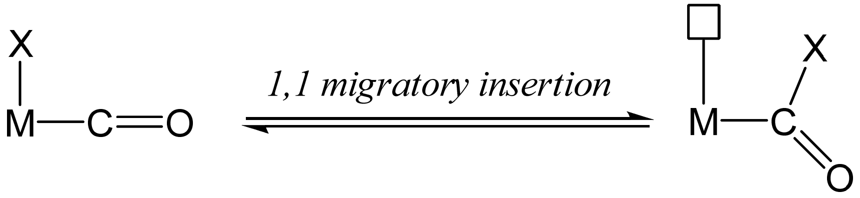
Insertion Reactions

- ***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

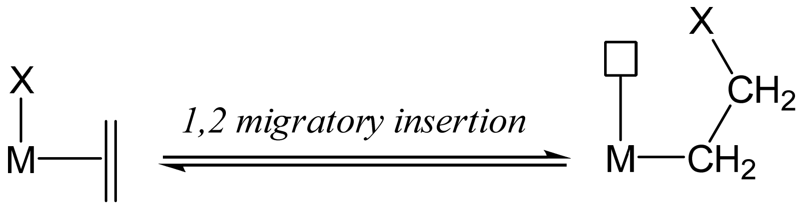


$\Delta\ EC = -2$

$\Delta\ CN = -1$

$\Delta\ OS = 0$

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.



$\Delta\ EC = -2$

$\Delta\ CN = -1$

$\Delta\ OS = 0$

- 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, *η^1 ligands tend to give 1,1 insertion and η^2 ligands give 1,2 insertion*

- SO_2 is the only common ligand that can give both types of insertion; as a ligand, SO_2 can be η^1 (S) or η^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 ***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.

$\Delta\, EC = -2$

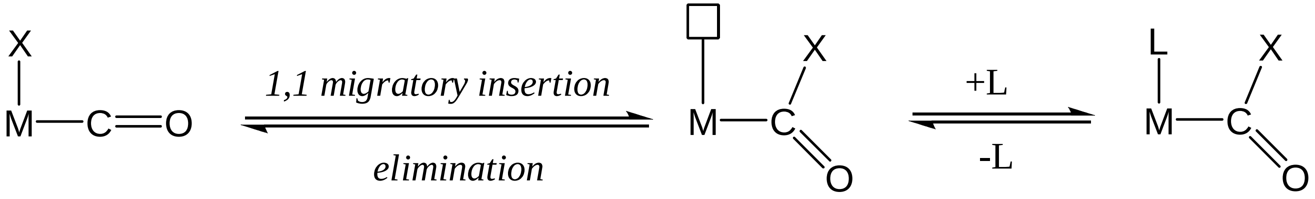
$\Delta\, CN = -1$

$\Delta\, OS = 0$

$\Delta\, EC = +2$

$\Delta\, CN = +1$

$\Delta\, OS = 0$



$\Delta\, EC = +2$

$\Delta\, CN = +1$

$\Delta\, OS = 0$

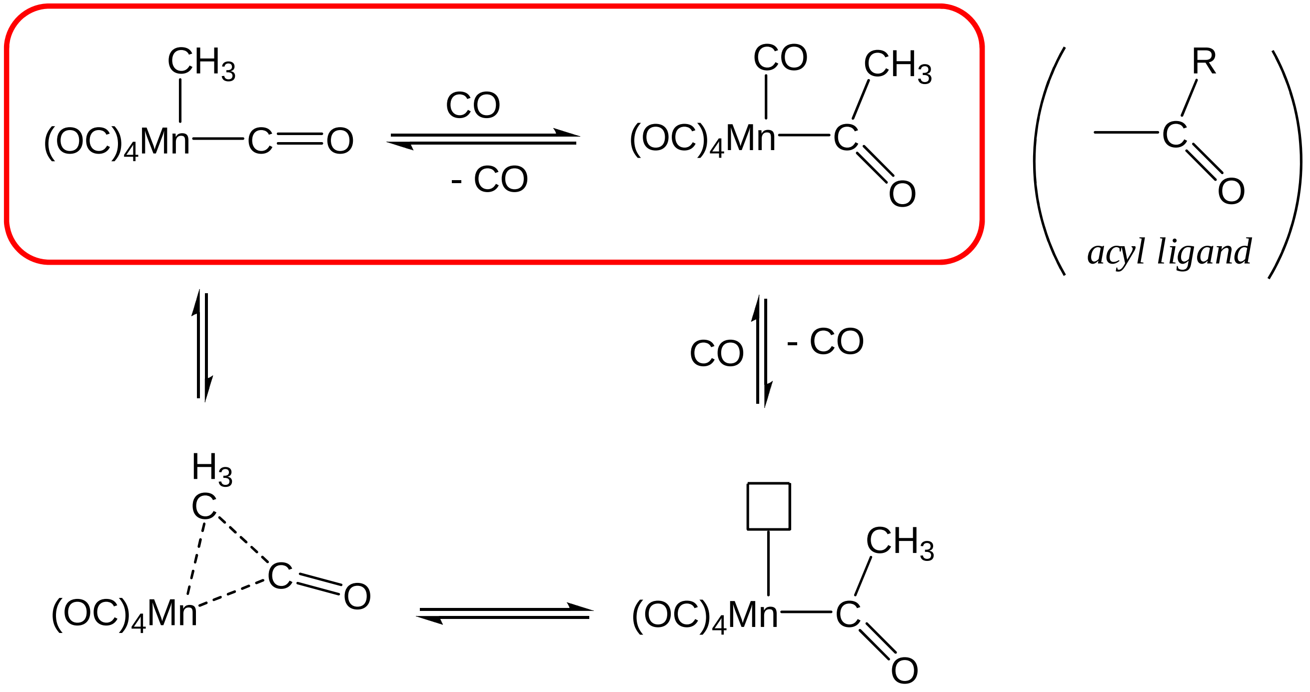
$\Delta\, EC = -2$

$\Delta\, CN = -1$

$\Delta\, OS = 0$

CO insertion reactions

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



- When the incoming ligand is ^{13}CO, the product contains only one labeled CO, which is *cis* to the newly formed acetyl group.

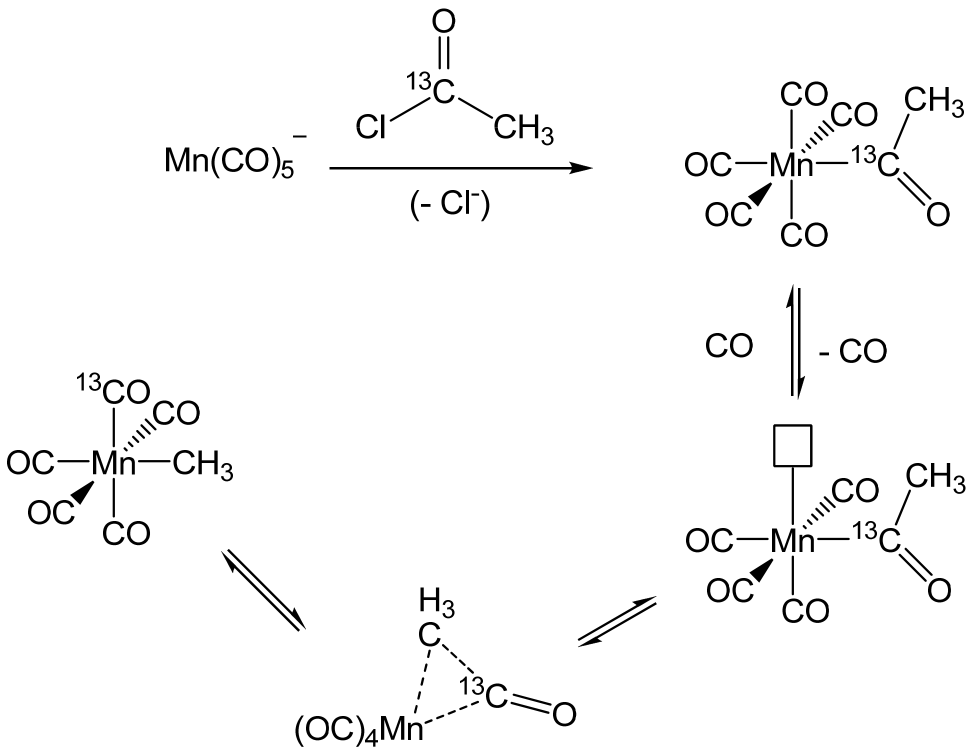
- This shows that ***the methyl group migrates to a coordinated CO***, rather than free CO attacking the Mn−Me bond.

