1. Classify the following reactions as migratory insertion, elimination, oxidative addition, reductive elimination, β-hydride elimination, oxidative coupling, reductive coupling, ligand substitution (associative or dissociative if important), ligand dissociation, ligand addition, etc. Note that there may be more than one step and classification per reaction. If there is more than one step to label, make sure you list the steps in the correct order if the order is important. NO discussion or justification is necessary.

a) $PtBr(CH_3)_3(PMe_3)_2 \longrightarrow PtBr(CH_3)(PMe_3)_2 + CH_3CH_3$

b) $CpRu(CH_2CH_3)(PPh_3)_2 \longrightarrow CpRu(H)(PPh_3)_2 + CH_2{=}CH_2$

c) $Cr(CO)_6 + PMe_3 \longrightarrow Cr(CO)_5(PMe_3) + CO$

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a) $$PtBr(CH_3)_3(PMe_3)_2 \longrightarrow PtBr(CH_3)(PMe_3)_2 + CH_3CH_3$$

1. **Ligand dissociation** **PMe_3)**
2. **Reductive elimination**
3. **Ligand association** **PMe_3)**

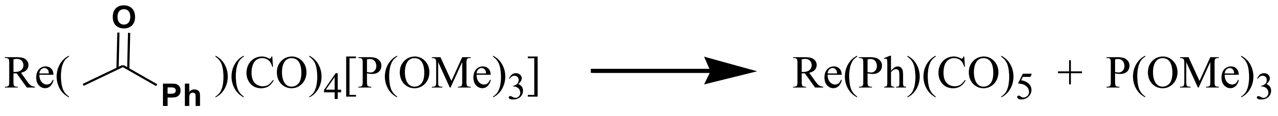
b) $$CpRu(CH_2CH_3)(PPh_3)_2 \longrightarrow CpRu(H)(PPh_3)_2 + CH_2{=}CH_2$$

1. **Ligand dissociation (PPh_3)**
2. **β-hydride elimination**
3. **Alkene ligand dissociation**
4. **Ligand addition (PPh_3)**

You must first have ligand dissociation, as this is an 18e- saturated complex. You need an empty orbital (16e- count or lower) to have a β-hydride elimination.

c) $$Cr(CO)_6 + PMe_3 \longrightarrow Cr(CO)_5(PMe_3) + CO$$

1. **Dissociative ligand substitution (18e- complex)**

d) 

$$Re(C(O)Ph)(CO)_4[P(OMe)_3] \longrightarrow Re(Ph)(CO)_5 + P(OMe)_3$$

1. P[OMe]$_3$ ligand dissociation

2. CO/Ph elimination from acyl

e) $CpRh(PMe_3)_2 + C_6H_6 \longrightarrow CpRh(C_6H_5)(H)(PMe_3) + PMe_3$

1. PMe$_3$ ligand dissociation
2. oxidative addition of benzene C-H bond

- $[Fe(CO)4]^{2-}$ reacts with CH_3Br to produce $[Fe(CH_3)(CO)_4]^-$ + Br–, but does ***not*** react with H_2. What kind of reaction this is, and why Br^- is not binding; why there is no reaction with H2.

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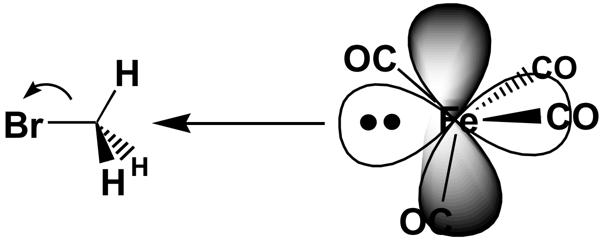
Answer: SN2 Oxidative Addition , Br- does not bind because the complex has 18 e-,
H_2 need an empty orbital at the metal center for concerted OA ,
not needed for CH_3Br

