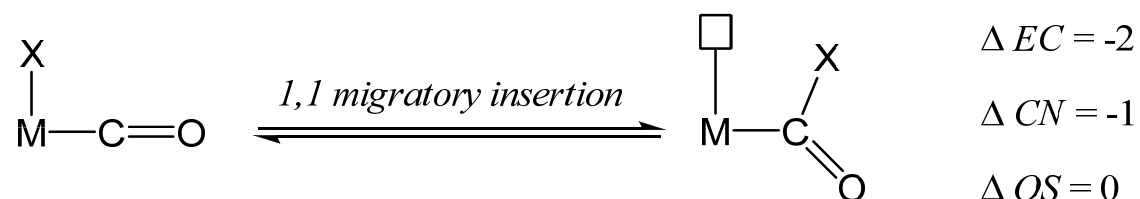


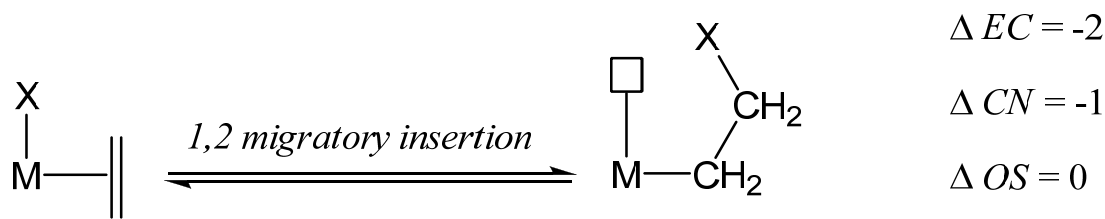
# Insertion Reactions

- **Oxidative addition** and **substitution** allow us to assemble 1e and 2e ligands on the metal, respectively.
- With **insertion**, and its reverse reaction, **elimination**, we can now *combine and transform these ligands within the coordination sphere*, and ultimately expel these transformed ligands to form free organic compounds.
- There are two main types of insertion

1) **1,1 insertion** in which the metal and the X ligand end up bound to the same (1,1) atom



2) **1,2 insertion** in which the metal and the X ligand end up bound to adjacent (1,2) atoms of an L-type ligand.

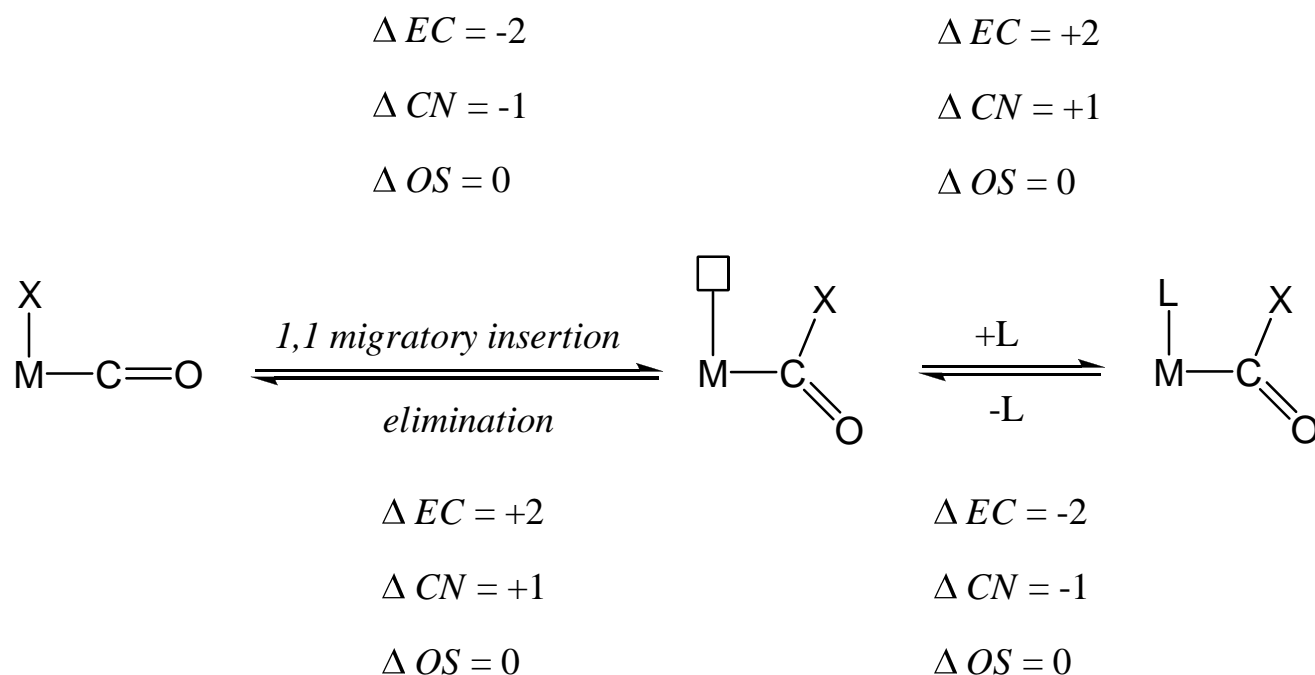


- The type of insertion observed in any given case depends on the nature of the 2e inserting ligand.
- For example:
  - ***CO gives only 1,1 insertion***
  - ***ethylene gives only 1,2 insertion***, in which the M and the X end up on adjacent atoms of what was the 2e X-type ligand.

