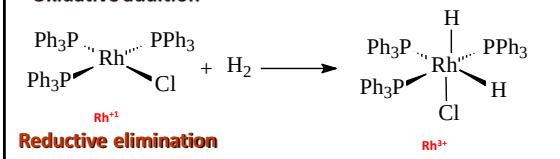
II. Reaction chemistry of complexes

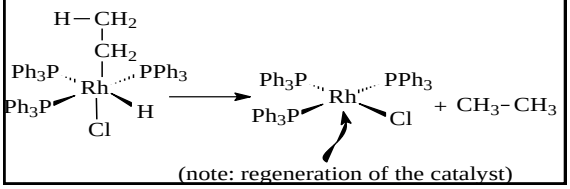
Three general forms:

1. **Reactions involving the gain and loss of ligands**
   - a. Oxidative Addition
   - b. Ligand Dissociation. and Association.
   - c. Reductive Elimination
   - d. Nucleophillic displacement
2. **Reactions involving modifications of the ligand**
   - a. Insertion
   - b. Carbonyl insertion (alkyl migration)
   - c. Hydride elimination (equilibrium)
3. **Catalytic processes by the complexes**
   - Wilkinson, Monsanto
   - Carbon-carbon bond formation (Heck etc.)

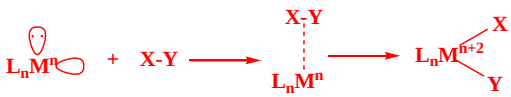
Oxidative addition

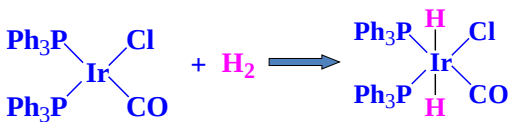


Reductive elimination



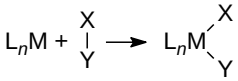
Oxidative addition





Oxidative Addition

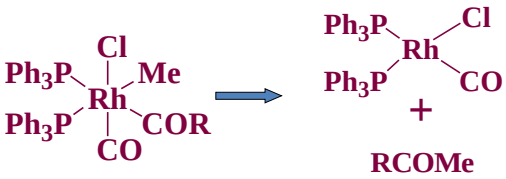
Basic reaction:



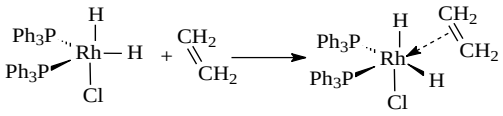
- Electron count changes by +/- 2 (assuming the reactant was not yet coordinated)
- Oxidation state changes by +/- 2
- Mechanism *may* be complicated The new M-X and M-Y bonds are formed using:
- the electron pair of the X-Y bond
- one metal-centered lone pair

(d) Reductive elimination

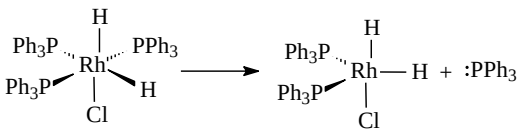
Involves decrease in the oxidation and coordination number



(b) Ligand Association

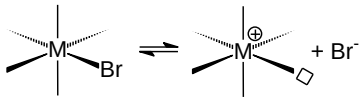


(b) Ligand Dissociation

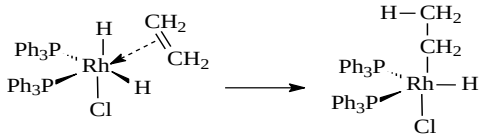


a) Ligand dissociation/association

- Electron count changes by -/+ 2
- No change in oxidation state
- Dissociation easiest if ligand stable on its own (CO, olefin, phosphine, Cl^-, ...)
- Steric factors important

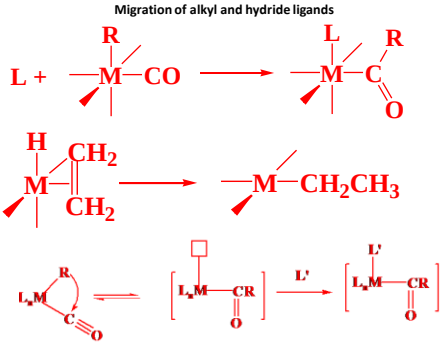


C- Migration/Insertion



(c) Insertion or migration

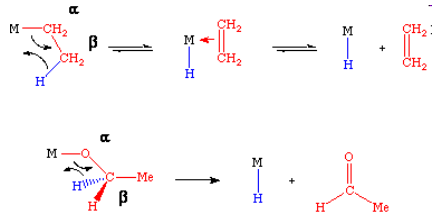
Migration of alkyl and hydride ligands



(e) Hydride elimination (usually by B hydrogens)

