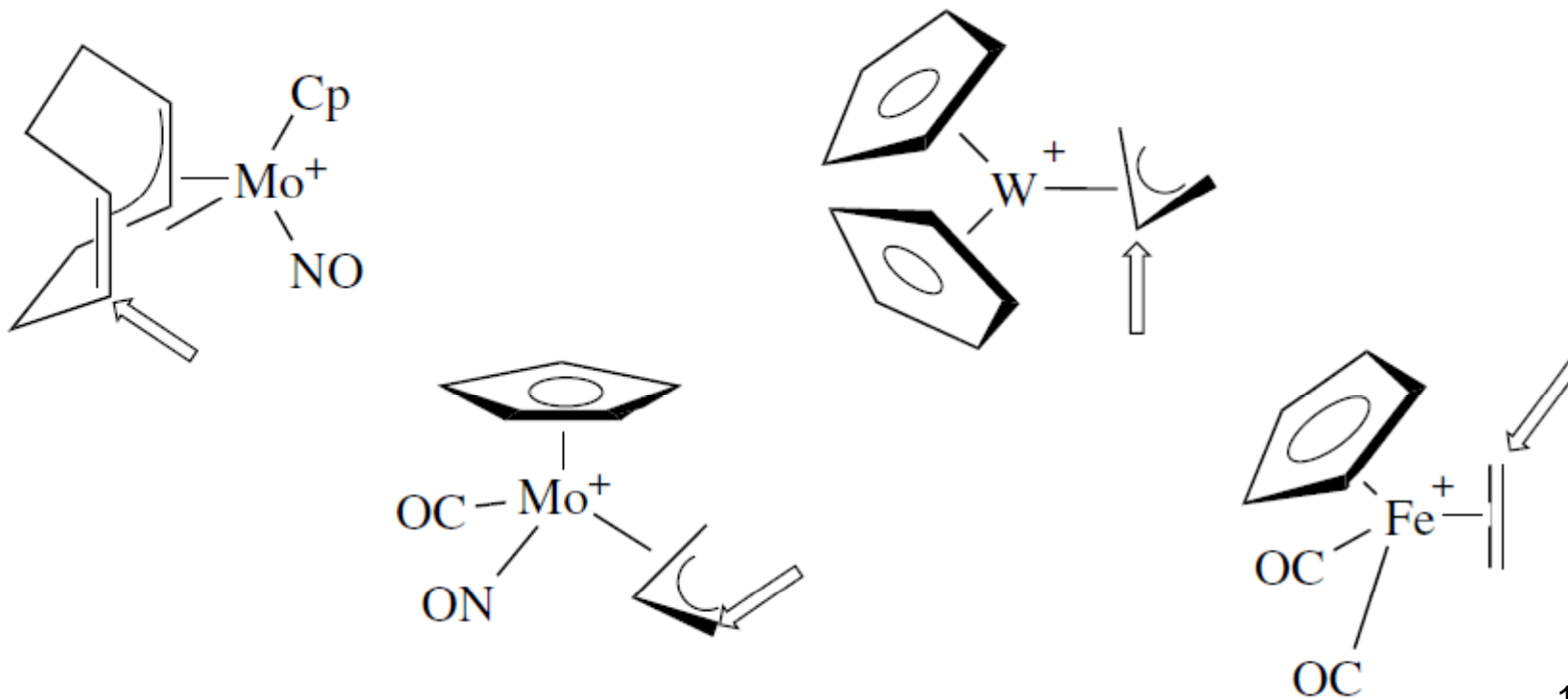
Attack at a Cp ring is rare; as an odd, closed system, this only happens if there is no other  $\pi$  bonded ligand present. Typically Cp is very resistant to attack and directs addition to other ligands present on the metal.

