Organometallic Chemistry and Homogeneous Catalysis

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Lecture N8

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Types of reactions in the coordination sphere of TMC

3. Reductive elimination

$$X\text{-}ML_n\text{-}Y \rightarrow ML_n + X\text{-}Y$$

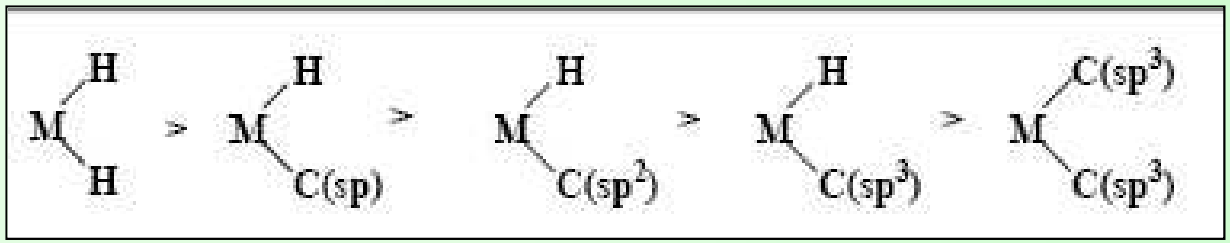
In the process of reductive elimination:

1) TM reduces its oxidation state by 2 points

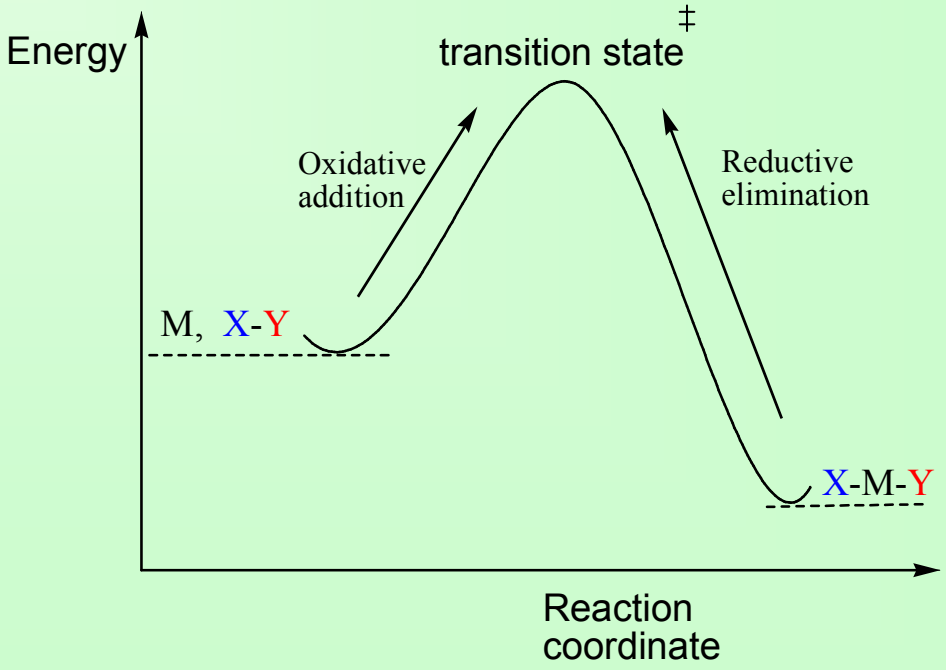
2) TM reduces coordination number by 2 points

Reductive elimination is a key transformation in transition metal mediated catalysis, often representing the product forming step in a catalytic cycle.

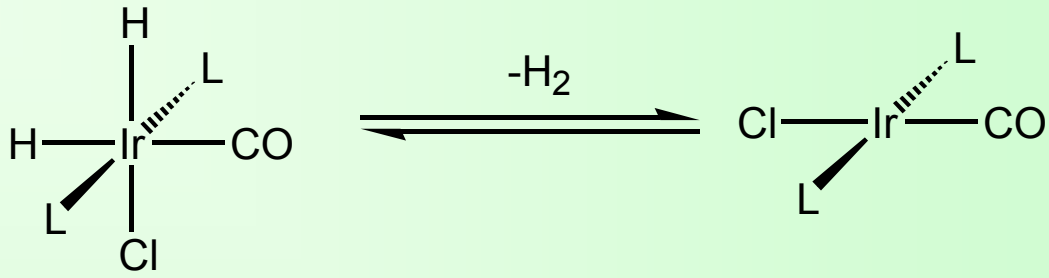
General trend for reductive elimination from d^8 square planar complexes:



Reductive elimination is a reverse reaction to oxidative addition. If two opposite reactions can take place at one and the same reaction conditions – they usually proceed through the same transition state (*microscopic reversibility* principle)



Features of Reductive Elimination



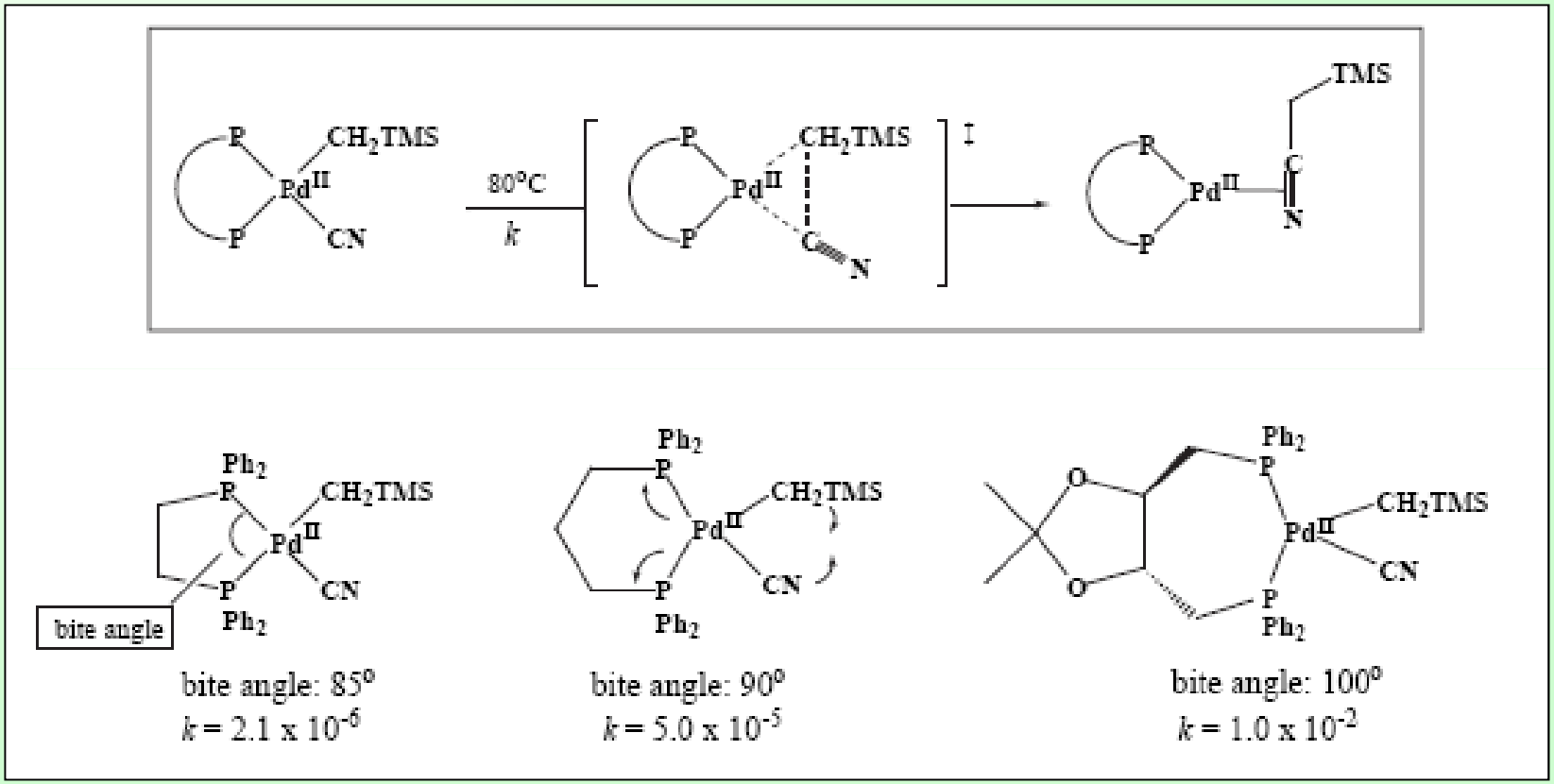
Reductive elimination is promoted by presence of:

- larger ligands L such as PPh_3 since (i) steric crowding is reduced on elimination and (ii) the product, which has a lower coordination number, is stabilized
- electron withdrawing ligands such as CO since these stabilize the low oxidation state (in the case of CO this is particularly effective because of π-backbonding).

Similarly, if you want to design a complex that will not undergo oxidative addition readily, use big and/or electron withdrawing ligands

RE can be promoted by:

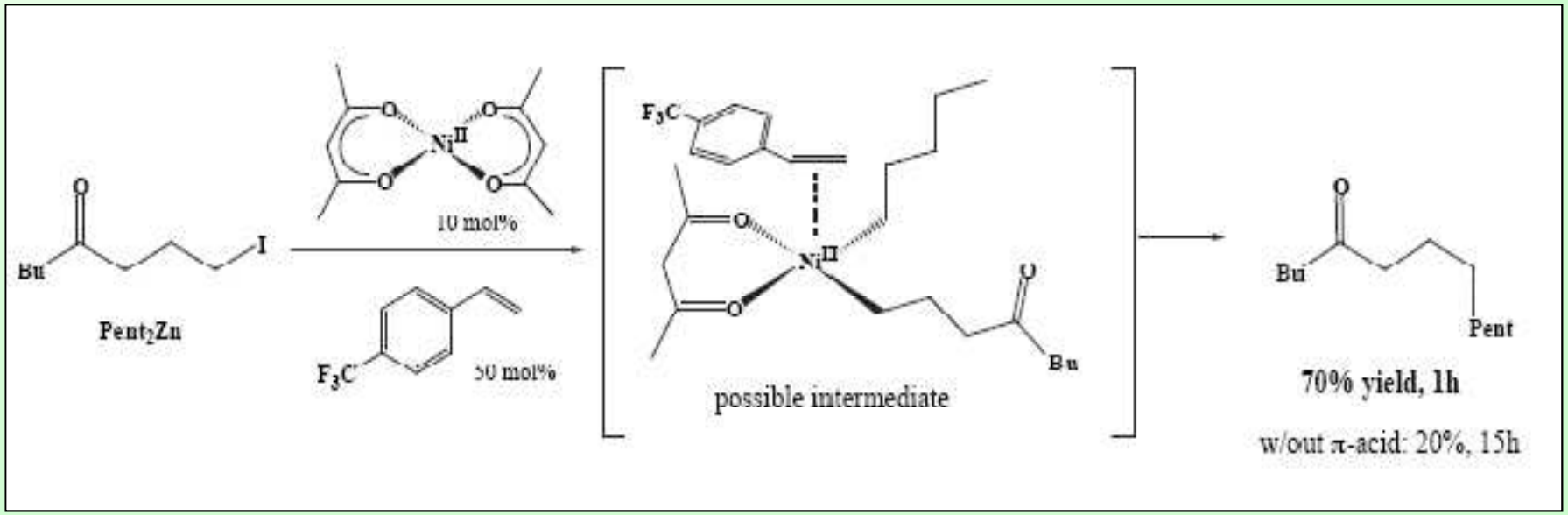
- **Increasing the bite angle of the ligand**
- Increasing electrophilicity of metal center (*e.g.* π-acids)
- *cis*-orientation of ligands (for concerted RE) is required



Large bite angles of diphosphines have been shown to enhance the rates of reductive elimination from square planar complexes presumably by bringing the two departing ligands closer together.

RE can be promoted by:

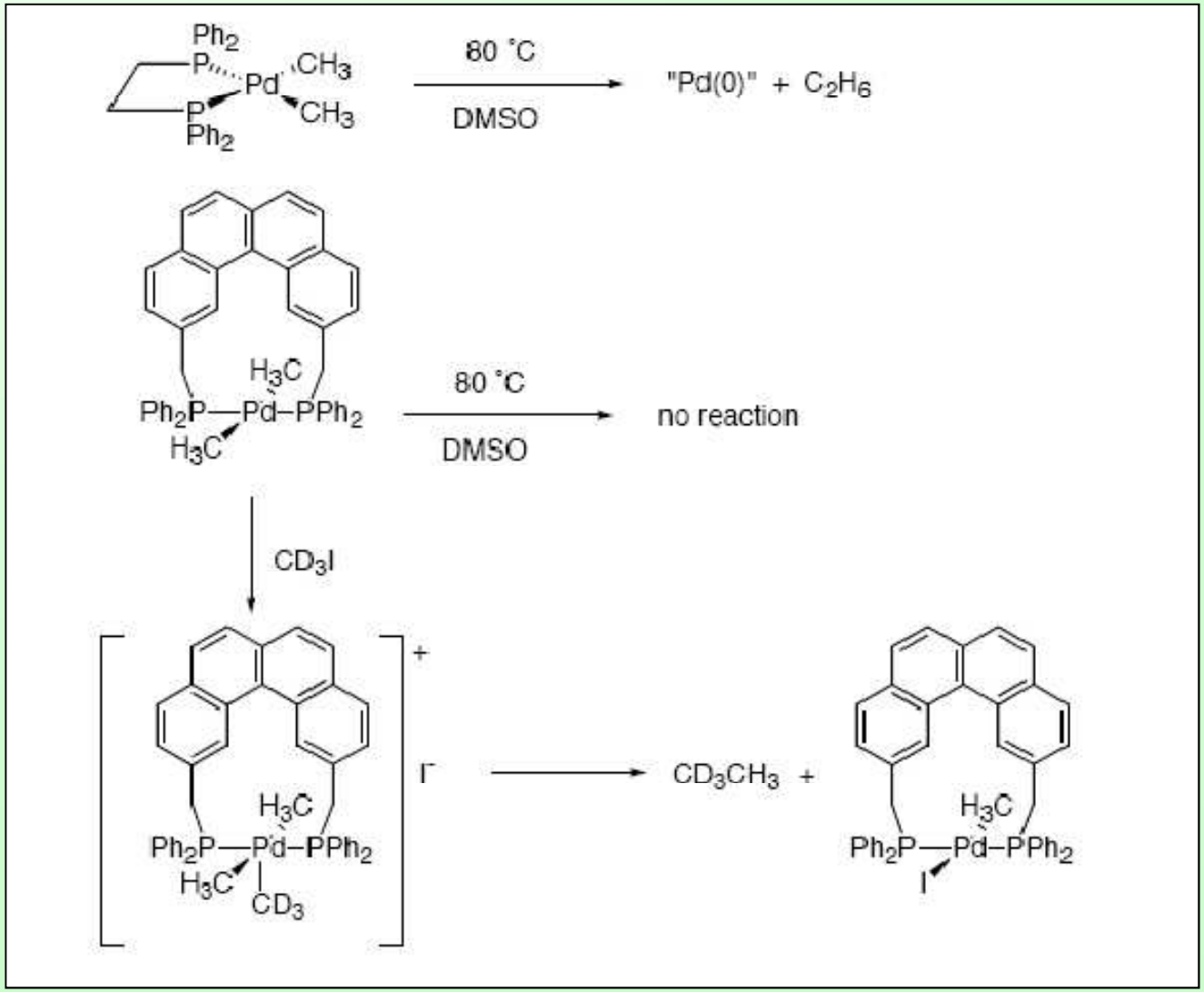
- Increasing the bite angle of the ligand
- **Increasing electrophilicity of metal center (*e.g.* π-acids)**
- *cis*-orientation of ligands (for concerted RE) is required



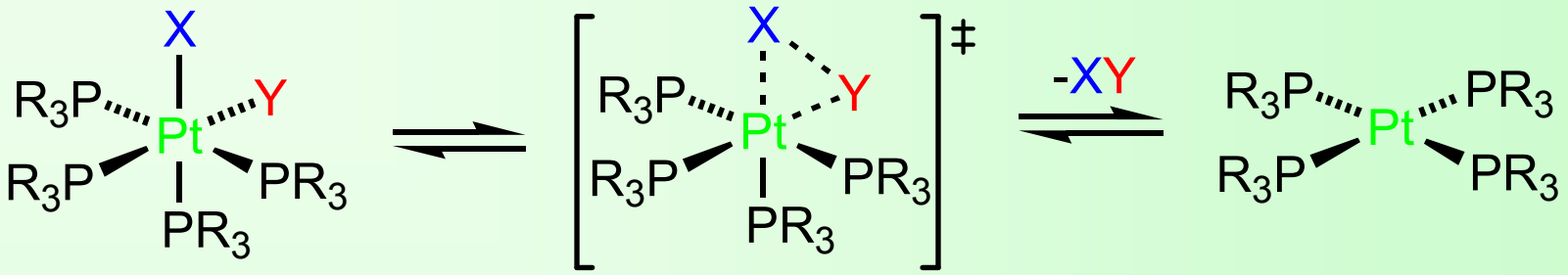
Coordination of π-acidic ligand CF_3-C_6H_4-$CH{=}CH_2$ to the Ni-catalyst increases the rate of reductive elimination and the yield of the coupling product.

