Summary of Principal Reaction Types:

Organometallic Complexes can be stabilised over a range of oxidation states, and show a range of reactions with organic molecules to make catalysts and other useful compounds or reagents:

1) Salt Elimination

2) Protonolysis

3)Substitiution

4) Oxidative Addition

5) Reductive Elimination

6) Oxidative Coupling

7) Reductive Cleavage

8) Migratory Insertions

9) Elimination Reactions

10) σ-Bond Metathesis

There is a simple formal relationship between 4 and 5, 6 and 7, and 8 and 9 in that they are the *reverse* of each other, respectively.

Salt Elimination (often known as salt metathesis):

M-Cl + Li-R → M-R + LiCl

Metal halide + group 1 alkyl   soluble   insoluble in organic solvent, lattice enthalpy

M-Cl + RMgCl → M-R + $MgCl_2$

Protonolysis:

M-R + HNR_2 → M-NR_2 + RH

Metal alkoxide, + anything with   M-N stronger   volatile, entropy

amide or alkyl   an acidic H   Le Chatelier’s Principle

Ligand Substitution Reactions

$$ML_n + {}_xP \rightleftharpoons ML_{n-x}P_x + {}_xL$$

The mechanism of this substitution will almost always depend on whether the parent ML_n complex is coordinatively saturated or not!

Saturated Complex: Dissociative Pathway!

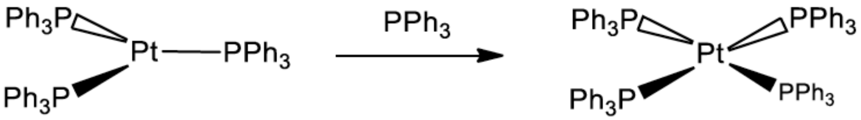
Unsaturated Complex: Associative Pathway (usually)
Dissociative pathway (sometimes)

Most of the substitutions involve 2e- pathways.

Ligand Association and Dissociation Reactions

Coordinatively Saturated complexes have 18 VE.
Coordinatively Unsaturated complexes have less than 18 VE - typically will have 16 or 14 VE.

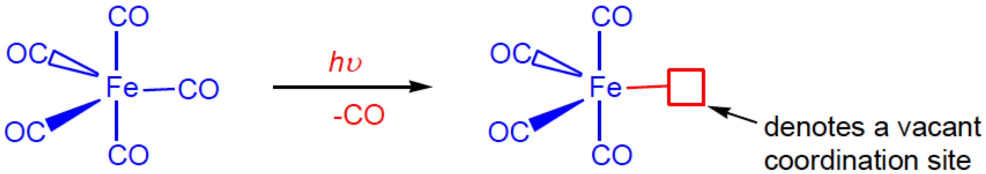
Ligand association – is the addition of a ligand to a transition metal centre that does not involve a change in the oxidation state at the metal centre.



Pt( ), VE

Pt( ), VE

Ligand dissociation – is the loss of a ligand from a transition metal centre which does not involve a change in the oxidation state.



Fe( ), VE

Fe( ), VE

Oxidative Addition (O.A.):

- ***This is the simultaneous addition of two ligands into the coordination sphere of a metal, it is an <u>overall</u> process with no mechanistic implications.***

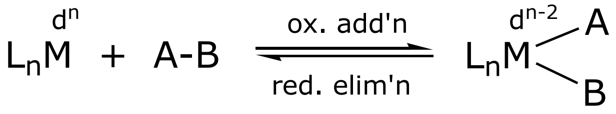
e.g. the synthesis of Grignard reagents, RMgX, from Mg and RX is an O.A. reaction.

Oxidative addition, which is most common for d^8 and d^{10} metals, requires:

- Non-bonding electron density at the metal.

- A vacant coordination site.

- A metal with accessible oxidation states separated by 2 units.



Δ O.S. = **+2**

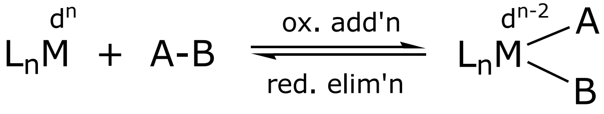
Δ C.N. = **+2**

Δ V.E. = **+2**

Δ d^n = **-2**

For 16-electron complexes it is an equilibrium process dependent on the nature of M, ligands, M-A, M-B and A-B bonds, and the solvent.
O. A. is favoured for:

- Heavier elements of a group.
- When the metal is electron rich (π-basic).
- Whit hard or strong σ-donor ligands present.
- Small ligands are present.
- The metal is large.
- For strong M-A and M-B and weak A-B bonds.



Δ O.S. = **+2**

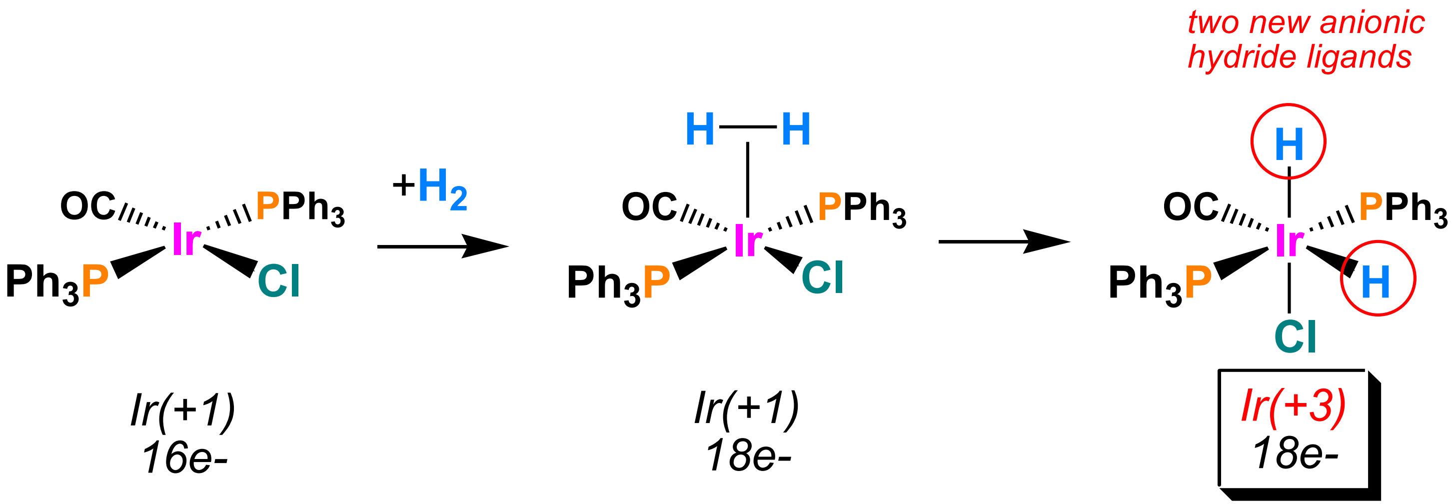
Δ C.N. = **+2**

Δ V.E. = **+2**

Δ d^n = **-2**

4 types of mechanism: concerted (H_2, *cis*-addition), S_N2 (MeI, addition is solvent dependent), ionic (HCl, RCO_2H, *trans*-addition), radical ($PhCH_2I$).