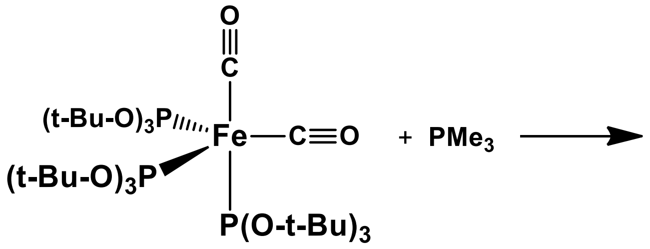
$[Fe(CO)_4]^{2-}$ is an 18e- complex. Although it has 4 electron-withdrawing CO ligands, the dianionic charge indicates that it is quite electron-rich. The CO's will be strongly π-backbonding and will not easily dissociate to make an unsaturated 16e- complex. In order to react with a non-electrophillic substrate, you need an empty orbital on the metal and enough d-electron density to do an oxidative addition reaction. Therefore, it will not react with H_2 due to the lack of an empty orbital (16e- or lower count) and too-strong Fe.

It can, however, directly react with CH_3Br to produce $[Fe(CH_3)(CO)_4]^-$ + Br^- because CH_3Br is an electrophillic substrate that can be directly attacked by one of the filled d-orbitals of an 18e- saturated metal complex (so long as it is not sterically blocked) to do a S_N2 type substitution and oxidative addition reaction. The Br- anion does not coordinate to the Fe because it attains an 18e- count when the CH_3 coordinates after the oxidative addition.

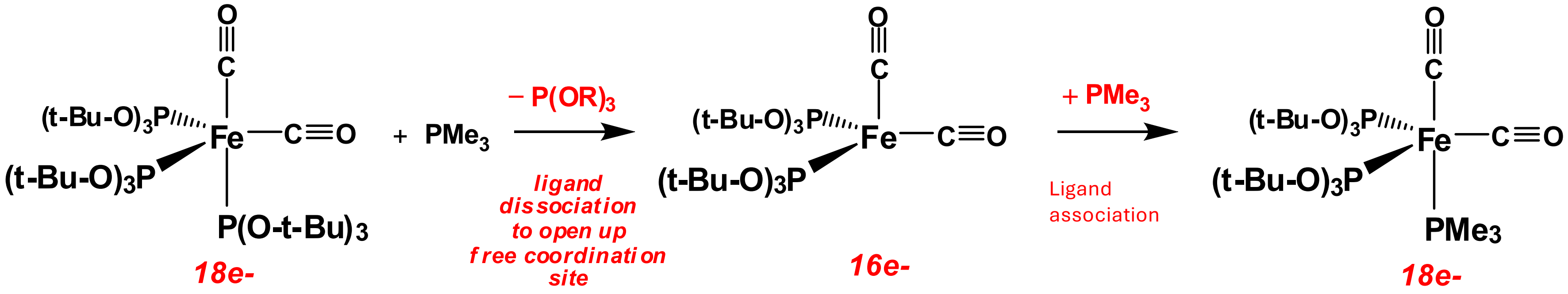


Consider the following two substitution reactions. Sketch out the most likely reaction steps to produce the most stable product (substitute only one ligand with that shown).

a)



a)



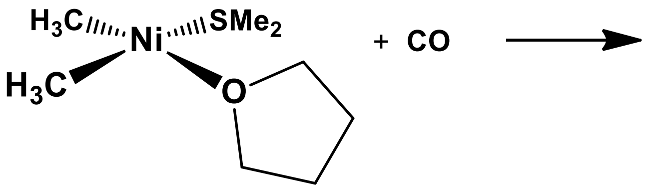
ligand dissociation to open up free coordination site