- We can tell where the labeled CO is located in the product because there is a characteristic shift of the *v(CO)* stretching frequency to lower energy in the IR spectrum of the complex as a result of the greater mass of ^{13}C over normal carbon.

- By studying the reverse reaction, elimination of CO from $Me^{13}COMn(CO)_5$, where we can easily label the acyl carbon with ^{13}C (by reaction of Mn(CO)5− with $Me^{13}COCl$), we find that the label ends up in a CO *cis* to the methyl.

$$\nu = \frac{1}{2\pi c}\left\{\sqrt{\frac{k}{m_r}}\right\} \qquad m_r = \frac{m_1 m_2}{m_1 + m_2}$$

- Bands in the IR spectrum correspond to vibrational modes of a molecule where the position or *wavenumber* of the band, *v*, 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.

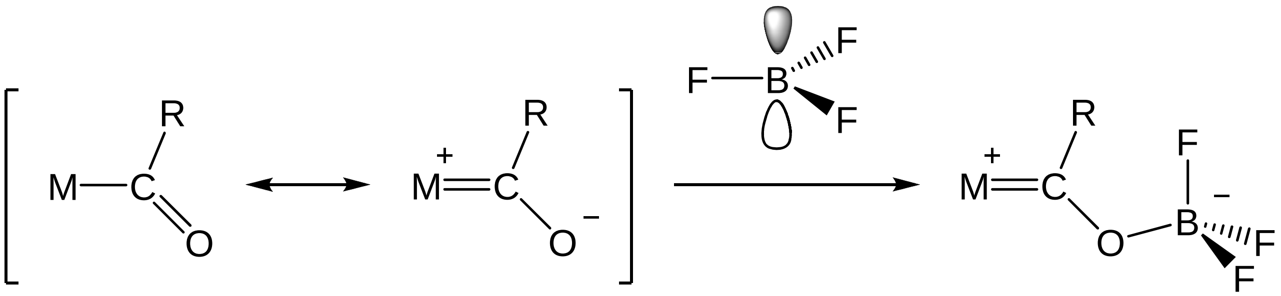
- If a subsequent scrambling of the COs had been fast, we could have deduced nothing.

- The methyl also migrates when the reaction is carried out in the direction of insertion.

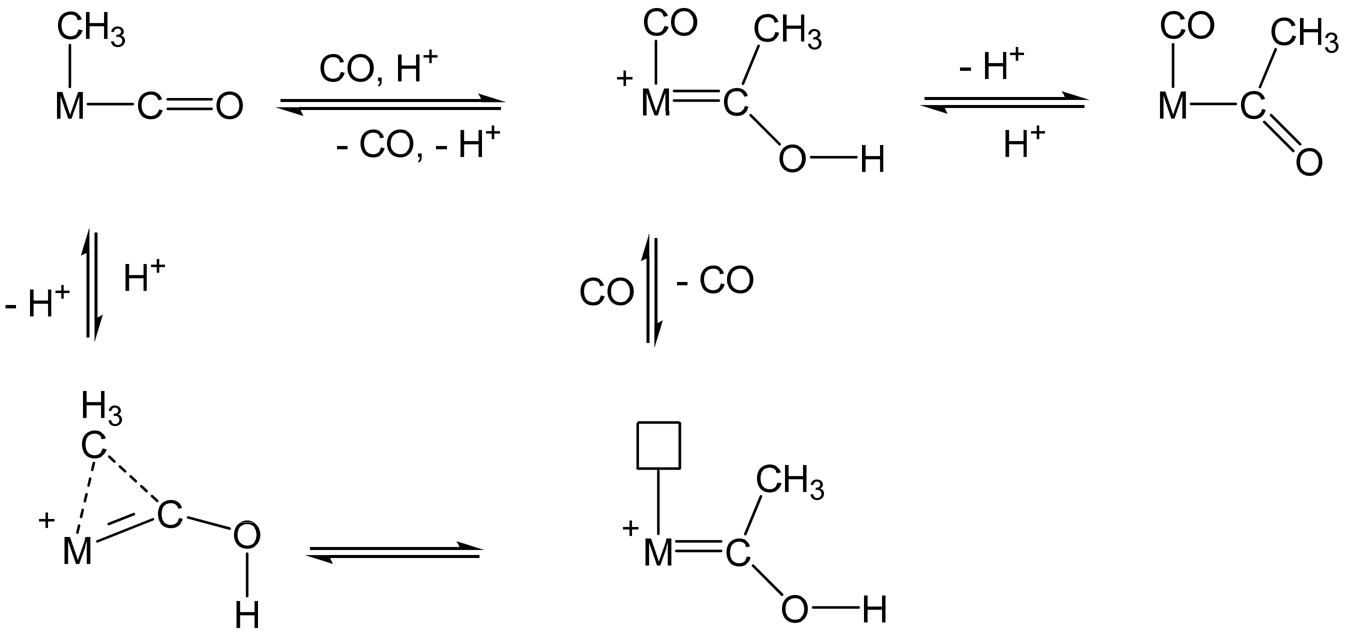
- We again use the IR spectrum to tell where the label has gone in the products.

Enhancing insertion rates

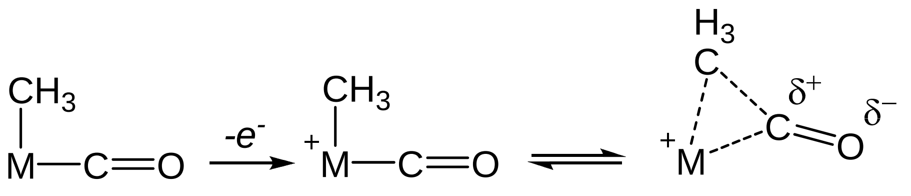
- ***Steric bulk in the ligand set accelerates insertion***, no doubt because the acetyl in the $L_nM(COMe)$ product, occupying one coordination site, is far less bulky than the alkyl and carbonyl, occupying two sites.
- ***Lewis acids*** such as $AlCl_3$, BF_3 or H^+ can increase the rate of migratory 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.