Oxidative Addition



There are three main classes of molecules (substrates) that can perform oxidative additions to metal centers:

- Non-Electrophilic
- Non-Electrophilic “Intact”
- Electrophilic

Non-electrophilic: these molecules do NOT contain electronegative atoms and/or are not good oxidizing agents. These molecules usually require the presence of an **empty orbital** on the metal in order for them to pre-coordinate prior to being activated for the oxidative addition rxn.

H_2, C-H bonds, Si-H bonds, S-H bonds,
B-H bonds, N-H bonds, S-S bonds, C-C bonds, etc.

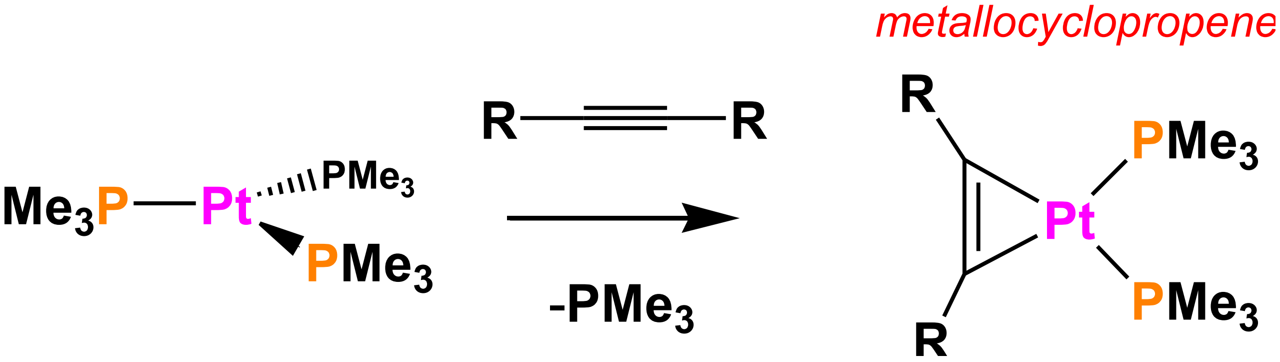
H_2 is by far the most important for catalytic applications, followed by Si-H bonds, B-H, N-H, and S-H bonds.

C-H bond activation and functionalization is very important, but still not practical.

Non-electrophilic "Intact": these molecules may or may not contain electronegative atoms, but they do need to have a **double** or **triple bond** present. One also needs a metal center with an **empty orbital** (16e- or lower count) in order to pre-coordinate the ligand before the oxidative addition occurs.

Typical "intact" ligands that can perform an oxidation addition without fragmenting apart are (O_2 can also act as an **electrophilic** substrate):

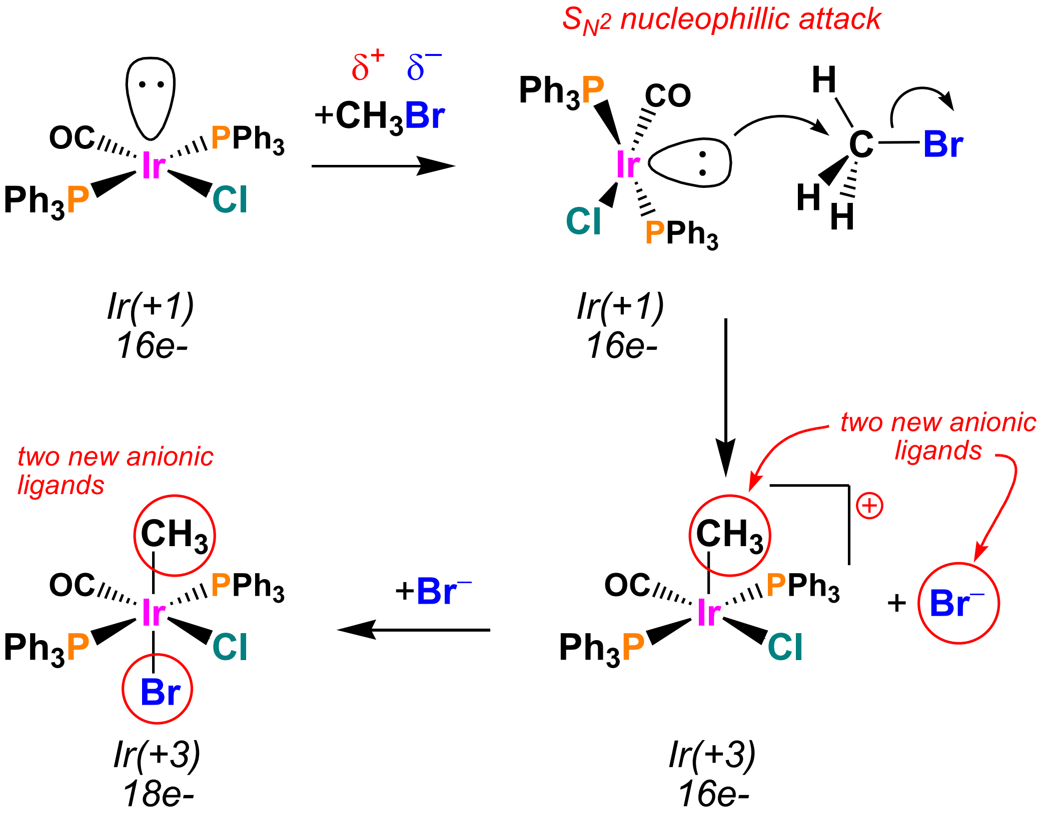
alkenes, alkynes, and O_2



Electrophilic: these molecules ***do*** contain electronegative atoms and are good oxidizing agents. They are often considered to be *“reactive”* substrates.

These molecules do ***NOT*** require the presence of an **empty orbital** (18e- is OK) on the metal center in order to perform the oxidative addition rxn.

X_2 (X = Cl, Br, I), R-X, Ar-X, H-X, O_2, etc.



S_N2 nucleophillic attack

Ir(+1)
16e-

Ir(+1)
16e-

two new anionic ligands

Ir(+3)
16e-

two new anionic ligands

Ir(+3)
18e-

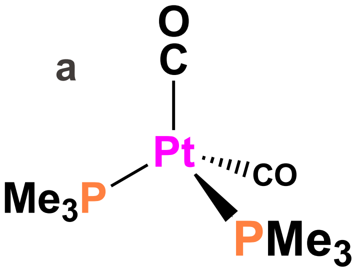
d^0 metals can ***NOT*** do ***oxidative additions***!!

So always electron count the starting and final metal complexes to check out the overall electron-count, metal oxidation state and *d*-electron count!

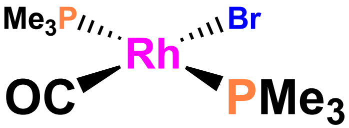
Oxidative additions are easy to identify **IF YOU ELECTRON COUNT** the metal complexes. When an oxidative addition rxn occurs the metal will be oxidized, usually by 2e-. So, if you start with a metal in the 0 oxidation state (d^8), after the oxidative addition the metal will be in the +2 oxidation state (d^6). Once you get used to looking at organometallic rxns you will be able to identify common oxidative additions quite quickly. **H_2, R-X, and H-SiR$_3$ are three of the most common substrates that perform oxidative addition reactions in catalytic cycles.**

Problem: H_2 will do an oxidative addition most readily to which of the following complexes. Why?

a

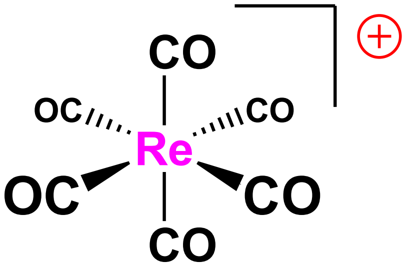


b)

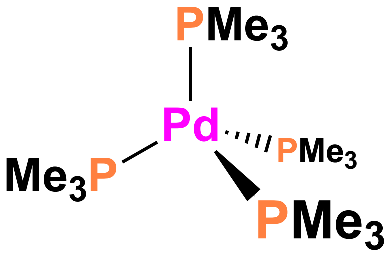


Problem: Cl_2 will do an **oxidative addition** most readily to which of the following complexes. Why?