Ligand association

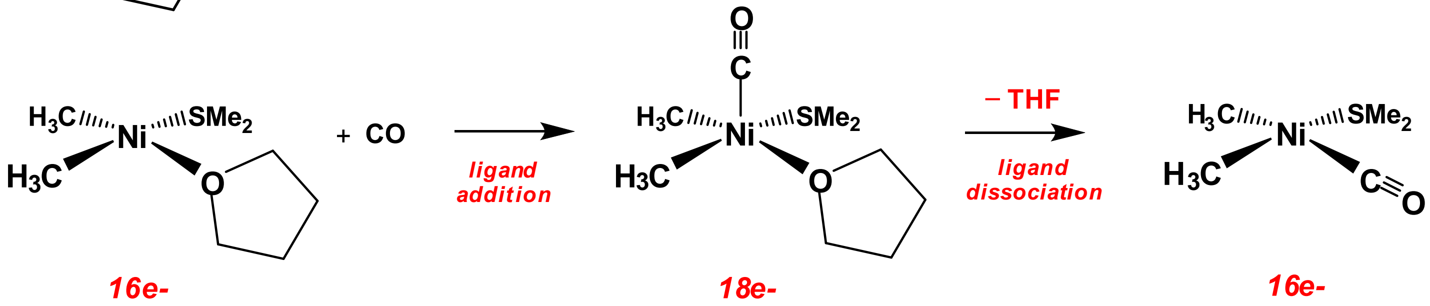
Since we are starting with an 18e- complex, we <u>have</u> to proceed by a dissociative substitution reaction. The phosphite ligand is the more weakly coordinated and somewhat bulky due to the t-butyl groups. Thus it is the most likely ligand to fall off first. This opens up a coordination site for the PMe_3 ligand to coordinate.

Consider the following two substitution reactions. Sketch out the most likely reaction steps to produce the most stable product (substitute only one ligand with that shown). Briefly & clearly state your reasoning/explanation for each reaction and the final product shown.

b)

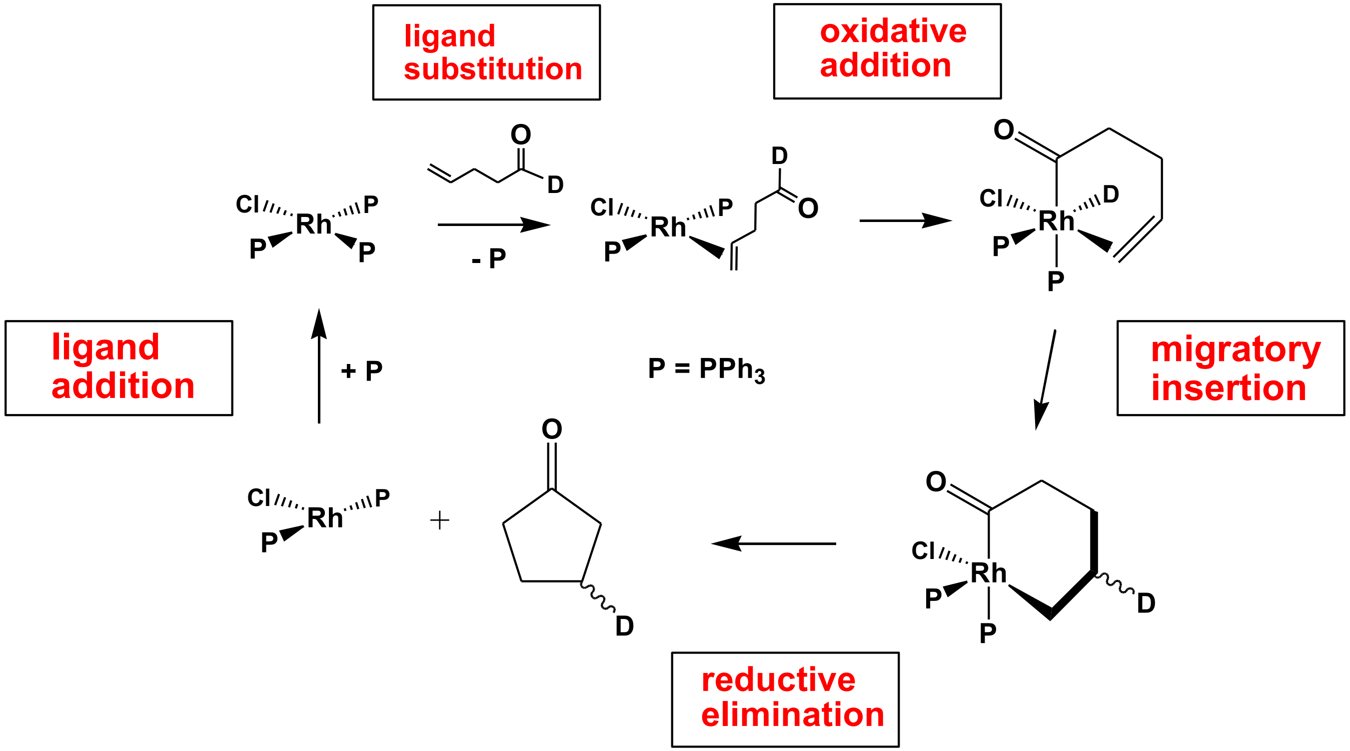


b)