Many transition metal alkyls are unstable (the reverse of insertion) the metal carbon bond is weak compared to a metal hydrogen Bond Alkyl groups with β hydrogen tend to undergo β elimination

Two examples $M\text{-}CH_2\text{-}CH_3 \rightarrow M\text{-}H + CH_2{=}CH_2$



Ligand Substitution Rxns

"A mechanism is a theory deduced from the available experimental data. The experimental results are facts; the mechanism is conjecture based on those facts"
Lowry & Richardson

"You can never prove that your mechanism is right - only wrong."
Guy in the audience asking about your proposed mechanism

$$ML_n + xP \rightleftharpoons ML_{n-x}P_x + xL$$

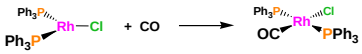
The mechanism of this substitution will almost always depend on whether the parent ML_n complex is coordinatively saturated or not!

Saturated Complex: Dissociative Pathway!

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

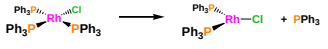
Most of the substitutions we will study will involve 2e- pathways. Odd e- or radical pathways are known, but less common.

Ligand Addition (association): this is when an incoming ligand coordinates to a metal center that has one or more empty orbitals available.

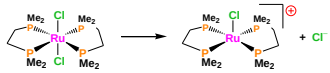


This Rh(+1) complex is d^8 and only 14e-. Adding a ligand takes one to the more stable 16e- square-planar complex.

Ligand Dissociation: this is when a ligand coordinated to a metal dissociates (falls off). The probability of a specific ligand dissociating depends on how strongly or weakly it is coordinated to the metal center and steric effects.

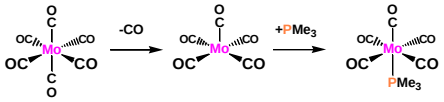


The steric hindrence of the three bulky PPh_3 ligands favors dissociation of one to form the 14e- $RhCl(PPh_3)_2$ complex. The moderate electron-donating ability of the PPh_3 ligand (not a strongly coordinating ligand) makes this fairly facile.

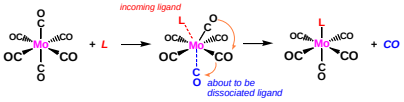


The strongly donating ability of the dmpe ligands combined with their strong chelate effect makes it difficult to dissociate one of the PMe_2 arms. In this case the Cl- anion is the one that dissociates, leaving a cationic complex behind. The two dmpe ligands donate enough electron-density to the Ru center to make it reasonable to dissociate a Cl-.

A **ligand substitution** can occur either by an ***associative*** or ***dissociative*** route. The exact mechanism depends in large part on the electron-count of the metal complex undergoing the ligand substitution. The simplest case is when one is dealing with an **18e-** metal complex. In this case one almost always has a ***dissociative substitution***.

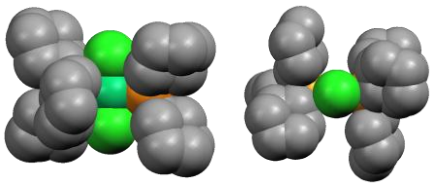


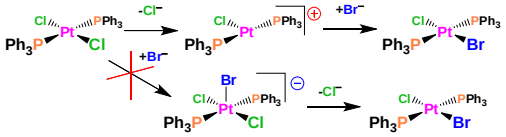
Almost NO evidence for this type of rxn:



Dissociative substitution can also occur in 16e- (or in very unusual cases, lower electron count systems) complexes. These cases either involve sterically bulky ligands that block the open coordination site, or third row square planar d^8 complexes like Pt(+2) where there are strong electronic factors that limit the coordination of an additional ligand to the empty axial site.

The large PCy_3 ligands sterically block access to the empty axial p_z orbital

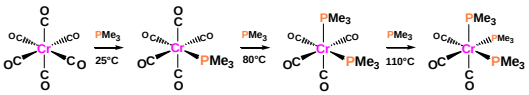




The spatially extended filled axial Pt d_{z^2} orbital partially blocks coordination of ligands via the empty axial p_z orbital. This limits ligand association, although it can occur.

Problem: The rate of substitution reactions on square planar d^8 complexes goes in the order: Ni > Pd >> Pt. Explain why.