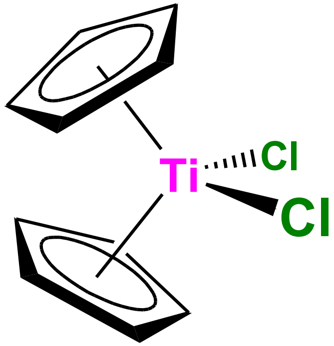
a)



b)

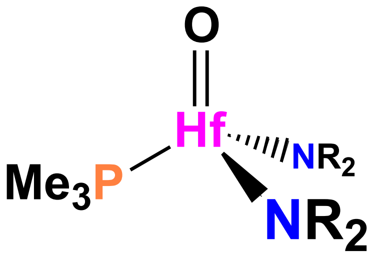


c)

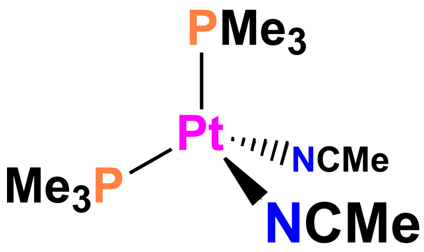


Problem: CH_3Br will do an **oxidative addition** most readily to which of the following complexes. Why?

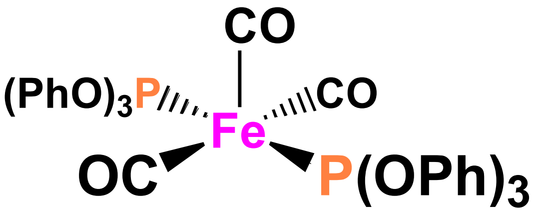
a)



b)

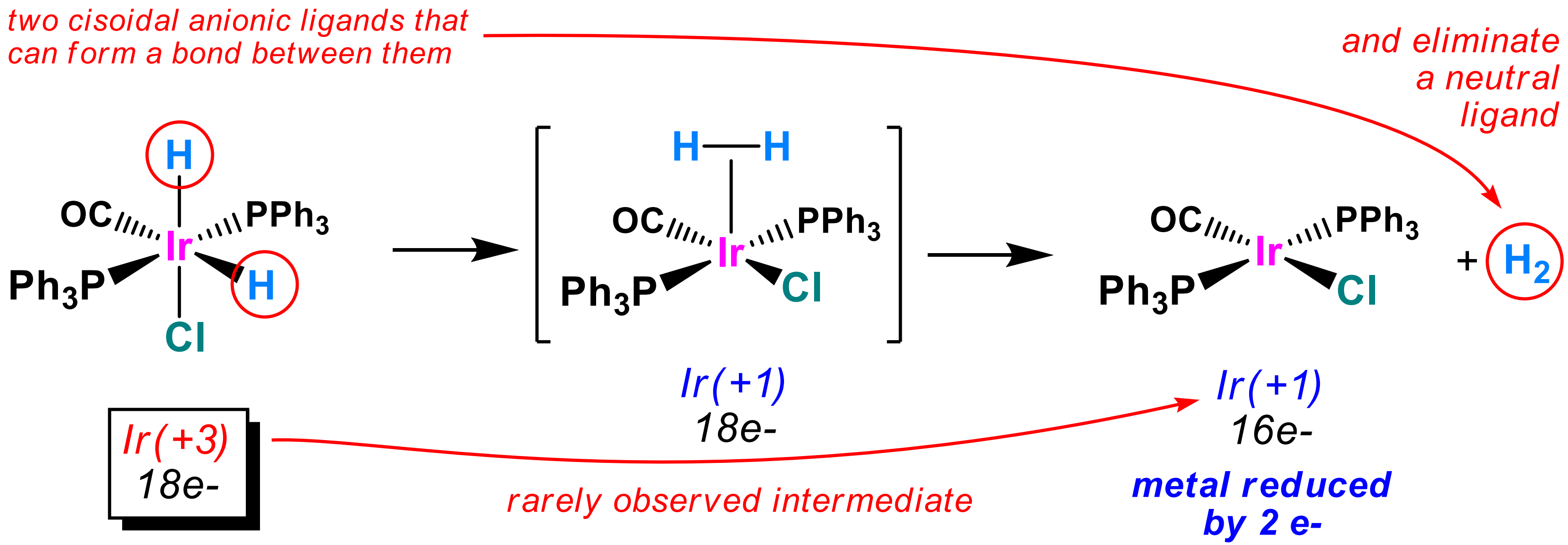


c)



Reductive Elimination

A ***reductive elimination*** reaction is the reverse of an oxidative addition. It is a reaction in which **two cisoidal anionic ligands** on a metal center couple together. Each anionic ligand pushes one electron back onto the metal center (in the case of a monometallic complex) to reduce it by 2e-. The coupled anionic ligands then usually fall off the metal center as a **neutral** molecule.