- Although the rules were first developed empirically, an MO study has shown that they often successfully predict the location of the atom having the highest coefficient of the LUMO.
- Under kinetic control, we would expect addition at the point where this empty acceptor orbital is largest.
- Qualitatively, we can understand the rules as follows:

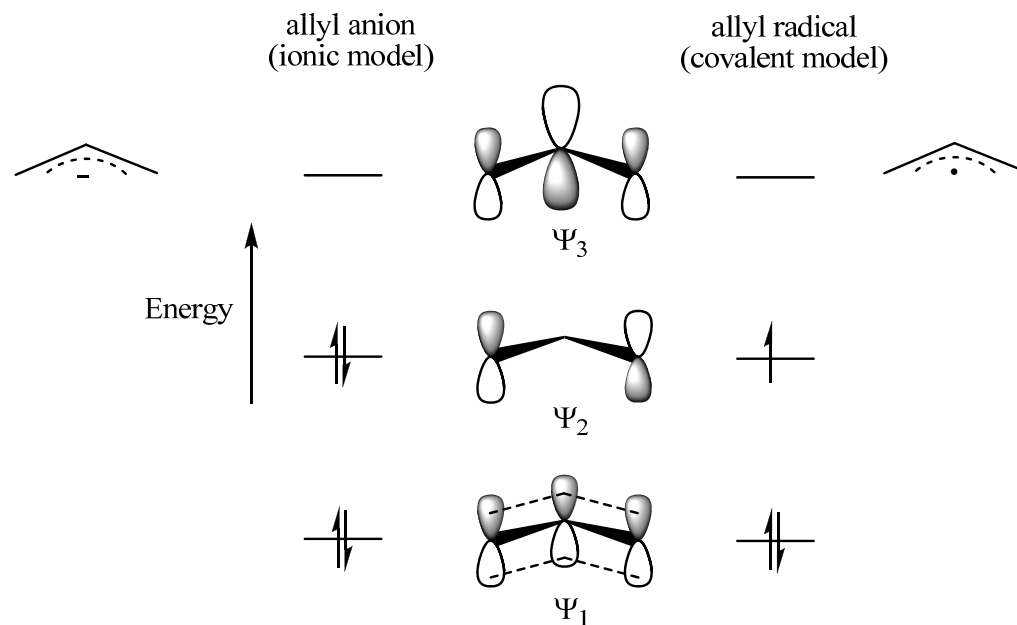
***Ligands having a higher X character will tend to be more negatively charged and therefore will tend to resist nucleophilic attack relative to L ligands.***

- The coordinated allyl group, as an LX ligand, has more anionic character than ethylene, an L ligand.
- This picture even predicts the relative reactivity of different ligands in the same class, a point not covered by the rules. ***For example, it is found that pentadienyl ( $L_2X$ ) reacts before allyl (LX); we can understand this because the former has the lower X character.*** Ethylene reacts before butadiene; the  $LX_2$  form is always a significant contributor to the structure of butadiene complexes.
- The reason the terminal carbons of even-open ligands are the sites of addition is that the ***coefficients of the LUMO*** are larger there. As an example, look at  $\Psi_3$  in butadiene.
- An odd, open polyenyl gives terminal addition only if the metal is sufficiently electron withdrawing.

- We can treat the alkene and the allyl parts of the bicyclooctadienyl as independent entities; the even alkene part is attacked.
- CO is an even ligand but is among the least reactive of these.
- The examples below also illustrate what might be called the “zeroth rule” of nucleophilic addition:
  - A nucleophile usually adds once to a monocation, twice to a dication, and so on....etc.



- Reference to the MO picture for the allyl group shows that the usual LUMO,  $\Psi_2$  (covalent model *aka* SOMO), has a large coefficient at the terminus, but  $\Psi_3$  has a large coefficient at the central carbon.
- As we go to a less electron-withdrawing metal, we tend to fill  $\Psi_2$  and to the extent that  $\Psi_3$  becomes the new LUMO, and so we may no longer see terminal attack.



- An example of non-terminal attack in an allyl is shown by  $[\text{Cp}_2\text{W}(\eta^3\text{-C}_3\text{H}_5)]^+$ ; as a  $d^2$  fragment,  $\text{Cp}_2\text{W}$  is strongly electron donating in character.