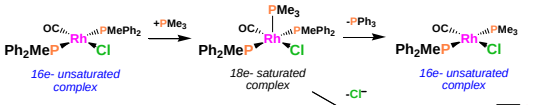
Problem: **Consider the following series of substitution reactions.**



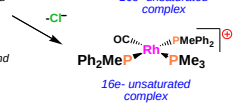
As one replaces each CO ligand with a PMe_3, the next CO substitution is progressively more and more difficult requiring higher temperatures and longer times. Once one forms $Cr(CO)_3(PMe_3)_3$, it is extremely difficult to replace another carbonyl ligand. Why? Give all the major reasons?

Associative Substitutions

These occur first by a **ligand addition** to the metal complex followed by the **dissociation** of one of the original ligands. You typically need to have an **unsaturated** (17e- or lower) **complex** in order to propose an associative substitution mechanism.



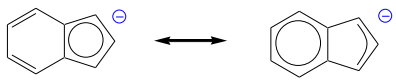
This rxn could proceed by two different likely substitution routes. Cl- is not that strong a ligand and can be substituted off by stronger donating neutral ligands like PMe_3.



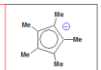
The filled axial Pt d_{z^2} orbital partially blocks coordination of ligands via the empty axial p_z orbital. This limits, but does not stop ligand association, which is quite common for Rh(I) and Pd(II).

Indenyl Effect

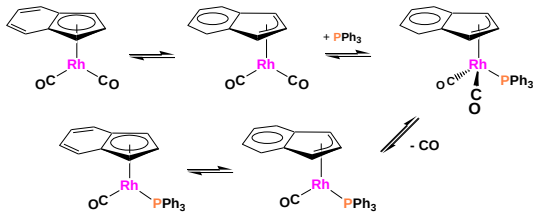
The indenyl ligand family, however, shows dramatically enhanced substitution reactions due to the ability to switch the aromaticity between the Cp and arene ring via the following resonance structures:



indenyl resonance/aromaticity switch

Ligand:					
Relative rate of substitution:	$> 10^{10}$	3.8×10^8	6.1×10^5	1	2.2×10^{-2}

The indenyl effect dramatically lowers the barrier for the η^5-Cp to η^3-Cp resonance structure, opening up a free coordination site and allowing far easier ligand additions and substitution reactions.

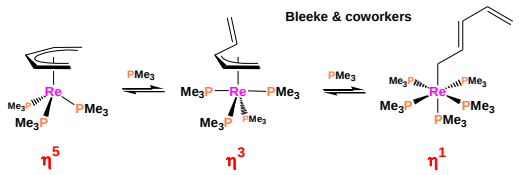


Pentadienyl

The pentadienyl ligand is an acyclic version of Cp that does not have any aromatic stabilization. This has two important effects:

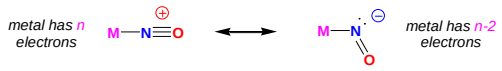
1) No aromatic stabilization means that the π-orbitals are higher in energy and are, therefore, better donors than Cp^-. Similarly, the π*-antibonding orbitals are lower in energy and are better π-acceptors than Cp^- (but the low electronegativity limits the amount of π-backbonding that can occur).
2) The lack of aromatic stabilization means that there is a much smaller barrier for η^5-pentadienyl ⇌ η^3-pentadienyl ⇌ η^1-pentadienyl transformations.

Bleeke & coworkers

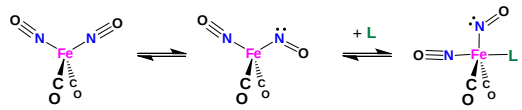


Nitrosyl

We usually count the nitrosyl ligand as a cationic 2e- donor, isoelectronic with CO. But it can adopt an anionic 2e- configuration with a bent coordination geometry:

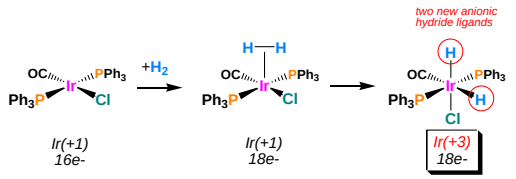


The nitrosyl ligand can shift from linear to bent, cationic to anionic, and open up a coordination site on the metal by essentially oxidizing it (shuttling 2e- from the metal to the NO^+ turning it into NO^-). The linear NO^+ form can usually be easily differentiated from the bent anionic form by IR spectroscopy because of the large change in NO bond order (triple to double bond).