RE can be promoted by:

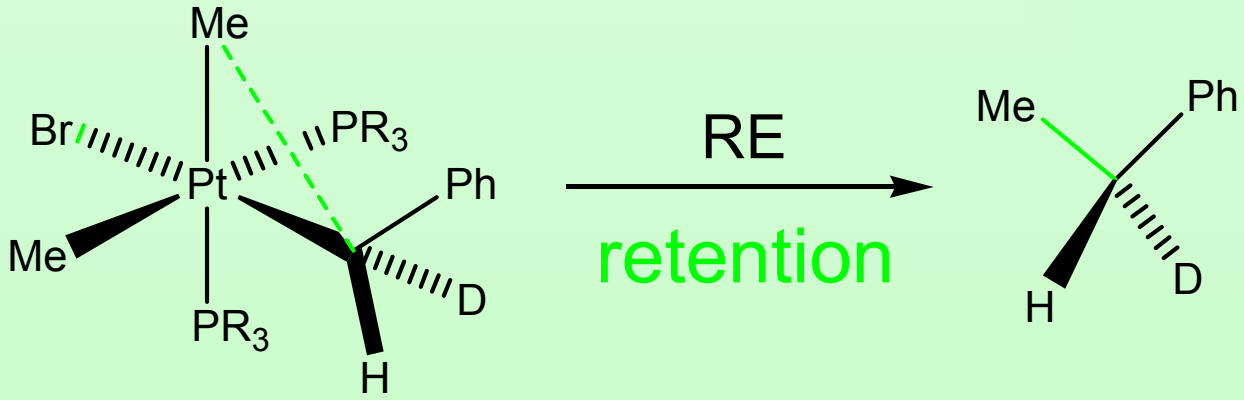
- Increasing the bite angle of the ligand
- Increasing electrophilicity of metal center (*e.g.* π-acids)
- ***cis*-orientation of ligands (for concerted RE) is required**



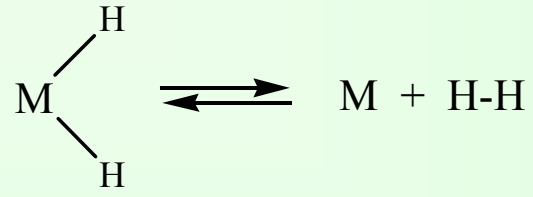
Cis-elimination

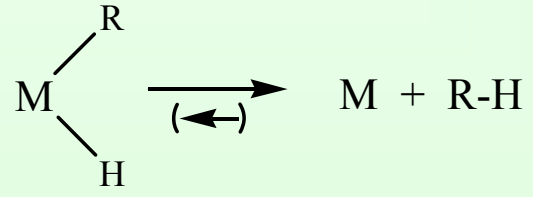


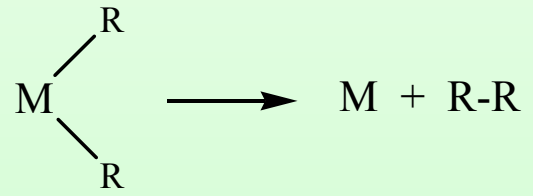
- Most eliminations occur by this 3-centre process
- Reverse of 3-centre OA
- The two X-type ligands must be *cis*



Some examples of reductive elimination:

a) 

b) 

c) 

M-H bond strength: 50-60 kcal/mole

M-C(sp^3) bond strength: 30-40 kcal/mole

H-H bond strength: 104 kcal/mole

C(sp^3)-H bond strength: 95 kcal/mole

C(sp^3)-C(sp^3) bond strength: 83 kcal/mole

Thermodynamics:

a) 2 bonds breaking: 50+50, 1 bond forming: 104, so ~ 4 kcal of profit

b) 2 bonds breaking: 50+30, 1 bond forming: 95, so ~ 15 kcal of profit

c) 2 bonds breaking: 30+30, 1 bond forming: 83, so ~ 23 kcal of profit

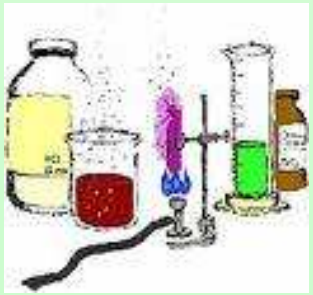
a) → b) → c) – thermodynamic favorability increases

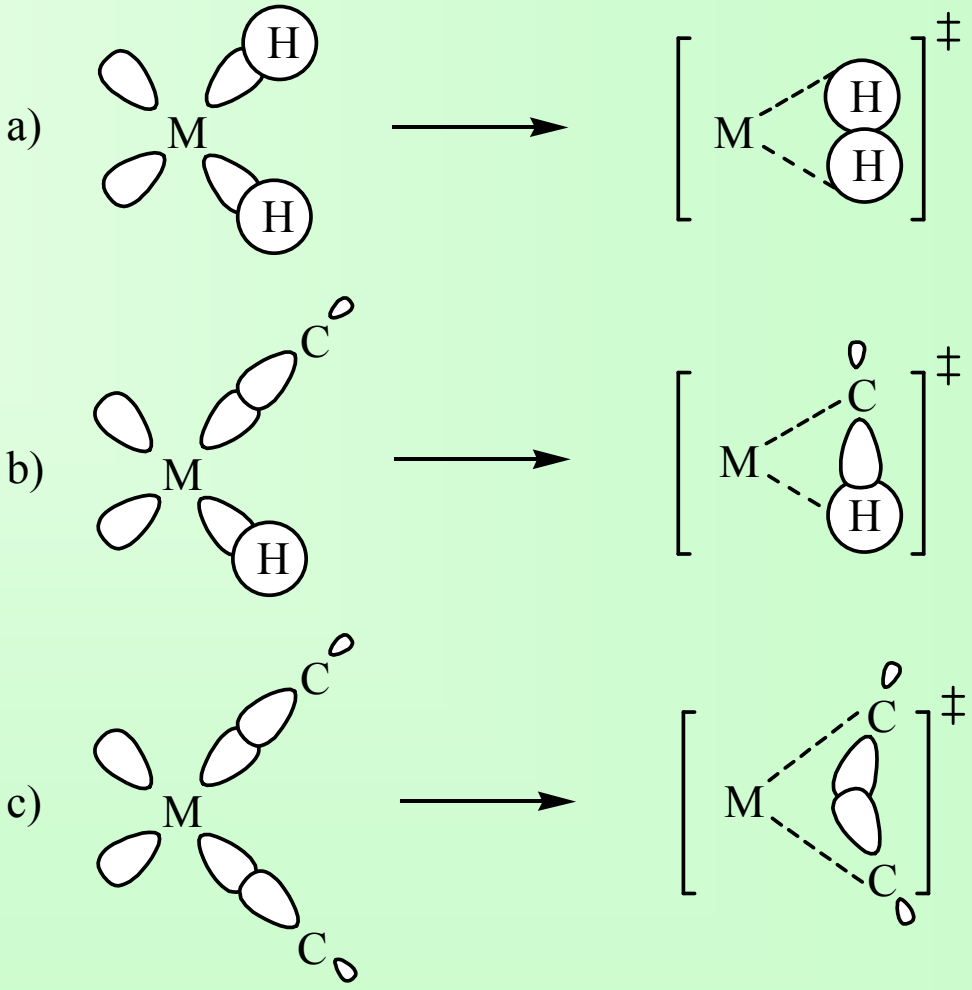
Kinetics:

a) → b) → c) – reaction rate decreases

Why the a) process is thermo-dynamically most unfavorable but it has the most high reaction rate?

To answer we should compare transition states of the process:

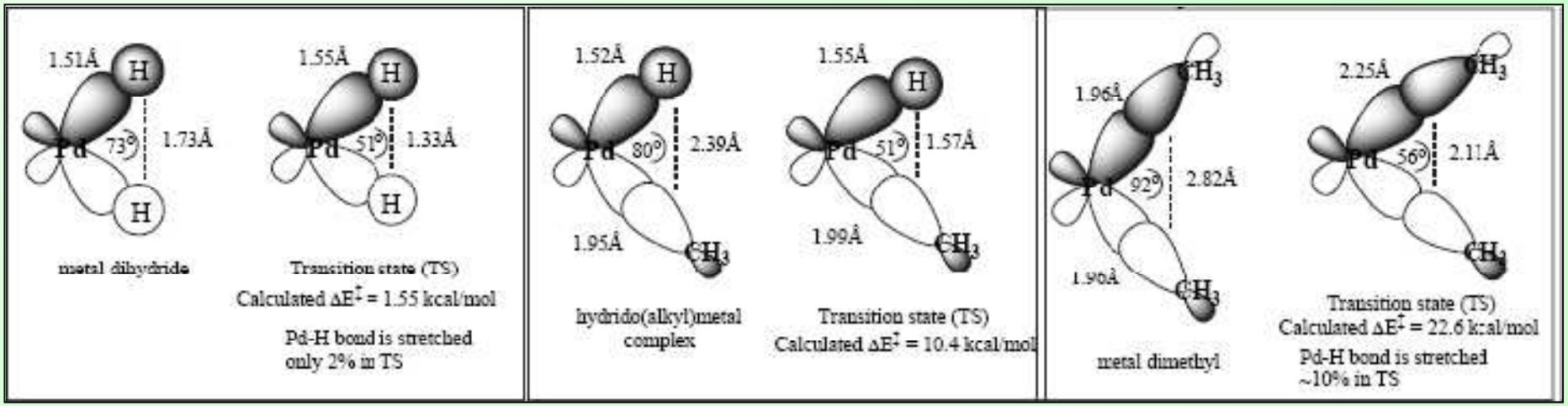




Computational studies (**Goddard** *JACS* **1984, Dedieu** *Chem. Rev.* **2000**): the spherical symmetry of the s orbitals of H allows the simultaneous breaking of the M-L σ-bonds while making the new σ-bond of the product.

Best overlap

Worst overlap



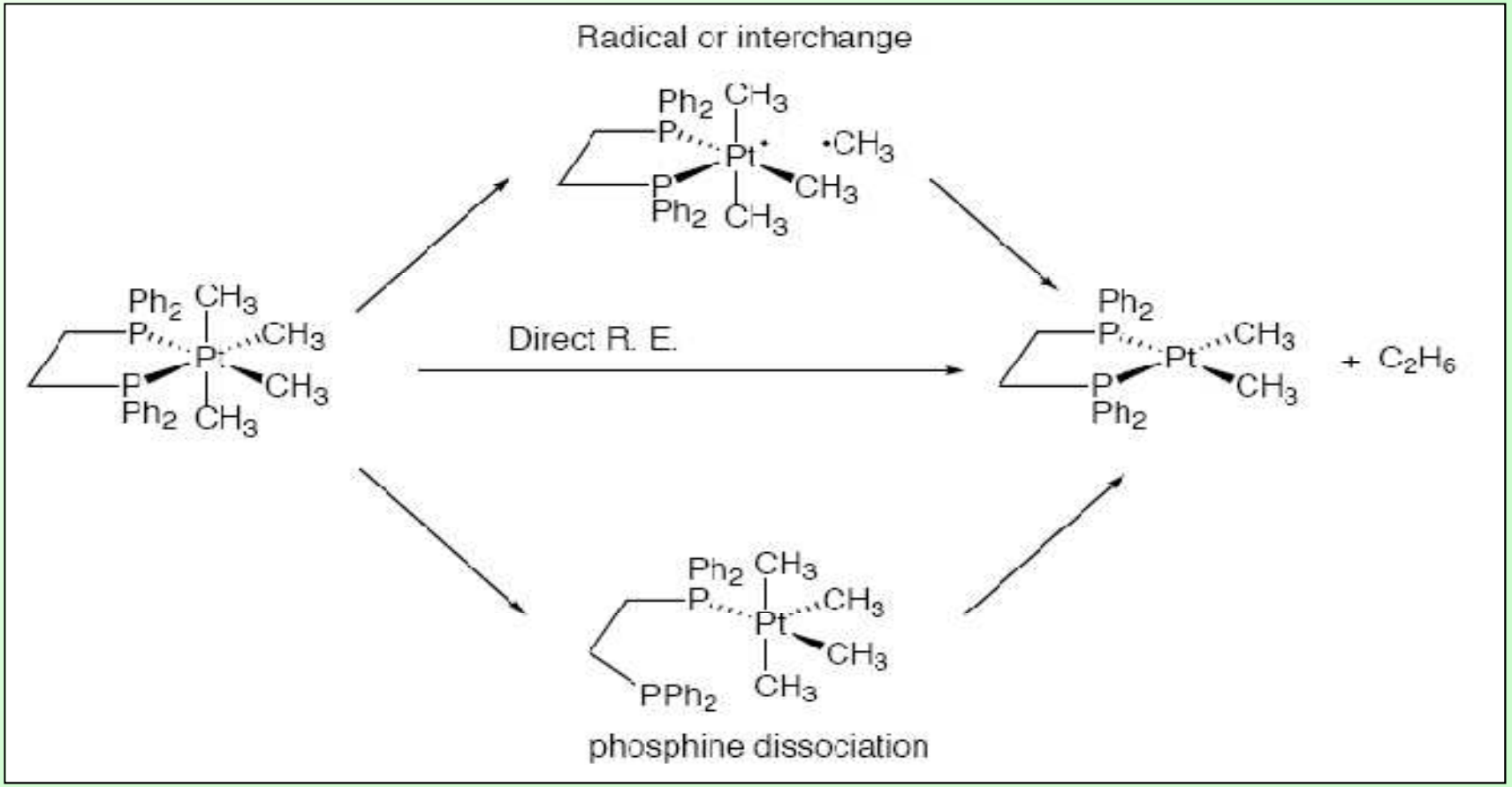
RE is usually easy for:

- H + alkyl / aryl / acyl
- alkyl + acyl
- SiR_3 + alkyl etc

RE is often slow for:

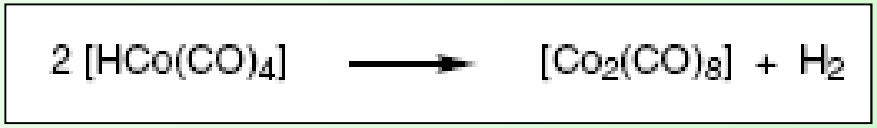
- alkoxide + alkyl
- halide + alkyl

Mechanistic possibilities of RE:

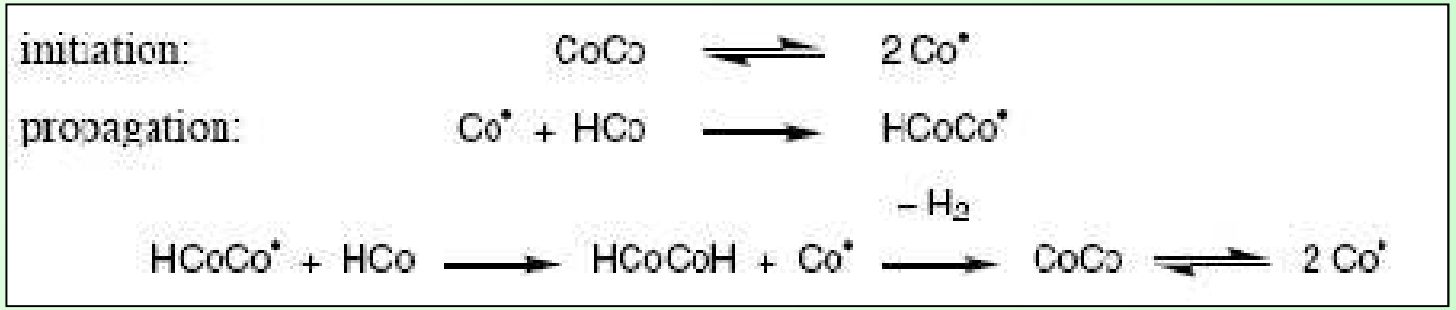


No cross-coupling products could be usually found in the corresponding experiments:

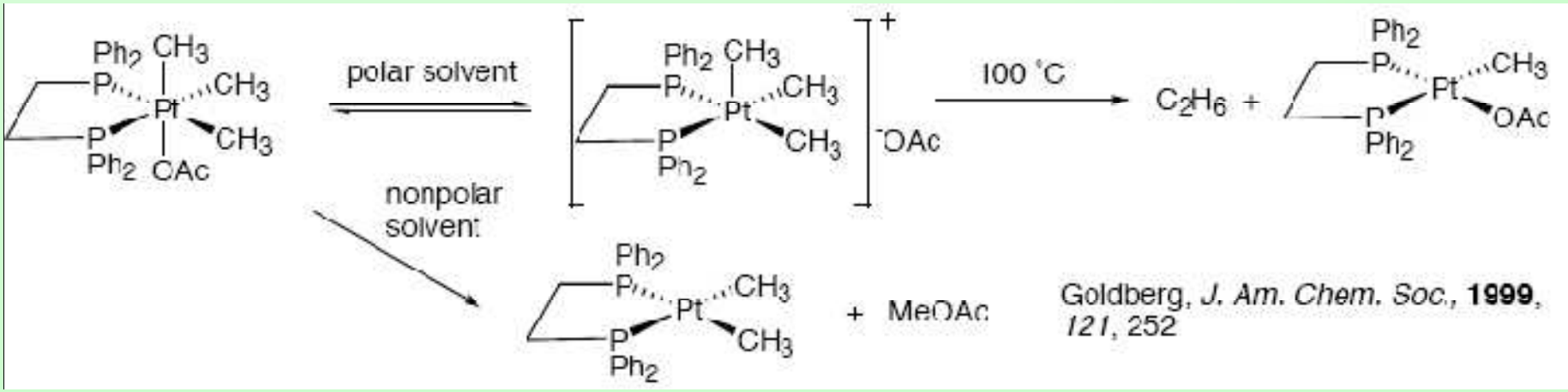
Radical mechanisms are also found in reductive elimination. An important example is the radical-chain mechanism of the dehydrogenation of cobalt carbonyl hydride:



Mechanistic scheme of the RE (carbonyls are omitted):

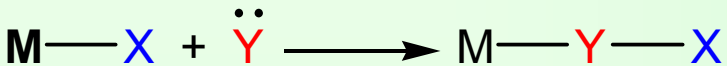


Interesting case of RE: solvent effect



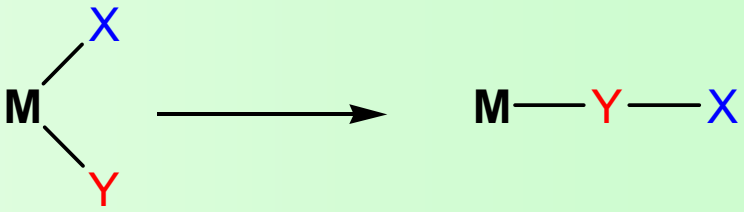
4. Insertion (Migratory insertion)

- Intermolecular insertion:



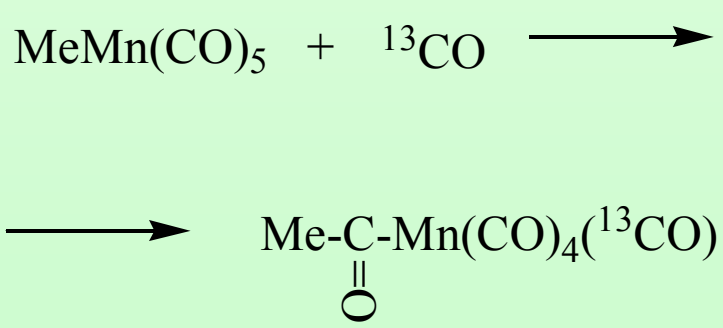
Nucleophile Y attacks X

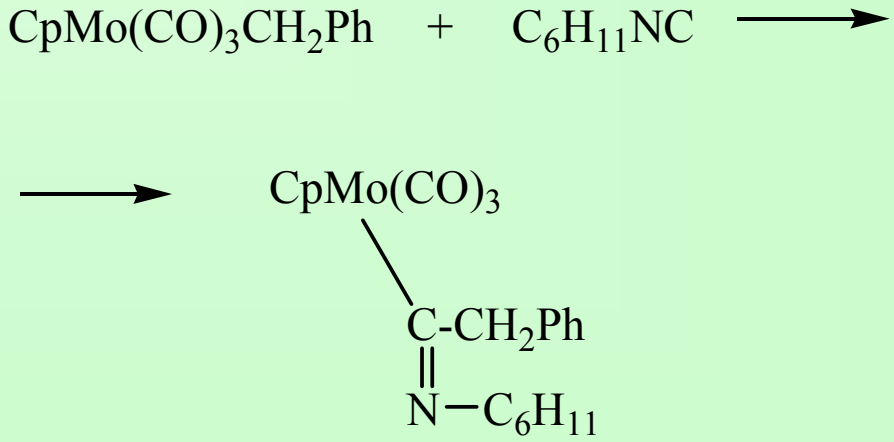
- Intramolecular insertion:

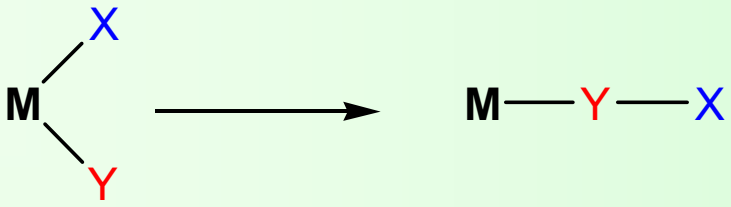


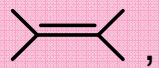
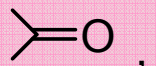
Unsaturated ligand Y insert into M-X

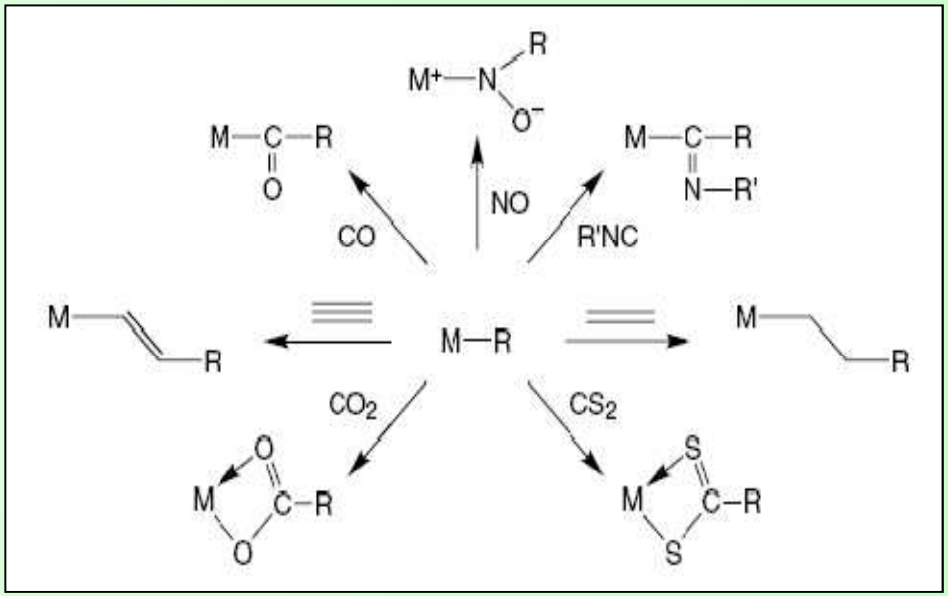
Examples:







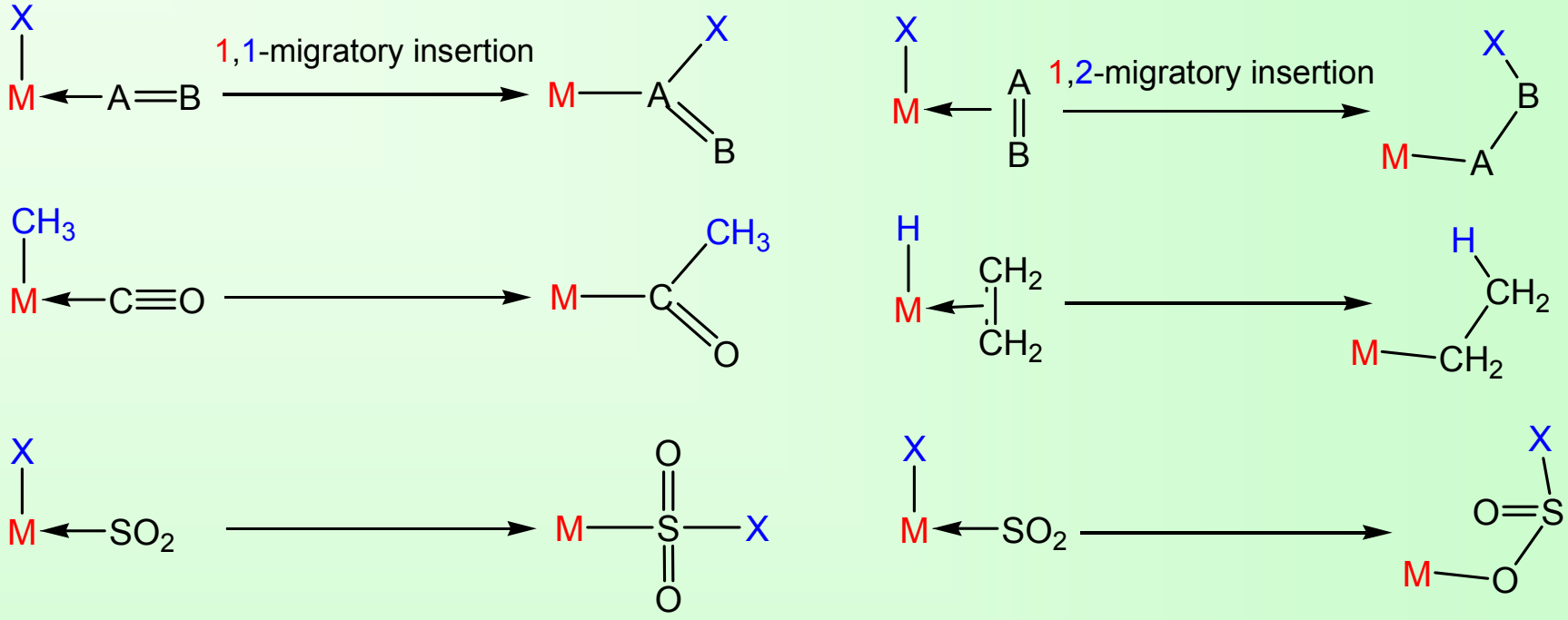
M—X	Y
M—H	 , C=C–C=C , C≡C
M—C	 ,  , –C≡N
M—Hlg	CO, CO_2, SO_2, CS_2
M—N	:CH_2 , 
M—O	CO, –C≡N



General Features:

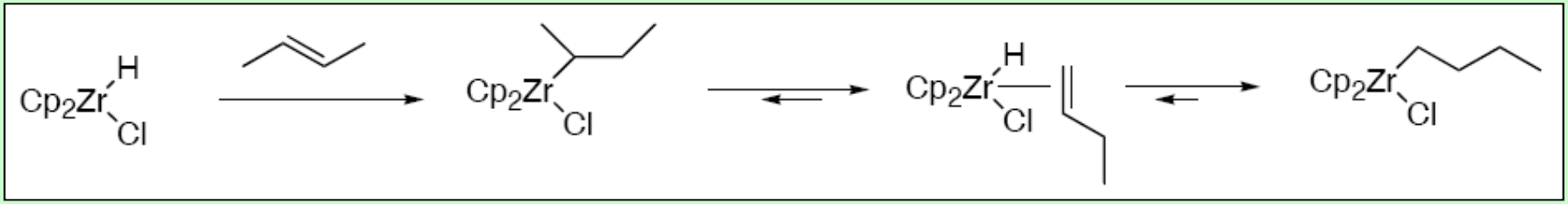
1) No change in formal oxidation state of the TM
2) The two groups that react must be *cisoidal* to one another
3) A vacant coordination site is generated by the migratory insertion.
4) Migratory insertions are usually favored on more electron-deficient metal centers.

Depending on the nature of the inserting group it is possible to recognize 2 types of intramolecular insertion:



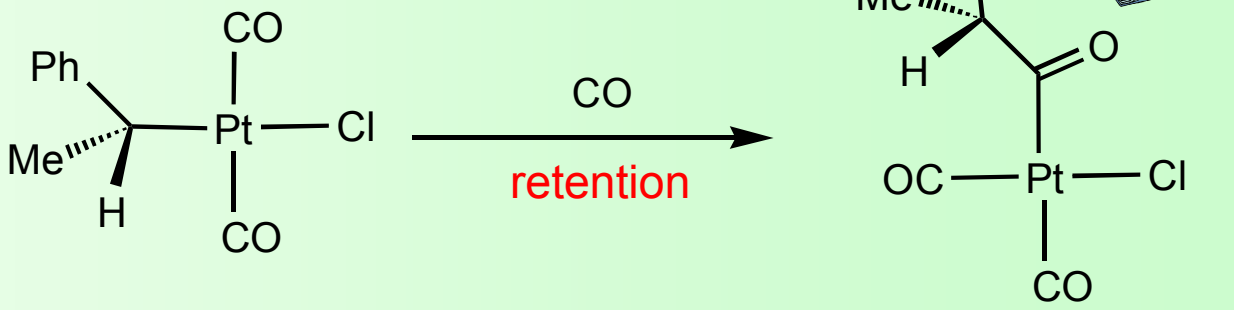
Regioselectivity of Insertion:

Typically steric factors will result in a thermodynamic preference for the sterically less hindered carbon to be bonded to the metal center. Hydrozirconation of alkenes with the Schwartz reagent is a good example of this thermodynamic preference:

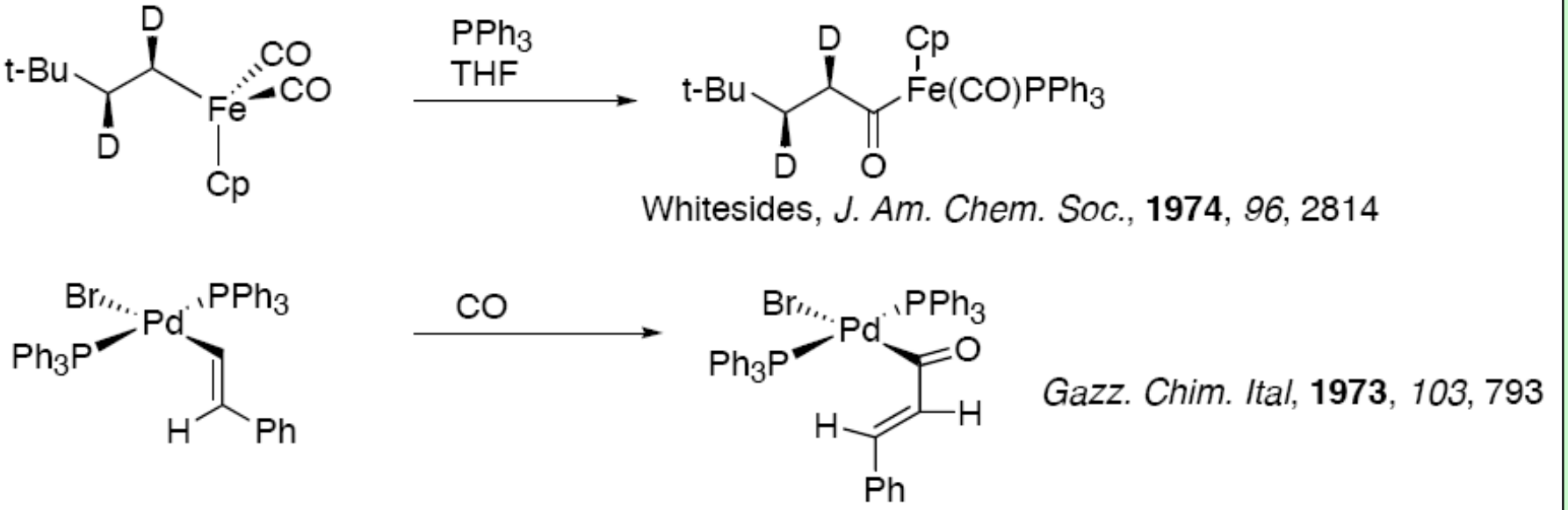


Stereochemistry:

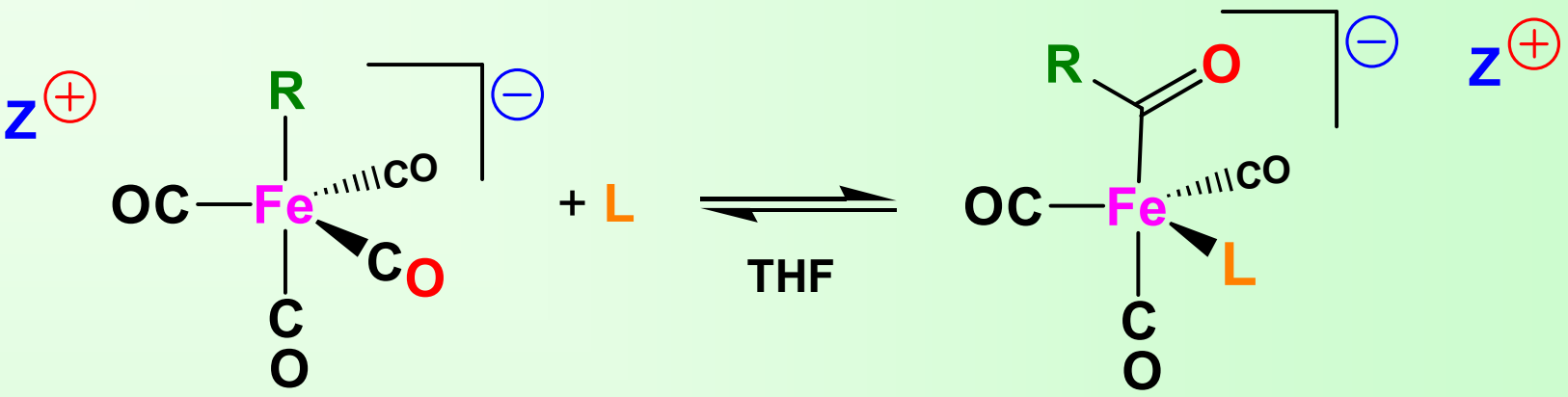
Retention of configuration



For concerted migratory insertion or elimination, carbon stereochemistry is nearly always retained:



Some Electronic effects



best Lewis acid - can coordinate to electron-rich CO ligands and drain off some e- density

$Z^+ = \mathbf{Li^+} > Na^+ > (Ph_3)_2N^+$

strongest coordinating ligand - best trapping ligand

$L = \mathbf{PMe_3} > PPhMe_2 > PPh_2Me > CO$

most electron-rich alkyl group makes the best nucleophile for migrating to the electron-deficient CO

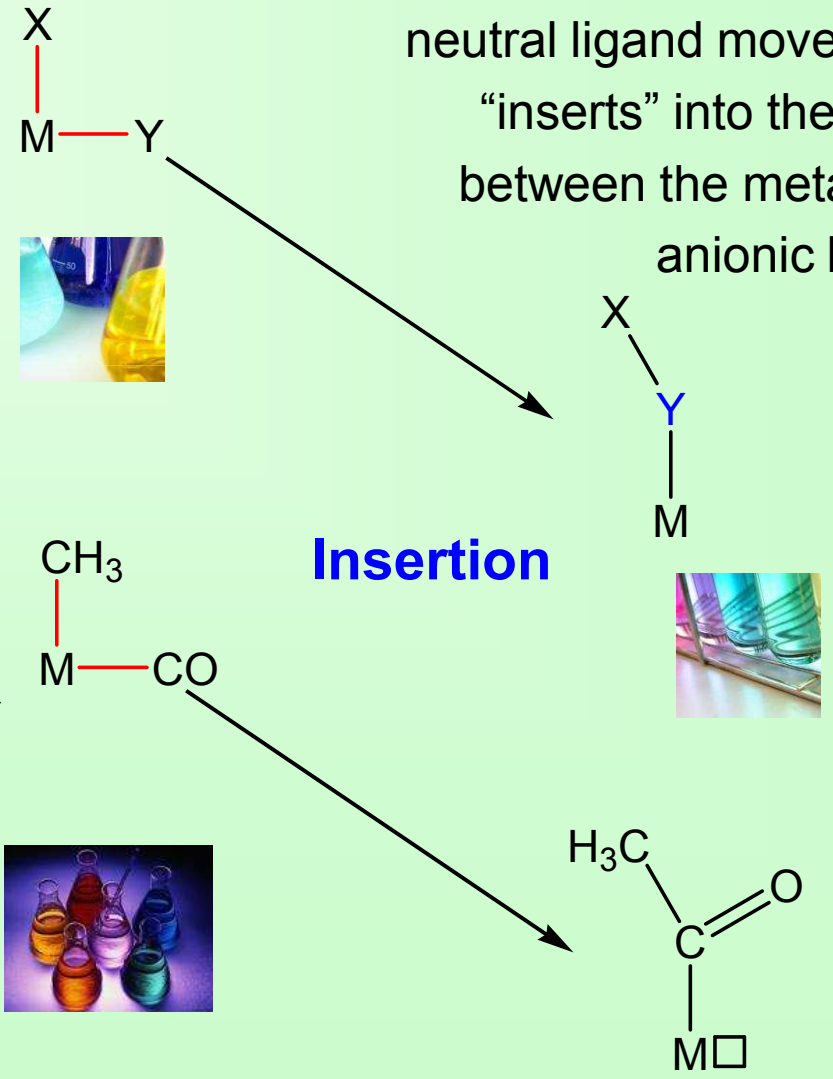
$R = \mathbf{n\text{-}alkyl^-} > PhCH_2^-$

Migration vs. Insertion

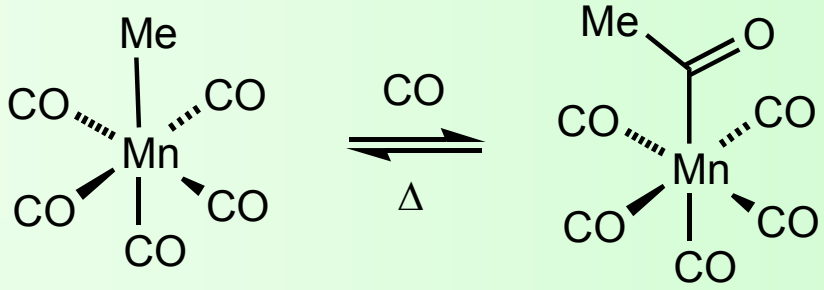
There are two different "directions" that a migratory insertion can occur:

A migration is when the anionic ligand moves and performs a nucleophillic-like intramolecular attack on the electrophillic neutral ligand

An insertion is when the neutral ligand moves and "inserts" into the bond between the metal and anionic ligand

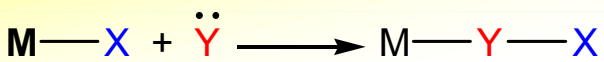


Let's have a look on the CO insertion into the Mn-CH_3 bond:



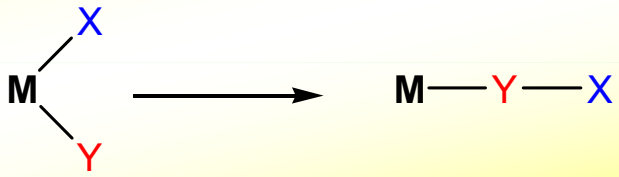
1. Question: What kind of insertion takes place – intermolecular or intramolecular?

- Intermolecular insertion:



Nucleophile Y attacks X

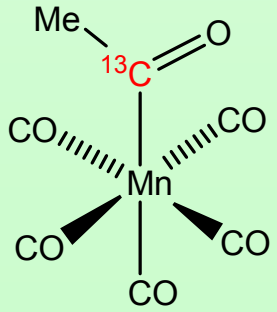
- Intramolecular insertion:



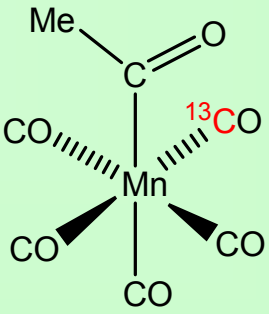
Unsaturated ligand Y insert into M-X

To answer this question ^{13}CO should be used:

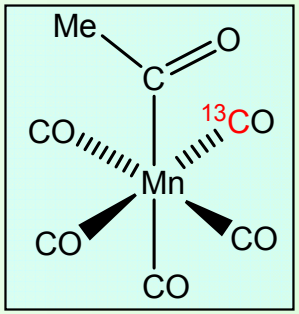
- In the case of inter-molecular insertion ^{13}C will go to acyl group



-In the case of intramolecular insertion unlabeled C appears in acyl group

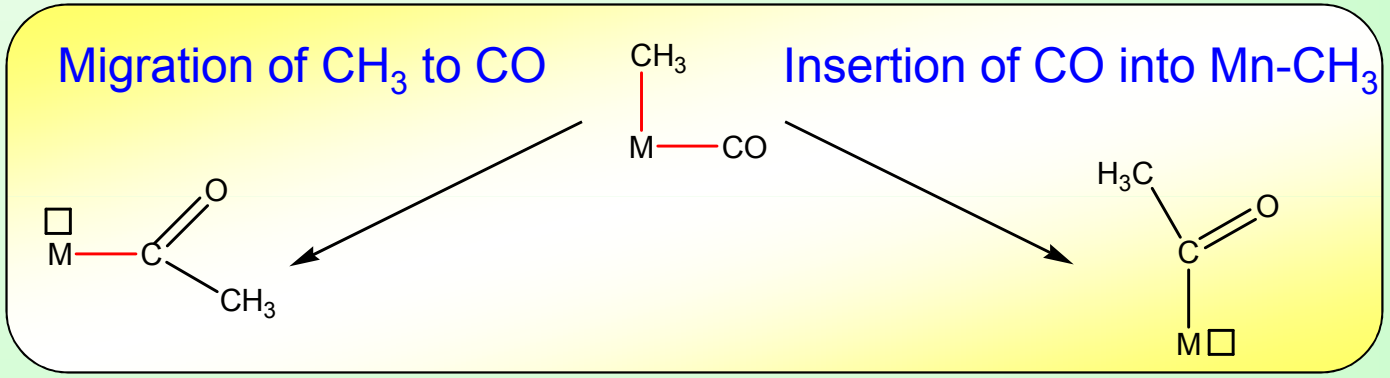


It was found that ^{13}C label exists only as a cabonyl ligand:

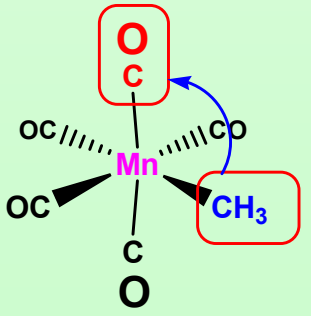


- Intermolecular insertion

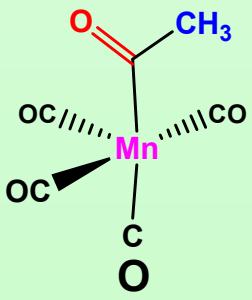
2. Question: How does insertion take place?



Migration

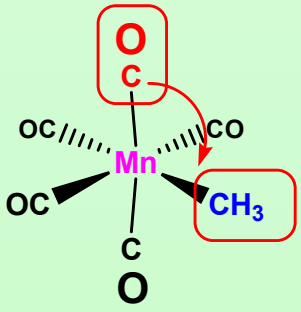


Mn(+1)
18e-

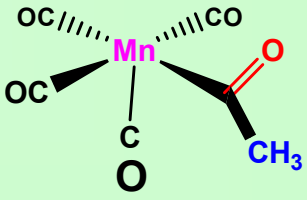


Mn(+1)
16e-

Insertion



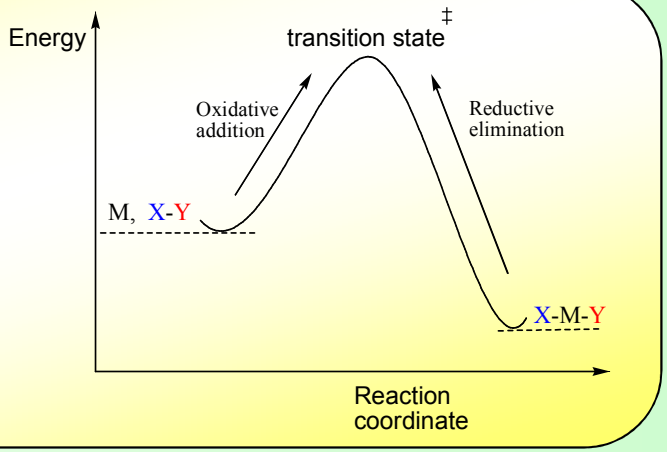
Mn(+1)
18e-



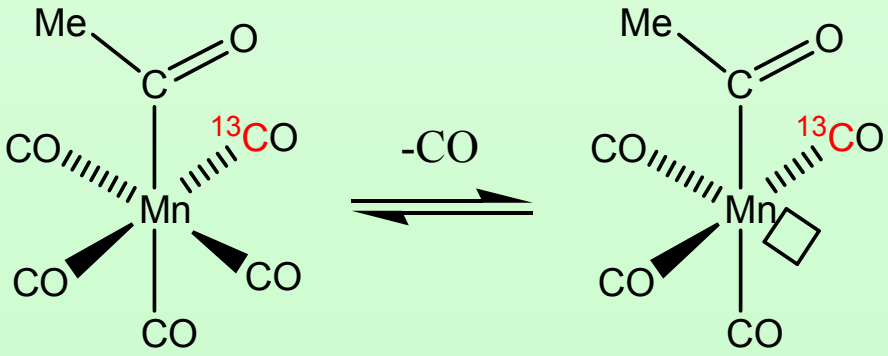
Mn(+1)
16e-

Just looking at the direct reaction you can not make a choice

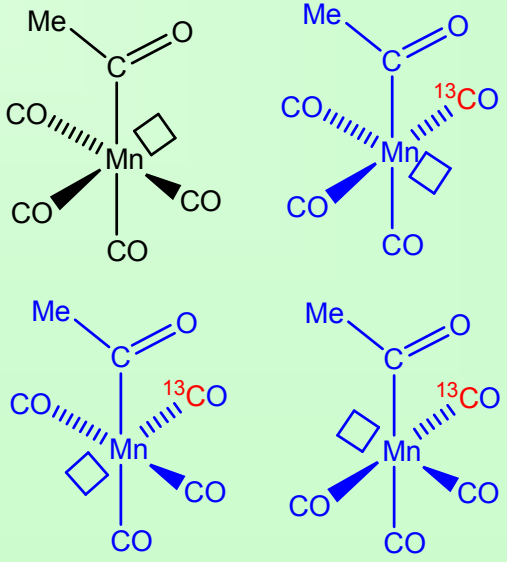
If two opposite reactions can take place at one and the same reaction conditions – they usually proceed through the same transition state (*microscopic reversibility* principle)



