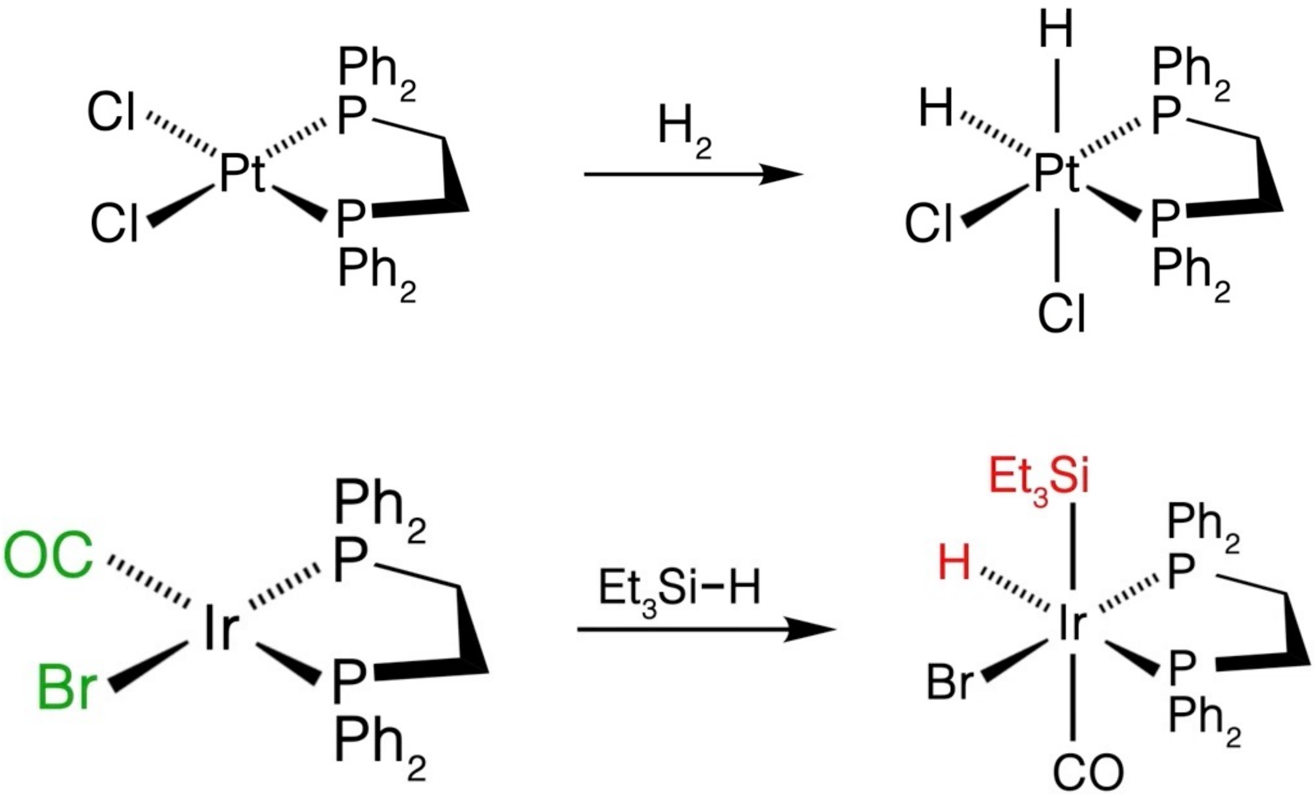
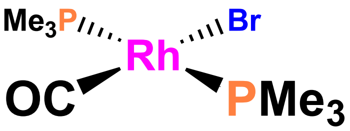

Cl
Cl
Pt
P
P
Ph$_2$
Ph$_2$
H$_2$
H
H
Pt
Cl
Cl
P
P
Ph$_2$
Ph$_2$
OC
Br
Ir
P
P
Ph$_2$
Ph$_2$
Et$_3$Si–H
Et$_3$Si
H
Ir
Br
CO
P
P
Ph$_2$
Ph$_2$