***In general,  $\eta^1$  ligands tend to give 1,1 insertion and  $\eta^2$  ligands give 1,2 insertion***

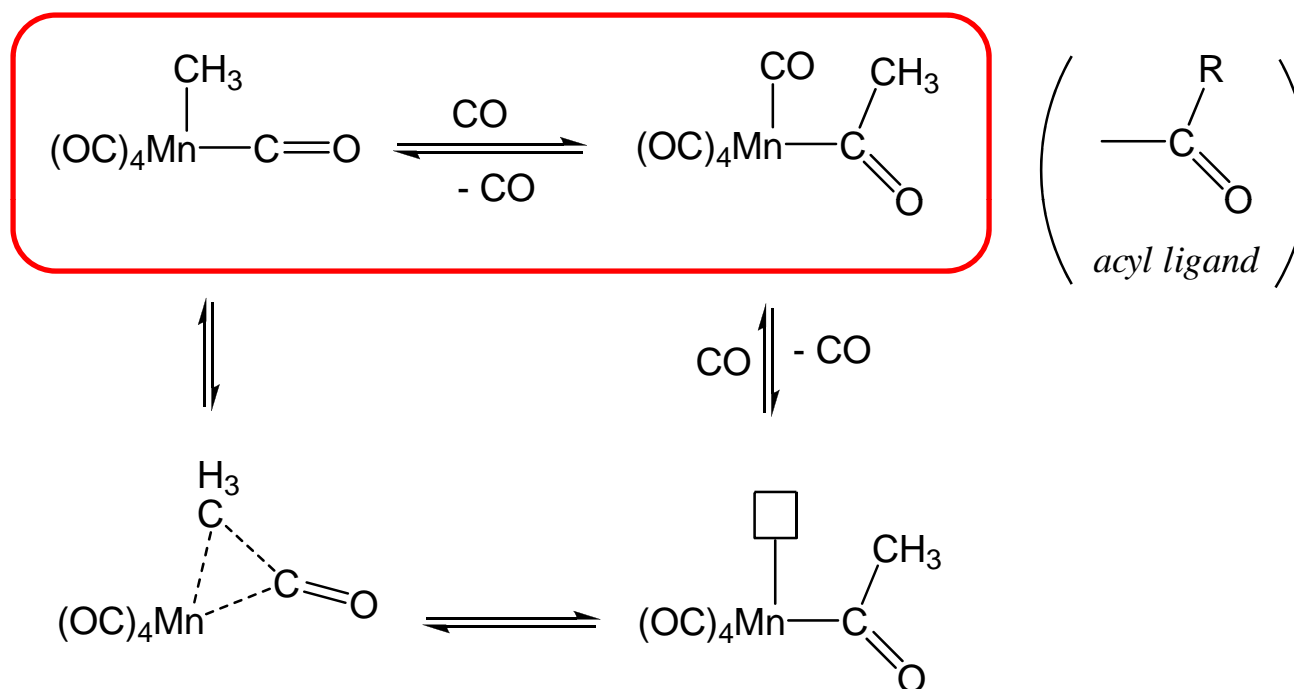
- $\text{SO}_2$  is the only common ligand that can give both types of insertion; as a ligand,  $\text{SO}_2$  can be  $\eta^1$  (S) or  $\eta^2$  (S, O).
- In principle, ***insertion reactions are reversible***, but just as we saw for oxidative addition and reductive elimination previously, for many ligands only one of the two possible directions is observed in practice, probably because this ***direction is strongly favored thermodynamically***.

- A **2e vacant site is generated** by 1,1 and 1,2 insertion reactions.
- This site can be occupied by an external 2e ligand and the insertion product trapped.
- Conversely, the **reverse elimination requires a vacant site**, so that an 18e complex will not undergo the reaction unless a ligand first dissociates.
- The **insertion requires a cis arrangement** of the ligands, while the **elimination generates a cis arrangement** of these ligands.
- The formal oxidation state does not change during the reaction.



# CO insertion reactions

- CO shows a ***strong tendency to insert into metal–alkyl bonds*** to give metal acyls.

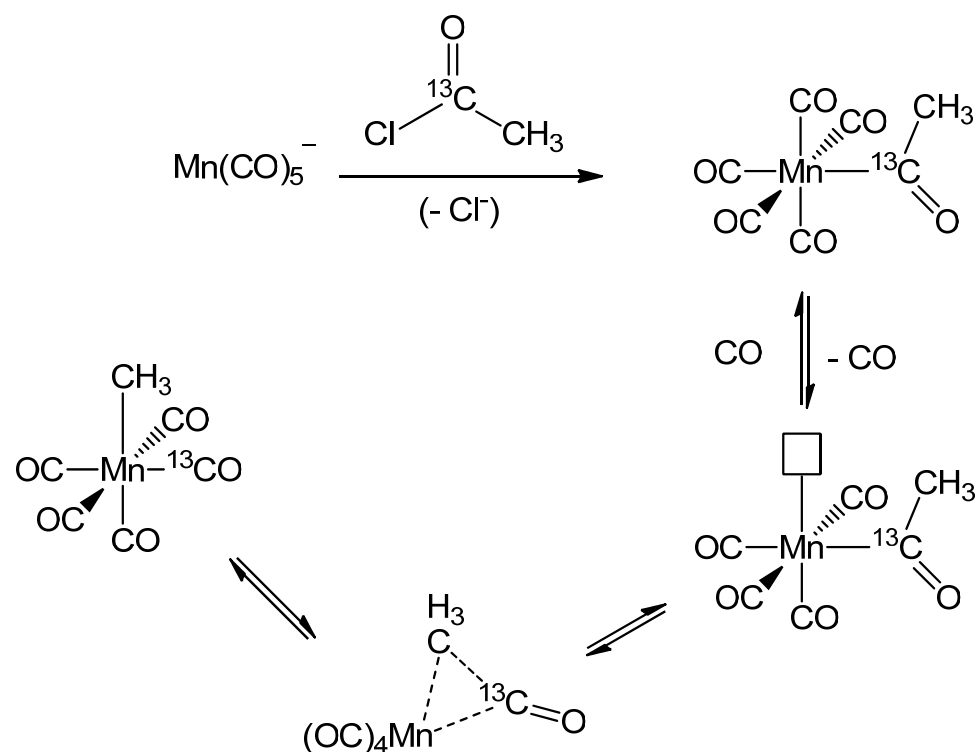


- When the incoming ligand is  $^{13}\text{CO}$ , the product contains only one labeled CO, which is *cis* to the newly formed acetyl group.
- This shows that ***the methyl group migrates to a coordinated CO***, rather than free CO attacking the Mn–Me bond.
- We can tell where the labeled CO is located in the product because there is a characteristic shift of the  $\nu(\text{CO})$  stretching frequency to lower energy in the IR spectrum of the complex as a result of the greater mass of  $^{13}\text{C}$  over normal carbon.
- By studying the reverse reaction, elimination of CO from  $\text{Me}^{13}\text{COMn}(\text{CO})_5$ , where we can easily label the acyl carbon with  $^{13}\text{C}$  (by reaction of  $\text{Mn}(\text{CO})_5^-$  with  $\text{Me}^{13}\text{COCl}$ ), we find that the label ends up in a CO *cis* to the methyl.

$$\nu = \frac{1}{2\pi c} \left\{ \sqrt{\frac{k}{m_r}} \right\}$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

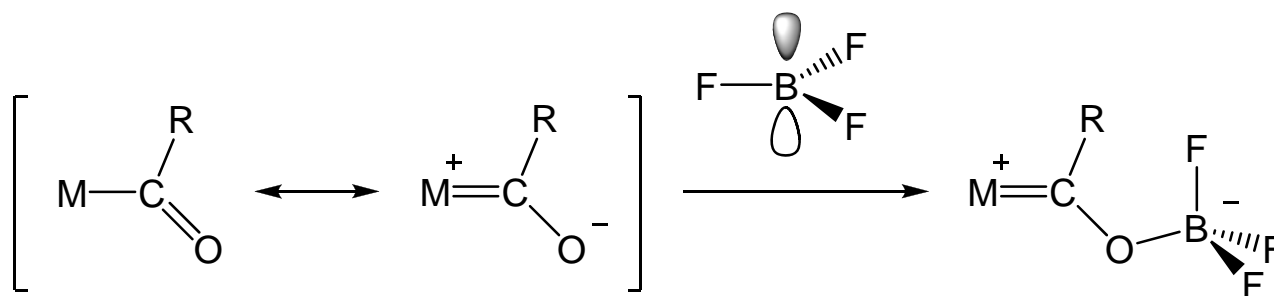
Bands in the IR spectrum correspond to vibrational modes of a molecule where the position or *wavenumber* of the band,  $\nu$ , depends on the strength of the bond(s) involved as measured by a force constant  $k$ , and on the reduced mass of the system,  $m_r$ . The reduced mass is calculated for a simple diatomic molecule as shown, where  $m_1$  and  $m_2$  are the atomic weights of the two atoms.