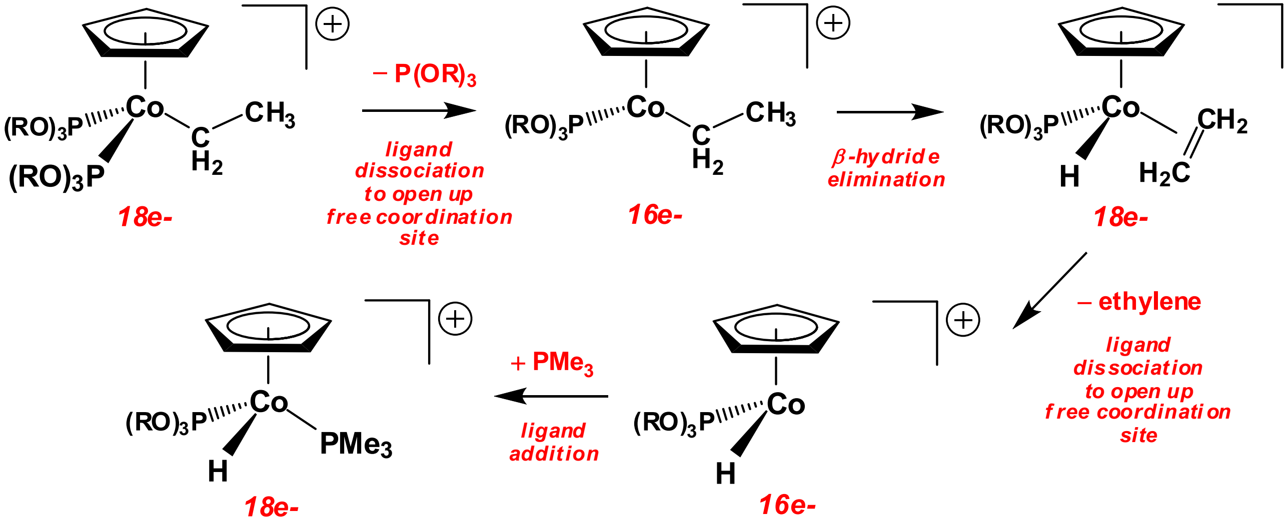
Since we are starting with a 16e- Ni complex without any steric problems we can proceed by an associative substitution reaction. Once the CO ligand coordinates, the weakest ligand that should fall off is the THF. Late transition metals have a far stronger preference for S over O-based ligands. I will also accept a dissociative mechanism where you lose a THF first to make a 14e- complex, then coordinate CO.

Label the reaction steps in the following catalytic cycle. Use the boxes provided and print clearly. The reactant is labeled with a deuterium to assist in tracking the mechanism. The squiggly line for the deuterium location on the product indicates that there is no specific stereochemistry associated with its placement. P = PPh_3



5. $[\mathrm{CpIr(Et)(dmpe)}]^+$ is quite stable while $[\mathrm{CpCo(Et)[P(OMe)_3]_2}]^+$ readily reacts with one equivalent of $\mathrm{PMe_3}$ to produce $\{\mathrm{CpCo(H)(PMe_3)[P(OMe)_3]}\}^+$ plus a gas that bubbles off the solution.

a) Write out a mechanism for the reaction of $[\mathrm{CpCo(Et)[P(OMe)_3]_2}]^+$ to form $\{\mathrm{CpCo(H)(PMe_3)[P(OMe)_3]}\}^+$.



The phosphite, $\mathrm{P(OR)_3}$, is the weakest coordinating ligand and can fall off the easiest promoting the β-hydride elimination rxn.

Why is [CpIr(Et)(dmpe)]$_+$ considerably more stable?

The strong chelating dmpe ($Me_2PCH_2CH_2PMe_2$) ligand will not easily dissociate to open up an empty orbital to allow β-hydride elimination to occur. The considerably more weakly coordinating phosphine ligand in (a) can far more easily dissociate allowing the β-hydride elimination to occur.