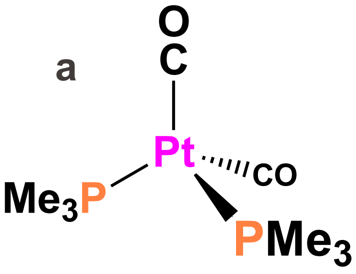
Oxidative additions are easy to identify **IF YOU ELECTRON COUNT** the metal complexes. When an oxidative addition rxn occurs the metal will be oxidized, usually by 2e-. So, if you start with a metal in the 0 oxidation state (d^8), after the oxidative addition the metal will be in the +2 oxidation state (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?

b)



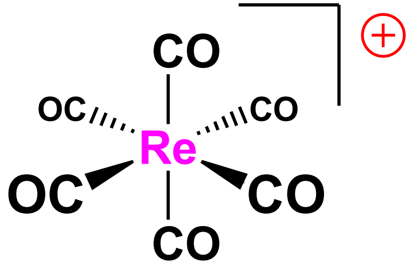
a



H_2 is a non-electrophilic substrate and needs an empty orbital (or an easily dissociable ligand) to pre-coordinate. a) is 18e- with strongly coordinating ligands and is eliminated as a choice. B is a 16e- complexes, B) is the far better choice as it is more electron-rich and can more easily do an oxidative addition.

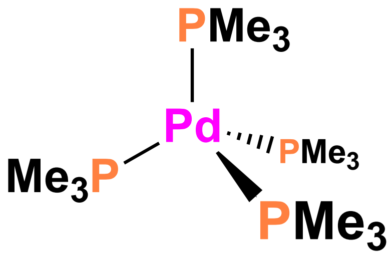
Problem: Cl_2 will do an **oxidative addition** most readily to which of the following complexes. Why?

a)



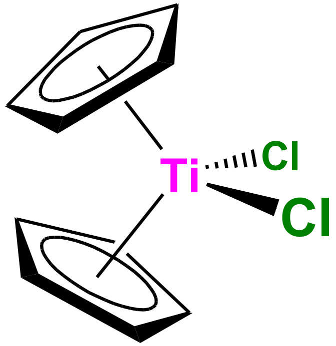
Re(I) d^6 18 EV

b)



Pd(o) d^{10} 18 EV

c)



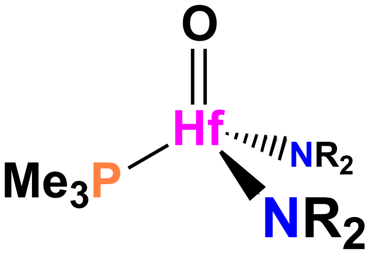
Ti(IV) d^0 16 EV

Cl_2 is a highly electrophilic & oxidizing substrate that can oxidatively add to an 18e- complex so long as it has filled d-orbitals and is sterically accessible. C) is d ^{0} and can't do an oxidative addition. Between A) and B), both 18e- complexes, B) is the far better choice as it is more electron-rich and can more easily do an oxidative addition.

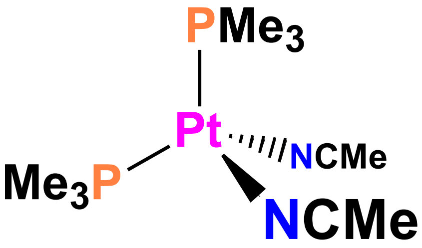
Problem: CH_3Br will do an **oxidative addition** most readily to which of the following complexes. Why?

Hf(IV)
d^0

a)



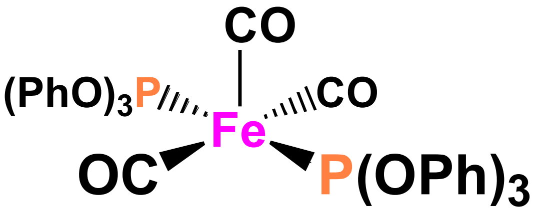
b)



Pt d^{10} +8 e =18

Fe d^8
10 +8=18

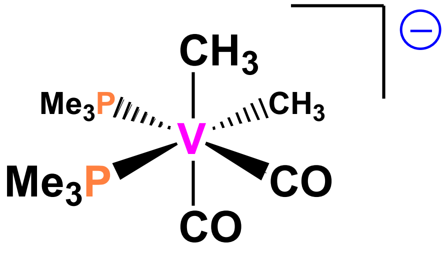
c)