two cisoidal anionic ligands that can form a bond between them

and eliminate a neutral ligand

Ir(+3)
18e-

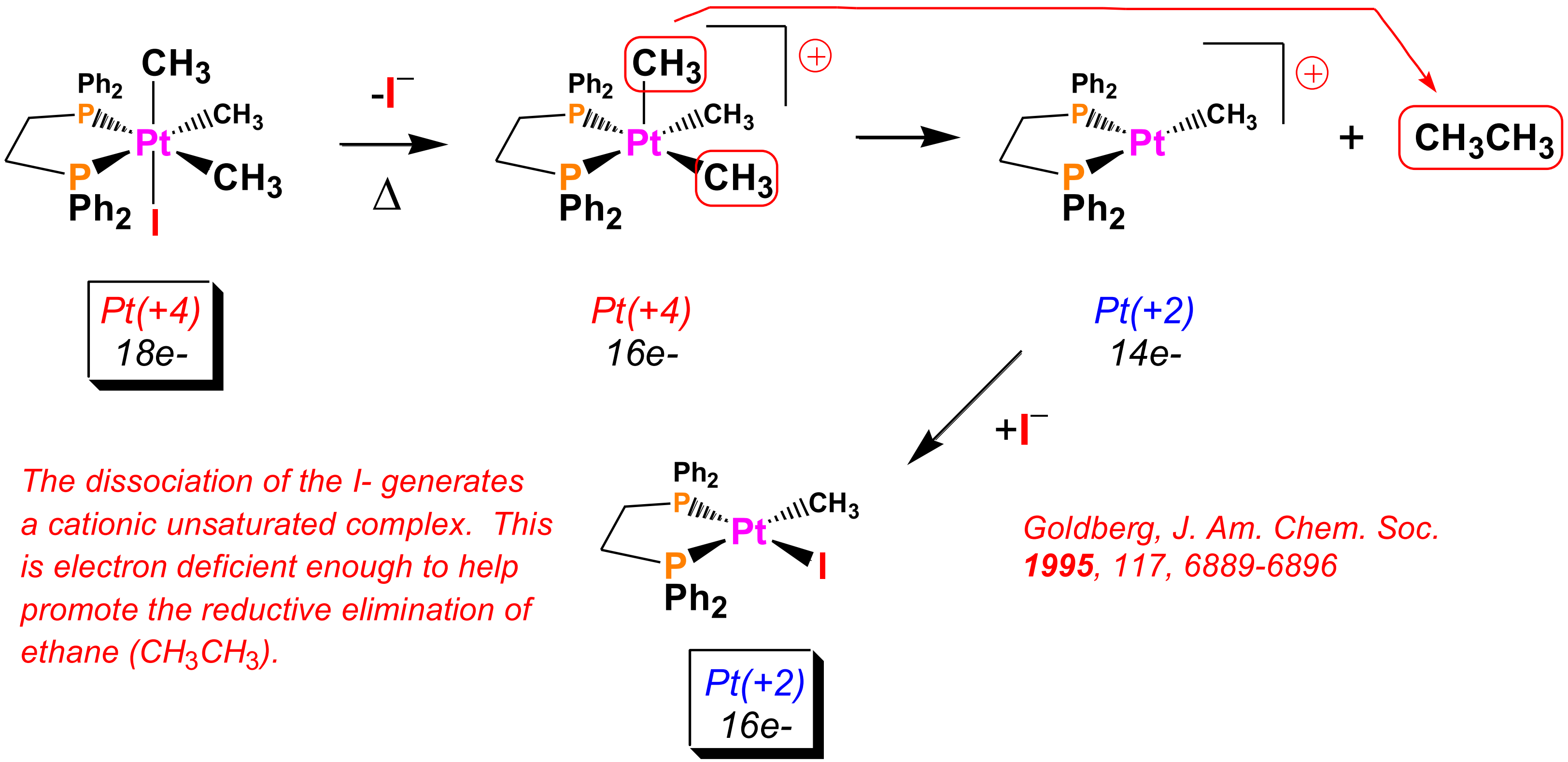
Ir(+1)
18e-

rarely observed intermediate

Ir(+1)
16e-

metal reduced by 2 e-

While reductive elimination can occur from saturated 18e- complexes (so long as the two ligands that you want to reductively eliminate are **cisoidal** to one another), it has been shown that reductive elimination can be promoted by a ligand dissociation generating an unsaturated and more electron-deficient metal center.

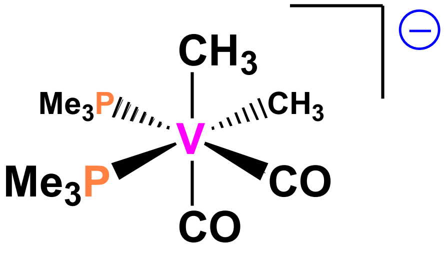


The dissociation of the I- generates a cationic unsaturated complex. This is electron deficient enough to help promote the reductive elimination of ethane (CH_3CH_3).

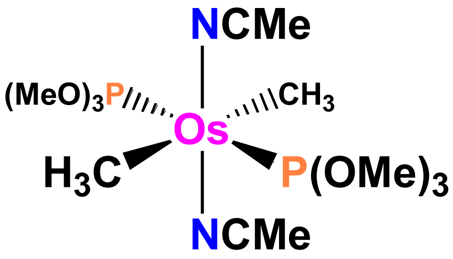
Goldberg, J. Am. Chem. Soc. ***1995****, 117, 6889-6896*

Problem: Which of the following compounds will be most likely to do a reductive elimination of ethane (CH_3-CH_3)? Why?

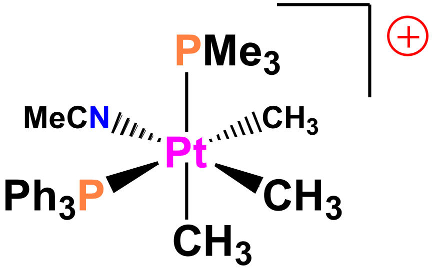
a)



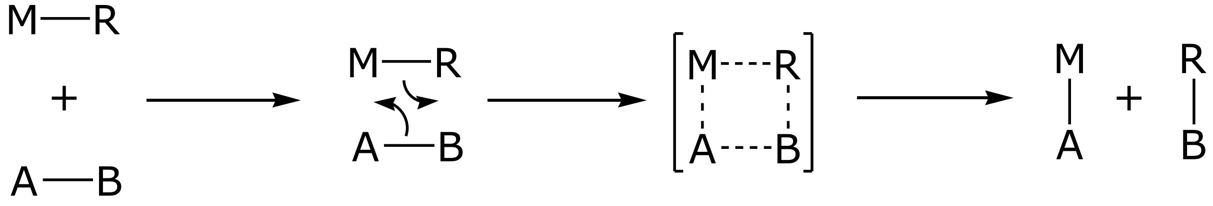
b)



c)



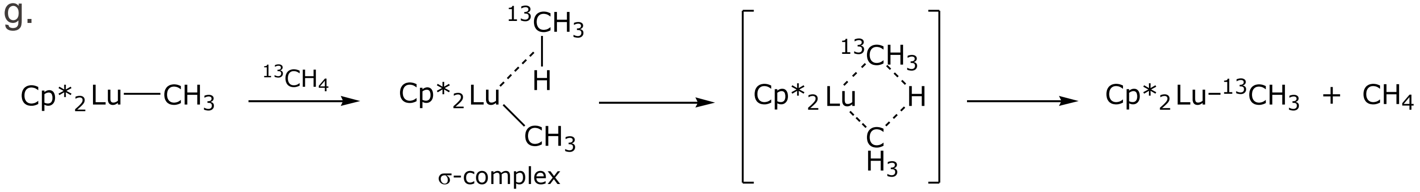
σ-Bond Metathesis:



Notice this four-centred mechanism *does not* involve a change in oxidation state. The metal centre polarises bonds sufficiently to rupture them.

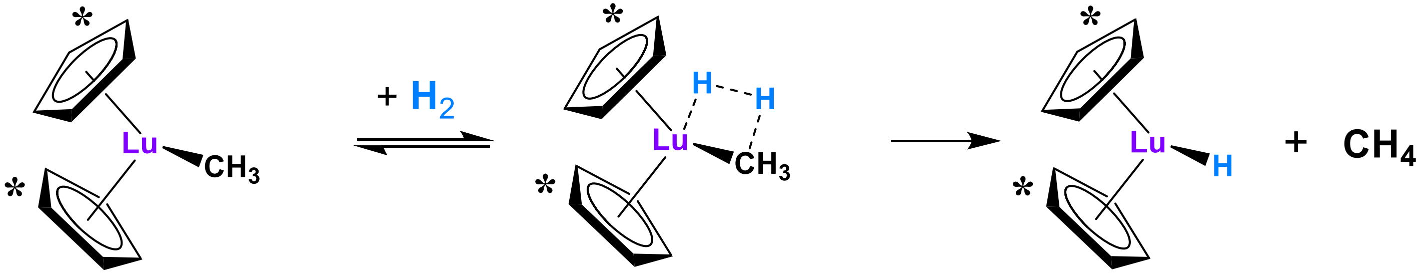
This is a common reaction for early transition metals, lanthanides, and actinides in high oxidation states, and is usually confined to complexes where oxidative addition and reductive elimination are not viable mechanistic reaction pathways.

e.g.