18e- (Fe^{2-}) 16e- (Fe^0) 18e- (Fe^0)

Oxidative Addition/Reductive Elimination



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

- Non-Electrophillic
- Non-Electrophillic "Intact"
- Electrophillic

Non-electrophillic: 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.

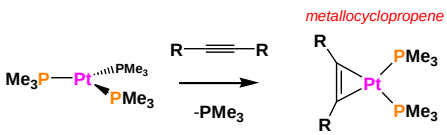
H_2 is by far the most important for catalytic applications, followed by Si-H bonds, B-H, N-H, and S-H bonds.

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

Non-electrophillic "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 **electrophillic** substrate):

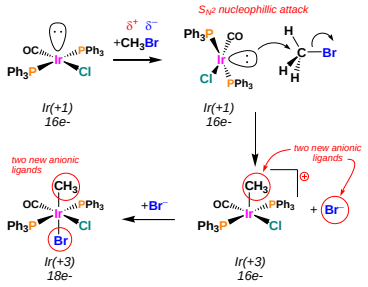
alkenes, alkynes, and O_2



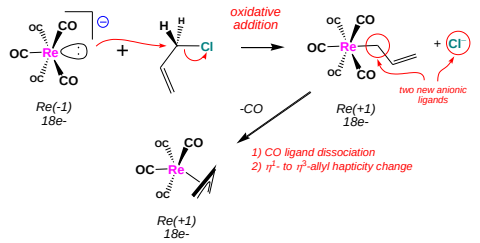
Electrophillic: these molecules ***do*** contain electro-negative atoms and are good oxidizing agents. They are often considered to be *"reactive"* substrates.

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.



In the case of a starting **18e-** complex (shown below) only ***one*** of the two anionic ligands (usually the strongest binding) generated from the oxidative addition will end up coordinated to the metal unless a separate substitution reaction occurs.



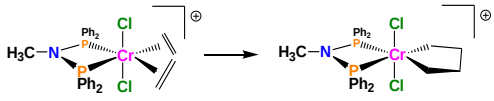
WARNING:

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.**

Oxidative Coupling

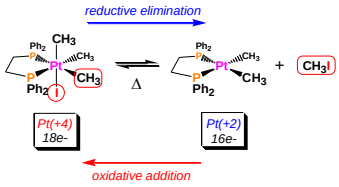


Cr(+3) d^3 **15e-** **Cr(+5) d^1** **13e-**

The Cr on the right now has two new anionic alkyl ligands forming a metallocyclopentane ring system. We have done an oxidative addition, but in forming a new bond between the two ethylene ligand (and losing the original double bonds) we have coupled the two ligands together.

While this is an oxidative addition, there is a special term for this type of reaction called **oxidative coupling**. The metal is being oxidized to create two new anionic ligands, but the original two neutral ligands also form a new bond between them, instead of fragmenting apart to make two new independent anionic ligands.

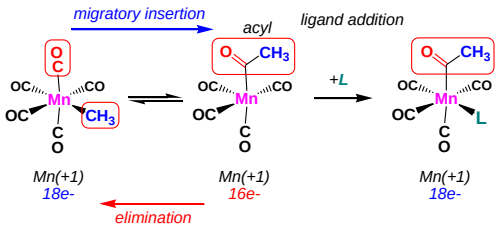
In studying the above system, it was also found that one could have reductive elimination of CH_3I from the starting 18e- complex. This reaction, however, is very reversible due to the high reactivity of CH_3I for doing an oxidative addition back reaction with the electron-rich neutral Pt(+2) complex to make the Pt(+4) octahedral compound.



The reductive elimination of the CH_3I is kinetically favored. This is because the orbitals around the iodide anion are spherically symmetric and this makes it much easier to overlap with the alkyl group orbital to perform the reductive elimination. The sp^3 directed orbitals on the two CH_3 groups are more difficult to overlap in order to get the reductive elimination to occur. But the reductive elimination of the CH_3CH_3 is thermo-dynamically considerably more favorable and the back oxidative addition much more difficult.

Migratory Insertion & Elimination Rxns

A ***migratory insertion*** reaction is when a **cisoidal anionic and neutral** ligand on a metal complex couple together to generate a new coordinated **anionic** ligand**.** This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another. ***There is NO change in the oxidation state or d electron-count of the metal center.***



General Features of Migratory Insertions:

1) No change in formal oxidation state (exception: alkylidenes)

2) The two groups that react must be cisoidal to one another

3) A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g., β-hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the back elimination reaction.

4) Migratory insertions are usually favored on more electron-deficient metal centers.

