ORGANOMETALLICS

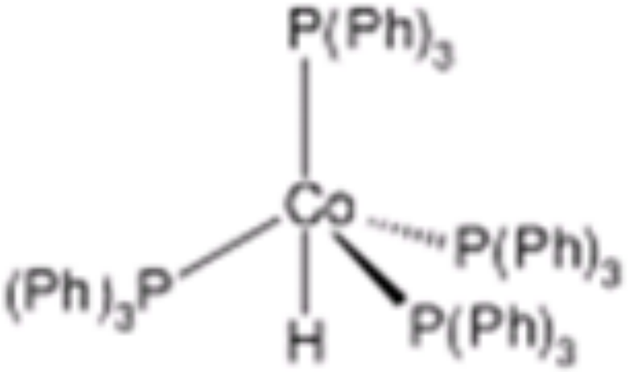
MFT Ch 13

Other common ligands in organometallic complexes

Hydride ligand, H^-

- What orbital(s) does H^- have available for bonding with a metal center?

- What kind of bonding interaction(s) will you observe between a transition metal and a hydride? (sigma? pi bonding? pi backbonding?)



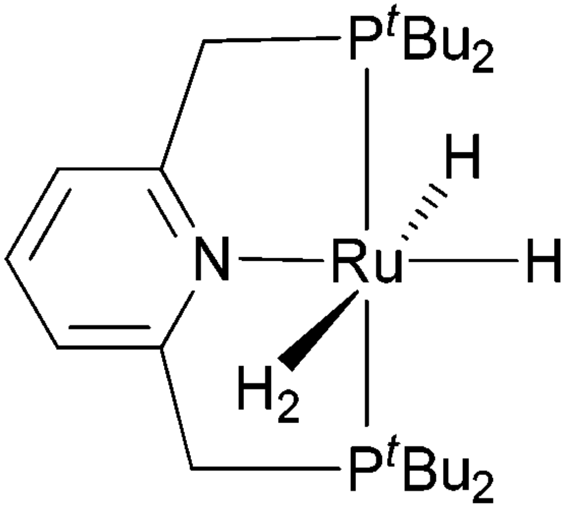
H- is a 2 electron donor

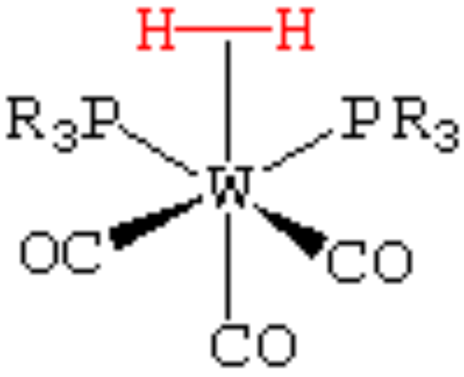
Dihydrogen ligand, H_2

- What orbital(s) does H_2 have available for bonding with a metal center?

- What kind of bonding interaction(s) will you observe between a transition metal and H_2? (sigma? pi bonding? pi backbonding?)

H_2 is a 2 electron donor



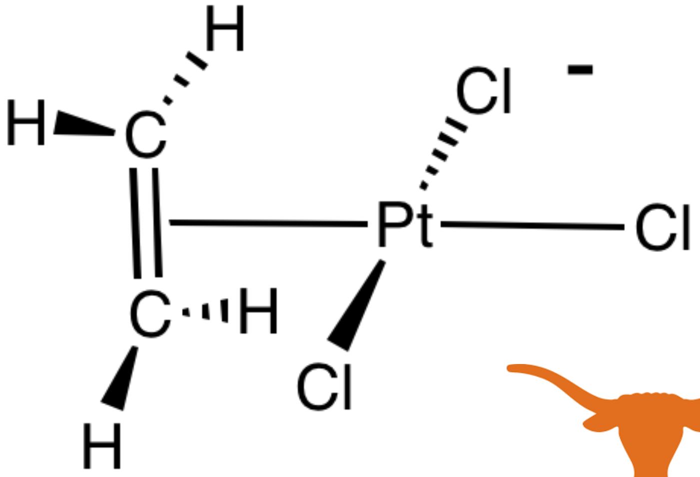


Ligands with pi systems

- In organometallic chemistry, you will often observe complexes between a metal center and the pi electrons of an alkene, an extended pi system (multiple double bonds), an aromatic system (Cp, benzene)

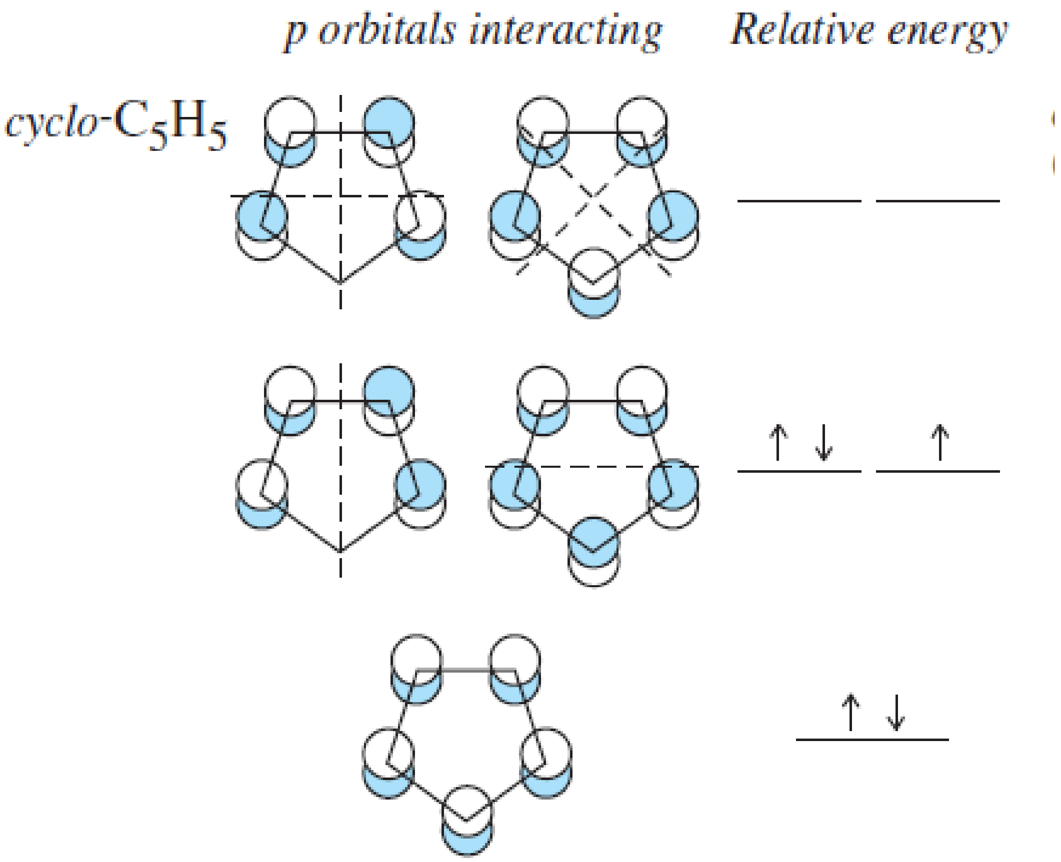
Ethlyene

- Ethylene typically interacts with metals in a side-on fashion, with the metal-ligand bond forming in between the two carbon atoms.
- This binding mode is a good indication that bond involves the pi electrons of ethylene
- Ethylene uses its pi bonding orbital for sigma interaction with metal and its pi* antibonding orbital for pi backbonding with metal