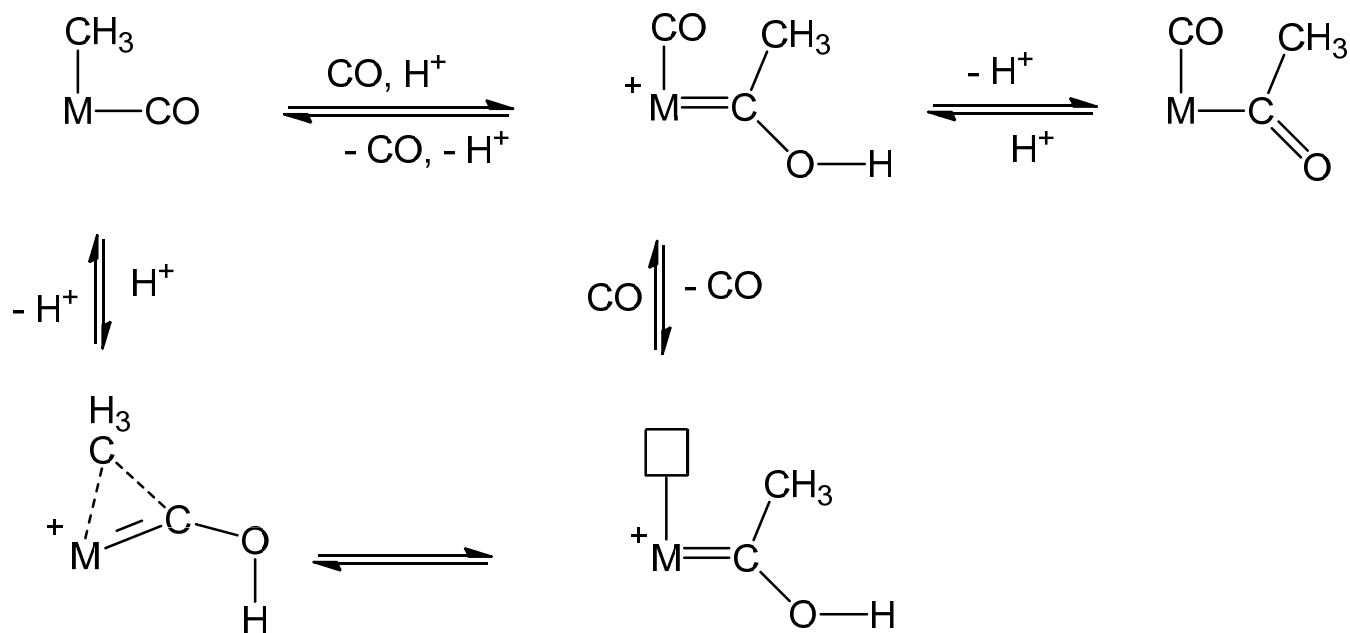
- This relies on *microscopic reversibility*, according to which the forward and reverse reactions of a thermal process must follow the same path.
- If a subsequent scrambling of the COs had been fast, we could have deduced nothing.
- The methyl also migrates when the reaction is carried out in the direction of insertion.
- We again use the IR spectrum to tell where the label has gone in the products.

# Enhancing insertion rates

- **Steric bulk in the ligand set accelerates insertion**, no doubt because the acetyl in the  $L_nM(COMe)$  product, occupying one coordination site, is far less bulky than the alkyl and carbonyl, occupying two sites.
- **Lewis acids** such as  $AlCl_3$ ,  $BF_3$  or  $H^+$  can increase the rate of migratory insertion by as much as 108-fold.
- Metal acyls are more basic at oxygen than are the corresponding carbonyls by virtue of the resonance form.

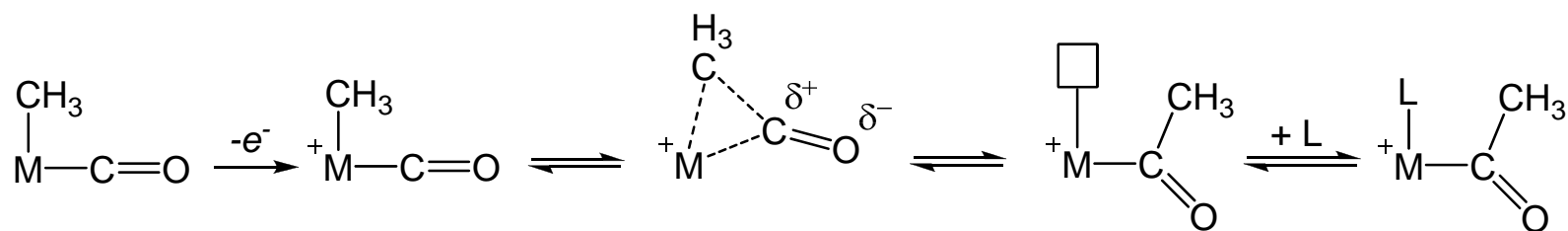


- By binding to the oxygen, the Lewis acid would be expected to stabilize the transition state and speed up trapping by L and therefore speed up the reaction.
- Polar solvents such as acetone also significantly enhance the rate due to stabilization of the zwitterionic form of the resonance structure.