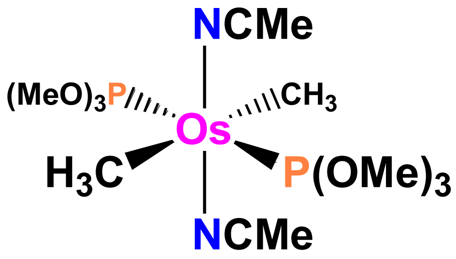
CH_3Br is an electrophilic substrate that can oxidatively add to an 18e- complex so long as it has filled d-orbitals and is sterically accessible. A) is d^0 and can't do an oxidative addition. Between B) and C), B) has the stronger σ-donor ligands and is more electron-rich.

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

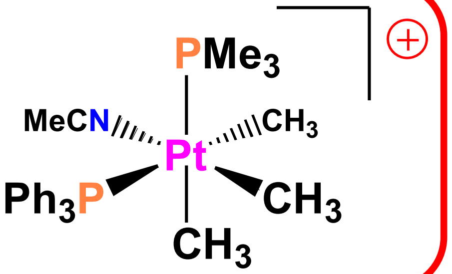
a)



b)

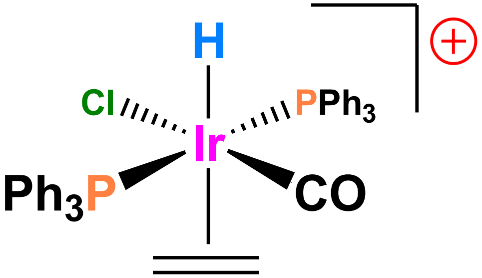


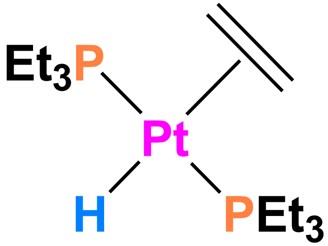
c)



Reductive eliminations are most favored from electron-poor complexes that have the two groups cisoidal to one another. A) is very electron-rich early transition metal complex that will not want to do a reductive elimination and go into the V(–1) oxidation state. B) has the two methyl groups trans to one another, making it more difficult to do a reductive elimination. C) has cis methyl groups and a cationic charge favoring reductive elimination to go from Pt(+4) to Pt(+2), a common oxidation state for Pt.

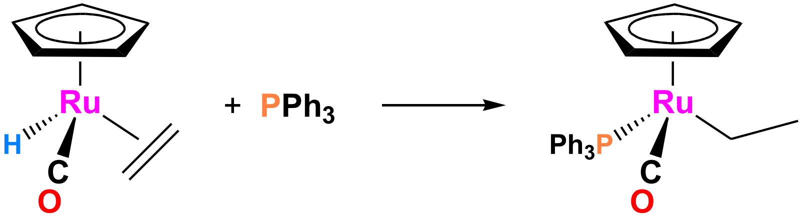
Problem: Why don’t either of the complexes shown below do alkene-hydride migratory insertions at room temperature?