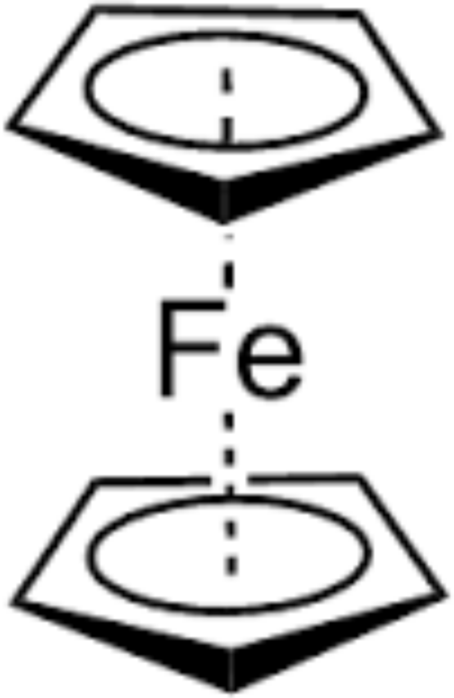


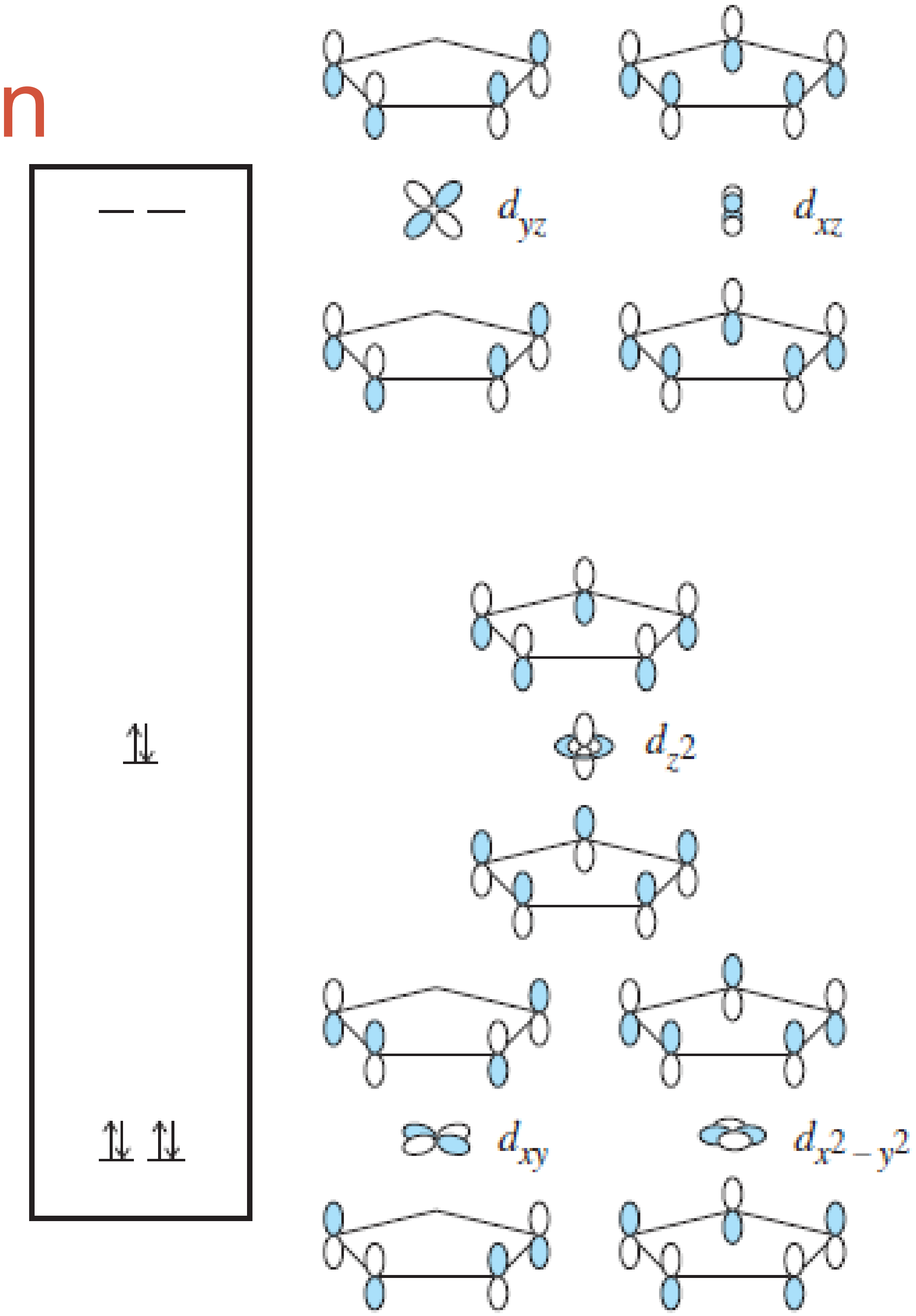
Cycolpentadienyl (Cp)

- Cp also interacts with metals using its pi system
- Orbitals used for bonding with metal are depicted or right (these will be provided for an exam question if they are needed)
- Based on these orbitals, and the geometry of a complex, can you figure out what metal d orbitals interact with what Cp orbitals?



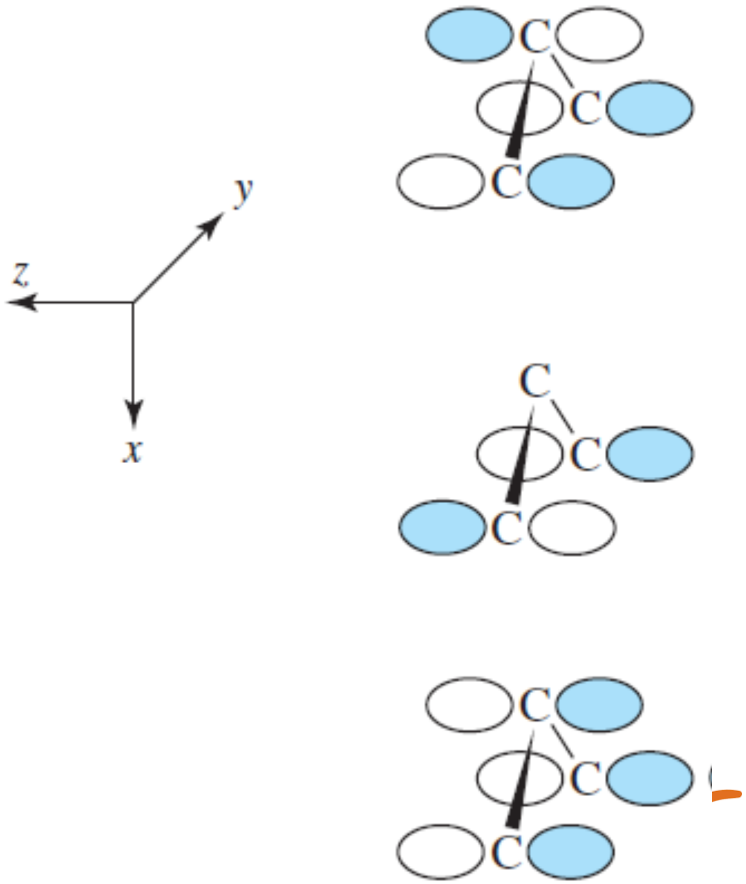
Orbital interactions in ferrocene: $FeCp_2$





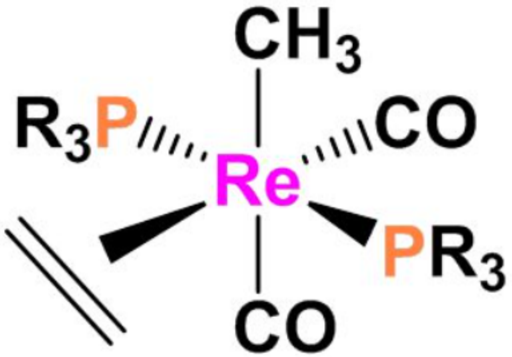
Example question:

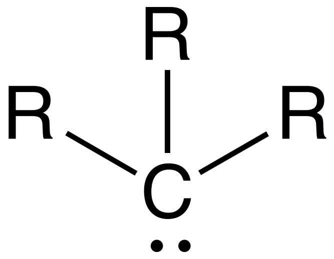
- The picture on the top right depicts the interactions between nickel and an allyl anion ($C_3H_5^-$)
- The allyl orbitals involved in bonding are depicted on the bottom right. Given the depicted coordinate axes, what metal d orbitals have the right symmetry to interact with the allyl orbitals in this complex? What metal s or p orbitals?

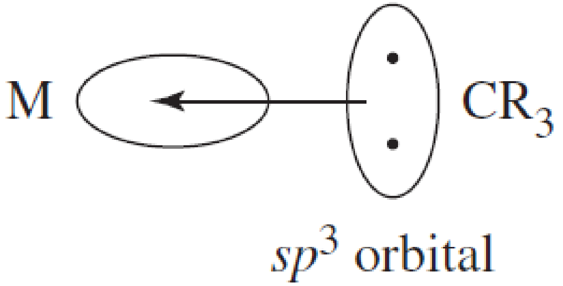


Metal-alkyls M-CR_3

- Metal alkyl complexes contain a metal-carbon single bond
- Alkyl ligand can be thought of as :CR_3^-
- Much like H^- (hydride), alkyl ligands are 2-electron donors and interact with metals in a sigma fashion
- This is similar to how η^1-Cp and η^1-benzene ligands interact with metal centers

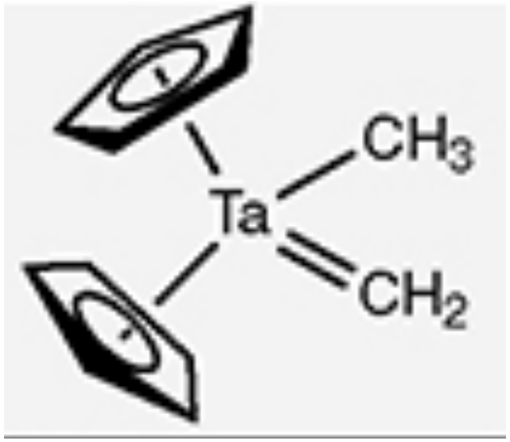




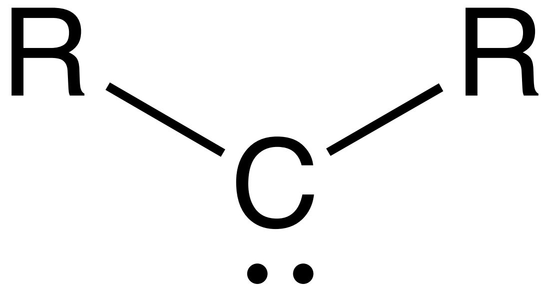


(R=H, alkyl, aryl)

Metal-carbenes $M{=}CR_2$



- Metal-carbene complexes contain a metal carbon double bond $M{=}CR_2$
- For electron counting purposes, we consider the CR_2 ligand to be a two electron donor because carbenes actually have only one lone pair, their structures are $:CR_2$