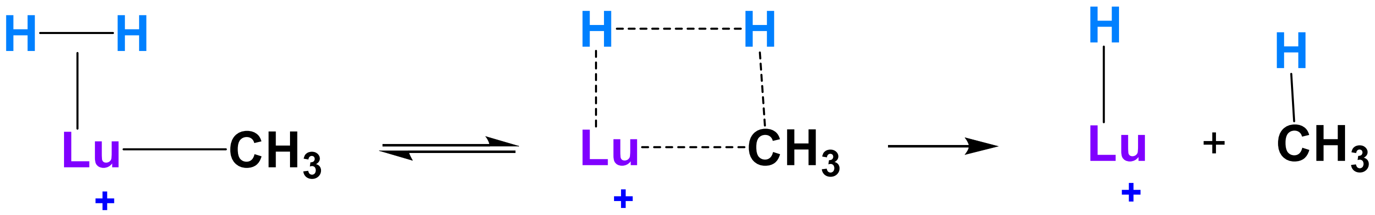


Hydrogenolysis (sigma bond methatesis)

The only way that early transition metals with d^0 counts can activate H_2. Lanthanides and actinides also typically use hydrogenolysis. As with oxidative addition, the metal center needs to have an empty orbital to bind the H_2 and an anionic ligand (e.g., alkyl, halide) that can be protonated off. No change in oxidation state of the metal.



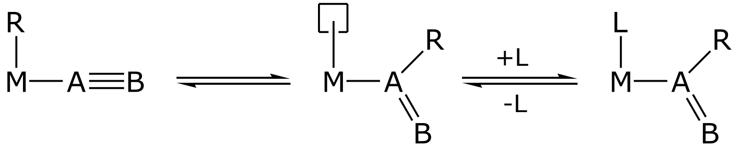
hydrogenolysis



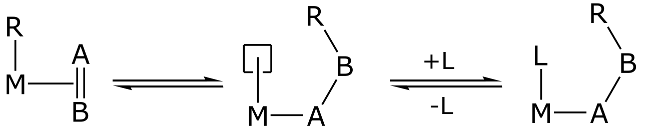
Migratory Insertion Reactions:

Migratory insertion is one of the most important reactions which occurs in homogeneous catalysis. It is an easy way to form C–C and C-N bonds. Reactions often look like *insertion* has occurred, but *it is usually migration which occurs.* Examples where both mechanisms operate are known!

1,1-migratory insertion:



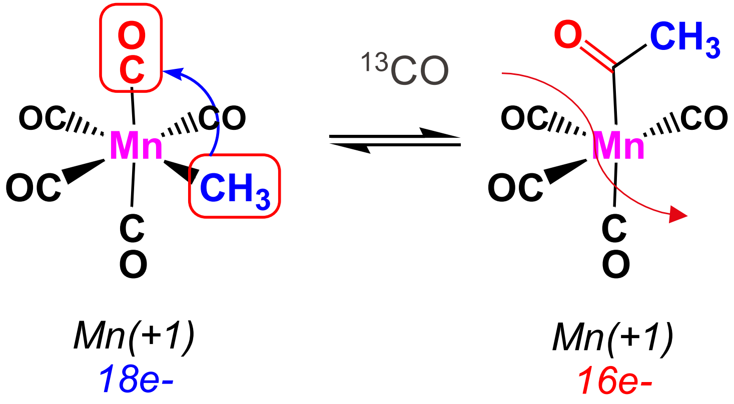
1,2-migratory insertion:



☐ = vacant coordination site

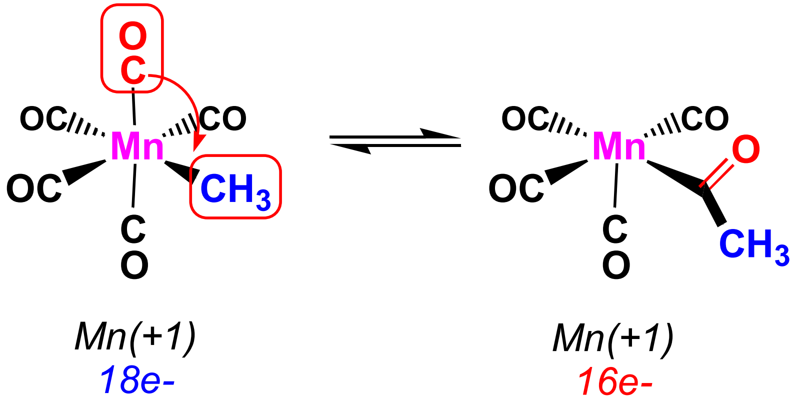
Migration vs. Insertion

Migration



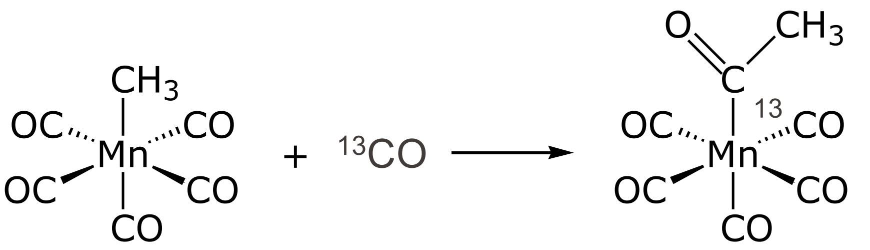
a MIGRATION rxn involves the anionic ligand doing a nucleophillic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

Insertion



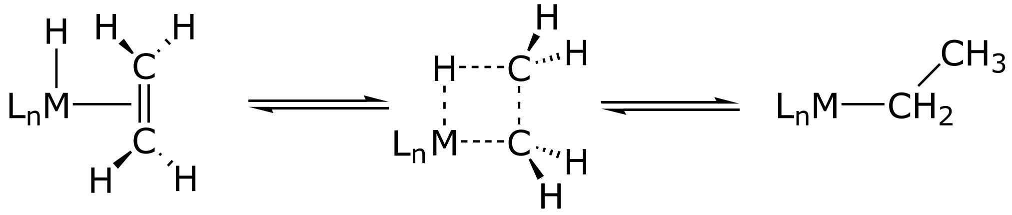
an INSERTION rxn involves the neutral ligand moving over to where the anionic ligand is coordinated and "inserting" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind from where the neutral ligand originally was located.

Acyl Formation (1,1):



^{13}C labelling experiments show the CH_3 migrates

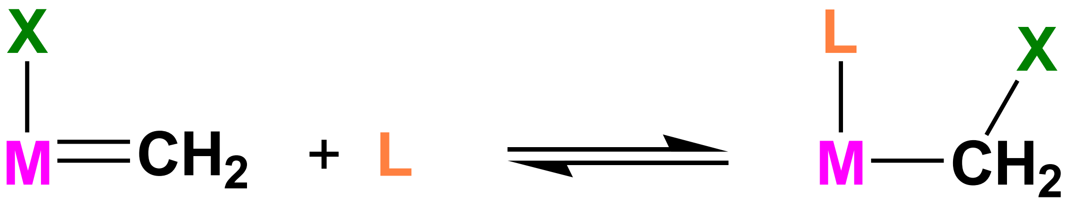
Migration of H to Alkenes (1,2):



This is the reverse of β-hydride elimination (see later).