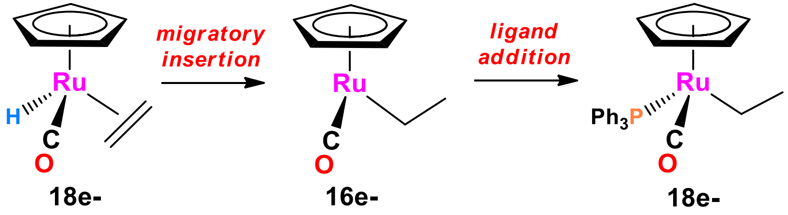




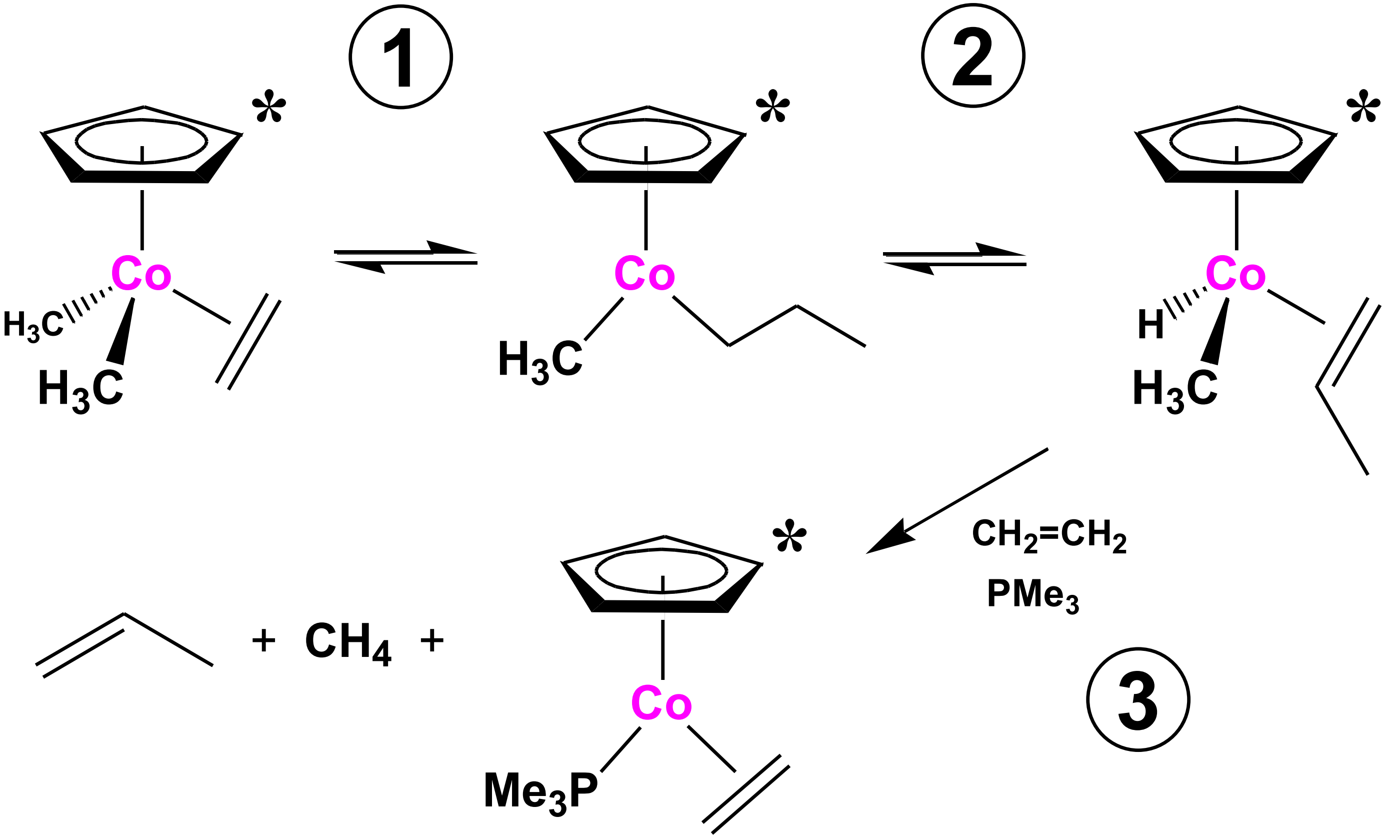
Both complexes have groups that are trans to one another. In order to do a migratory insertion the hydride and alkene must be cisoidal. Ligand rearrangements can occur to put them cis, but both of these complexes are third-row with relatively strong metal-ligand bonds that will make rearrangements less likely.

Problem: Sketch out and label the two mechanistic steps (in the correct order) that are occurring for the following reaction.