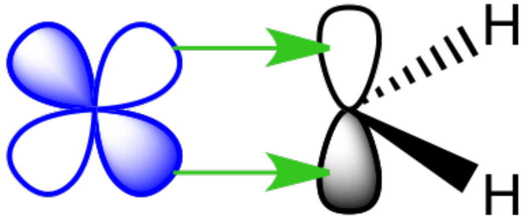


Metal-carbenes $M{=}CR_2$

- This lone pair is used for sigma bonding with metal

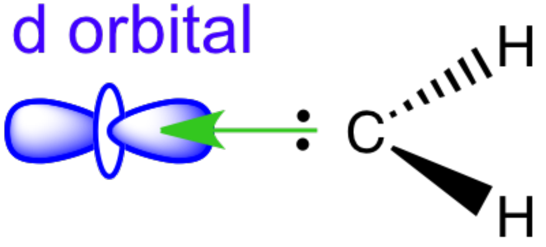
- The second bond comes from interactions between a metal d orbital and an empty p orbital on the carbene

Metal d orbital



Empty Carbon p orbital

Vacant Metal d orbital

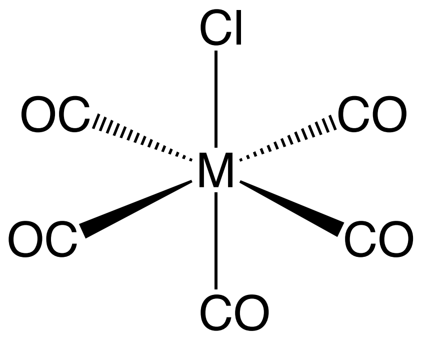


Carbon lone pair

Throwback to symmetry

- Now that we know more about organometallic complexes, we can look at a complex, understand aspects of its bonding, and predict its spectroscopic properties (i.e. number of IR stretches!)

- We can also use symmetry concepts to predict how many NMR peaks an organometallic complex might have



How many different CO stretches would you expect this complex to have? (Make reducible representation)

How many different ^{13}C NMR peaks will this complex have? (How many different CO ligands are there?)

ORGANOMETALLIC REACTIONS AND CATALYSIS

MFT Ch 14

CH 431

Organometallic complexes and catalysis

- Organometallic complexes, much like other inorganic complexes, can undergo a variety of different reactions

- Some organometallic complexes are used widely for industrial reactions as well as in common reactions performed in synthetic labs

- This lecture will cover the basic kinds of reactions organometallic complexes can undergo

- Lectures after this will then cover important complexes used in catalytic cycles

Two main categories of organometallic reactions

1. Reactions involving a gain or loss of ligands

2. Reactions involving modification of ligands

Reactions involving gain or loss of ligands

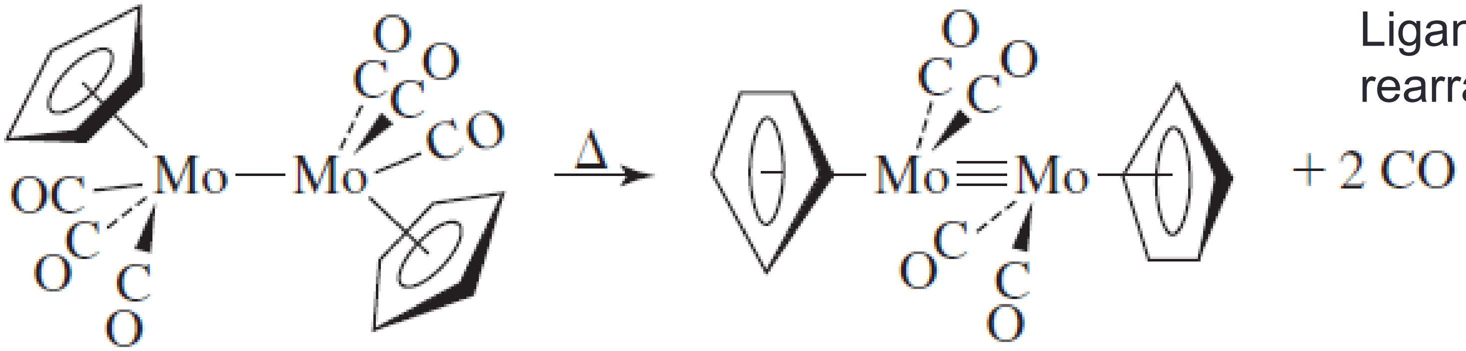
- Ligand dissociation
- Oxidative addition
- Reductive elimination
- Sigma bond metathesis

Ligand dissociation reactions

- Ligand dissociation reactions either involve the loss of a ligand or a ligand substitution reaction
- In reactions classified as ligand dissociation, metal oxidation state(s) do not change, however complexes may rearrange following ligand dissociation
- The same principles apply from what we have already learned about ligand substitution reactions
- If a reaction involves simply the gain of a ligand in the metal coordination sphere, this is called ligand association

Ligand dissociation: CO dissociation

- CO can be lost from a metal complex either thermally (with heat) or photochemically (with light)
- The reaction will either cause the metal complex to rearrange or for CO to be replaced by another ligand



Ligand dissociation, rearrangement

$$Fe(CO)_5 + P(CH_3)_3 \xrightarrow{\Delta} Fe(CO)_4(P(CH_3)_3) + CO$$

ligand substitution

Ligand dissociation: phosphines

- In some ligand dissociation reactions, steric bulk plays an important role, with bulkier ligands dissociating more quickly to relieve steric strain in the metal complex

- This can be observed in some phosphine dissociation reactions, where phosphines with bigger cone angles have faster ligand dissociation rates

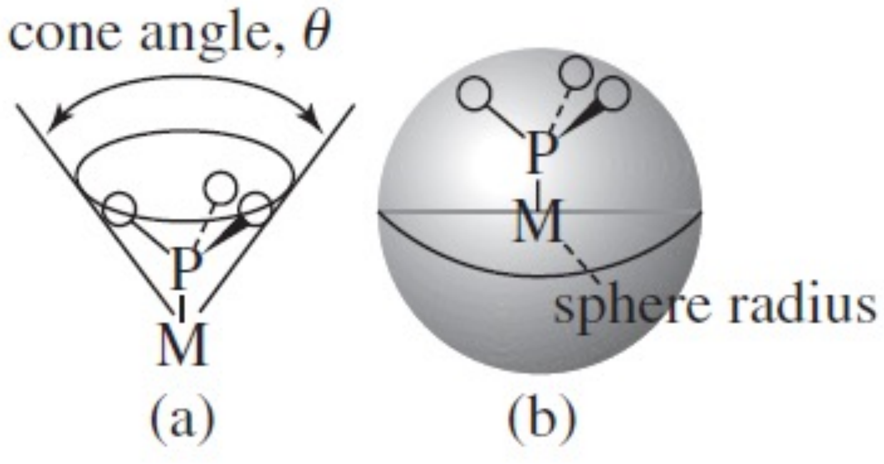
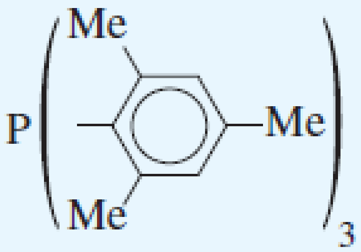
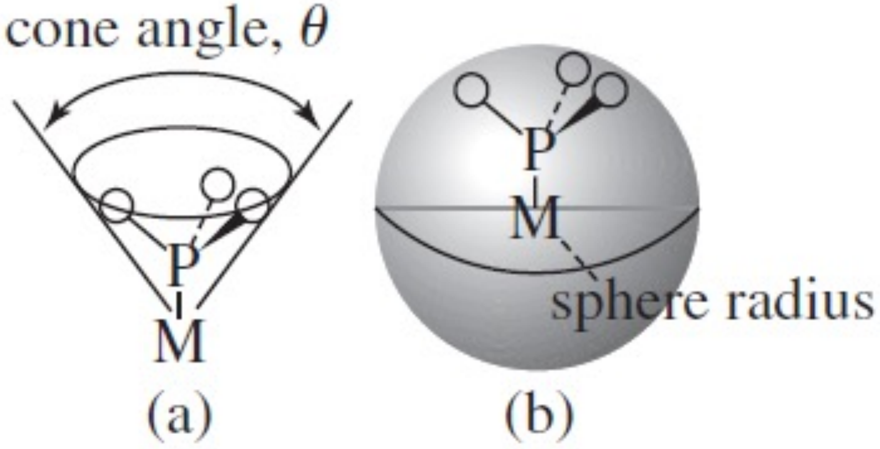
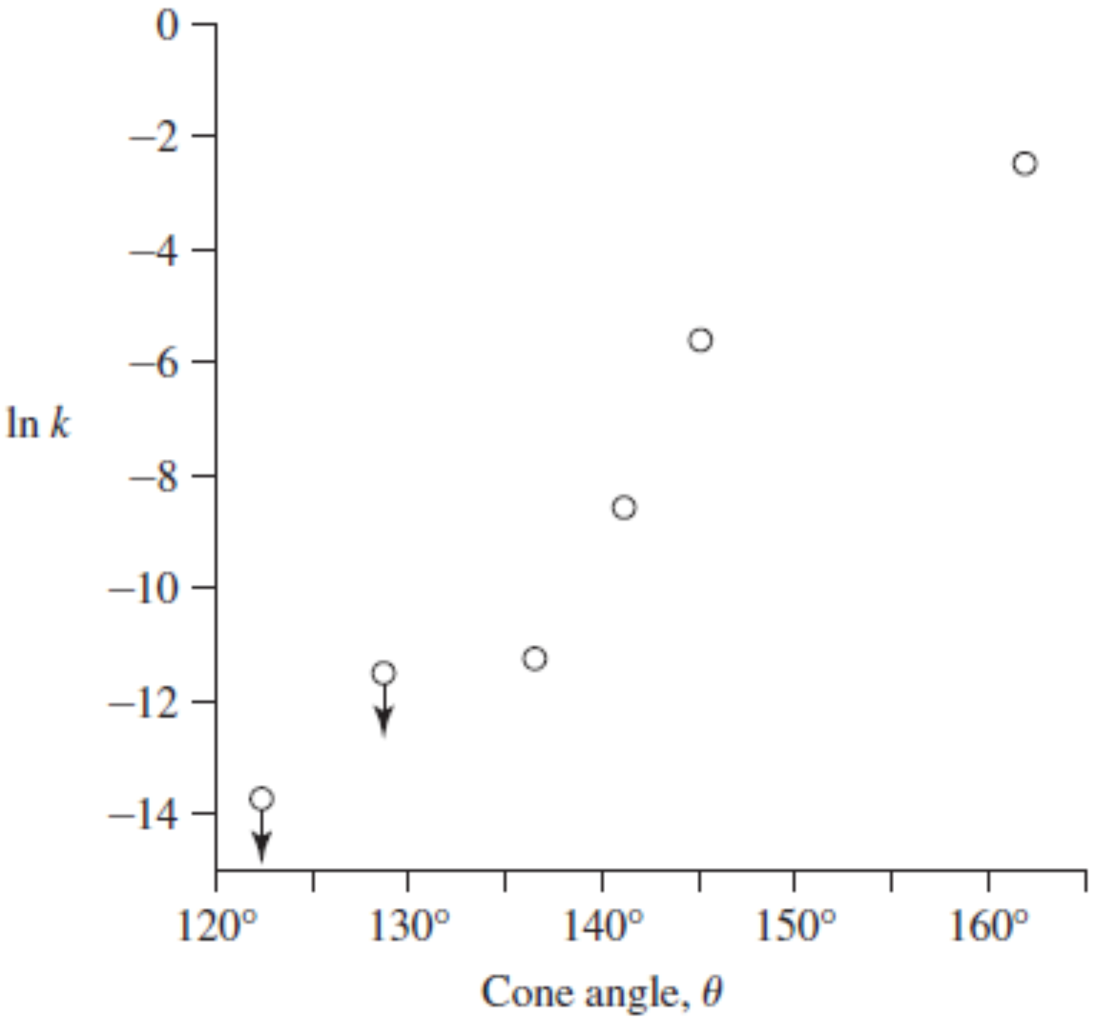