N.B. Insertion of CO into a metal hydride is exceedingly rare as this is thermodynamically unfavourable.

Carbene-Alkylidene Migratory Insertions



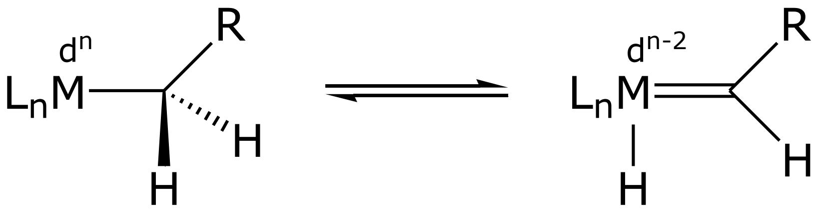
X = H^{-}, R^{-}, OR^{-}, halide^{-}

Normally a migratory insertion refers to a neutral ligand reacting with an anionic ligand to produce a new anionic ligand. But if we electron-count the carbene as a ***dianionic*** ligand (alkylidene), we are reacting a monoanionic ligand (**X**) with a dianionic ligand (alkylidene) to make a new monoanionic ligand. This changes the oxidation state of the metal center and is now formally a **reductive coupling reaction**.

In the case of **X** = H^{-}, the reverse reaction is called an α-hydride abstraction or elimination.

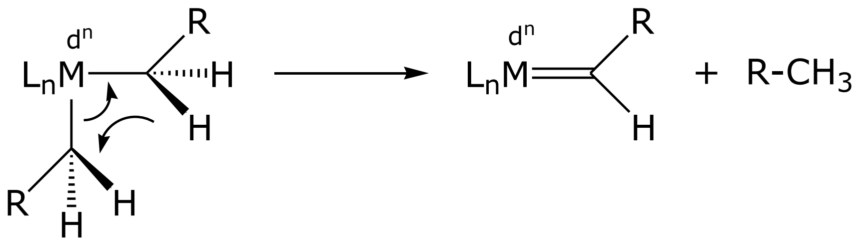
Elimination Reactions:

α-Hydride Elimination:



This is the transfer of a hydride from the α-position on a ligand to the metal centre. Formally, the process is a type of O.A. reaction. As the reaction involves a formal oxidation of the metal, α-elimination cannot occur in a d^0 or d^1 metal complex.

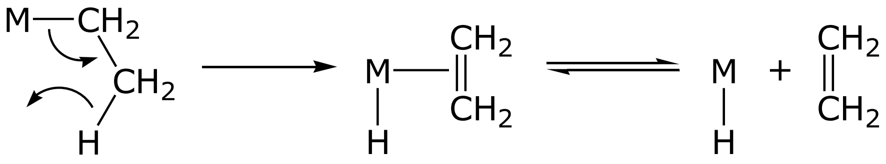
α-Hydride Abstraction:

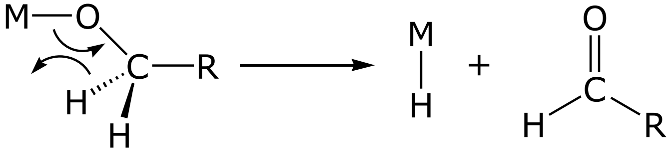


For d^0 and d^1 metal complexes α-abstraction does not result in a change in O.S. and the α-hydrogen transfers directly to an adjacent ligand instead of the metal centre.

β-Hydride Elimination:

β-hydride elimination is the most common way for a metal alkyl to decompose, and is the transfer of a hydride from the β-position on a ligand to the metal centre. While most common in alkyl complexes, it is also observed with other ligands, one example being alkoxides bound to late transition metals.

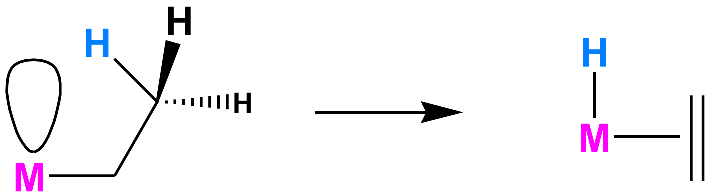




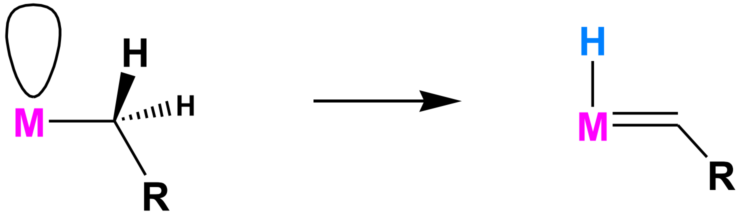
A complex must be coordinatively unsaturated for β-hydride elimination to occur. If no vacant site is available, ligand displacement must occur before the reaction can proceed. The metal complex must usually have < 18 electrons, otherwise a 20-electron alkene-hydride intermediate would be formed.

The microscopic reverse of β-hydride elimination is alkene insertion. In many systems there is a rapid, reversible equilibrium between the alkyl complex and the alkene-hydride that results from β-elimination. This is a very important chain termination step in the polymerisation of alkenes.