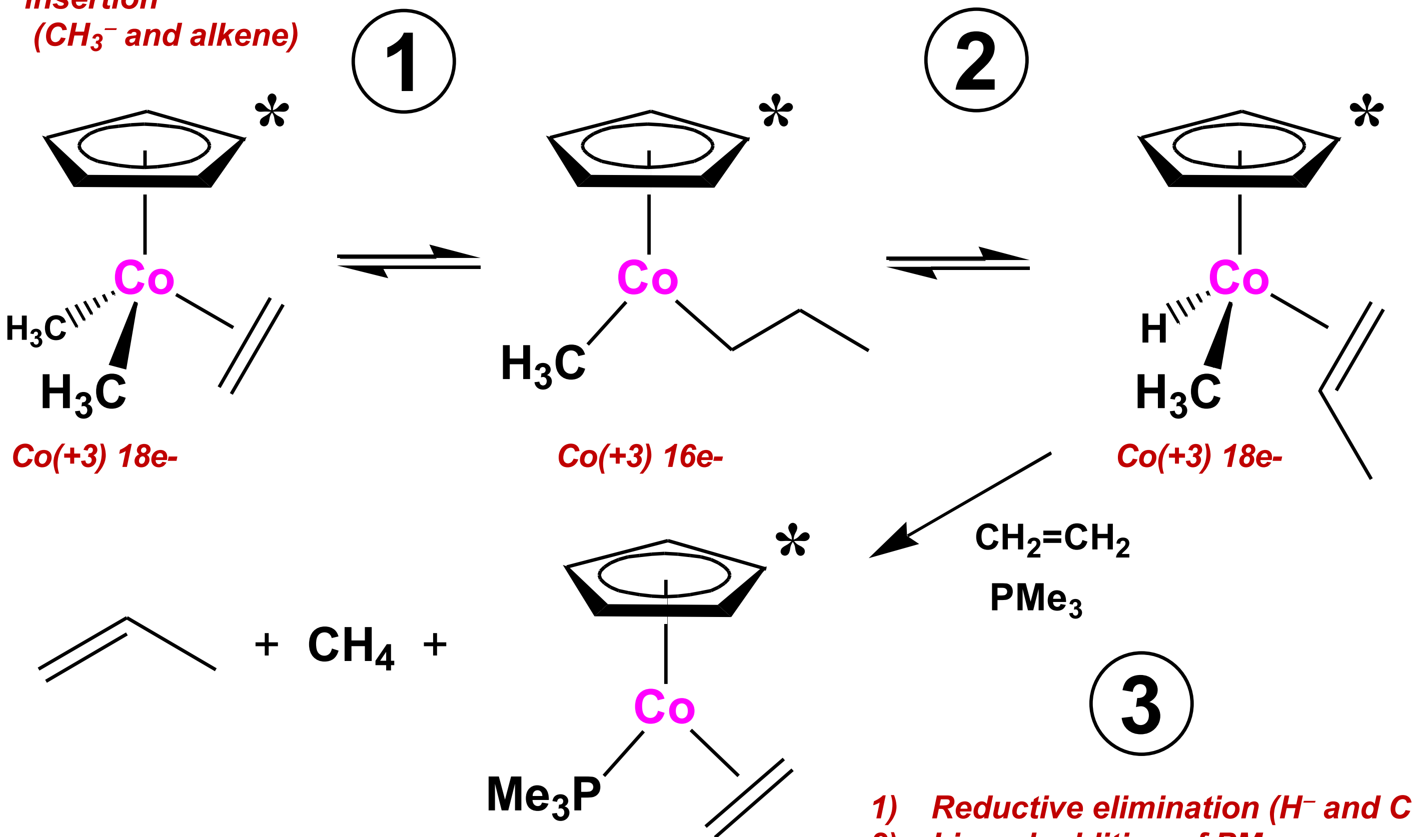




Problem: Identify each step in the following mechanism. Some steps may have several things occurring.



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



Migratory insertion (CH_3^- and alkene)

β-hydride elimination (propyl⁻ to H⁻ and propene)