TABLE 14.1 Ligand Cone Angles and %V_{bur} for Tertiary Phosphines

Ligand	Cone Angle θ	%V_{bur}	Ligand	Cone Angle θ	%V_{bur}
PH_3	87°		$P(CH_3)(C_6H_5)_2$	136°	
PF_3	104°		$P(CF_3)_3$	137°	
$P(OCH_3)_3$	107° (128°)[a]	26.4[b]	$P(C_6H_5)_3$	145°	29.6
$P(OC_2H_5)_3$	109°		$P(cyclo\text{-}C_6H_{11})_3$	170°	31.8
$P(CH_3)_3$	118°	22.2	$P(t\text{-}C_4H_9)_3$	182°	36.7
PCl_3	124°		$P(C_6F_5)_3$	184°	37.3
$P(OC_6H_5)_3$	128° (155°)[a]	30.7	$P(o\text{-}C_6H_4CH_3)_3$	194°	41.4
$P(C_2H_5)_3$	132°	27.8		212°	47.6

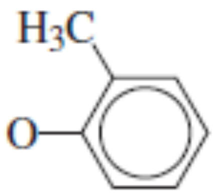


$$cis\text{-}Mo(CO)_4L_2 \quad + \quad CO \quad \longrightarrow \quad Mo(CO)_5L \quad + \quad L$$



L[a]	θ	k (s^{-1})
PPh_2Cy	162°	6.40×10^{-2}
PPh_3	145°	3.16×10^{-3}
$P(O\text{-}o\text{-}tol)_3$	141°	1.60×10^{-4}
$PMePh_2$	136°	1.33×10^{-5}
$P(OPh)_3$	128°	$<1.0 \times 10^{-5}$
PMe_2Ph	122°	$<1.0 \times 10^{-6}$

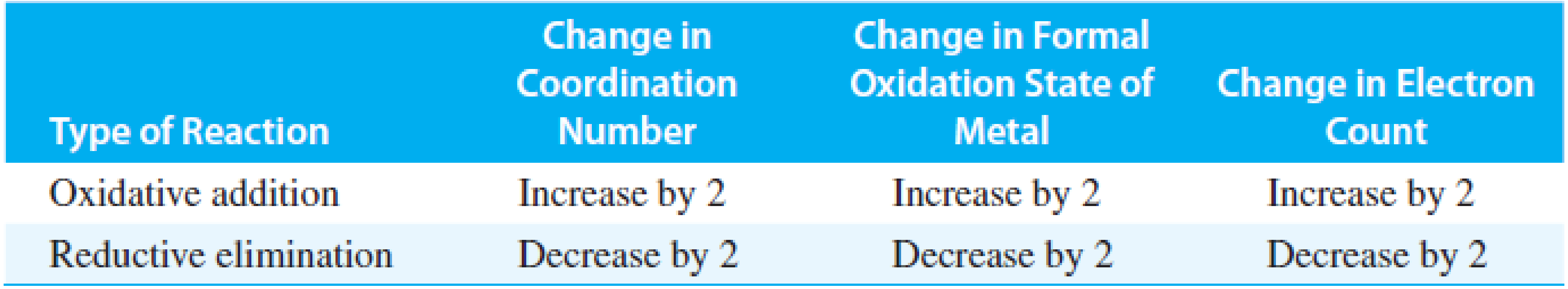
[a] Cy = cyclohexyl
Ph = phenyl
Me = methyl

O-*o*-tol =


Oxidative addition and reductive elimination

- **Oxidative addition (OA)** involves both *oxidation* of the metal center and *addition* of ligands to the metal coordination sphere
- The reverse reaction is called **reductive elimination (RE)** which involves both *reduction* of the metal center *elimination* of ligands from the metal coordination sphere

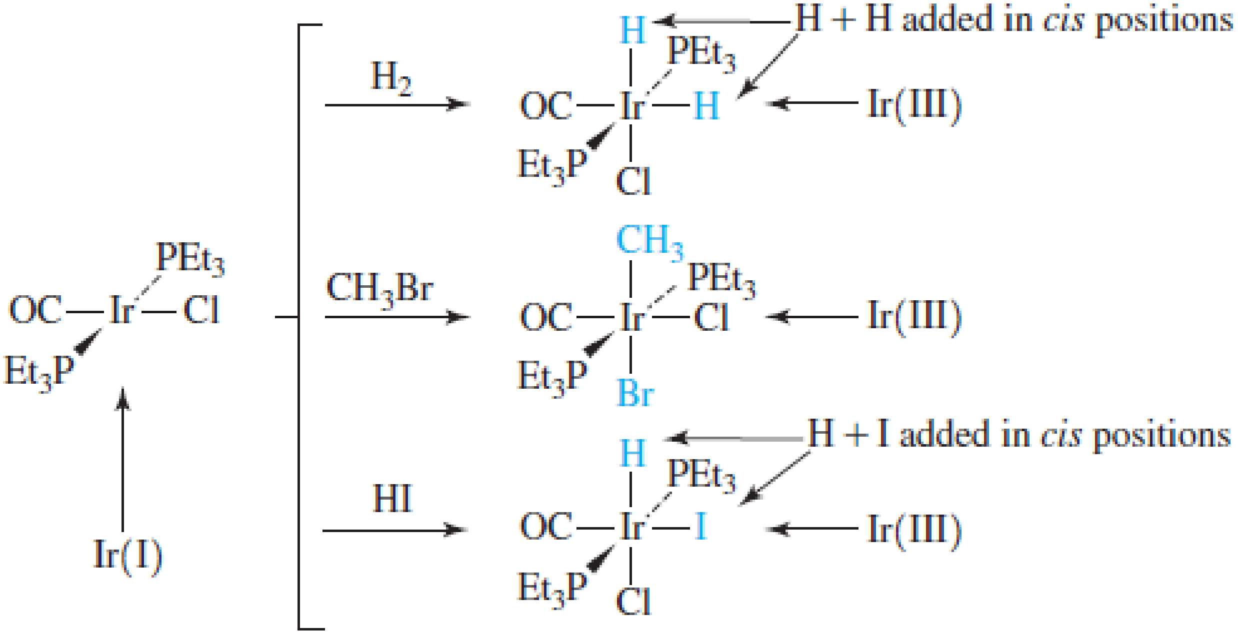
$$L_nM + X-Y \underset{RE}{\overset{OA}{\rightleftharpoons}} L_nM\begin{matrix}X\\Y\end{matrix}$$



Type of Reaction	Change in Coordination Number	Change in Formal Oxidation State of Metal	Change in Electron Count
Oxidative addition	Increase by 2	Increase by 2	Increase by 2
Reductive elimination	Decrease by 2	Decrease by 2	Decrease by 2