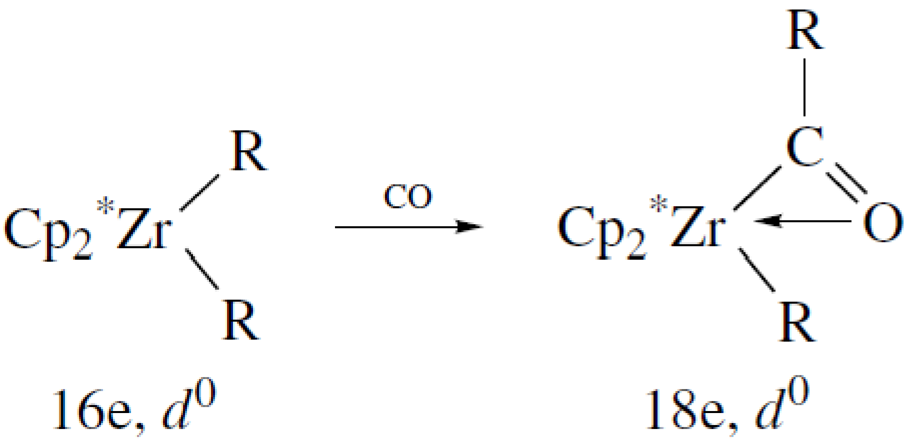


- Another important way of promoting the reaction is ***oxidation of the metal***.
- Increased electrophilicity (decreased π basicity) of the metal, leading to a larger partial positive charge on the CO carbon.
- The migration of H_3C^- to an electron deficient CO carbon seems to be a good description of the CO insertion, and so the rate of the reaction may increase in response to the increase in the δ^+ 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.



L = CO, PPh_3 , solvent etc.

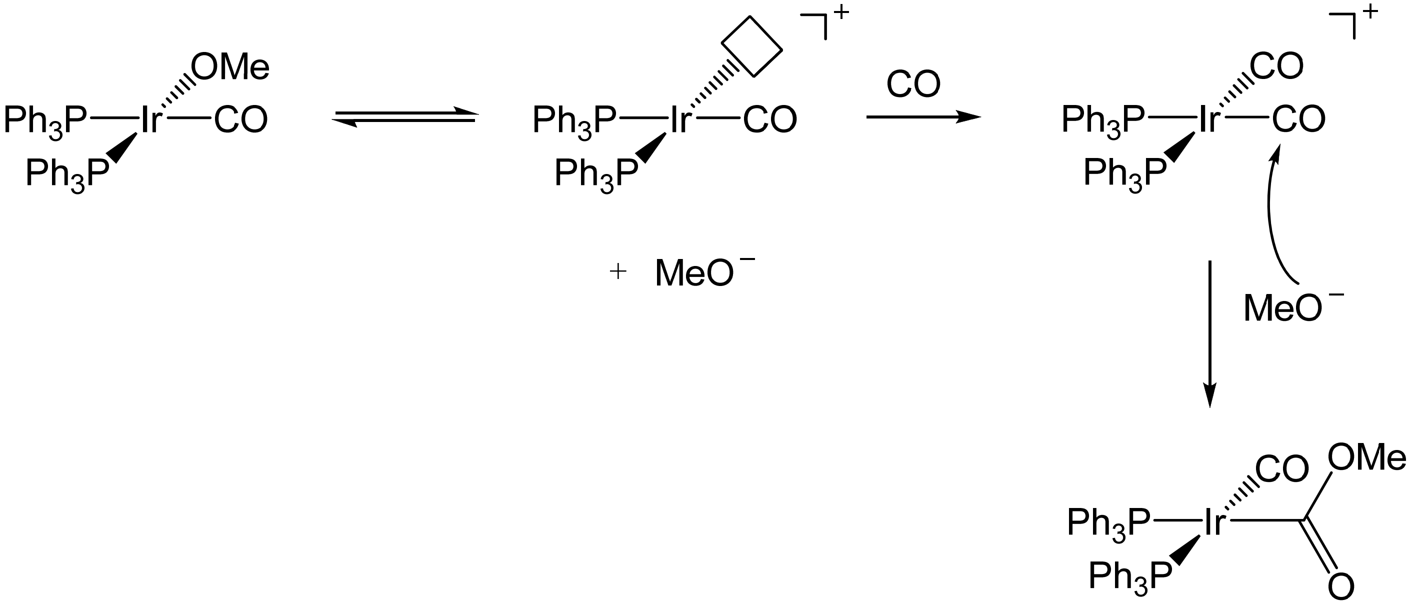
- ***Early metals are Lewis acids in their own right*** and tend to bind oxygen ligands. They can therefore act as their own Lewis acid catalysts for insertion.
- The product is an *η^2-acyl*



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

Apparent insertions

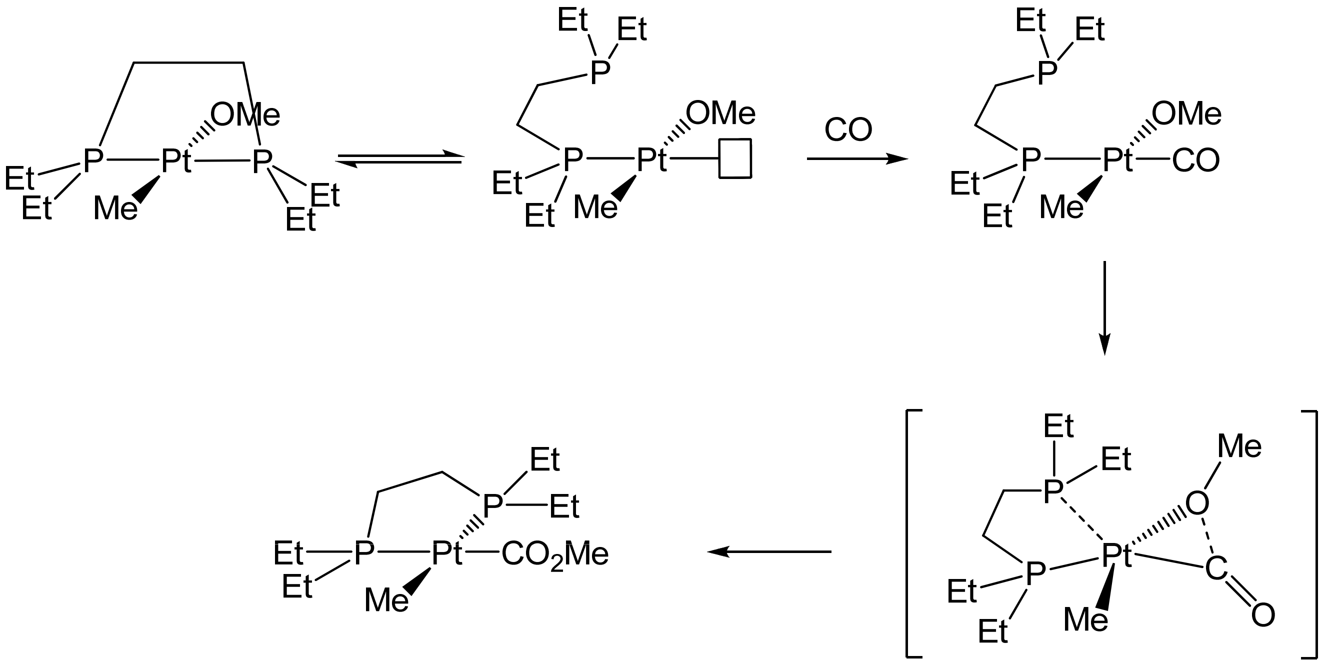
- These can in fact go by an entirely different route:

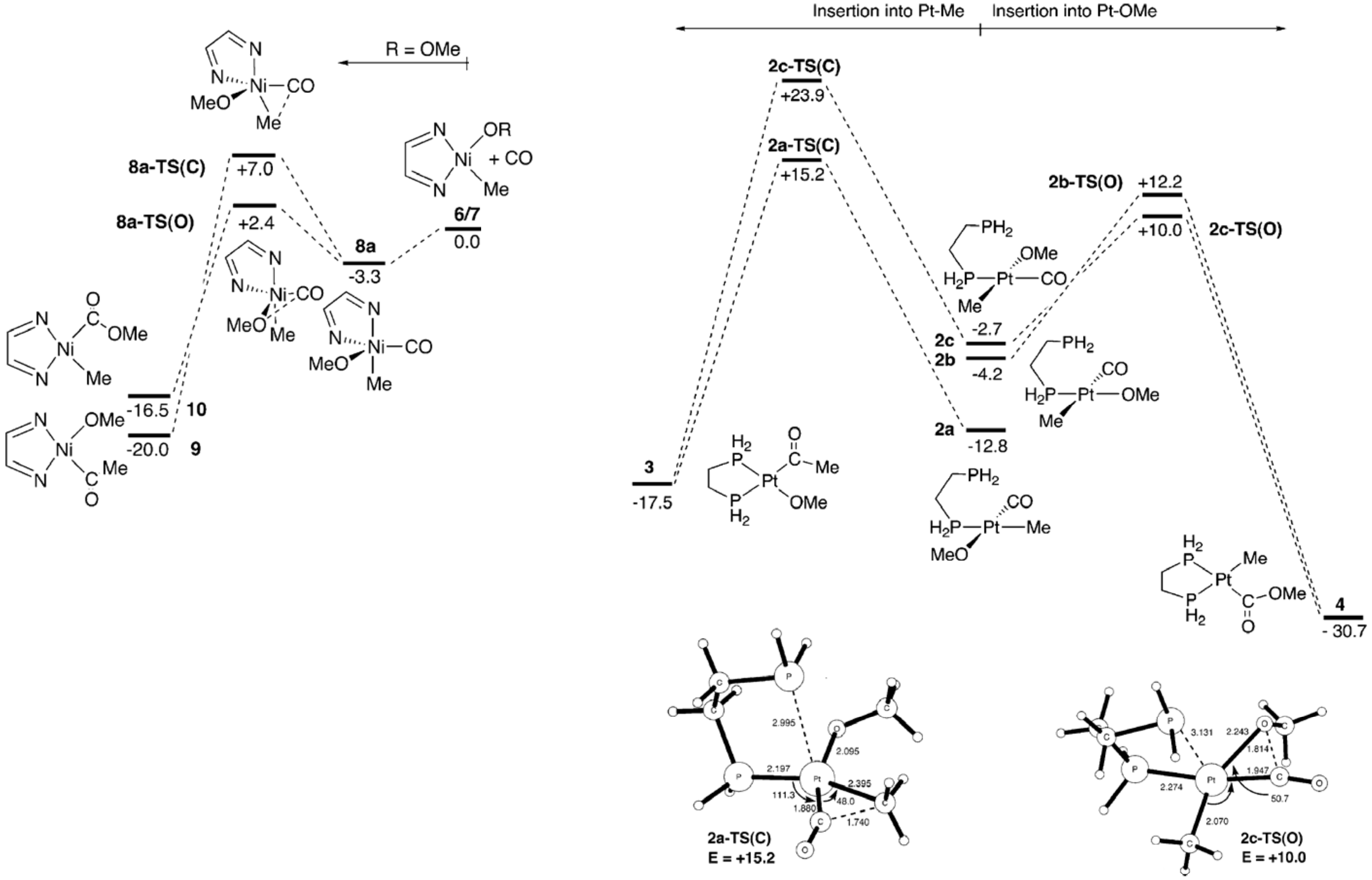


- The ***late metal alkoxide is unstable*** (since MeO$^-$ is a good π donor bound to a π donor metal) and the MeO$^-$ group dissociates to give an ion pair with a 2e vacancy at the metal.
- The free CO present then binds to this 2e site and is ***strongly activated toward nucleophilic attack at the 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_6H_4CN)(bipy)], CO inserts into Ni−Me. This follows from theoretical work.
- For Ni, the M−Me bond is significantly stronger than M−OMe, but migratory insertion with M−Me is marginally preferred owing to the weaker C−O bond of the aryloxycarbonyl.
- For Pt, M−Me and M−OMe bonds are equally strong, so the stronger methoxycarbonyl C−O bond results in reaction with the M−OMe bond.

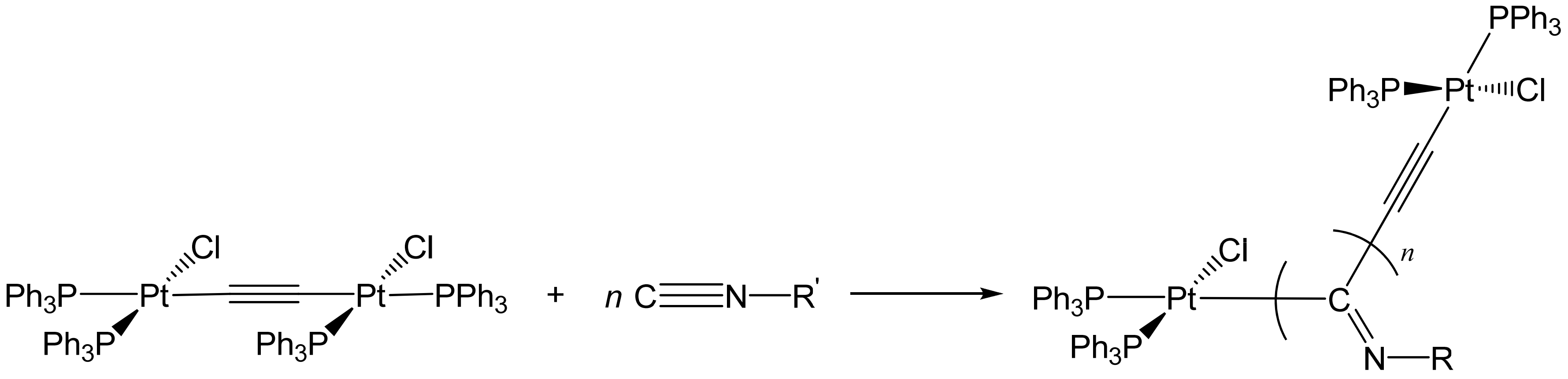




Computed reaction profiles (in kcal/mol) for the migratory insertion reaction CO. Energies are relative to the starting complex + free CO set to zero.