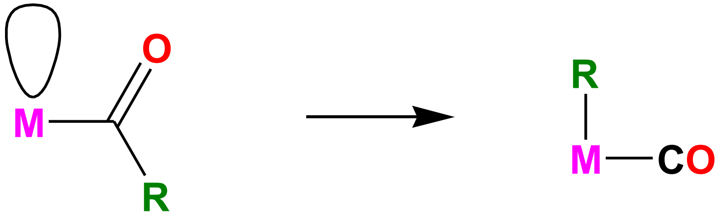
Elimination Reactions



β-hydride elimination



α-hydride elimination

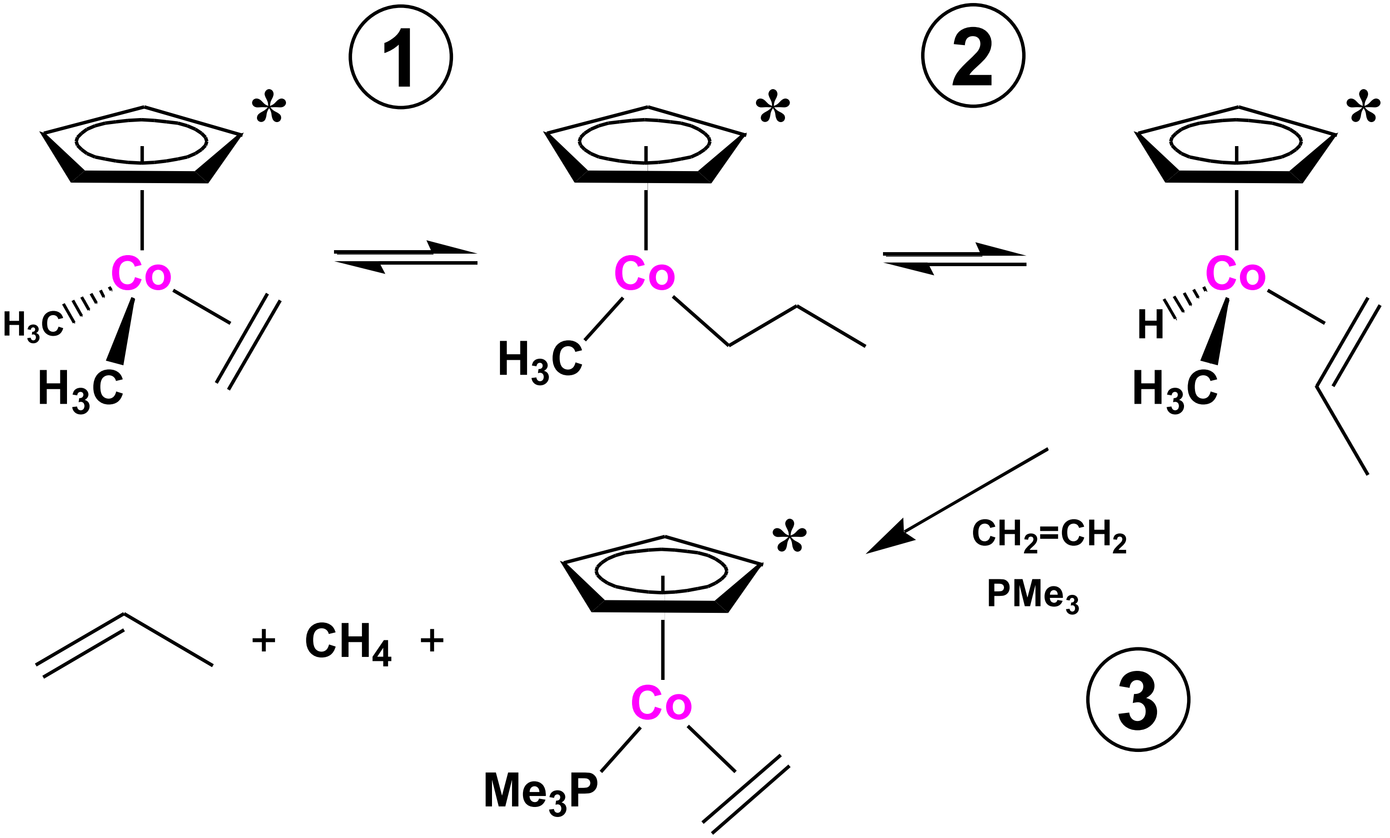


carbonyl elimination
***or* decarbonylation**

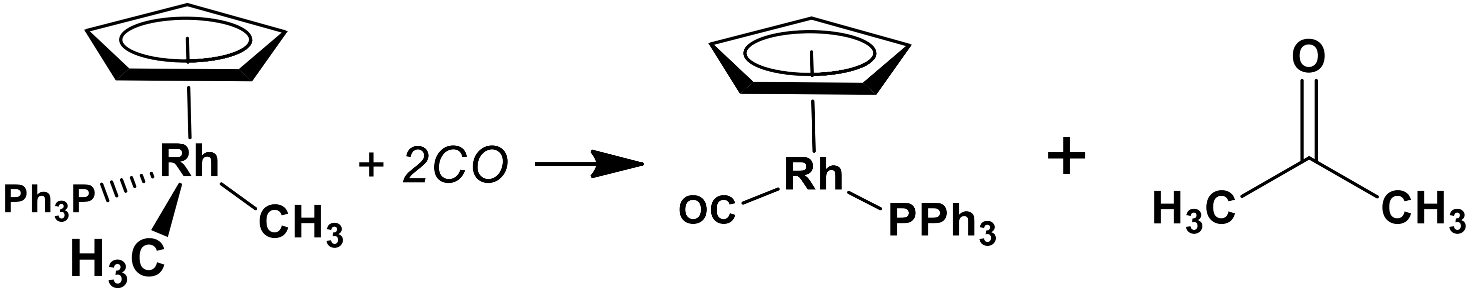
The key points are:

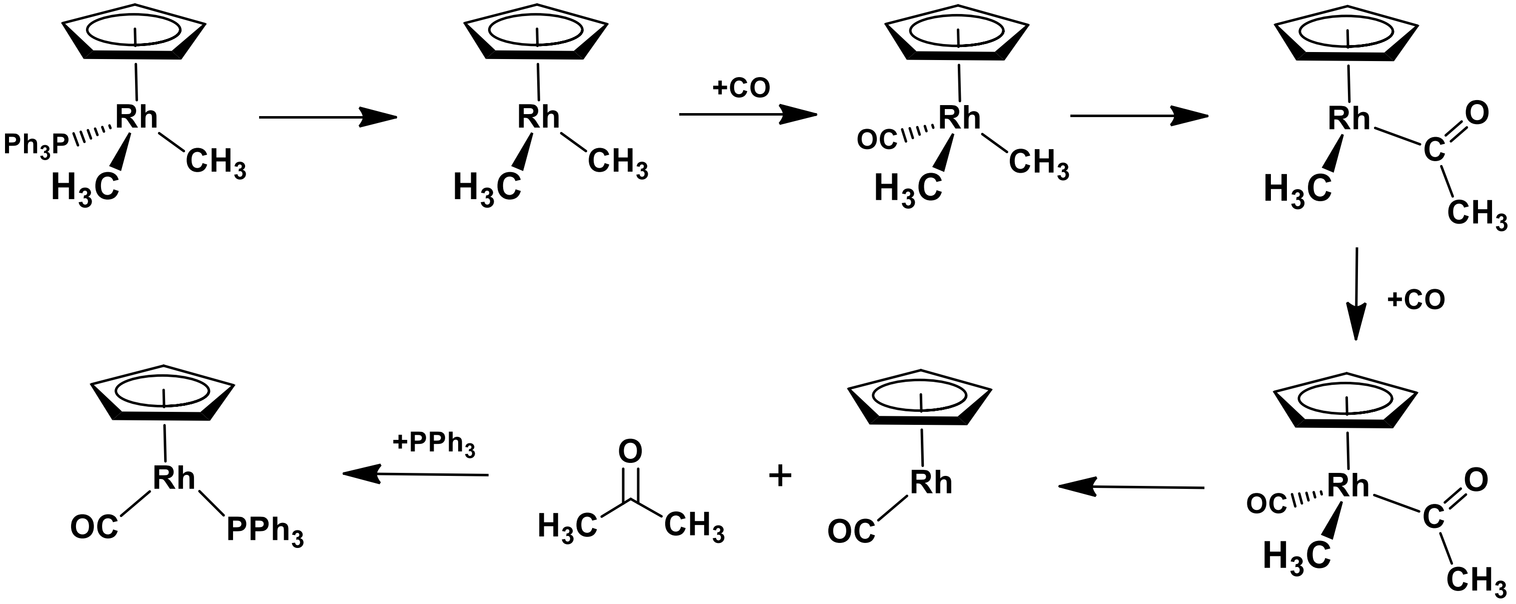
1) **No change in formal oxidation state (exception: alkylidenes)**
2) **You must have an empty orbital that is cisoidal to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.**

Problem: Identify each step in the following mechanism. Some steps may have several things occurring.



Problem: Sketch out a detailed mechanism and label each step for the following overall reaction.