Oxidative addition reactions

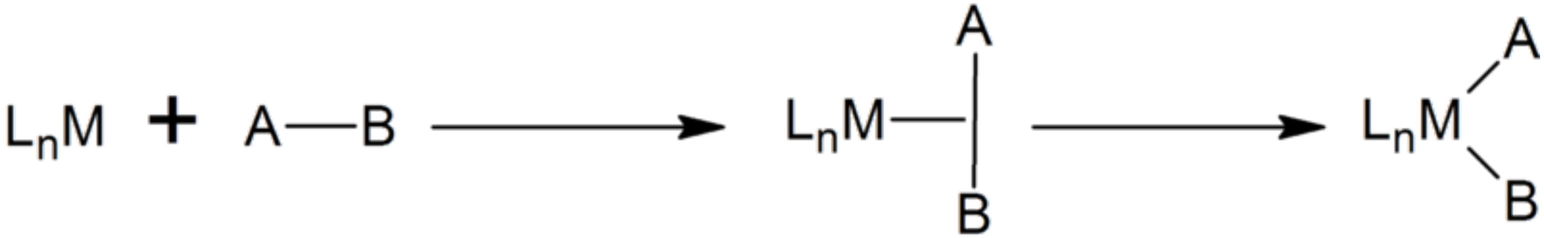
- OA reactions are very common with square planar complexes (why?)
- Example: OA reactions of *trans*-Ir(CO)Cl$(PEt_3)_2$



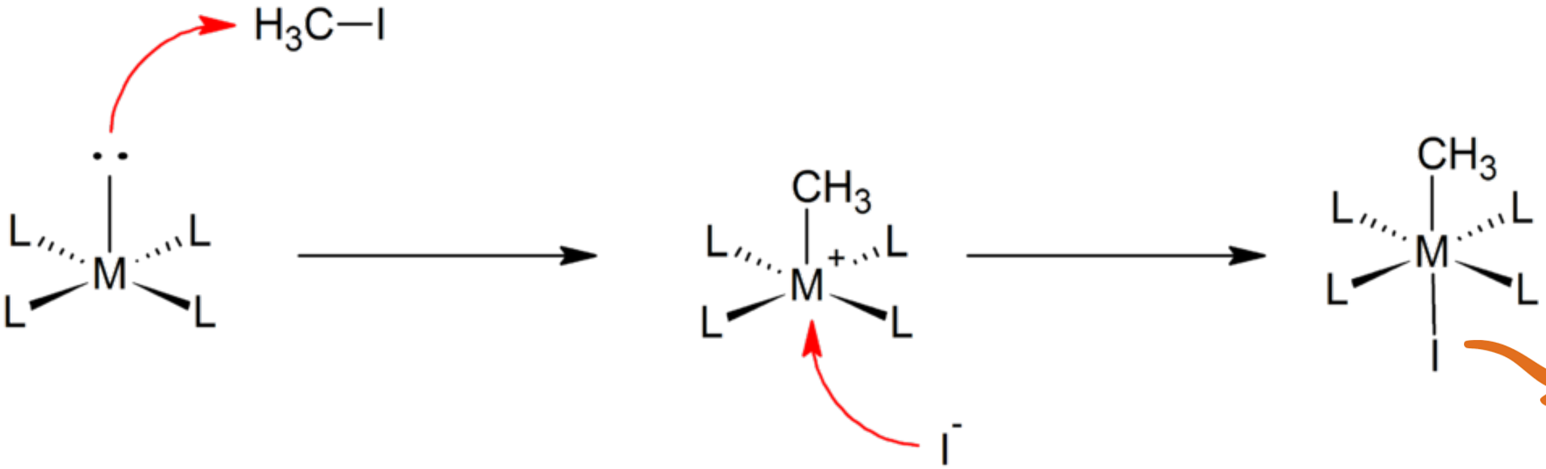
Depending on reactants, either trans or cis OA products can form

Oxidative addition reactions

- Different mechanisms possible including:
  - **Concerted pathway** (leads to cis addition)

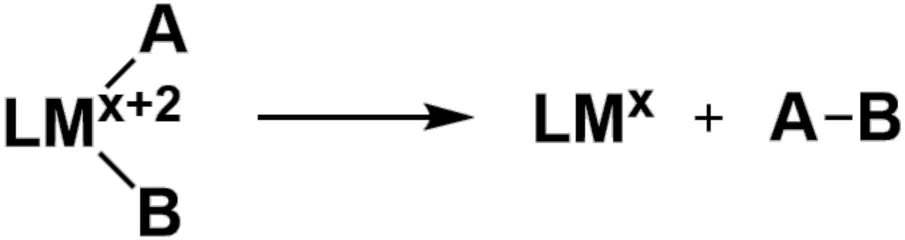


  - **S_N2-type** (leads to trans addition)



Reductive elimination reactions

- RE is reverse of OA

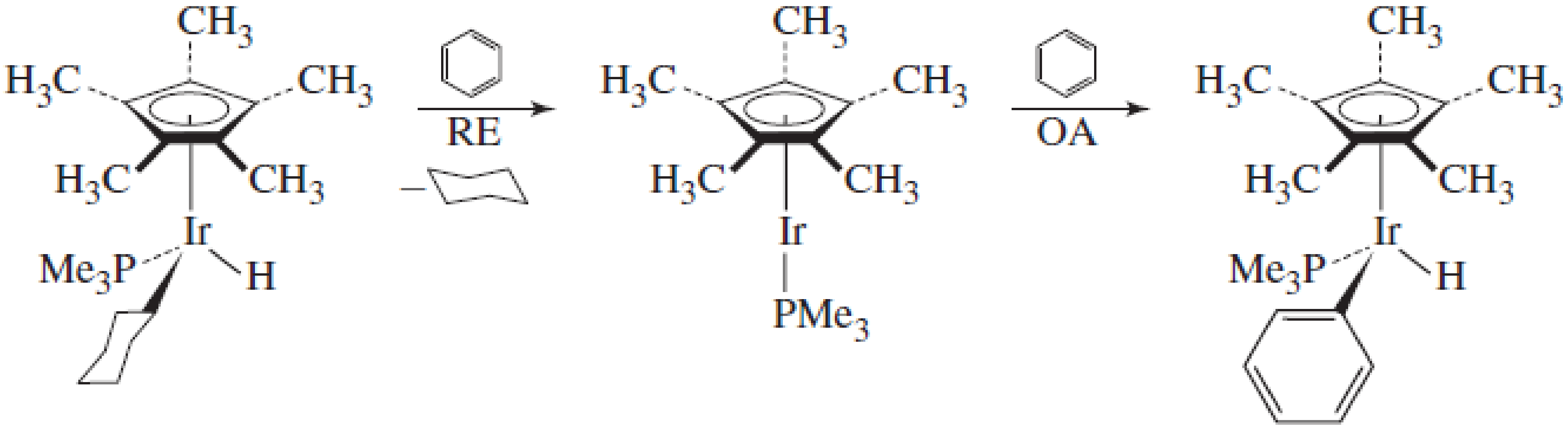


- Will go through similar reaction mechanisms to OA (*principle of microscopic reversibility*)
- RE can result in the formation of a variety of bonds including H-H, C-H, C-C, and C-X (X = halide, amide, alkoxide, thiolate, phosphide)

OA and RE in C-H bond activation

- C-H bond activation is a reaction in which a transition metal catalyst cleaves a strong C-H bond

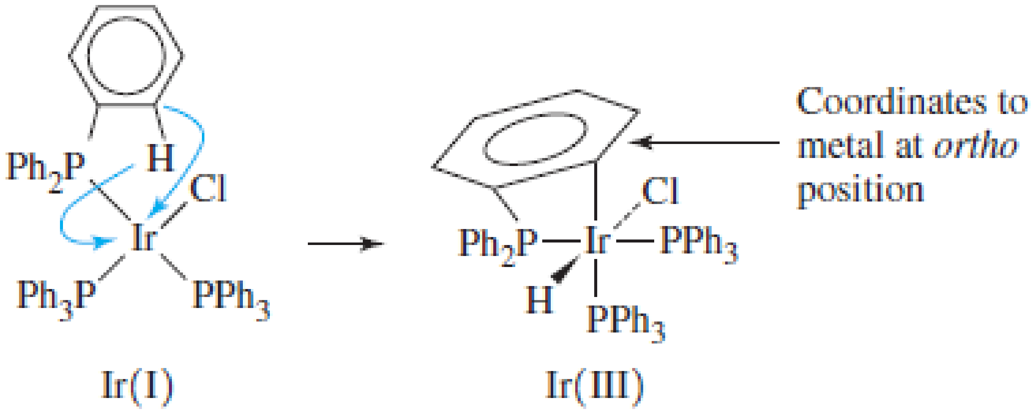
Activation of C-H bond in benzene (R.Bergman, UC-Berkeley)



Potential way to make benzene derivatives

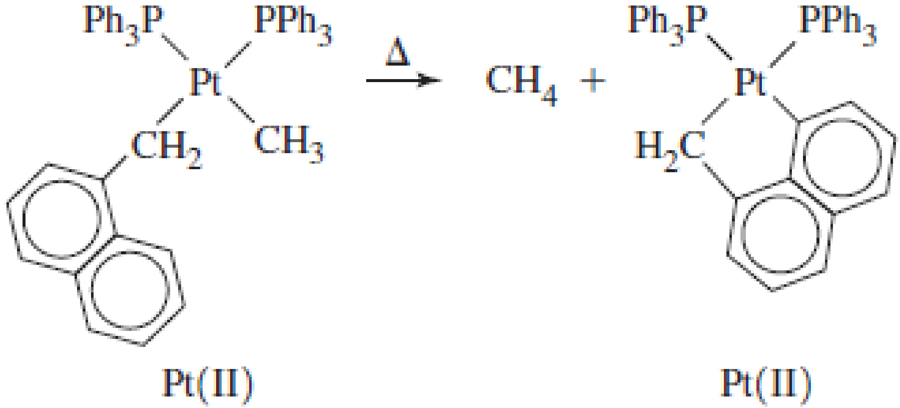
OA and RE in C-H bond activation

- Cyclometallation: C-H bond activations that incorporate metals into organic rings