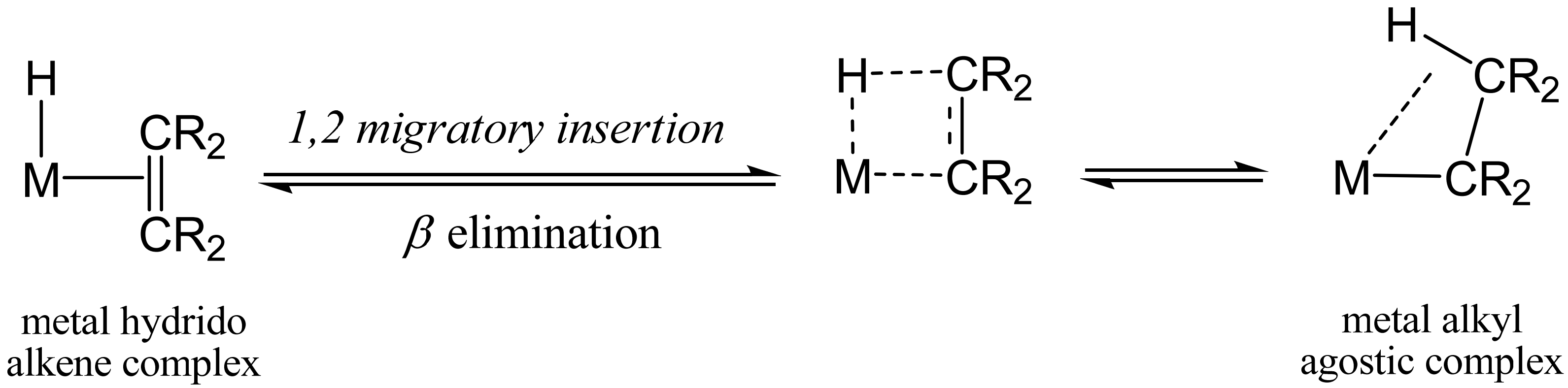
Double insertion

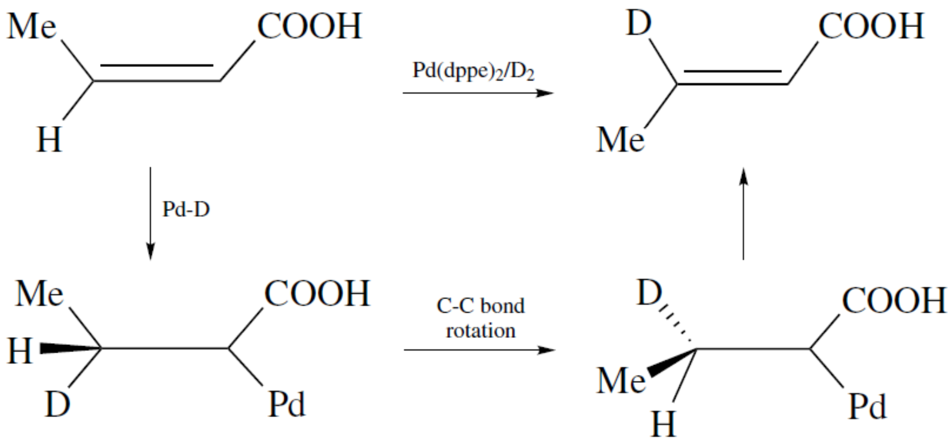
- Given that the methyl group migrates to the CO, why stop there? Why does the resulting acyl group not migrate to another CO to give an MeCOCO ligand?
- The complex that would have been formed in a double insertion can be made by an independent route from MeCOCOCl and $Mn(CO)_5^-$. ***It easily eliminates CO to give*** $\boldsymbol{MeCOMn(CO)_5}$***, which suggests that the double-insertion product is thermodynamically unstable*** with respect to $MeCOMn(CO)_5$.
- The −CHO and CF_3CO^- groups share with $MeCOCO^-$ the property of eliminating CO irreversibly to give hydride and trifluoromethyl complexes, respectively.
- ***The reason is again probably thermodynamic because the M−COMe, M−H, and M−***$\boldsymbol{CF_3}$ ***bonds are all distinctly stronger than M−***$\boldsymbol{CH_3}$***, the bond formed in CO elimination.***
- In contrast, isonitriles do undergo repeated migratory insertion to give polymers with as many as 100 isocyanide units inserted:



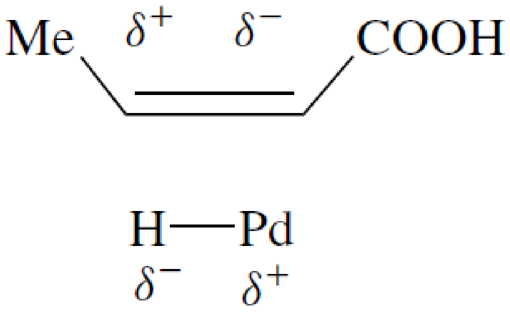
Alkene insertions reactions

- 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 *η^2-ligands, alkenes give 1,2* insertion. ***This is the reverse of the familiar β-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 β-eliminates), but for ***alkenes with electron-withdrawing ligands*** (e.g., C_2F_4), the alkyl is particularly stable, and the equilibrium lies entirely to the right;

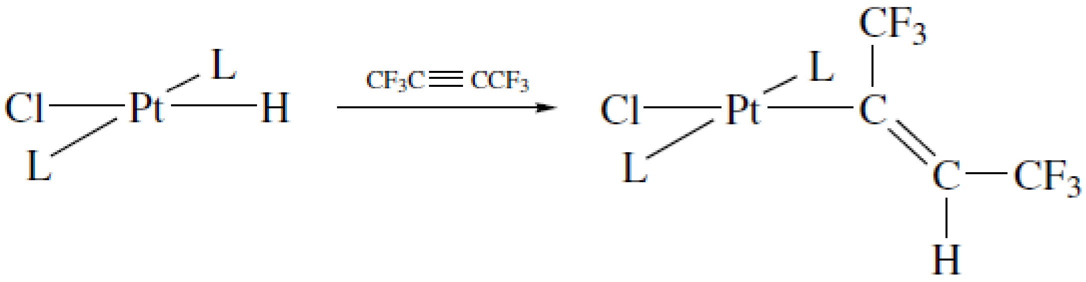




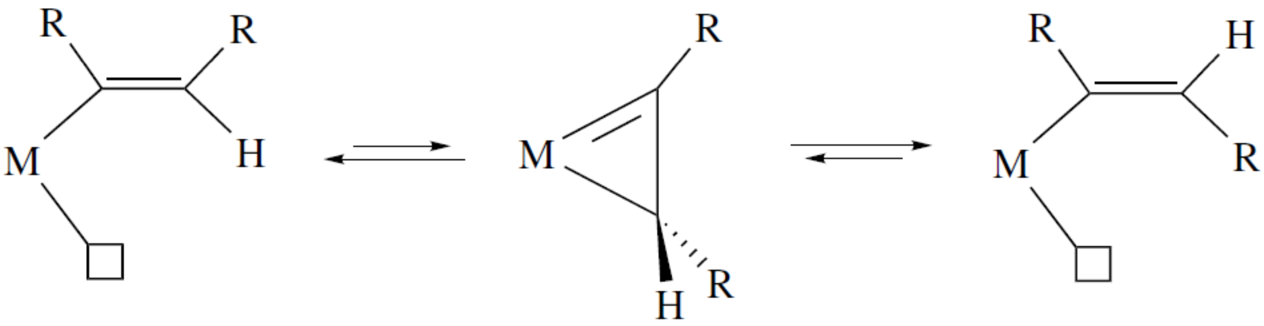
- Strategy that Spencer and co-workers have used to determine the mode of Pd−H addition to an unsymmetrical *cis* alkene.
- On isomerization to the *trans* form, the deuterium initially incorporated in the insertion step is retained by the substrate and labels the *β carbon of the product.*
- The mode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



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

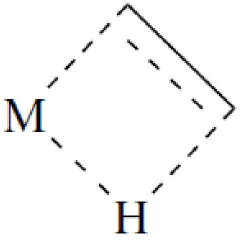


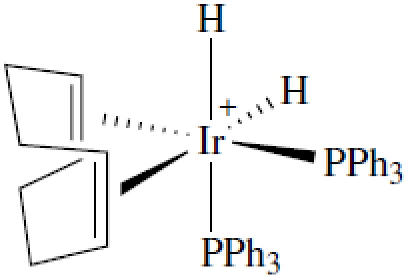
- But the initially formed *cis-vinyl complex, if 16e, can sometimes rearrange to the trans* isomer, via an *η*^{2}*-vinyl.*

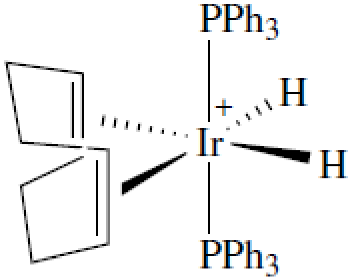


- *This can lead* to a net ***anti*** addition of a variety of groups to alkynes:

- 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)*.