The following are common **anionic** and **neutral** ligands that can do ***migratory insertion*** reactions with one another:

Anionic: H^-, R^- (alkyl), Ar^- (aryl), $acyl^-$, O^{2-} (oxo)

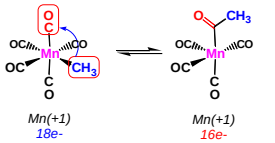
Neutral: CO, alkenes, alkynes, carbenes

CO and alkyl migratory insertions (as shown on previous slide) are extremely important and are often generically referred to as **carbonylation** reactions.

Hydride and CO migratory insertions to produce formyl groups are not common due to the *thermodynamic instability* of the formyl-metal interaction.

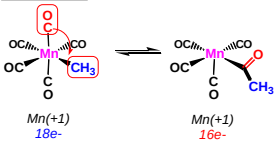
Migration vs. Insertion

Migration



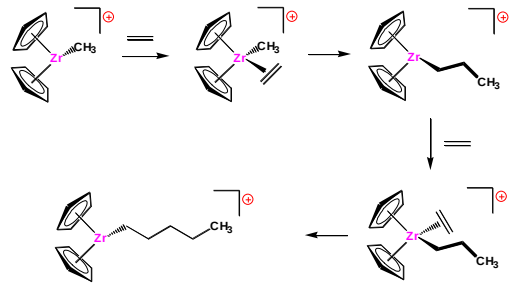
a MIGRATION rxn involves the anionic ligand doing a nucleophillic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

Insertion

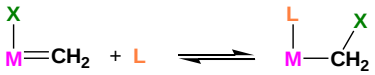


an INSERTION rxn involves the neutral ligand moving over to where the anionic ligand is coordinated and "inserting" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind from where the neutral ligand originally was located.

Alkene Migratory Insertions



Carbene-Alkylidene Migratory Insertions

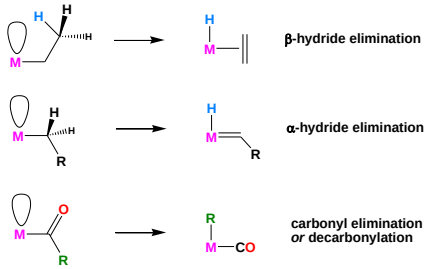


X = H^-, R^-, OR^-, halide$^-$

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.

Eliminations



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.**

Identify the following reactions by their type (migratory insertion, elimination, oxidative addition, reductive elimination, substitution, ligand addition, ligand dissociation, B-hydride elimination, ligand coordination change, etc.). Note that one may have to use more than one description for a reaction that may have several steps. For reactions with several steps, if the order is important you must list the steps in the correct order.

a) $Cp^*Ir(CO)_2 + CH_4 \xrightarrow{h\nu} Cp^*Ir(CO)(H)(CH_3) + CO$

b) $RhCl(PPh_3)_3 + dppe + CO \longrightarrow RhCl(CO)(dppe) + 3PPh_3$

c) $H_2RhCl(PPh_3)_2(CH_2CH_3) \longrightarrow HRhCl(PPh_3)_2 + CH_3CH_3$

d) $[Co(CO)_4]^- + CH_3Br \quad Co(CO)_4(CH_3) + Br^-$

e) $Mn(acyl)(CO)_5 + H_2 \longrightarrow HMn(CO)_5 +$ 

f) (η^5-indenyl)$Re(PMe_3)_3 + CO \longrightarrow$ (η^5-indenyl)$Re(CO)(PMe_3)_2 + PMe_3$

g) $Cp_2Hf(CH_3)_2 + H_2 \longrightarrow Cp_2Hf(H)(CH_3) + CH_4$

h) $H_2Ru(CO)_4 + CH_2{=}CH_2 \longrightarrow HRu(CH_2CH_3)(CO)_3 + CO$

a) $Cp^*Ir(CO)_2 + CH_4 \xrightarrow{h\nu} Cp^*Ir(CO)(H)(CH_3) + CO$

1) CO ligand dissociation (promoted by photolysis)

2) oxidative addition of methane C-H bond

Ir(+1) going to Ir(+3) indicates an oxidative addition rxn. CH_4 is a non-polar substrate and needs an empty orbital on the metal to bind to prior to oxidative addition.

b) $RhCl(PPh_3)_3 + dppe + CO \longrightarrow RhCl(CO)(dppe) + 3PPh_3$

1) PPh_3 substitution with CO

2) <u>two</u> PPh_3 substitutions by dppe (one arm at a time)