Coordinates to metal at *ortho* position

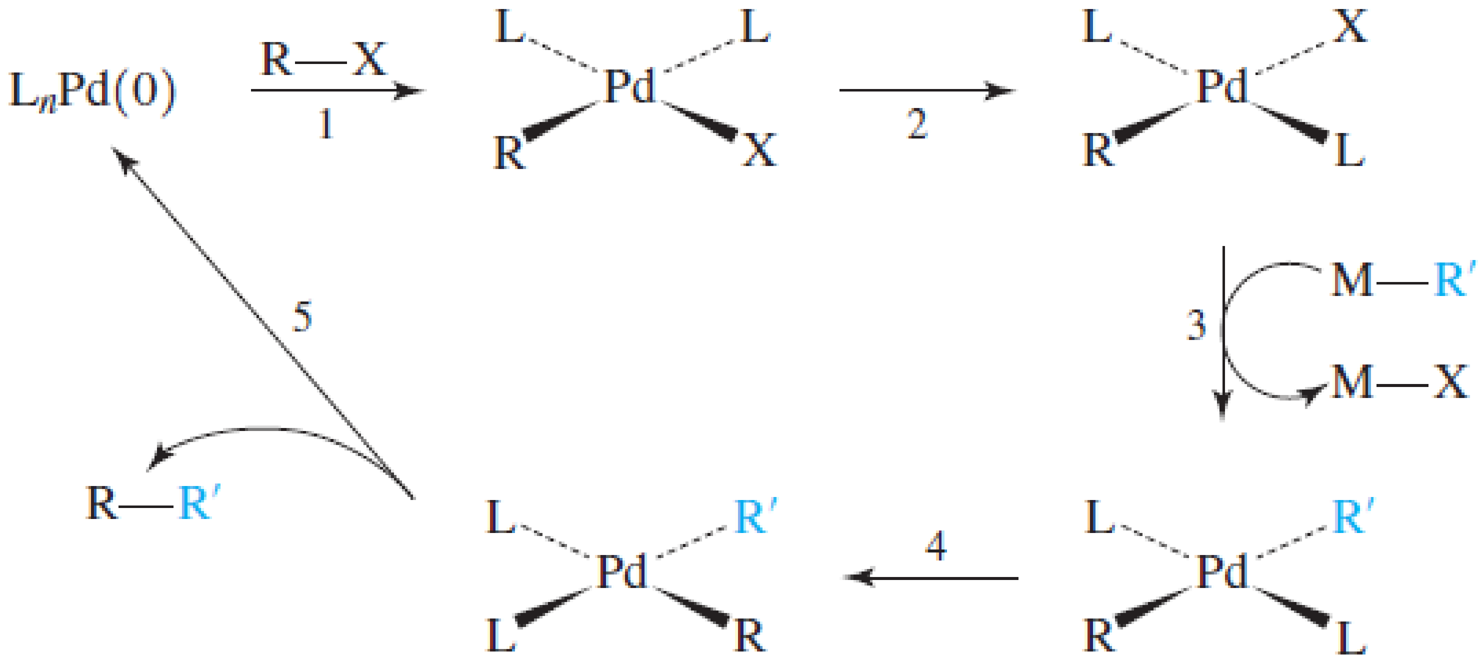
OA forms a 6-coordinate cyclometallated species



OA followed by RE of CH_4 forms a 4-coordinate cyclometallated species

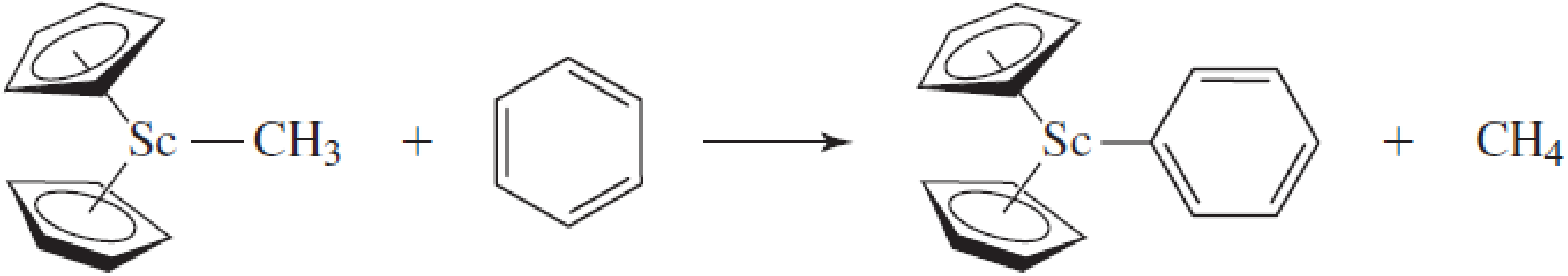
OA and RE in Pd-cross coupling

- Pd cross coupling reactions are widely used in organic chemistry, OA and RE are key steps
- Include important named reactions: Heck, Sonogashira, Negishi, Stille, Suzuki



Sigma bond metathesis

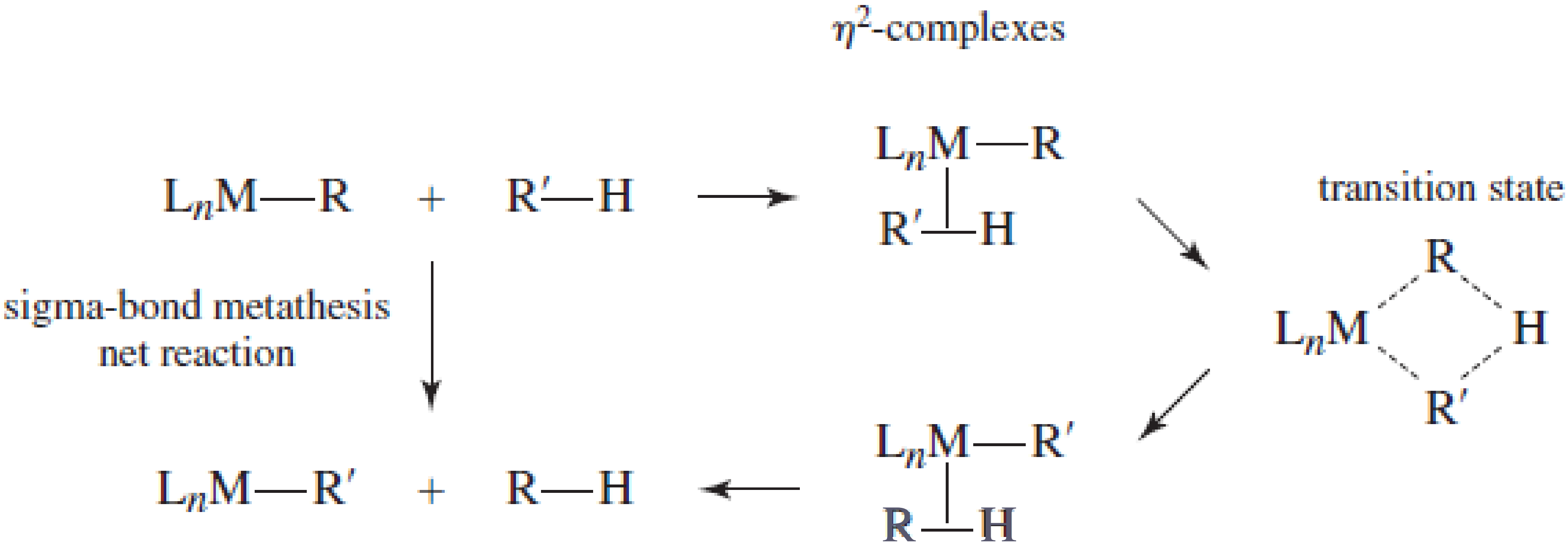
- In this type of reaction, two sigma bonded ligands are exchanged on a metal center without a change in metal oxidation state



  - In this reaction, C-H bond of methane is made and C-H bond of benzene is cleaved

Sigma bond metathesis

- The mechanism involves a 4-atom transition state that leads to exchange of ligands