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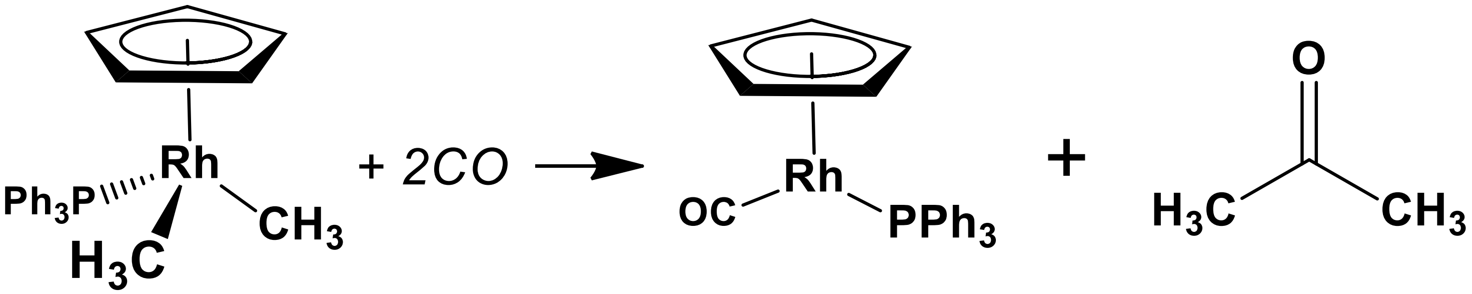
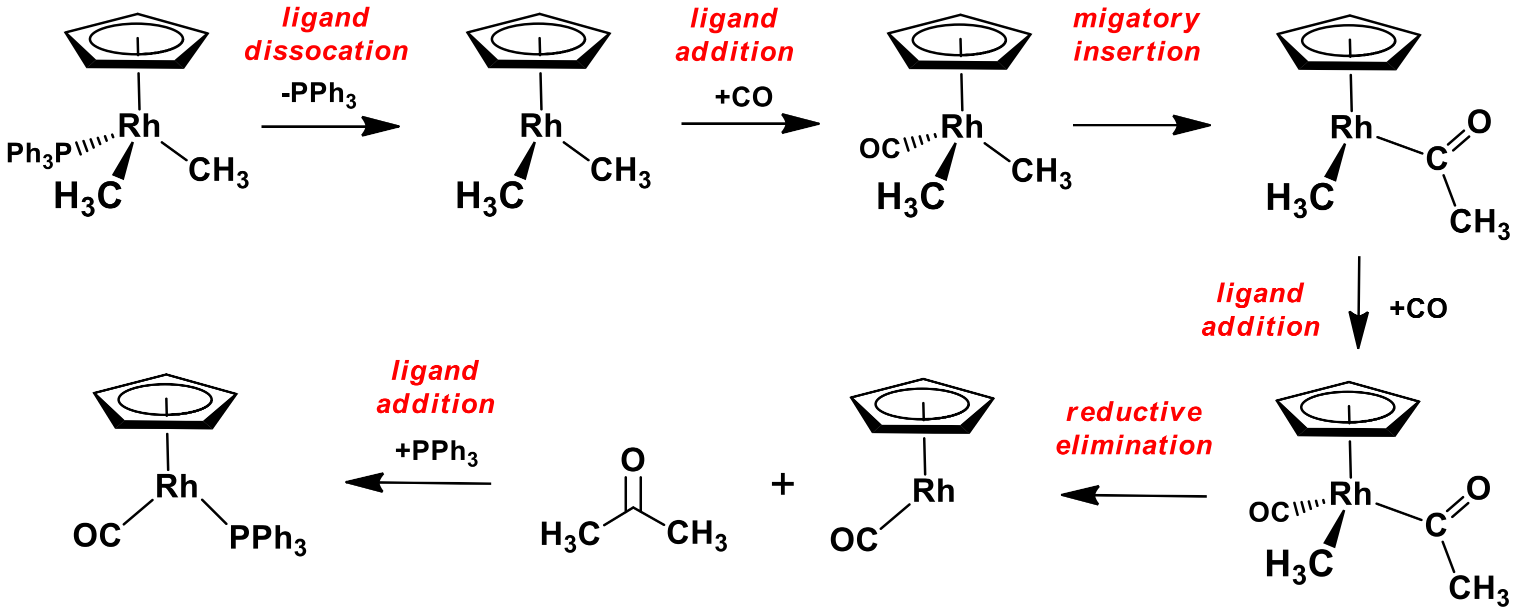
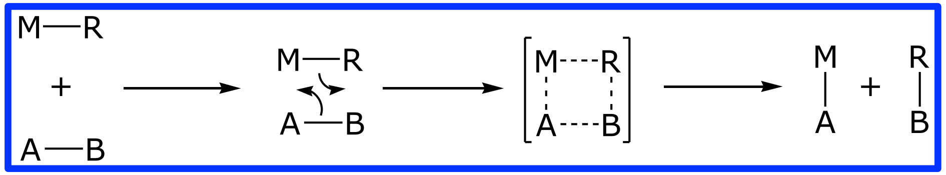




σ-Bond Metathesis:



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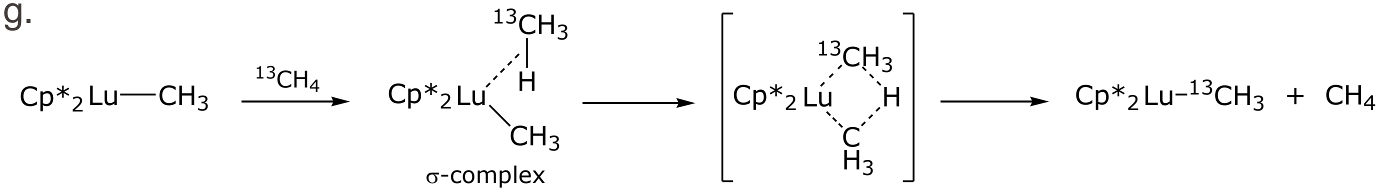
e.g.

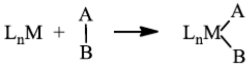
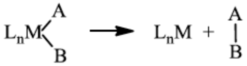
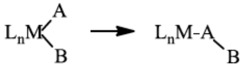
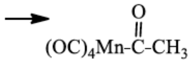
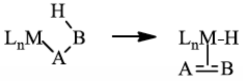


$Cp^*_2Sc{-}CH_3 + H_2 \longrightarrow Cp^*_2Sc{-}H + CH_4$

Watson, 1983

Bercaw, 1987

Summary of Principal Reaction Types:

		ΔVE	ΔOS	ΔCN	
Ligand association	$L_nM + L' \longrightarrow L_nM\text{-}L'$	+2	0	+1	$Pt(PPh_3)_3 + PPh_3 \longrightarrow Pt(PPh_3)_4$
Ligand dissociation	$L_nM\text{-}L' \longrightarrow L_nM + L'$	-2	0	−1	$Cr(CO)_6 \longrightarrow Cr(CO)_5 + CO$
Oxidative addition		+2	+2	+2	$IrCl(CO)(PPh_3)_2 + H_2 \longrightarrow IrCl(H)_2(CO)(PPh_3)_2$
Reductive elimination		-2	−2	−2	$IrCl(H)_2(CO)(PPh_3)_2 \longrightarrow IrCl(H)_2(CO)(PPh_3)_2 + H_2$
Migratory insertion		-2	0	−1	$(OC)_5Mn\text{-}CH_3 \longrightarrow$  $(OC)_4Mn\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3$
β-Elimination		+2	0	+1	$Cp_2Ta\text{-}CH_2\text{-}CH_3 \longrightarrow Cp_2Ta(H)(\eta^2\text{-}CH_2{=}CH_2)$