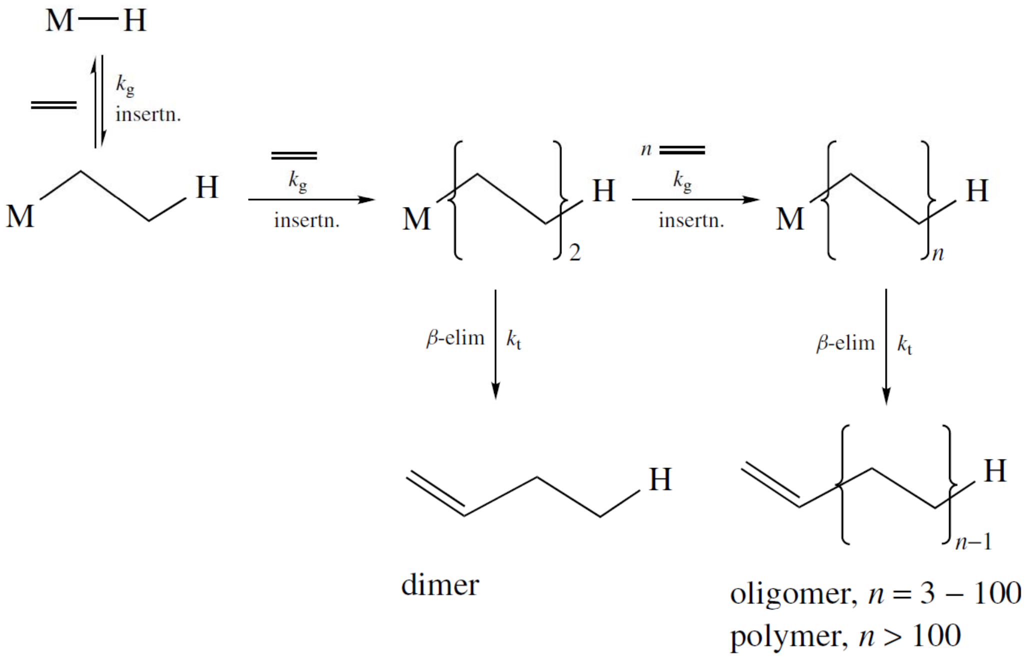




- We have seen how we can stabilize alkyls against *β elimination by having a non-coplanar* M−C−C−H system. The same principles apply to stabilizing alkene hydride complexes.
- The *cis*-phosphine complex above undergoes insertion at least 40 times more rapidly than the *trans*-phosphine isomer, although 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.

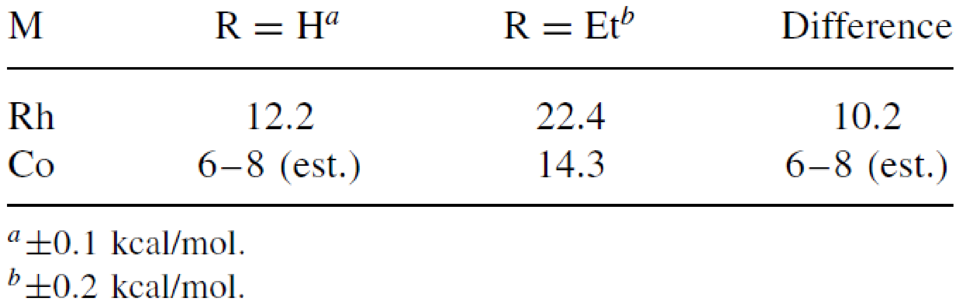
Insertion into M-H vs. M-R

- For thermodynamic reasons, CO insertion generally takes place into M−R but not into M−H bonds.
- ***Alkene insertion, in contrast, is common for M−H, but much less common for M−R.***
- Alkene polymerization is a reaction that involves repeated alkene insertion into an M−R bond.
- The thermodynamics still favor the reaction with M−H, so its comparative rarity must be due to kinetic factors.



Relative rates of insertion and *β elimination determine the value of n in* the products of di-, oligo-, and polymerization reactions in the Cossee mechanism. Slower *β elimination implies higher n.*

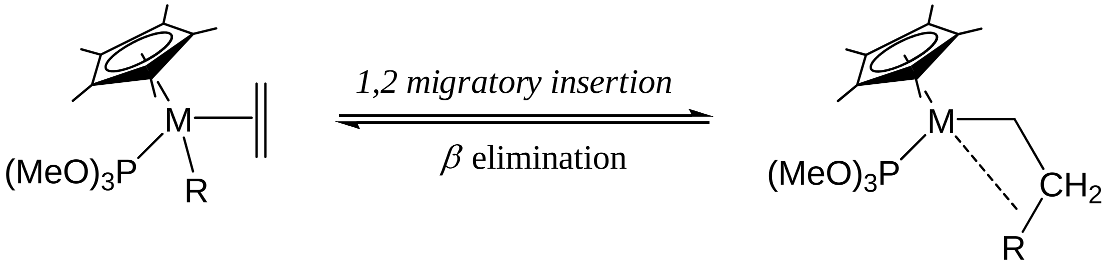
- Brookhart and co-workers have compared the barriers for insertion of ethylene into the M–R bond in $[Cp^*\{(MeO)_3P\}MR(C_2H_4)]^+$, where R is H or Et and M is Rh or Co.
- The reaction involving M–H has a 6–10-kcal/mol lower barrier. This corresponds to a migratory aptitude ratio k_H/k_{Et} of 106–108.



M	R = H[a]	R = Et[b]	Difference
Rh	12.2	22.4	10.2
Co	6–8 (est.)	14.3	6–8 (est.)

[a] ±0.1 kcal/mol.
[b] ±0.2 kcal/mol.