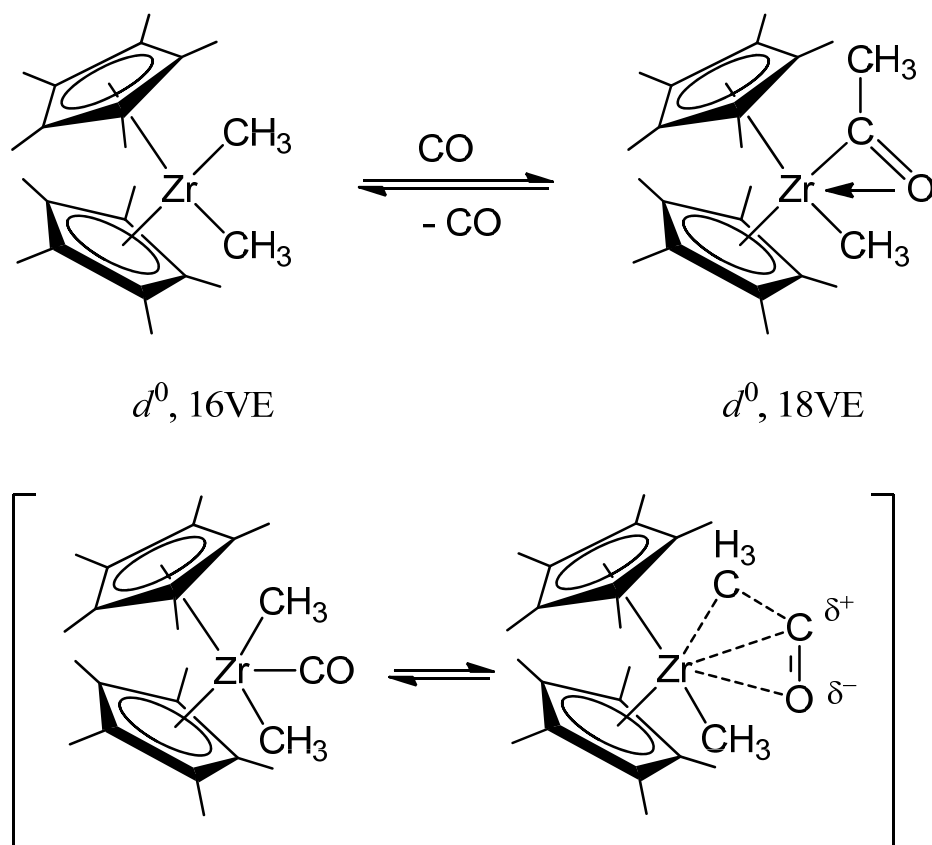


- Another important way of promoting the reaction is ***oxidation of the metal***.
- Increased electrophilicity (decreased  $\pi$  basicity) of the metal, leading to a larger partial positive charge on the CO carbon.
- The migration of  $\text{H}_3\text{C}^-$  to an electron deficient CO carbon seems to be a good description of the CO insertion, and so the rate of the reaction may increase in response to the increase in the  $\delta^+$  charge on the CO carbon.
- Oxidation would also speed up trapping by an external ligand such as phosphine, however, the solvent has also been known to play the role of incoming ligand.
- The rates of insertion are increased to some extent by using more nucleophilic solvents, suggesting that the solvent may act as a temporary ligand to stabilize an initial, solvated insertion product.



$\text{L} = \text{CO}, \text{PPh}_3, \text{solvent etc.}$

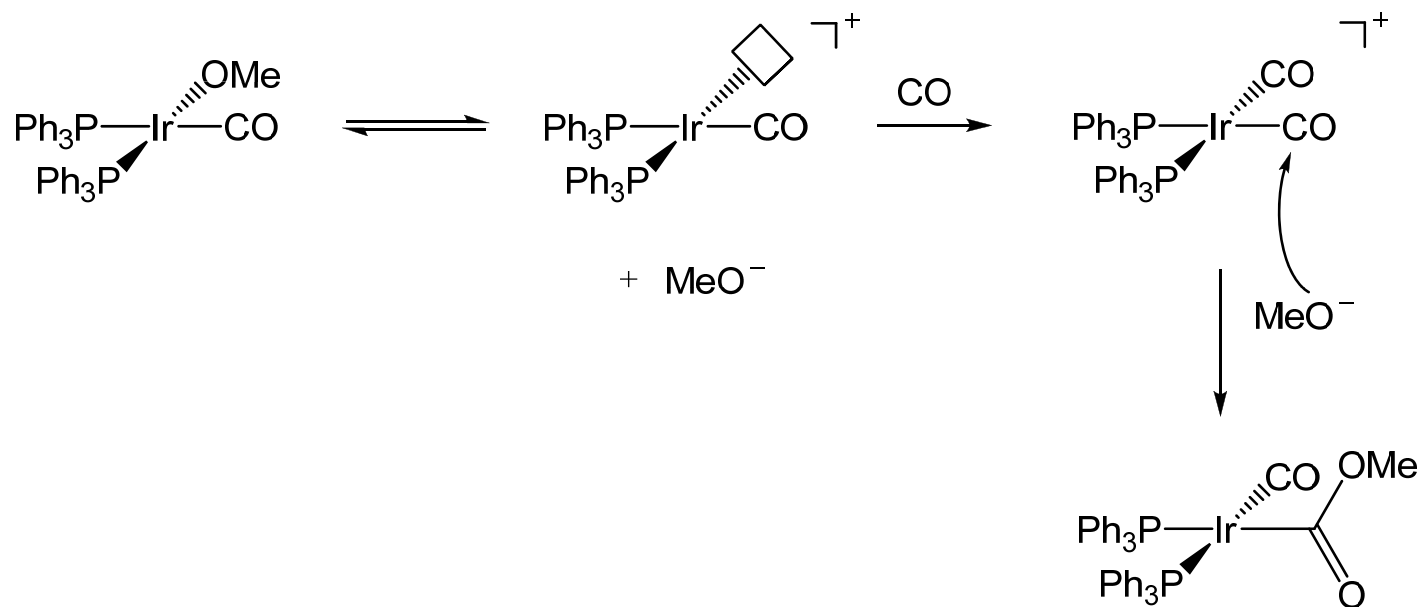
- **Early metals are Lewis acids in their own right** and tend to bind oxygen ligands. They can therefore act as their own Lewis acid catalysts for insertion.
- The product is an  $\eta^2$ -acyl



- In this reaction, formation of an intermediate carbonyl complex is proposed. Zr(IV) is a poor  $\pi$  base, and so the intermediate must be very unstable.
- **Limited back bonding should make the CO much more reactive toward insertion.**

# Apparent insertions

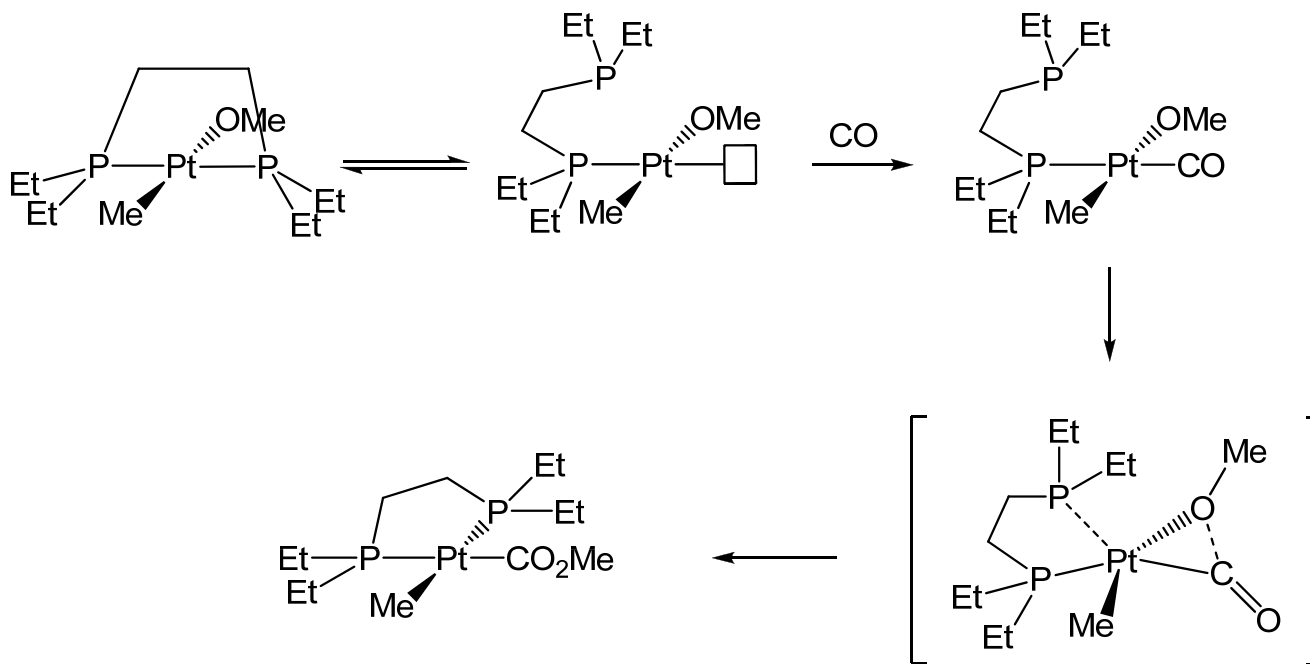
- These can in fact go by an entirely different route:

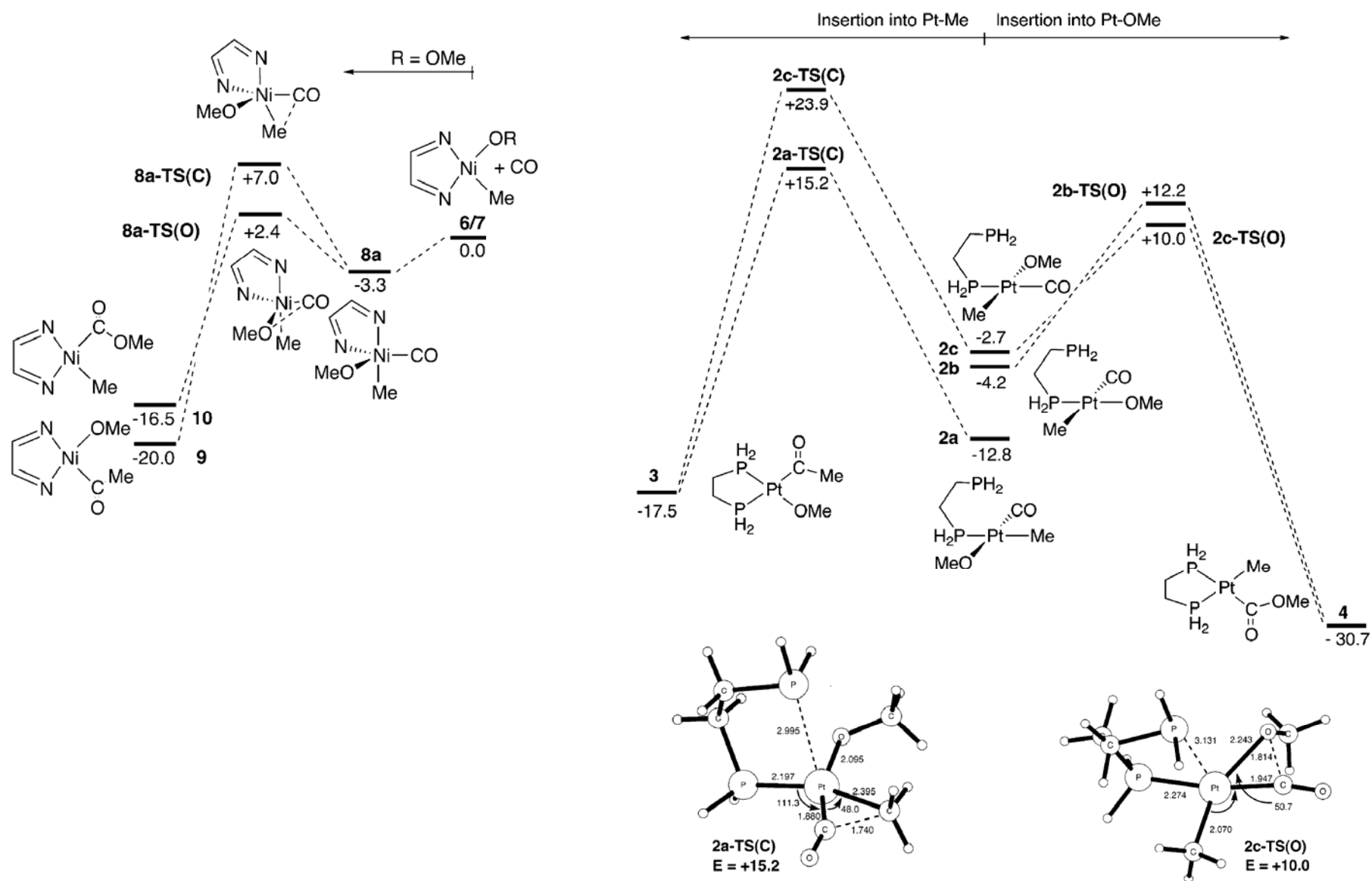


- The **late metal alkoxide is unstable** (since  $\text{MeO}^-$  is a good  $\pi$  donor bound to a  $\pi$  donor metal) and the  $\text{MeO}^-$  group dissociates to give an ion pair with a 2e vacancy at the metal.
- The free CO present then binds to this 2e site and is **strongly activated toward nucleophilic attack at the CO carbon owing to the positive charge on the metal**.

# CO insertion into M–O

- Genuine migratory insertions into M–O bonds are also possible.
- For *trans*-[Pt(Me)(OMe)(dppe)], CO inserts into the Pt–OMe bond, while for [Ni(Me)(*O*-*p*-C<sub>6</sub>H<sub>4</sub>CN)(bipy)], CO inserts into Ni–Me. This follows from theoretical work.
- The Ni–Me bond is significantly stronger than the Ni–OMe, but migratory insertion with Ni–Me is marginally preferred owing to the weaker C–O bond of the aryloxycarbonyl.
- The Pt–Me and Pt–OMe bonds are equally strong, so the stronger methoxycarbonyl C–O bond results in reaction with the Pt–OMe bond.