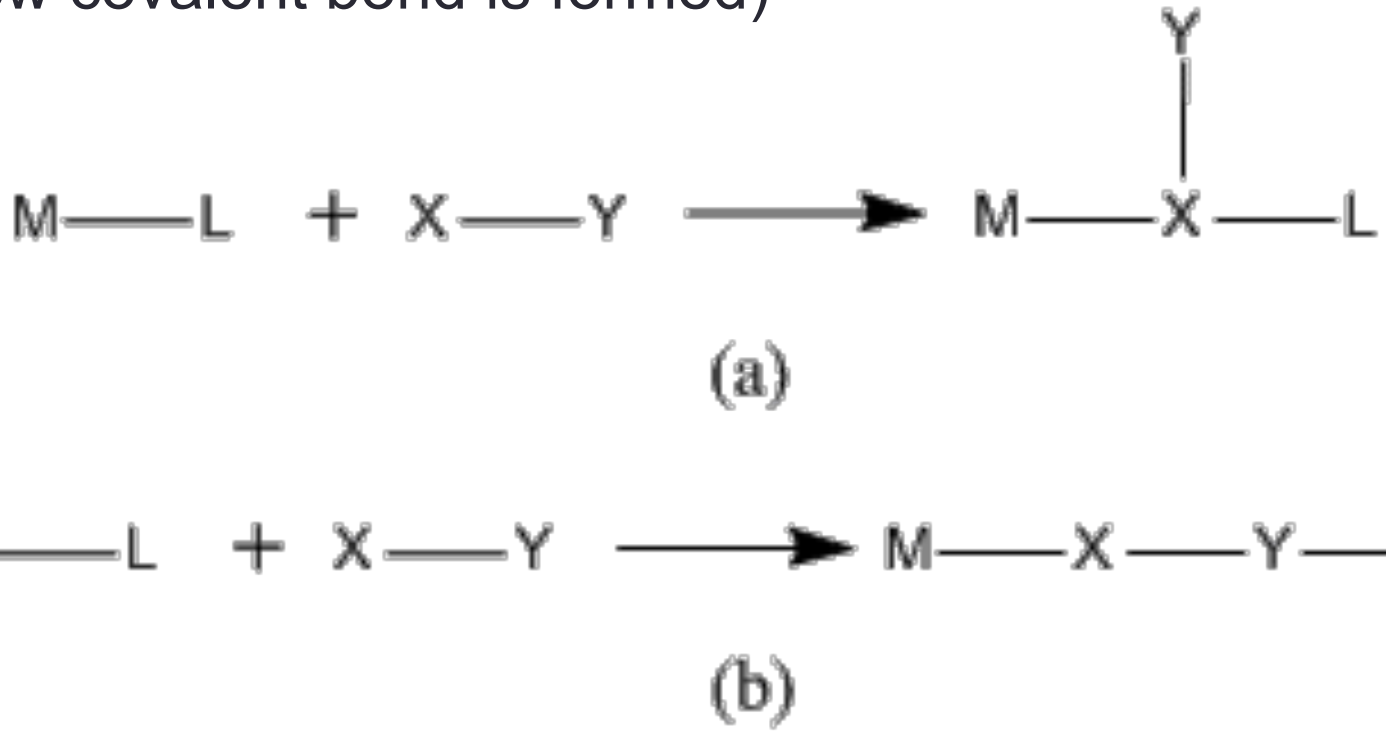


Reactions involving modification of ligands

- Insertion
- Migration
- Hydride elimination
- Abstraction

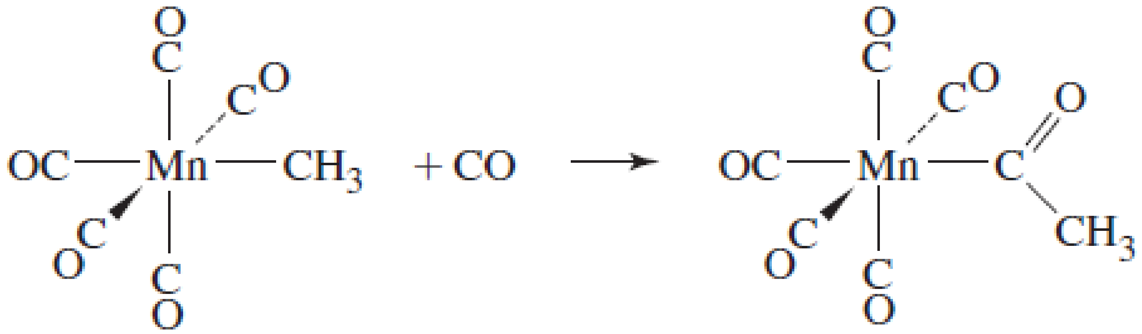
Insertion reactions

- In insertion reactions, an incoming molecule inserts into a metal-ligand bond (this is not a ligand substitution as a new covalent bond is formed)