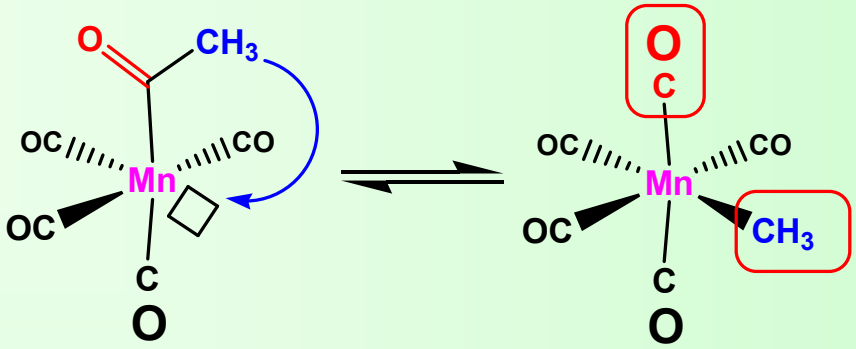
In the opposite direction first vacant place should be organized:

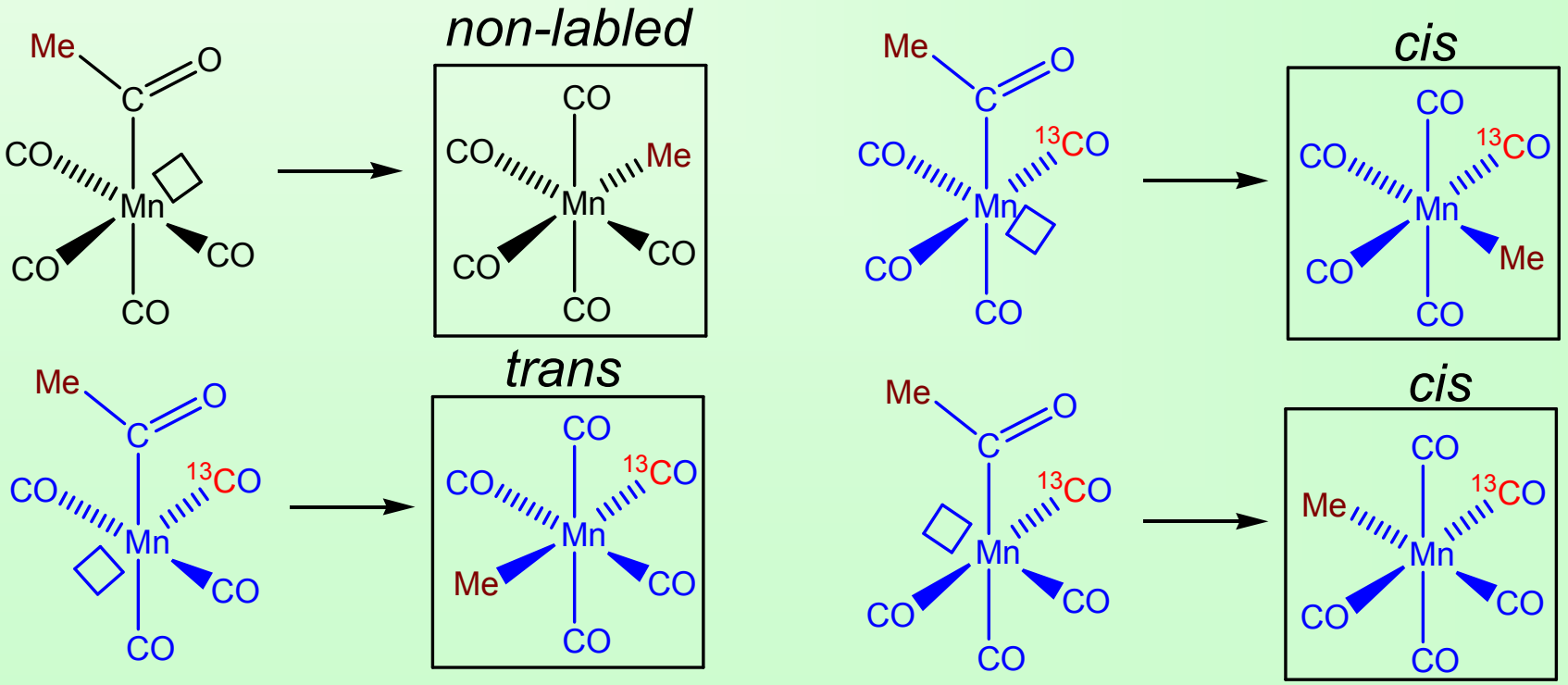


4 variants of CO dissociation are interesting for us:



a) Let's imagine that CH_3 migration takes place

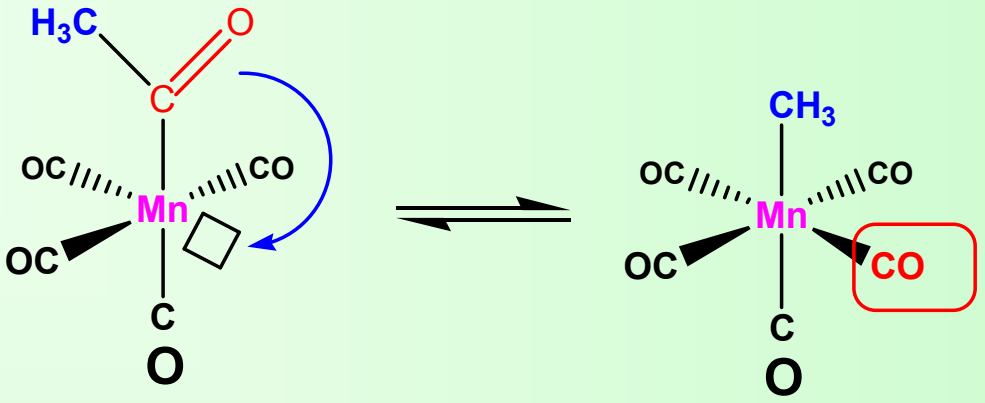


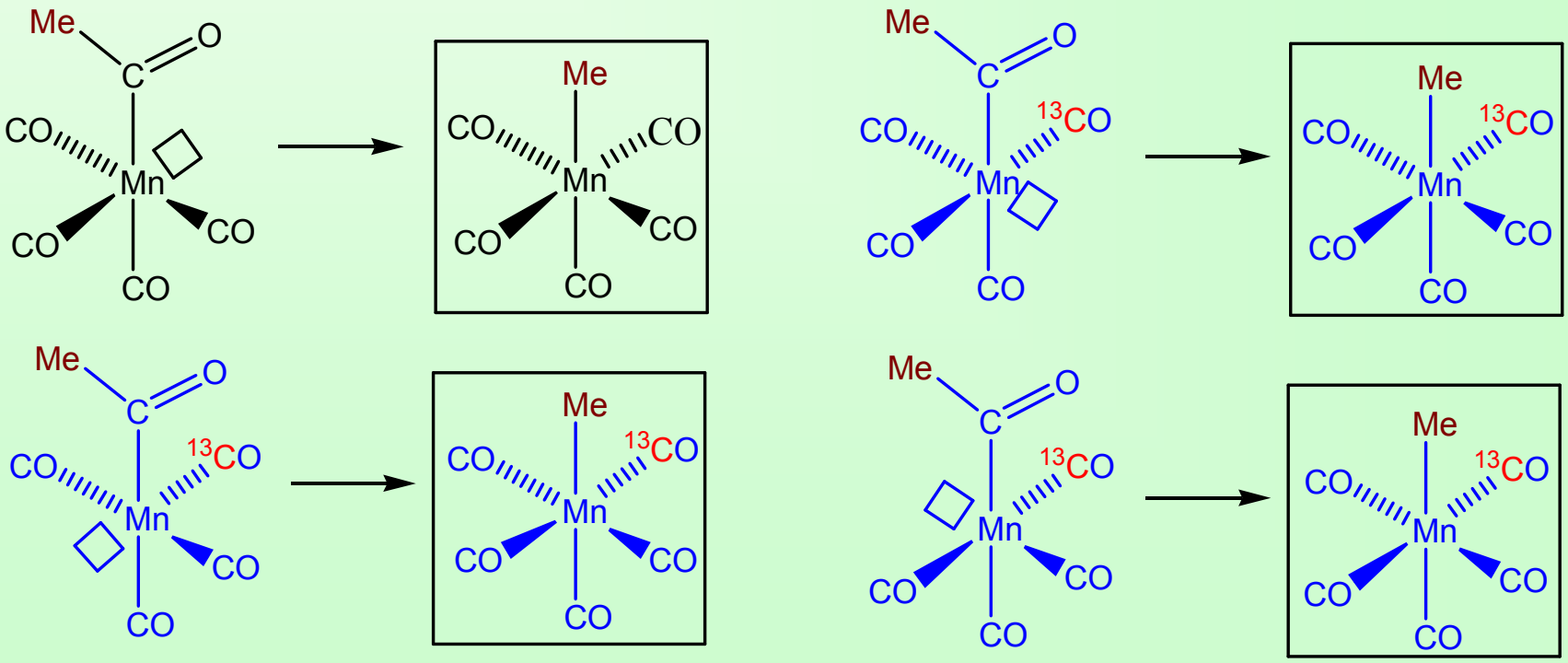


non-labled: 25%, labled cis: 50%, labled trans: 25%

cis:trans = 2:1

b) Let's think that CO insertion takes place



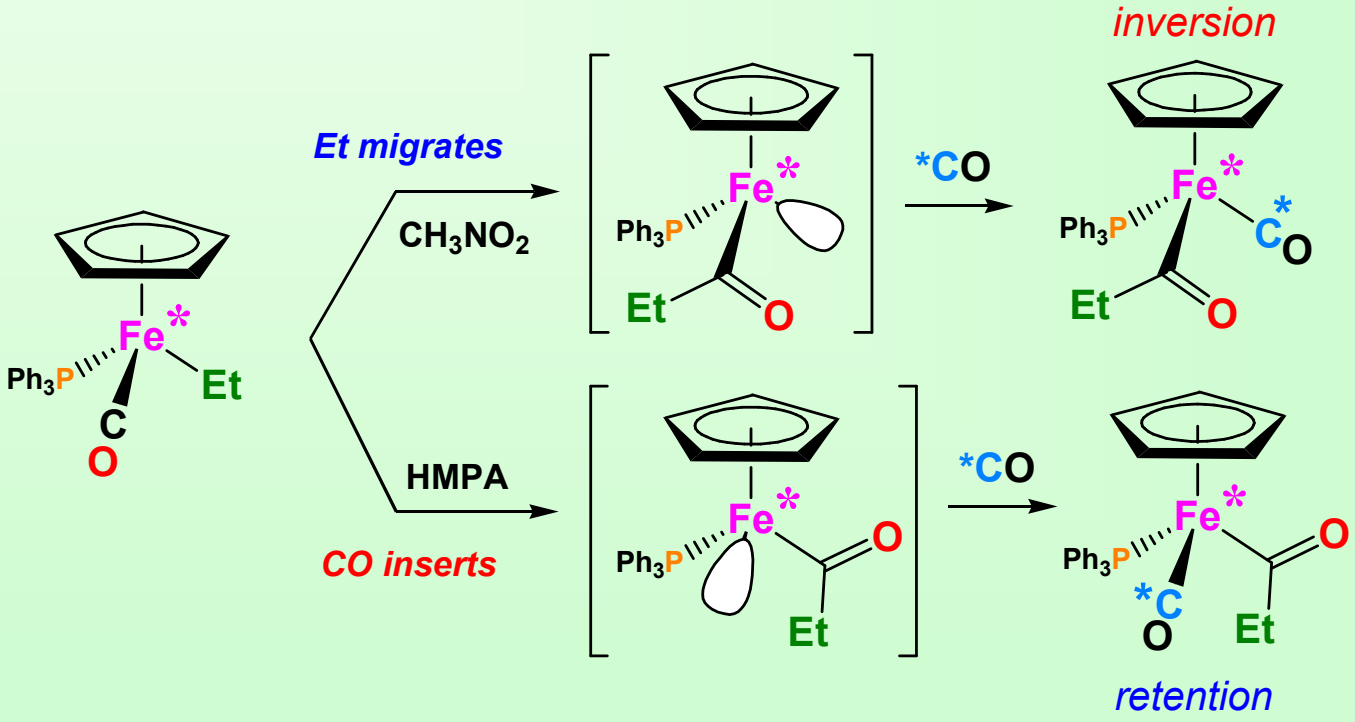


non-labled: 25%, labled cis: 75%, labled trans: 0%

all cis

It was found that cis and trans isomer are formed in 2:1 ratio, so **migration** of CH_3 takes place

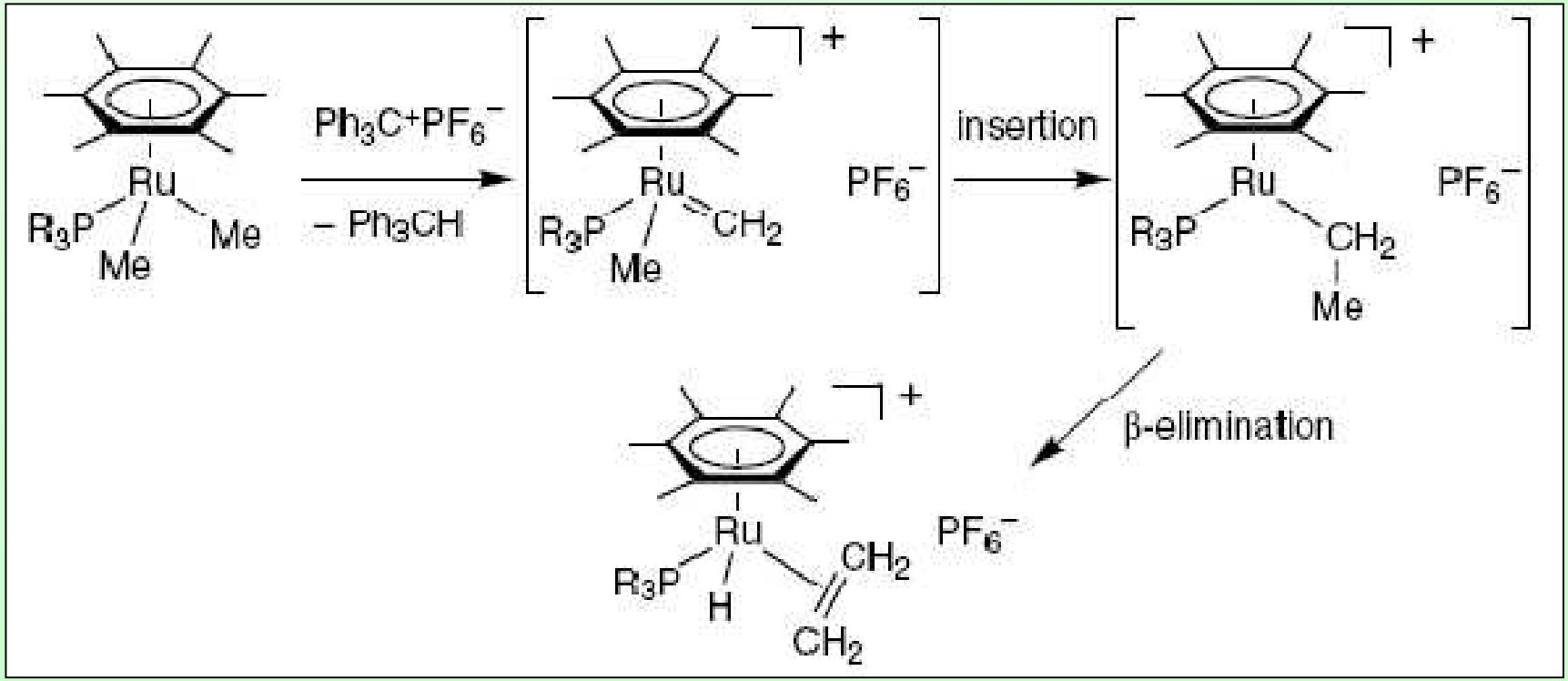
While most systems studied have been shown to do migrations, both are possible. The following example shows a system where both are very similar in energy and the solvent used favors one or the other:



In the line: Me > Et > Ph > CH_2Ph the ability of R to migrate decreases and the process of CO insertion to the M-R bond brings to a forefront

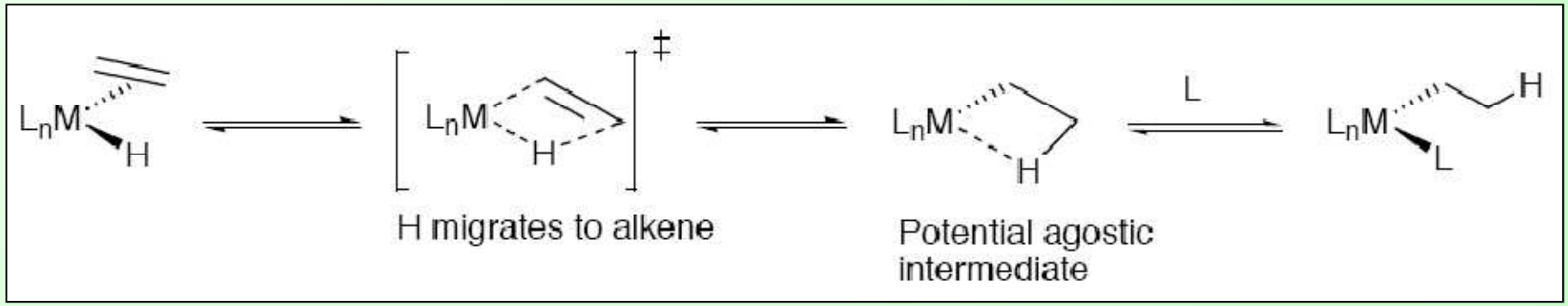
Other example of 1,1-insertion: methylene insertion

Since carbene ligands $=CH_2$ and $=CR_2$ have electronic structures related to that of CO, it is expected that methylene and carbene insertions are possible. There are only very few studies, however, because carbene ligands are more fragile than CO:



1,2-Migratory Insertion of Alkenes or Alkynes

Important catalytic processes such as alkene hydrogenation and olefin polymerization involved migratory insertion of alkenes:



Main features:

Insertion in M-H bonds is nearly always fast and reversible.

$\Rightarrow$ Hydrides catalyze olefin isomerization.

Regiochemistry corresponds to $M^{\delta+}$-$H^{\delta-}$

To shift the equilibrium:

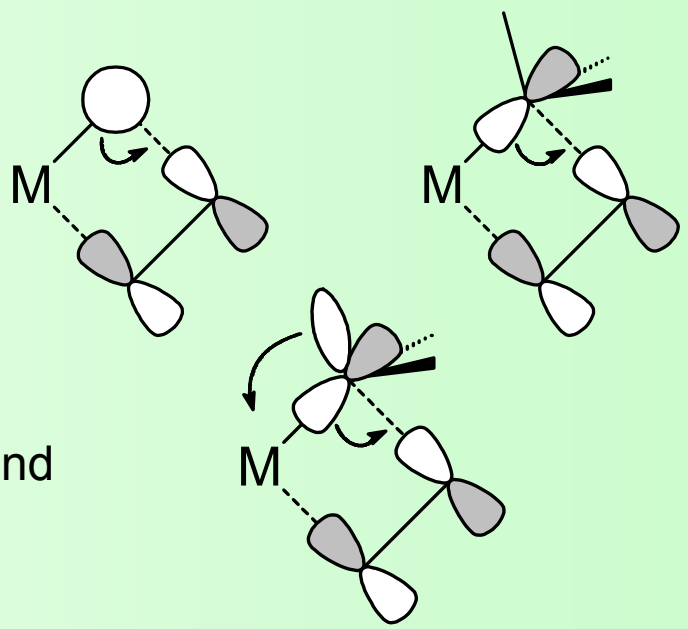
- Electron-withdrawing groups at metal
- Early transition metals
- Alkynes instead of olefins

Insertion in M-C bonds is slower than in M-H.

Barrier usually 5-10 kcal/mol higher

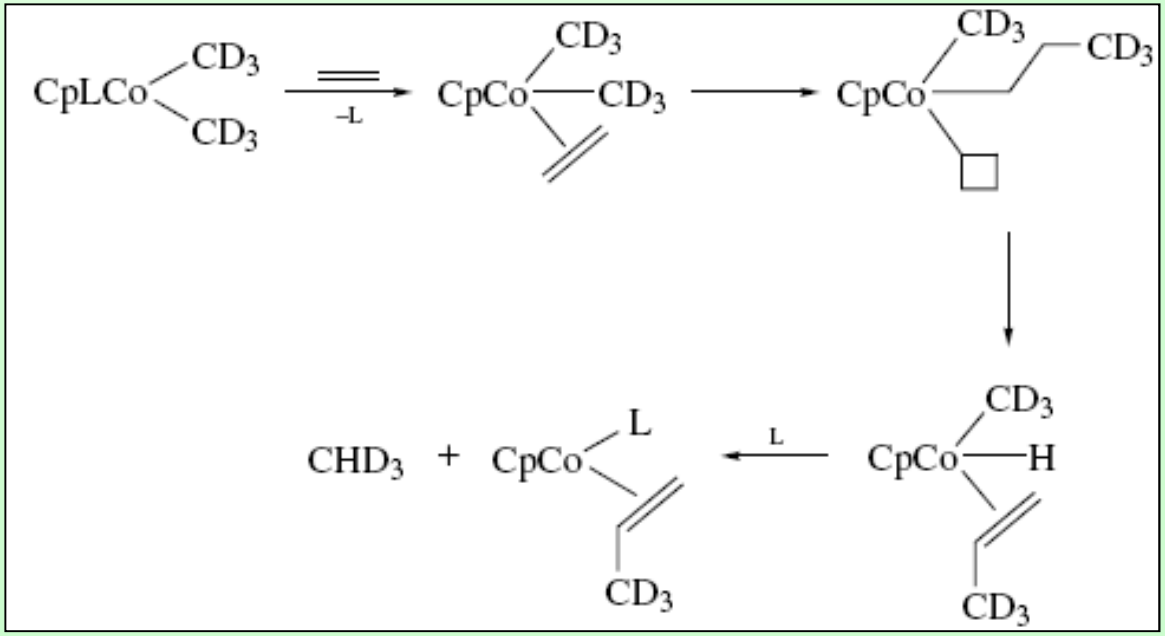
(factor 10^5-10^{10} in rate!)

Reason: shape of orbitals (*s* vs. sp^3)



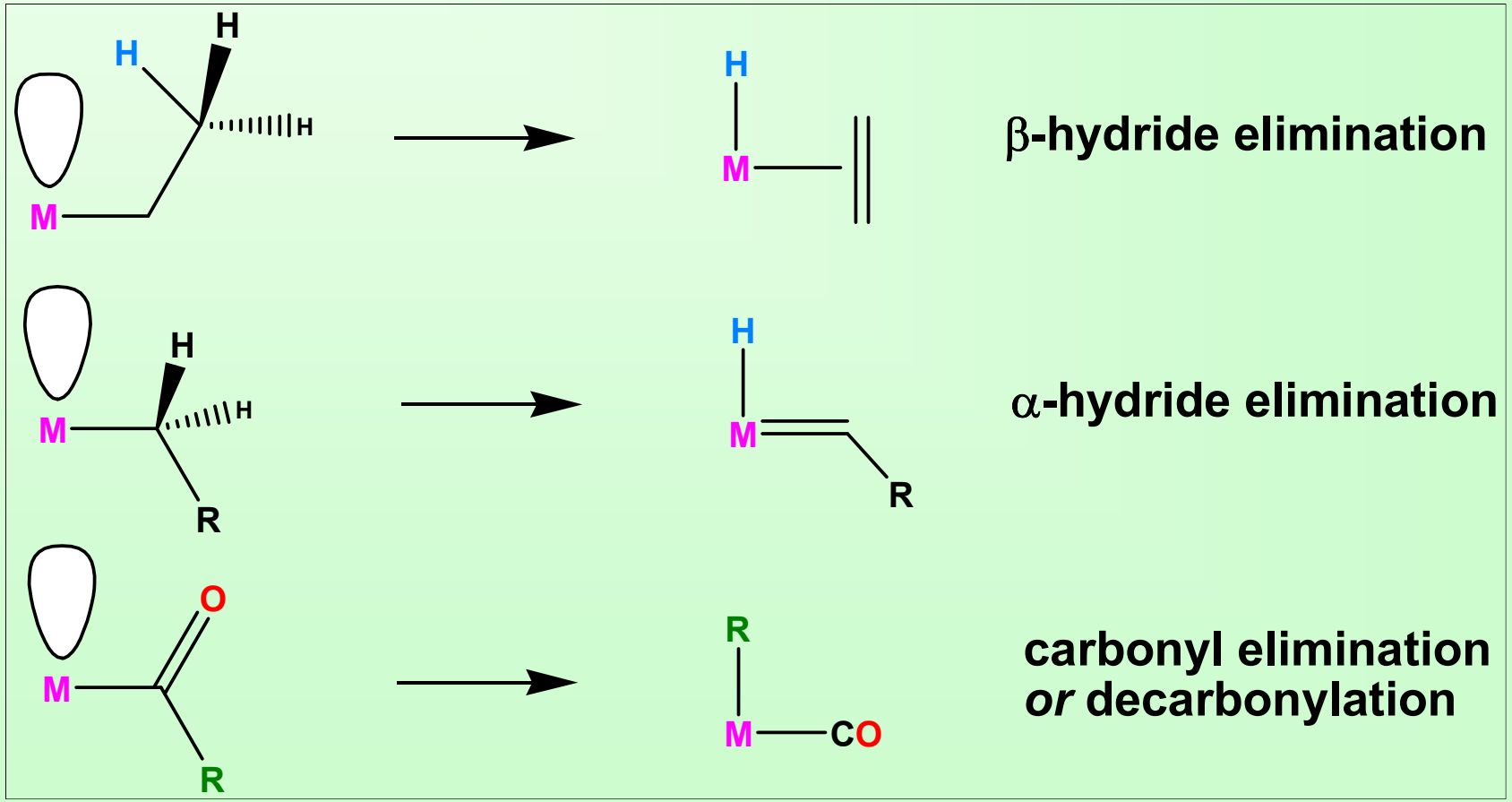
α-agostic interaction facilitates tilting of alkyl and accelerates insertion ("Green-Rooney")

The insertion mechanism was confirmed by the labeling scheme shown below:

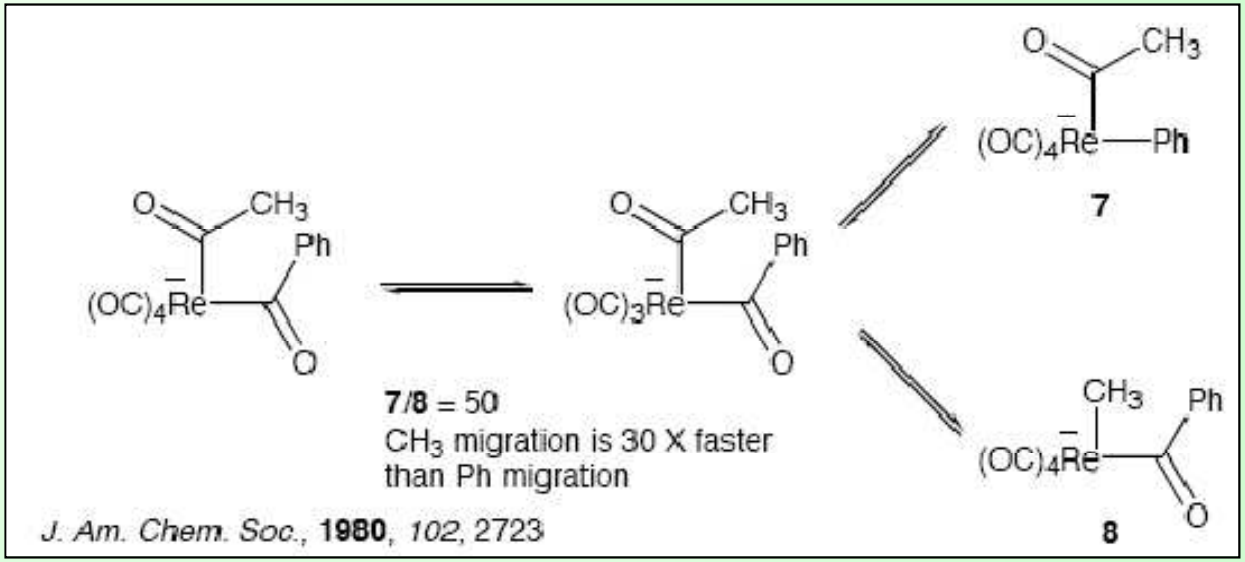


5. Elimination

Examples:



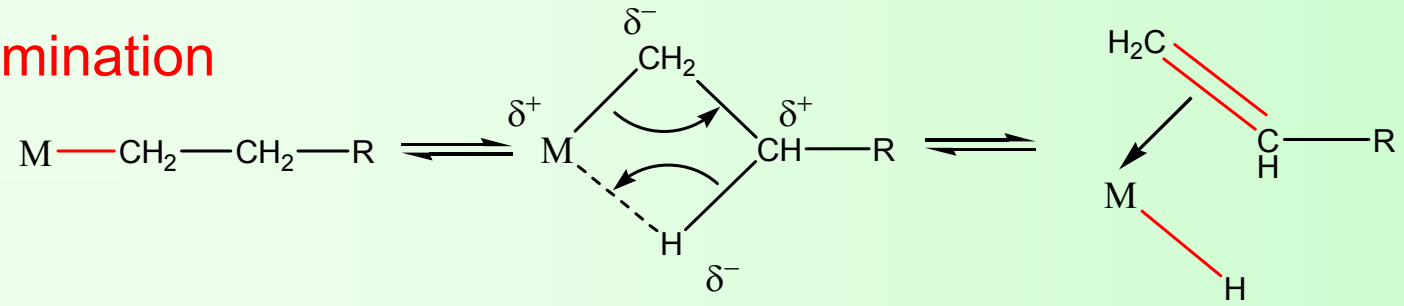
Elimination reactions are just the reverse of migratory insertion reactions:



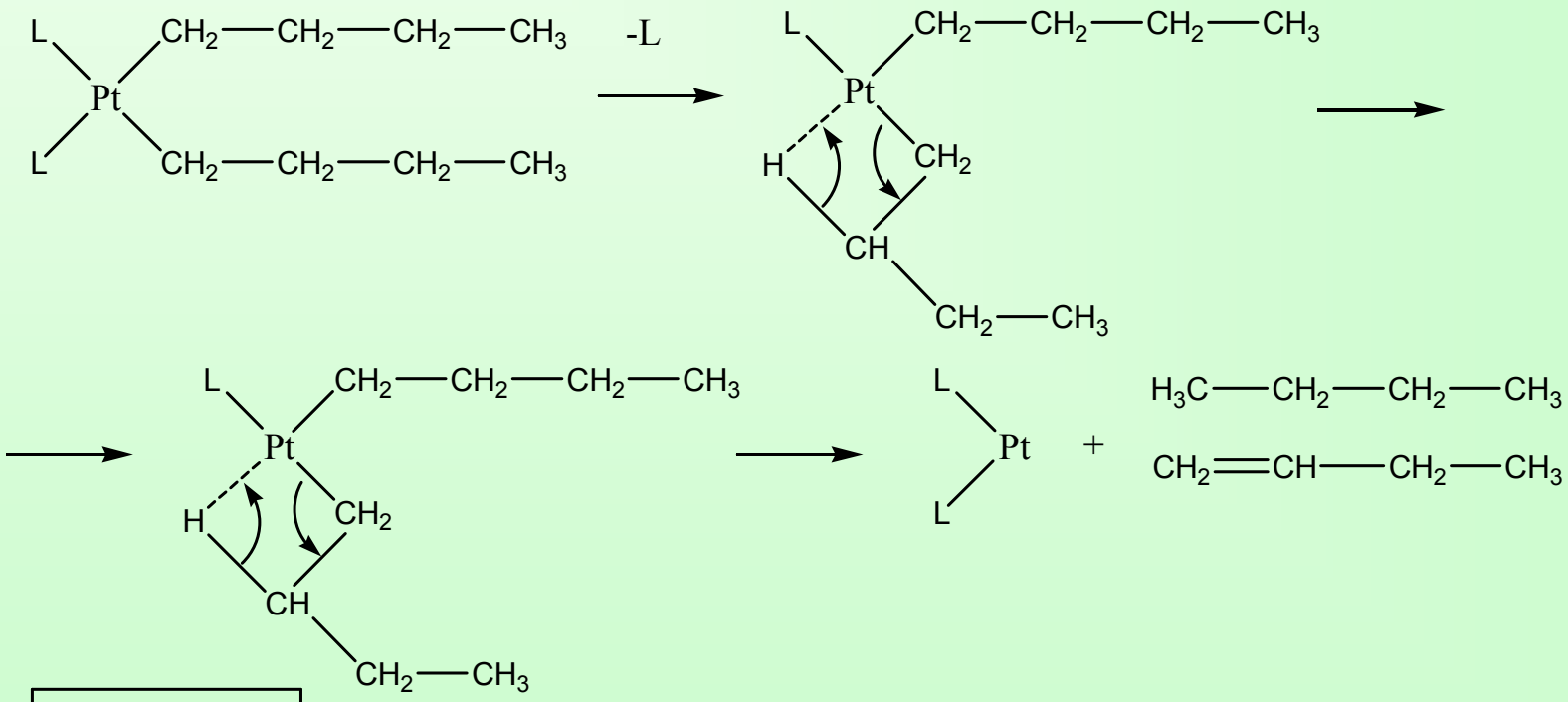
Main features:

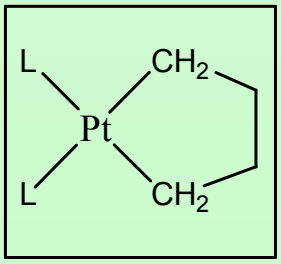
1) Retain of the TM oxidation state (hydrocarbyl ligand changes to hydride or acyl ligand changes to alkyl)
2) Vacant place in the coordination sphere of TMC is important for elimination
3) H-atom in the transition state should have an opportunity to reach the M-atom
4) High oxidative state of the TM and acceptor ligands facilitates elimination
5) In period from left to the right the ability to the elimination increases

β-limination



Example – dibutylplatinum complex (L = phosphine ligand):

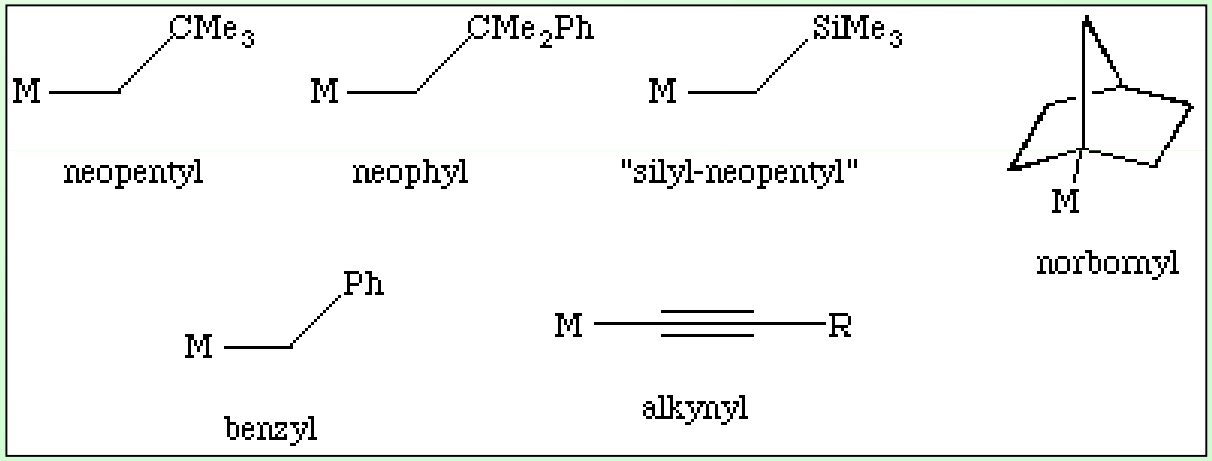




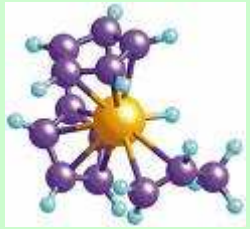
- platinumcyclopentane complex does not undergo β-elimination

Preventing β-elimination

- Although β-elimination is slightly endothermic, it is a common decomposition pathway for alkyls
- Can be prevented by
  - not having any β-hydrogens:

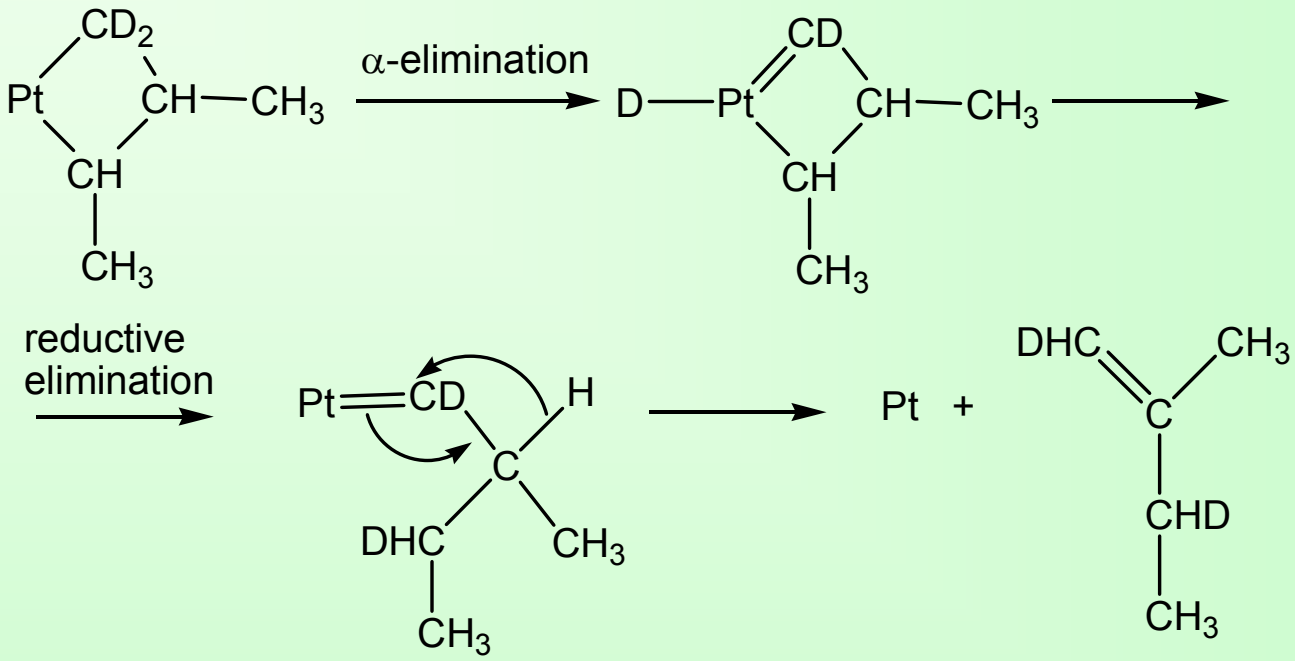


  - saturating the coordination sphere (*i.e.* no free coordination site available)
  - preventing planarization (metallacycle)
  - unstable alkene product



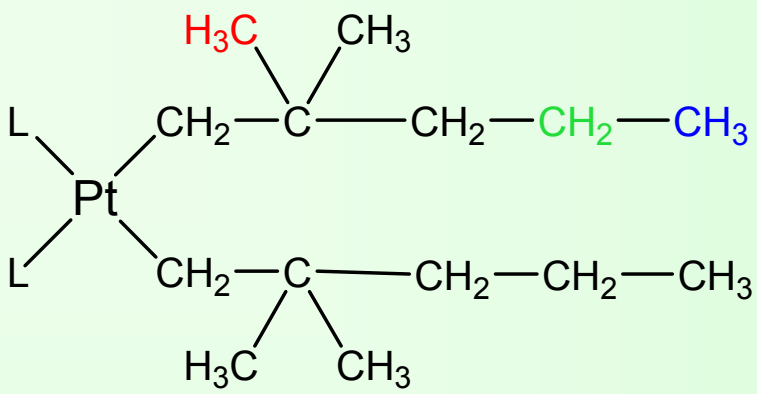
α-elimination

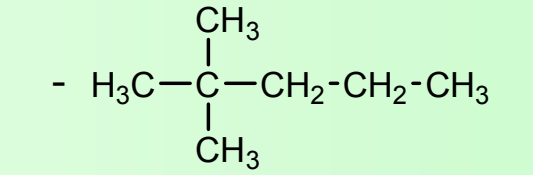
One of the possible root of decomposition of platinumcyclobutane complex is α-elimination:



γ, δ, ε, ... - elimination

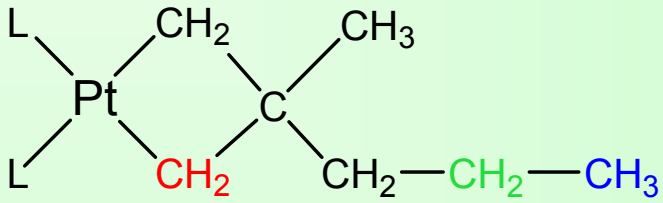
In the case of absence of β-hydrogen atoms γ, δ, ε, ... - elimination takes place (sometimes simultaneously)





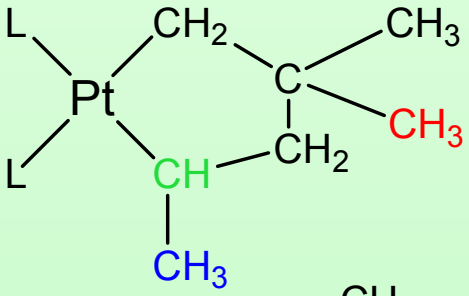
(reductive elimination)

γ - elimination



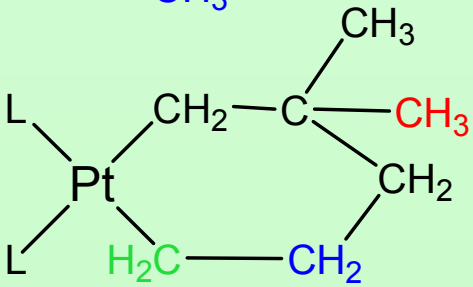
(30%)

δ - elimination



(60%)

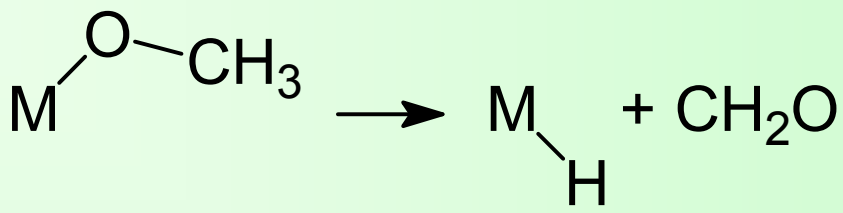
ε - elimination



(10%)

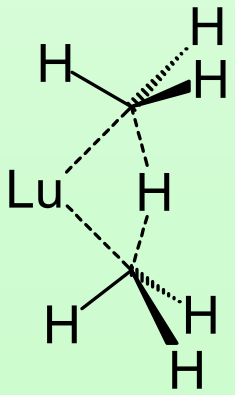
Less common elimination reactions

a) β-elimination from alkoxides of *late* transition metals:



b) σ-bond metathesis:

$$Cp^*_2Lu{-}CH_3 + CH_4 \rightleftharpoons Cp^*_2Lu{-}CH_3 + CH_3H$$

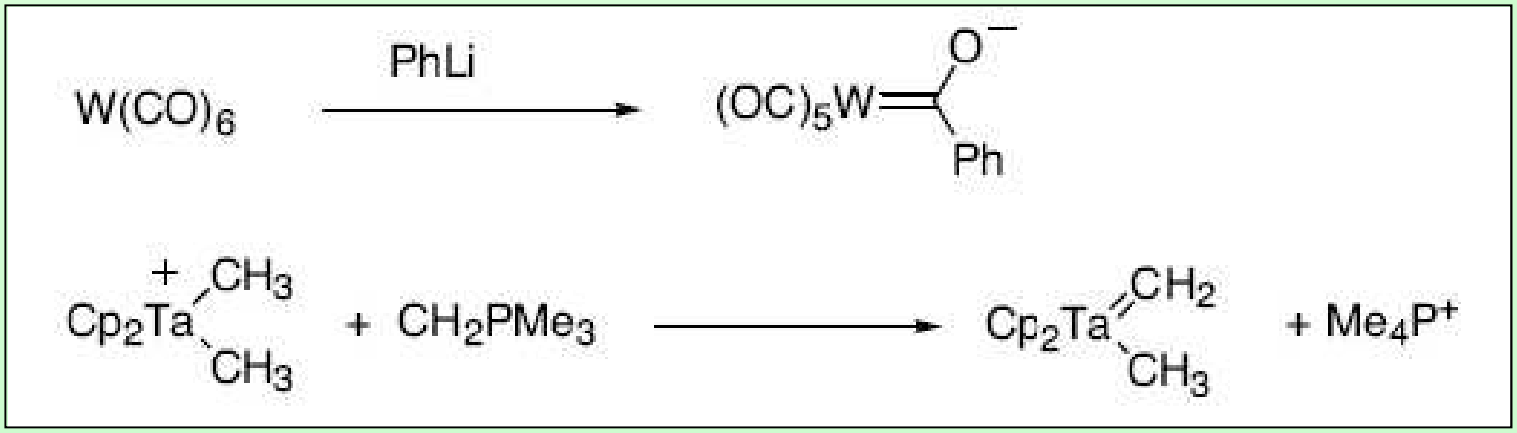


proton transfer from
alkane to alkyl

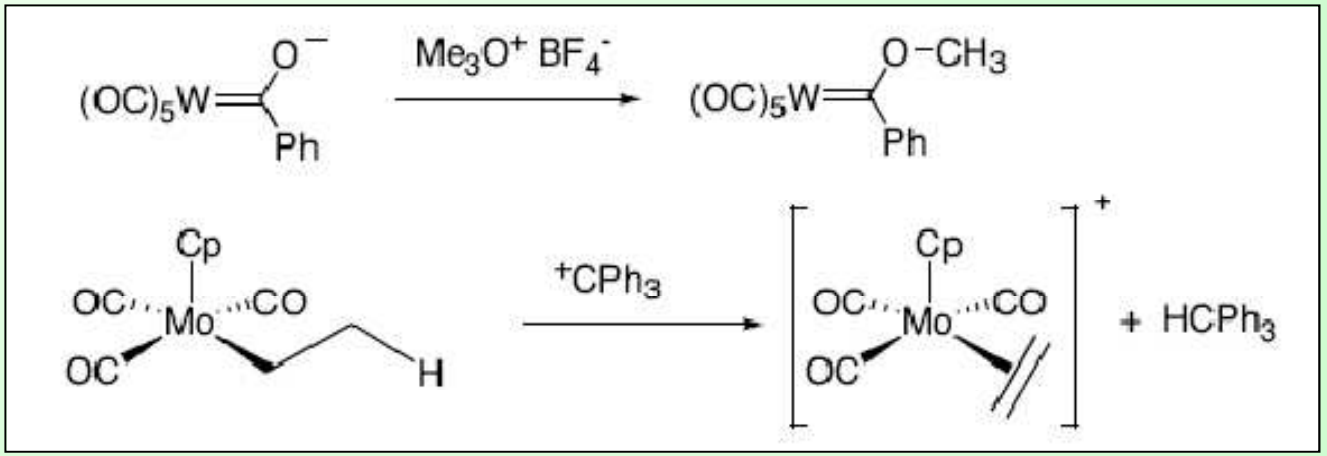
6. Nucleophilic attack on ligand

Ligands bound to metal centers often have quite different reactivity from the free compound. Many bound ligands can be modified or removed from the metal center by nucleophilic or electrophilic reactions. Often these reactions involve direct attack on the bound ligand.