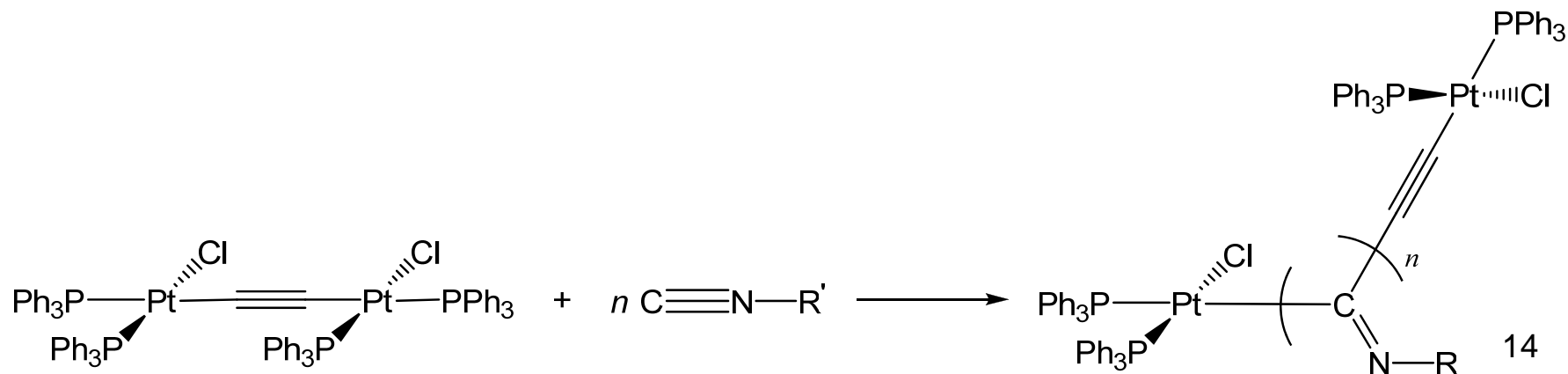




Computed reaction profiles (in kcal/mol) for the migratory insertion reaction CO. Energies are relative to the starting complex + free CO set to zero.

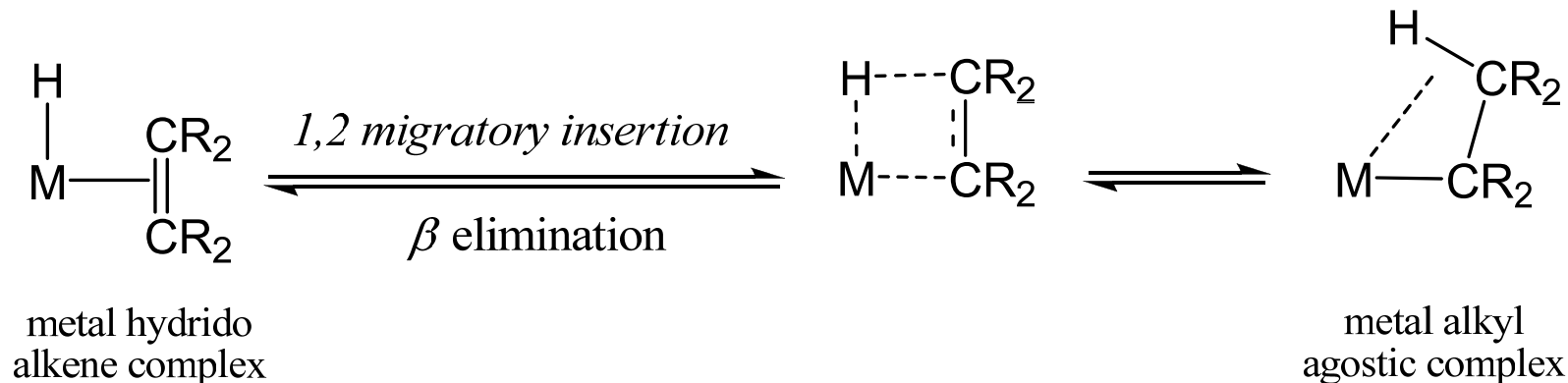
# Double insertion

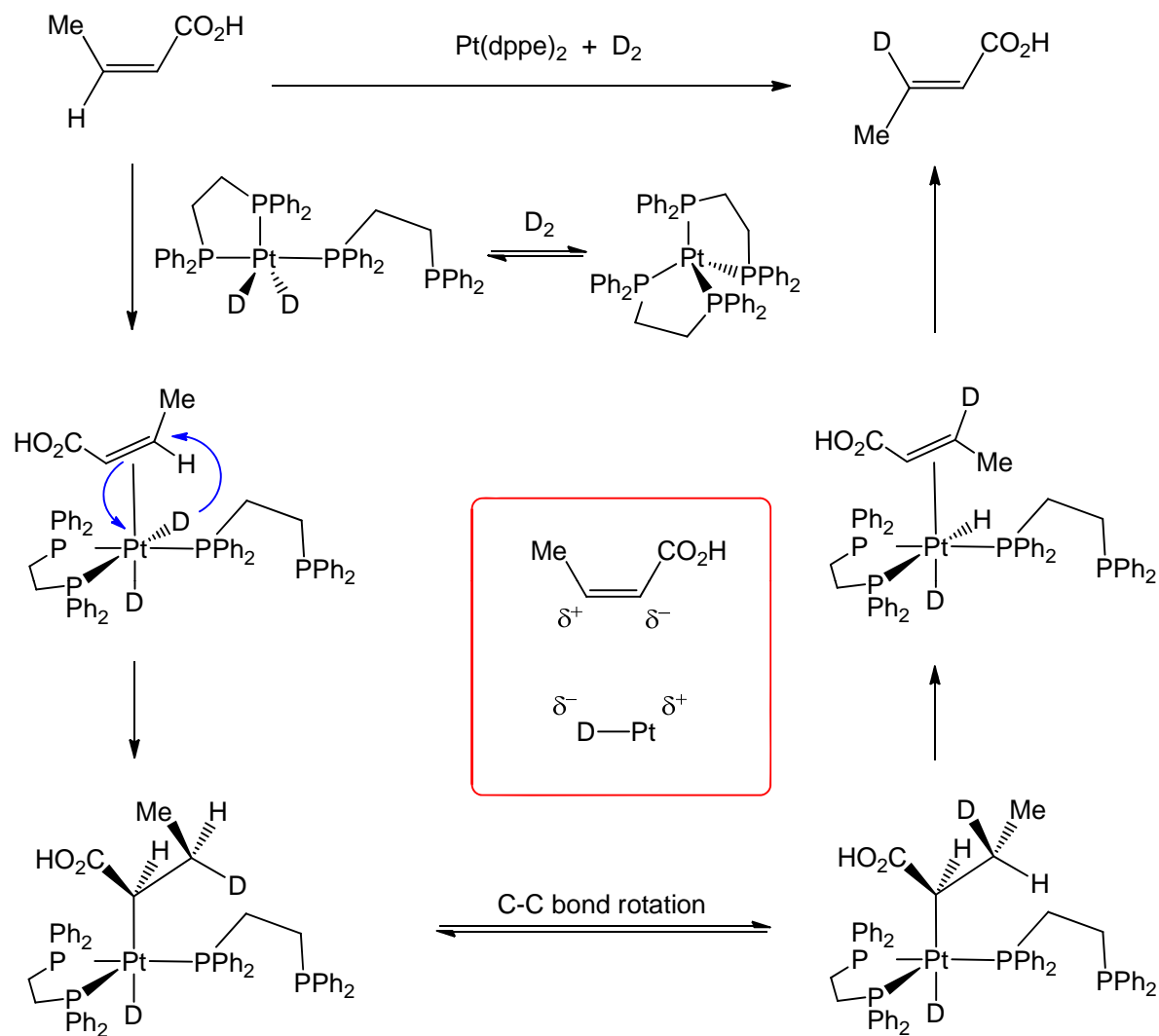
- Given that the methyl group migrates to the CO, why stop there? Why does the resulting acyl group not migrate to another CO to give an MeCOCO ligand?
- The complex that would have been formed in a double insertion can be made by an independent route from MeCOCOCl and  $\text{Mn}(\text{CO})_5^-$ . ***It easily eliminates CO to give  $\text{MeCOMn}(\text{CO})_5$ , which suggests that the double-insertion product is thermodynamically unstable*** with respect to  $\text{MeCOMn}(\text{CO})_5$ .
- The  $-\text{CHO}$  and  $\text{CF}_3\text{CO}^-$  groups share with  $\text{MeCOCO}^-$  the property of eliminating CO irreversibly to give hydride and trifluoromethyl complexes, respectively.
- The reason is again probably thermodynamic because the  $\text{M-COMe}$ ,  $\text{M-H}$ , and  $\text{M-CF}_3$  bonds are all distinctly stronger than  $\text{M-CH}_3$ , the bond formed in CO elimination.***
- In contrast, isocyanides do undergo repeated migratory insertion to give polymers with as many as 100 isocyanide units inserted:



# Alkene insertions reactions

- The insertion of coordinated alkenes into M–H bonds is a very important reaction because it gives alkyls and constitutes a key step in a variety of catalytic reactions including alkene polymerization, perhaps the most commercially important organometallic reaction.
- As  $\eta^2$ -ligands, alkenes give 1,2 insertion. ***This is the reverse of the familiar  $\beta$ -elimination reaction.***
- Some insertion reactions are known to give agostic rather than classical alkyls, and probably lie on the pathway for insertion into M–H bonds.
- The position of equilibrium is decided by the thermodynamics of the particular system, and depends strongly on the alkene involved.
- For simple alkenes, such as ethylene, the equilibrium tends to lie to the left (i.e., the alkyl  $\beta$ -eliminates), but for ***alkenes with electron-withdrawing ligands*** (e.g.,  $\text{C}_2\text{F}_4$ ), the alkyl is particularly stable, and the equilibrium lies entirely to the right;

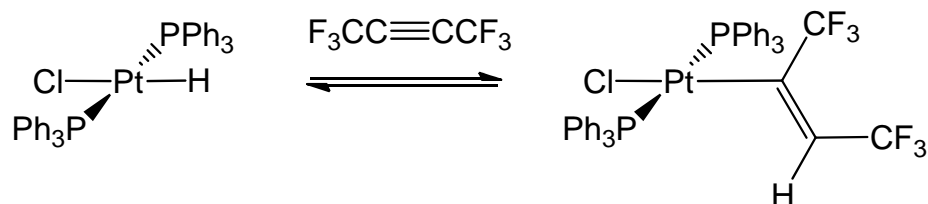




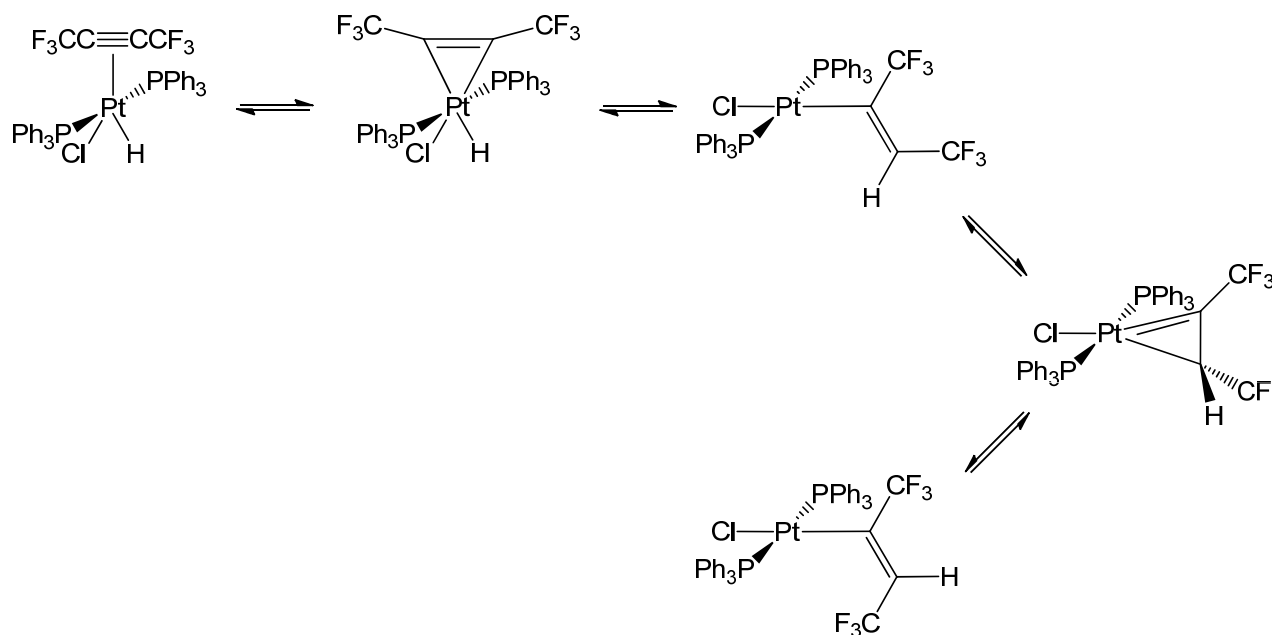
- Strategy that Spencer and co-workers have used to determine the mode of Pd-H addition to an unsymmetrical *cis* alkene.
- On isomerization to the *trans* form, the deuterium initially incorporated in the insertion step is retained by the substrate and labels the  $\beta$  carbon of the product.
- The mode of insertion is consistent with the Pd-H hydride acting as a hydridic  $\delta^-$  group.



- The usual stereochemistry of the insertion is **syn**, and so the stereochemistry at both carbons is retained.

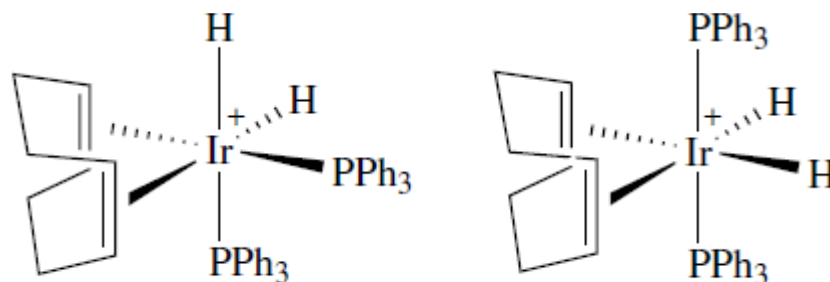
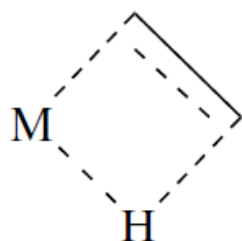


- But the initially formed *cis-vinyl* complex, if 16e, can sometimes rearrange to the *trans* isomer, via an  $\eta^2$ -vinyl.