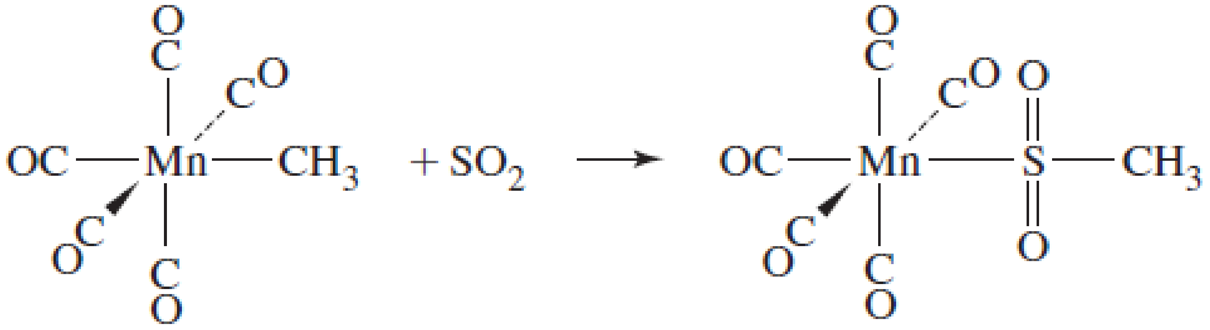


1,1 insertions

- Both new bonds formed are to the same atom



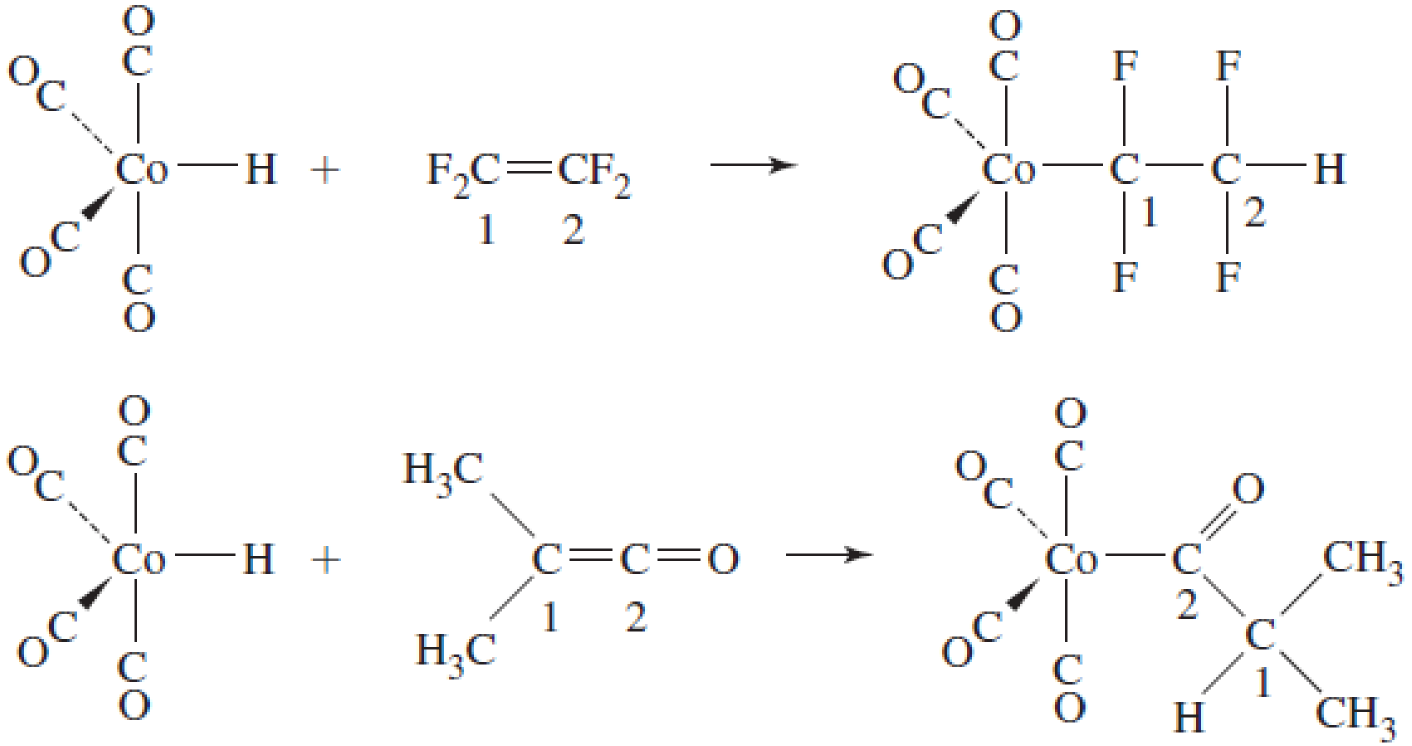
CO insertion into metal-alkyl bond



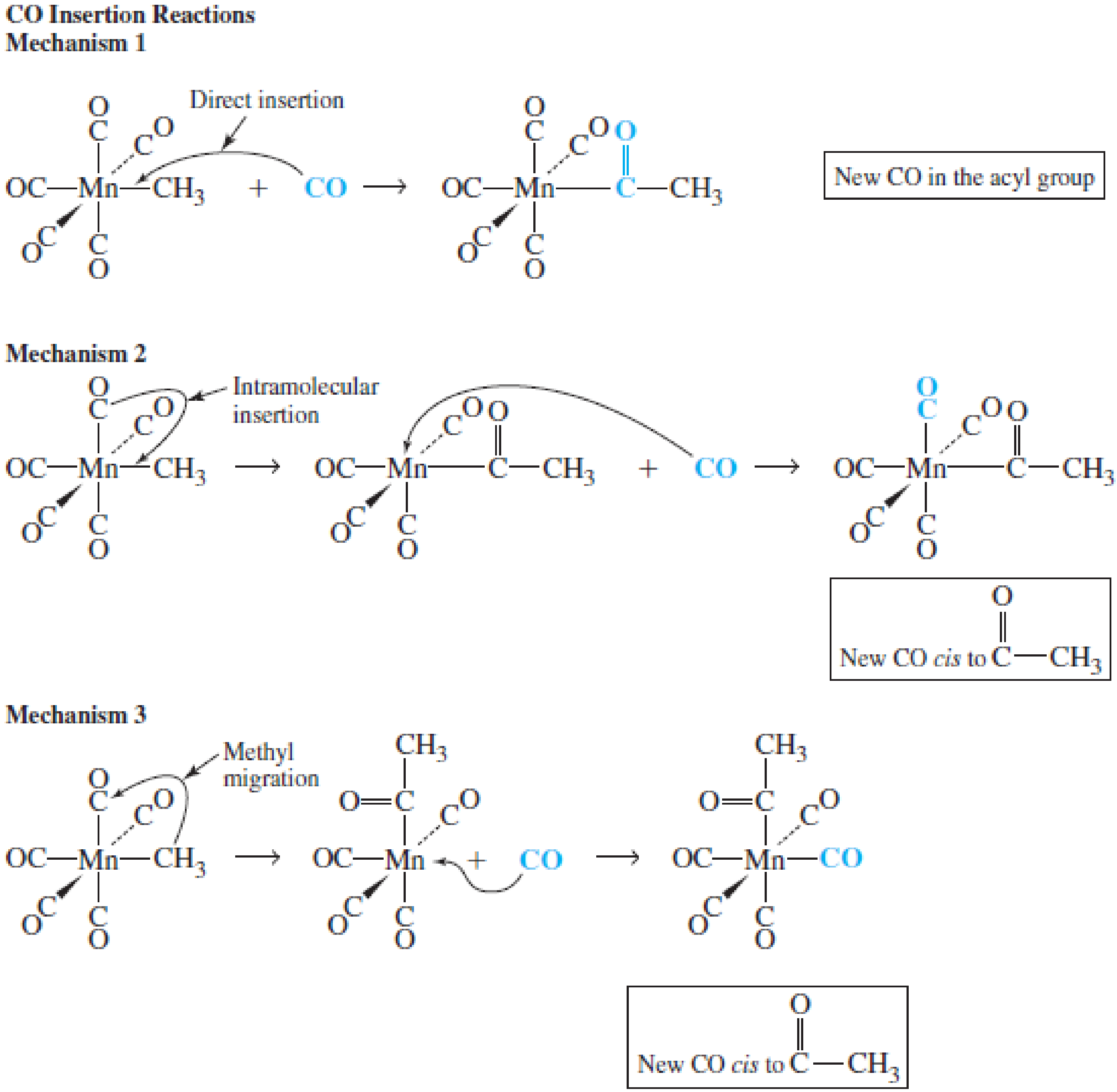
SO_2 insertion into a metal-alkyl bond

1,2 insertions

- New bonds are made to adjacent (1,2) atoms

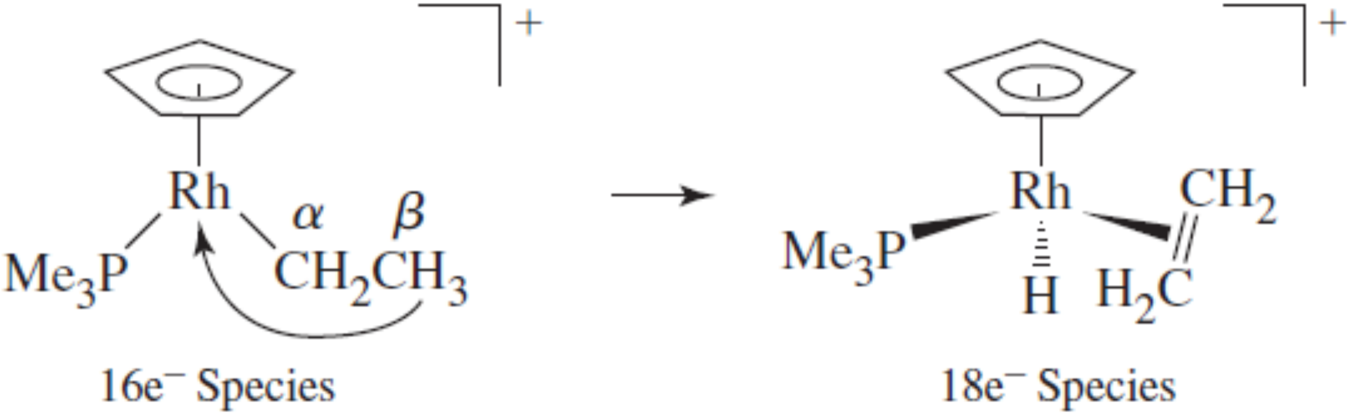


CO insertion may actually be alkyl migration



Hydride elimination

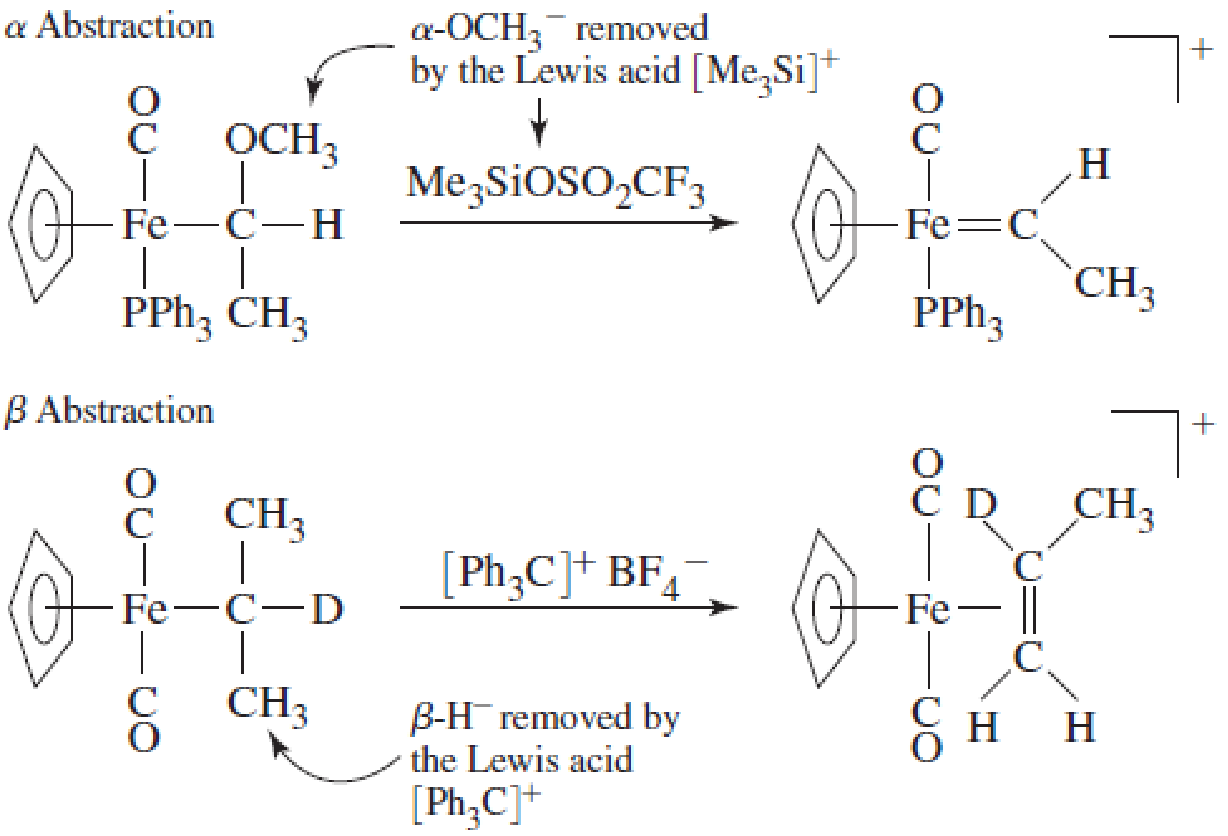
- In hydride eliminations, a hydrogen atom is transferred from a ligand to a metal
- The most common is **Beta hydride elimination**



  - Metal-alkyl complexes without beta hydrogens are more stable because they cannot undergo beta hydride elimination
- Alpha, gamma, and other hydride eliminations are also possible

Abstraction reactions

- These are elimination reactions in which the coordination number of the metal does not change
- Mediated by an external reagent like a Lewis acid



α Abstraction

α-OCH_3^- removed by the Lewis acid $[Me_3Si]^+$

$Me_3SiOSO_2CF_3$

β Abstraction

$[Ph_3C]^+ BF_4^-$

β-H^- removed by the Lewis acid $[Ph_3C]^+$

Organometallic catalysis

- Many of these single steps can be combined to form a catalytic cycle to convert one molecule into another

- This is of interest to industry: how to convert inexpensive feedstocks (e.g. petroleum) into $$$ molecules?

- One of the simplest examples is catalytic deuteration, a process catalyzed by H_3TaCp_2: this process is a series of RE and OA reactions