Nucleophilic attack: Favored for metals that are weak π-bases and good σ-acids (i.e., complexes with net positive charges or π-acidic ligands). Ligands bound to electrophilic metals will tend to be electrophilic themselves.

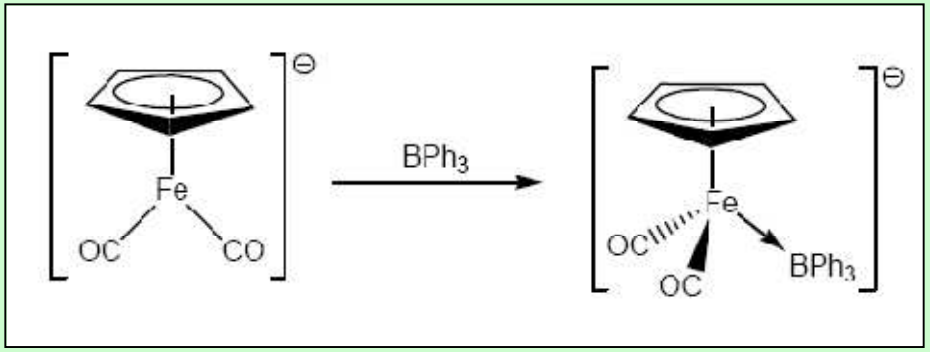


Electrophilic attack: Favored for electron rich metals that act as weak σ-acids, but strong π-bases (i.e. low valent metals, or those with net negative charges and/or electron donating ligands). Ligands bound to π-basic metals tend to be electron rich, and act as nucleophiles.



Zero-electron reagents (*e.g.* H^+, Me^+, CPh_3^+, AlR_3, BR_3, HgX_2, Cu^+, Ag^+, CO_2, SO_2 *etc.*) can attack at (a) the metal (even in 18 electron compounds), (b) the metal-ligand bond, or (c) the ligands.

Electrophilic addition of other zero-electron donor ligands (*e.g.* AlR_3 or BR_3) at the metal can also occur. However, the formation of stable complexes such as that shown below is extremely rare.



Direct nucleophilic addition to an unsaturated ligand
(e.g. CO, alkene, allyl, benzene)

Because they are electron rich, molecules such as CO, alkenes, polyenes and arenes generally **do not react with nucleophiles in the absence of a metal**.

• Once attached to a metal, these ligands give up some of their electron density and become susceptible to direct nucleophilic attack.

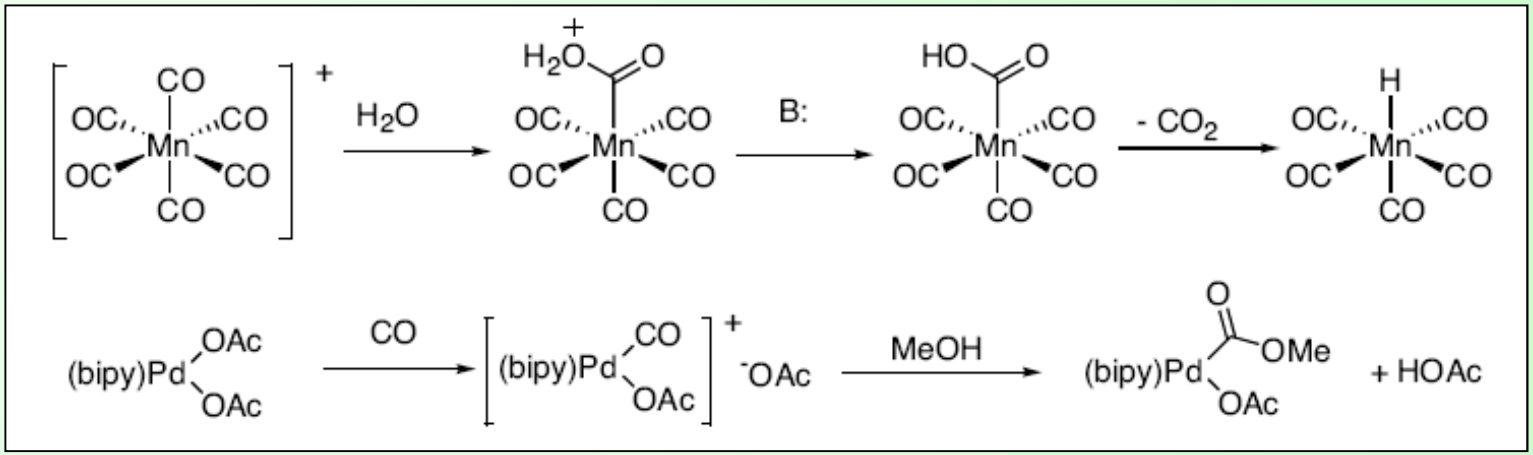
• Unsaturated ligands are more susceptible to direct nucleophilic attack when:

- there is less electron density on the metal (e.g. – π-acceptor co-ligands, overall positive charge).
- the metal is coordinatively saturated – this avoids nucleophilic attack at the metal centre.

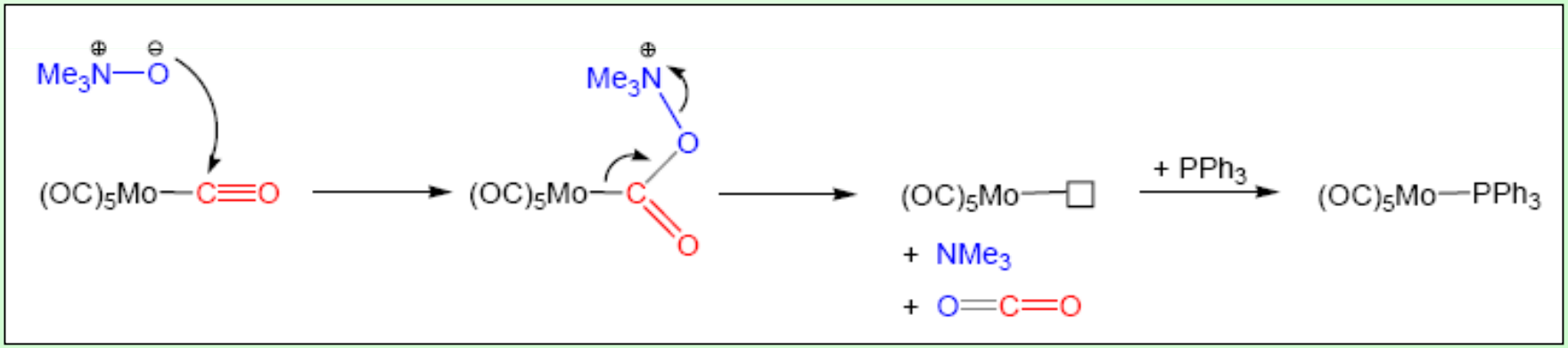
a) Direct nucleophilic addition at CO

CO is prone to attack by nucleophiles when coordinated to weakly π-basic metals. We have already seen that alkyl lithium reagents will alkylate CO. Increasing the electrophilicity of the metal center allows weaker nucleophiles like water or alcohols to attack.

H_2O, ROH attack:



N-oxide attack:

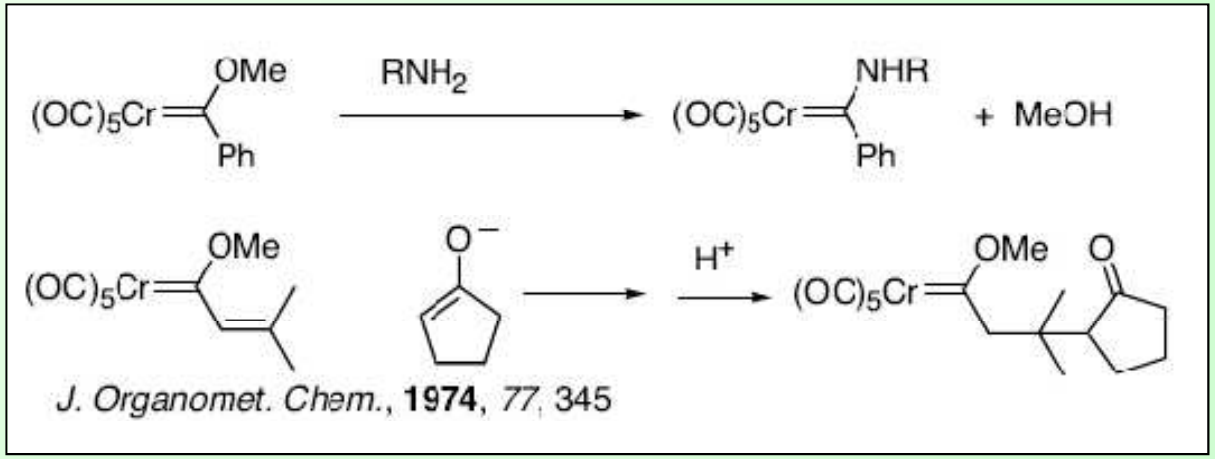


N-oxides are strongly nucleophilic reagents that can be used to abstract CO ligands. The ligand substitution occurs exclusively *cis* to the phosphine.

N-oxides (R = Me or Et) is commonly used instead of heat or UV-irradiation to remove CO ligands in order to speed up dissociative substitution reactions.

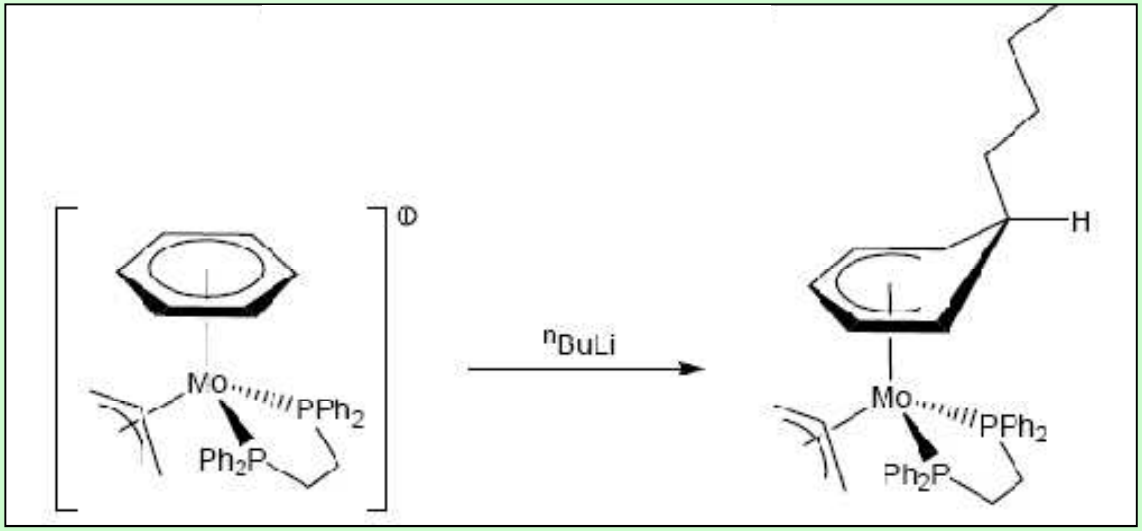
b) Direct nucleophilic attack on electrophilic carbenes:

Electrophilic carbenes are prone to nucleophilic attack. The reactivity is similar to that of carbonyl derivatives in organic chemistry.



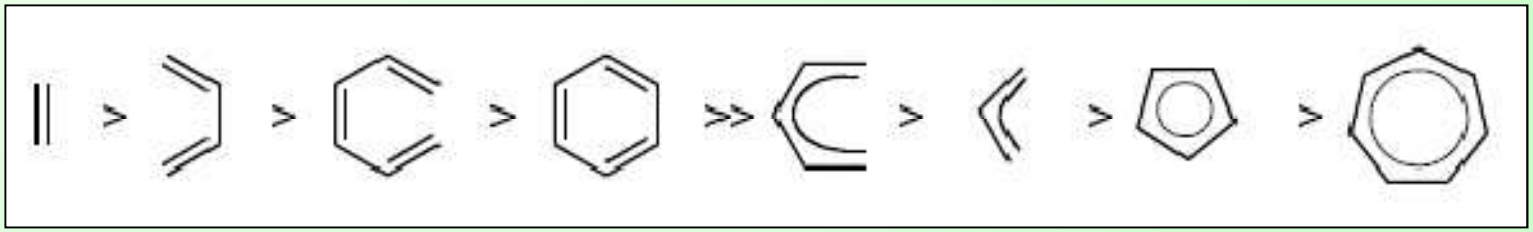
c) Nucleophilic addition at π-ligands

There are many examples of direct nucleophilic attack on coordinated π-ligands, and these transformations can be very useful in synthesis. For example:



Polyenes such as benzene and butadiene typically react with electrophiles rather than nucleophiles. Coordination to an electron deficient metal center reverses this normal reactivity. Coordinated polyenes and polyenyls tend to react with nucleophiles.

The order of polyene and polyenyl reactivity:



The regiochemistry of such reactions is predicted by the Davies / Green / Mingos (DGM) Rules.

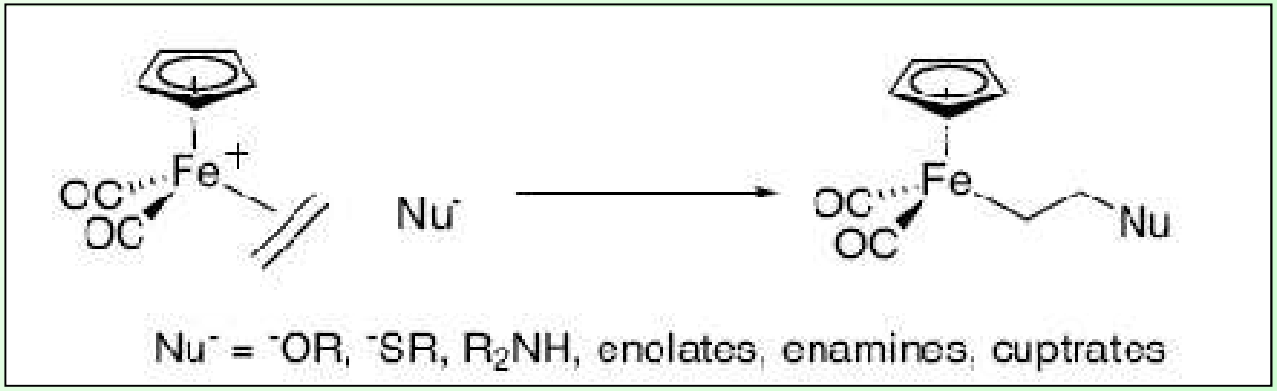
Rule 1 – Even before Odd: Nucleophilic attack occurs preferentially at even polyenes

Rule 2 – Open before Closed: Nucleophilic addition occurs preferentially to open polyenes (not closed).

Rule 3 - For open polyenes:

- If Even: attack occurs at a terminal position.
- If Odd: attack is usually NOT at a terminal position
  attack is only at a terminal position if the metal is very strongly electron withdrawing.

Alkenes bound to electrophilic metals, particularly Pd(II), Pt(II), Fe(II) are prone to attack by a wide range of nucleophiles:



There are two mechanisms by which nucleophilic attack on a bound alkene can occur. Direct attack on the bound ligand, or initial coordination to the metal followed by migratory insertion.