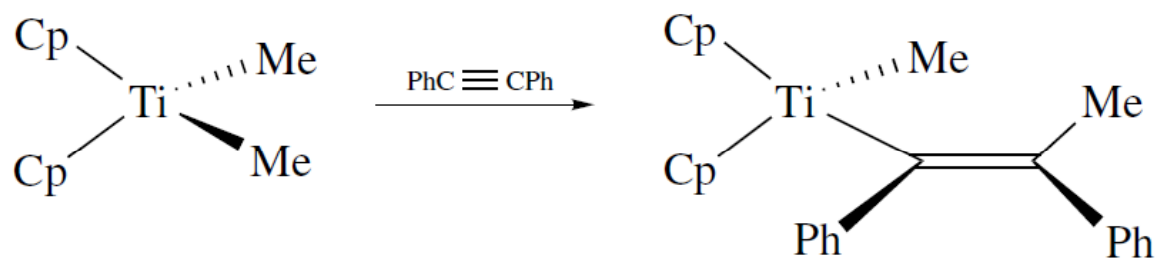
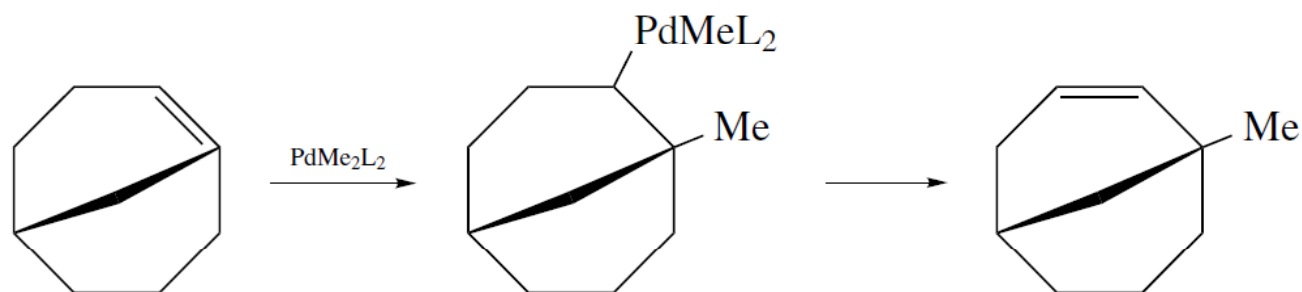
- This can lead to a net **anti** addition of a variety of groups to alkynes:

- As we saw for CO insertions and eliminations, **a 2e vacant site is generated by the insertion (and required for the elimination)**.
- Reversible insertion/elimination equilibria are also known. The vacant site may be filled by any suitable ligand, such as the solvent, excess alkene, an agostic C-H bond or a phosphine.
- The transition state for insertion, has an essentially **coplanar M-C-C-H arrangement**, and this implies that both insertion and elimination also require the M-C-C-H system to be capable of becoming coplanar (*microreversibility*).



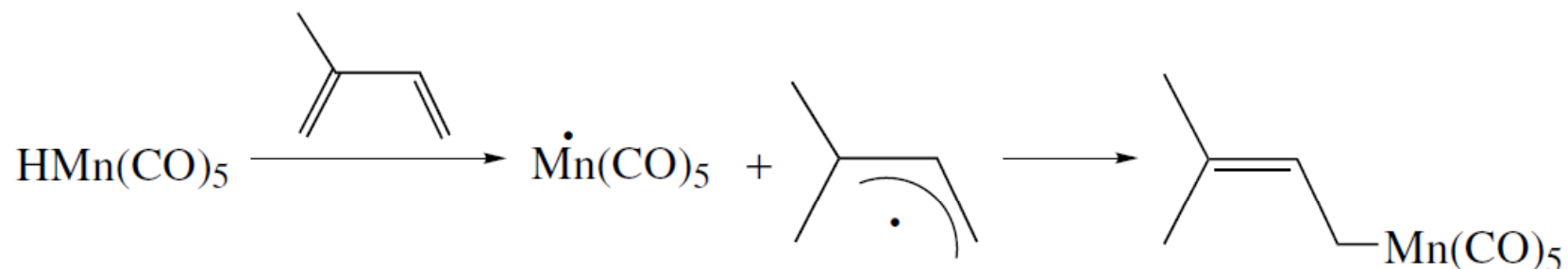
- We have seen how we can stabilize alkyls against  $\beta$  elimination by having a non-coplanar M-C-C-H system. The same principles apply to stabilizing alkene hydride complexes.
- The *cis*-phosphine complex above undergoes insertion at least 40 times more rapidly than the *trans*-phosphine isomer, although the alkene and M-H groups are *cis* in both cases, only in the *cis*-phosphine complex is there a coplanar M-C-C-H arrangement.

- Ring strain, or the presence of electronegative substituents on the alkene, or moving to an alkyne, are some of the other factors that can bias both the thermodynamics and the kinetics in favor of insertion.



# Diene Insertion

- Butadiene and allene react with a variety of hydrides by 1,2 insertion, but butadienes also react with  $\text{HMn(CO)}_5$  to give ***an apparent 1,4 insertion***.
- Since this 18e hydride has no vacant site and CO dissociation is slow, an indirect mechanism must be operating.
- This is thought to be H atom transfer to give a 1,1-dimethylallyl radical that is subsequently trapped by the metal.
- Only substrates that form especially stable radicals can react (e.g., 1,3-diene  $\rightarrow$  allyl radical).
- Chemically induced dynamic nuclear polarization (CIDNP) effects can be seen in such cases.

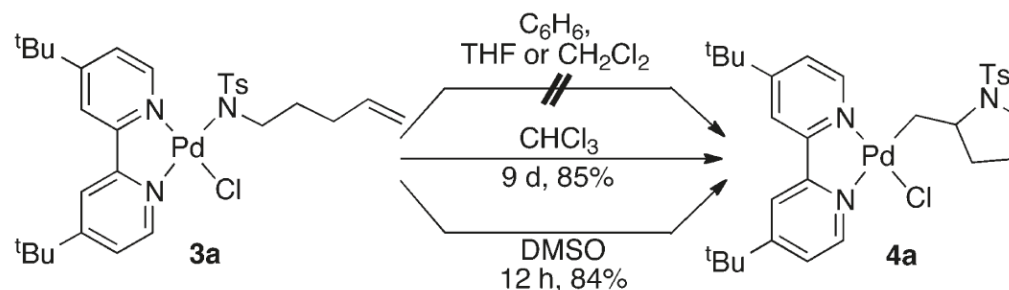


# Reversible Alkene Insertion into the Pd–N Bond of Pd(II)-Sulfonamidates and Implications for Catalytic Amidation Reactions

Paul B. White and Shannon S. Stahl\*

Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States

## Scheme 1. Amidopalladation of an Alkene



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