Co(+3) 18e-

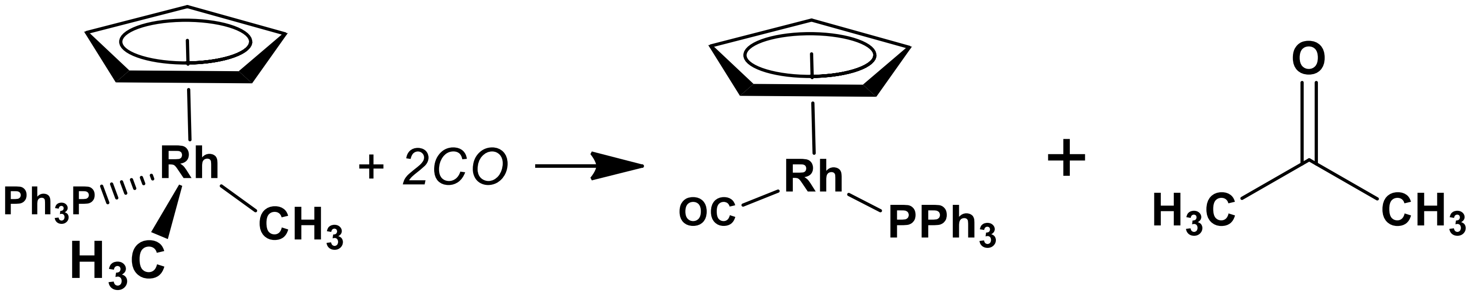
Co(+3) 16e-

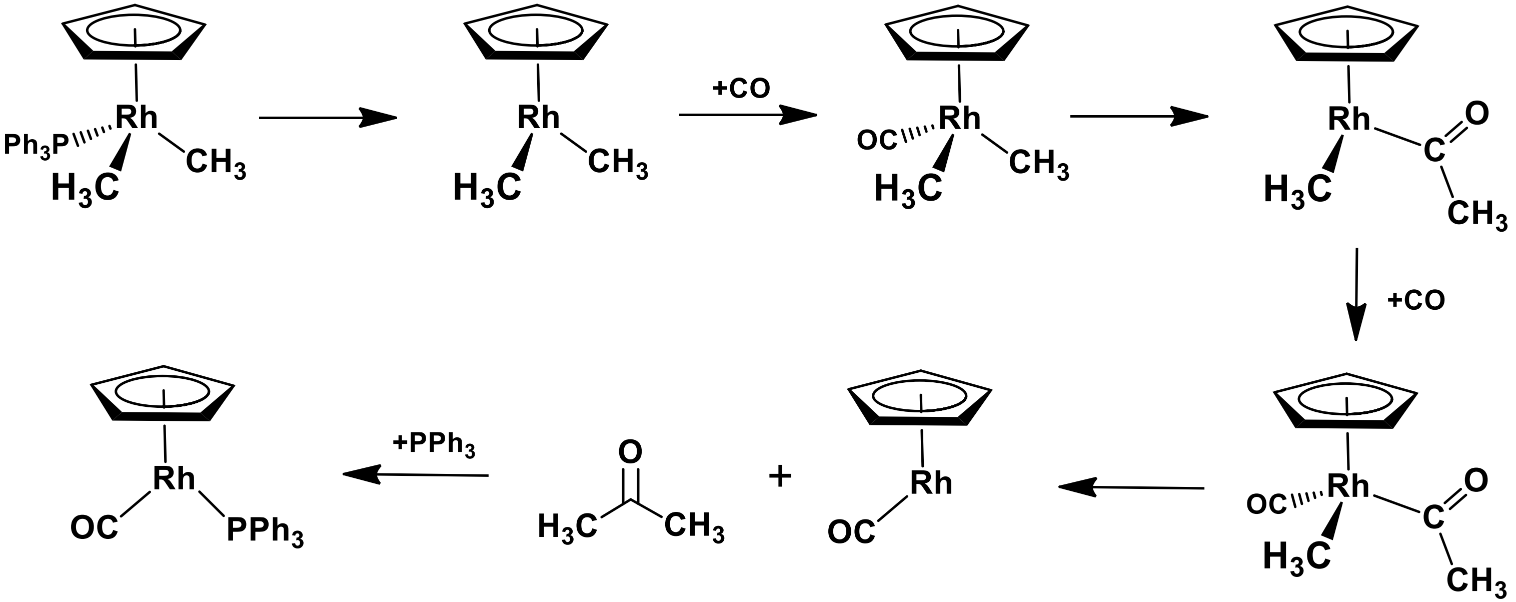
Co(+3) 18e-

Co(+1) 18e-

1) *Reductive elimination (H^- and CH_3^-)*
2) *Ligand addition of PMe_3*
3) *Dissociative substitution of propene with ethylene*

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





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