Comparison of Barriers (kcal/mol) for insertion in $[Cp^*\{(MeO)_3P\}MR(C_2H_4)]^+$ for R = H and R = Et



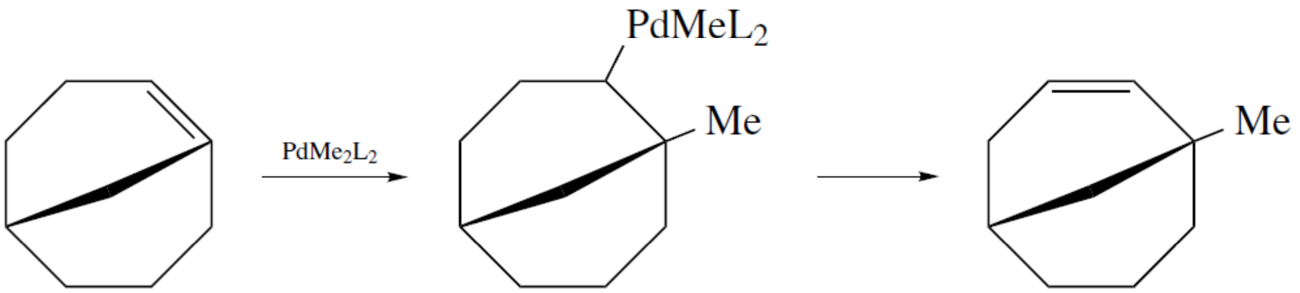
metal hydrido
alkene complex

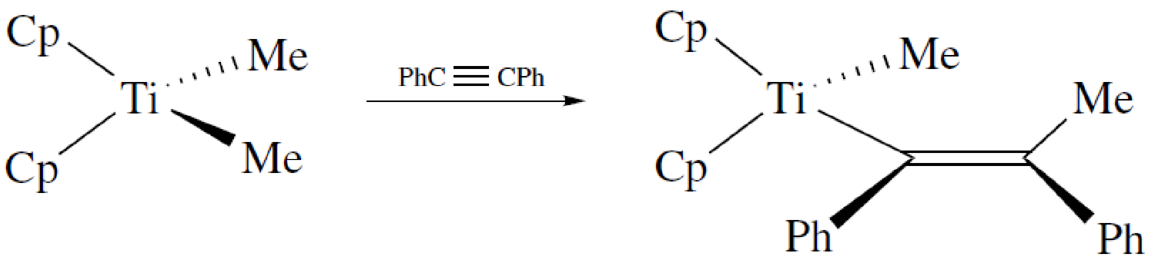
metal alkyl
agostic complex

R = H or Et

M = Rh or Co

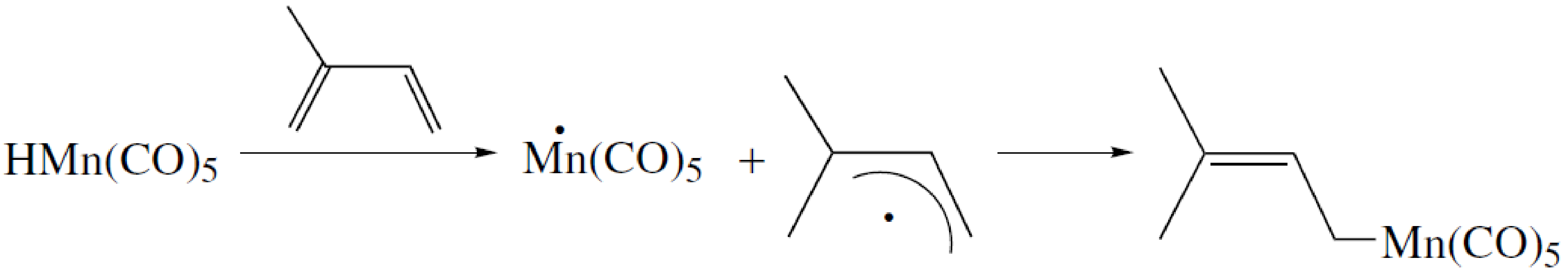
- Ring strain, or the presence of electronegative substituents on the alkene, or moving to an alkyne, are some of the other factors that can bias both the thermodynamics and the kinetics in favor of insertion.





Diene Insertion

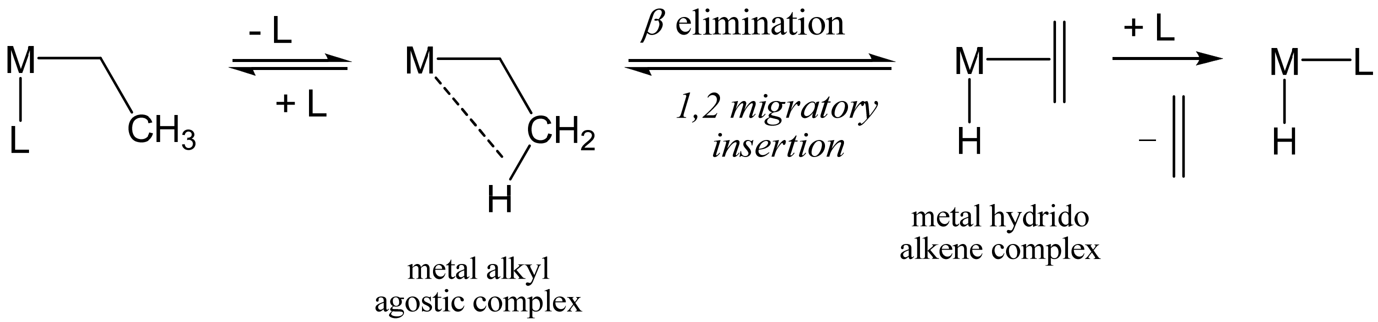
- Butadiene and allene react with a variety of hydrides by 1,2 insertion, but butadienes also react with $HMn(CO)_5$ to give ***an apparent 1,4 insertion***.
- Since this 18e hydride has no vacant site and CO dissociation is slow, an indirect mechanism must be operating.
- This is thought to be H atom 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 → allyl radical).
- Chemically induced dynamic nuclear polarization (CIDNP) effects can be seen in such cases.



α, β, γ, and σ elimination

β elimination

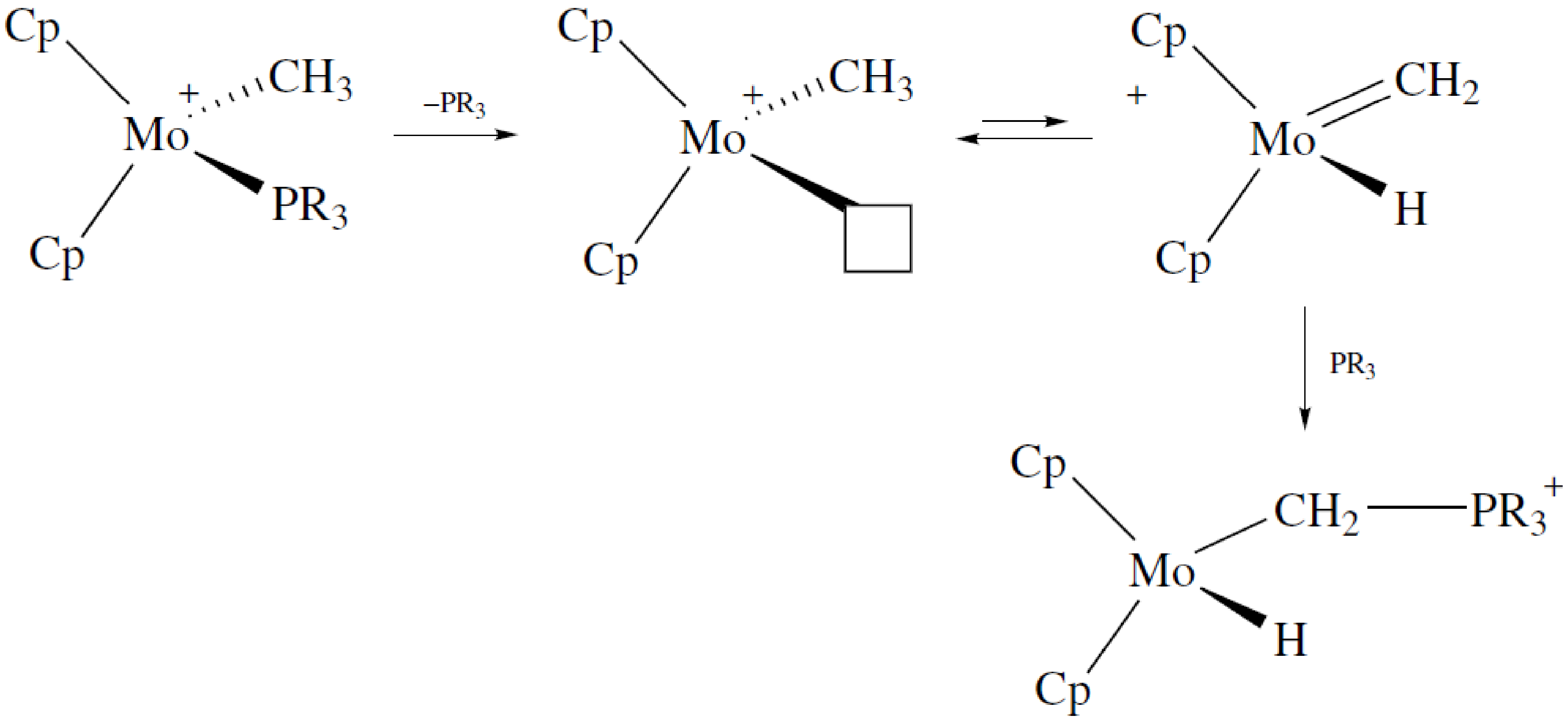
- *β elimination is the chief decomposition pathway for* alkyls that have *β-H substituents.*
- *A 2e vacant site is required at the metal, and* there has to be a roughly coplanar M−C−C−H arrangement that brings the *β-H* close to the metal.
- A complicating feature of this process is that the alkene may reinsert into the metal hydride, and this can give rise to isomerization of the alkene or of the starting alkyl.
- The alkene is rarely coordinated in the final products of a *β elimination,* however, because it is usually displaced by the ligand that originally dissociated to open up a 2e vacant site at the metal, or by some other ligand in the reaction mixture.



- An 18e complex has to lose a ligand to open up a site for elimination. In each case the addition of excess ligand inhibits the reaction by quenching the open site.

α elimination

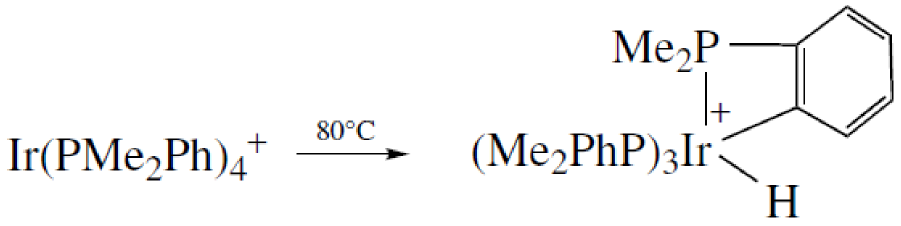
- If an alkyl has no β hydrogens, it may ***break a C–H bond in the α, γ, or δ position***.
- The simplest case is a methyl group, which has no β hydrogens and can undergo only α elimination to give the methylene hydride.
- While the β process gives an alkene, a stable species that can dissociate from the metal, the methylene ligand ($M{=}CH_2$) formed from the α elimination is very unstable in the free state and so does not dissociate.
- Methylene hydride complexes are unstable with respect to the starting methyl complex, and so the products of α elimination can be intermediates in a reaction but are seldom seen as isolable species.
- For this reason, the α-elimination process is less well characterized than β elimination.
- Studies of both molybdenum and tantalum alkyls suggest that α elimination can be up to 106 times faster than β elimination even in cases in which both α- and β-H substituents are present (Schrock carbene synthesis).
- In some cases, a coordinatively unsaturated methyl complex seems to be in equilibrium with a methylene hydride species, which can sometimes be trapped, either by nucleophilic attack at the carbene carbon or by removing the hydride by reductive elimination with a second alkyl present on the metal.

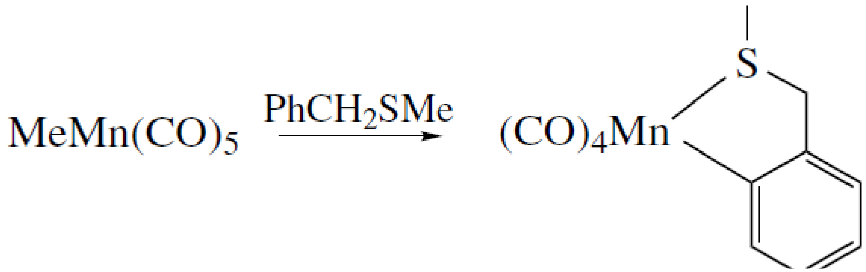


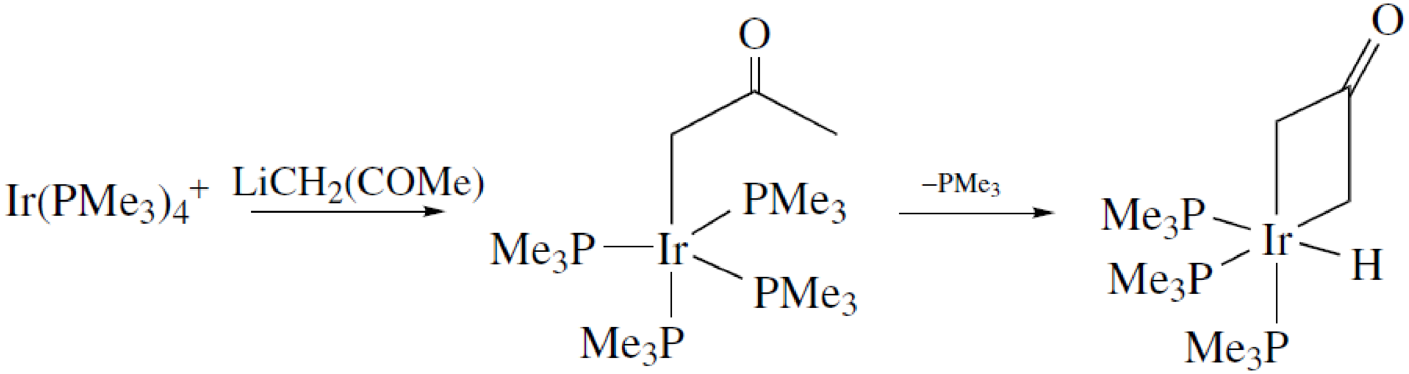
$$\mathrm{TaCl_2(CH_2Ph)_3} \xrightarrow{\mathrm{LiCp^*}} \mathrm{Cp^*TaCl(CH_2Ph)_3} \xrightarrow{-\mathrm{PhCH_3}} \mathrm{Cp^*Ta({=}CHPh)Cl(CH_2Ph)}$$

Other Eliminations

- In addition to alkyls, a great variety of other ligands have no β-H but do have γ- or δ-H's and can undergo γ or δ elimination to give cyclic products.







- All these elimination reactions can be thought of as being related to oxidative additions of a C–H bond to the metal.
- This is seen more clearly for β elimination if we write the metalacyclopropane (X_2) form of the alkene hydride product, and for α elimination if we consider the X_2 form for the product carbene hydride.
- Both γ and δ elimination are more obvious examples of oxidative addition.