The first PPh_3 substitution probably occurs via a dissociative route due to the steric bulk of the 3 PPh_3 groups. The incoming order of CO or dppe is not important.

c) $H_2RhCl(PPh_3)_2(CH_2CH_3) \longrightarrow HRhCl(PPh_3)_2 + CH_3CH_3$

1) reductive elimination

Rh(+4) going to Rh(+2). One could also first have a ligand dissociation of PPh_3 or Cl- to help promote the reductive elimination rxn. But the dissociated ligand needs to recoordinate after the reductive elimination.

d) $[Co(CO)_4]^- + CH_3Br \longrightarrow Co(CO)_4(CH_3) + Br^-$ **1) oxidative addition**

Co(−1) going to Co(+1) indicates an oxidative addition rxn. CH_3Br is an electrophillic reactive substrate that can react directly with an 18e- metal center via an S_N2 type attack of the metal on the CH_3-side of CH_3Br. This ejects the Br^- anion that does not coordinate to the metal since it is 18e- and does not need another ligand.

e) $Mn(acyl)(CO)_5 + H_2 \longrightarrow HMn(CO)_5 +$ 

1) CO ligand dissociation
2) oxidative addition of H_2
3) reductive elimination of H^- and acyl$^-$
4) CO ligand addition

This is a bit tricky because there appears to be no change in the oxidation state on the Mn. But the major rxn of H_2 with a $d^{2\text{-}10}$ metal is via oxidative addition. You need an empty orbital to do this because H_2 is a non-electrophillic reagent, thus the initial CO ligand dissociation from the 18e- starting complex.

f) $(\eta^5\text{-indenyl})Re(PMe_3)_3 + CO \longrightarrow (\eta^5\text{-indenyl})Re(CO)(PMe_3)_2 + PMe_3$

1) η^5- to η^3-hapticity (ligand coordination) change
2) CO ligand addition
3) PMe_3 ligand dissociation
4) η^3- to η^5-hapticity change

The indenyl ligand can readily change its hapticity from η^5 to η^3. This opens up a free coordination site on the metal allowing ligand addition.

a) $CpIrCl(\eta^3\text{-allyl}) + PMe_3 \longrightarrow CpIrCl(PMe_3)(\eta^1\text{-allyl})$

1. Ligand coordination change (η^3-allyl to η^1-allyl)
2. PMe_3 ligand addition.

b) $CpRh(CO)_2 + CF_3CF_2Br \longrightarrow CpRh(CO)(CF_2CF_3)Br + CO$

1. oxidative addition to produce $[CpRh(CO)_2(CF_2CF_3)]^+$ (18e-) + Br^-
2. CO ligand dissociation (favored by higher oxidation state and cationic charge on Rh)
3. bromide ligand addition

c) $H_2Rh(PPh_3)_2(Cl)(CH_2CH_3) \longrightarrow HRh(PPh_3)_2(Cl) + CH_3CH_3$

reduction elimination of H and CH_2CH_3
- or –
1. PPh_3 ligand dissociation (makes 16e- metal that is more likely to reductively eliminate)
2. reduction elimination of H and CH_2CH_3
3. PPh_3 ligand addition

d) $CpFe(CO)_2(Me) + PPh_3 \longrightarrow CpFe(CO)(acyl)(PPh_3)$ (acyl =)

1. migratory insertion of CO and Me ligands to make acyl
2. PPh_3 ligand addition

e) $PtCl_2(CH_2CH_3)_2(PMe_3)_2 \longrightarrow PtCl_2(PMe_3)_2 + CH_2{=}CH_2 + CH_3CH_3$

1. Cl^- ligand dissociation (must make empty orbital for β-hydride elimination, Cl^- is weakest binding ligand)
2. β-hydride elimination to make Pt-H(ethylene) complex
3. $CH_2{=}CH_2$ ligand dissociation
4. reduction elimination of H and CH_2CH_3 (steps 3 and 4 in either order)
5. Cl^- ligand addition

f) $[Cp_2Mo(H)(CH_2{=}CH_2)]^+ + PPh_3 \longrightarrow [Cp_2Mo(CH_2CH_3)(PPh_3)]^+$

1. migratory insertion of H and ethylene ligand to make Mo-CH_2CH_3
2. PPh_3 ligand addition

g) $Cp_2Hf(CH_3)_2 + H_2 \longrightarrow Cp_2Hf(H)(CH_3) + CH_4$

1) hydrogenolysis — *d^0 metals can NOT do an oxidative addition rxn.*

h) $H_2Ru(CO)_4 + CH_2{=}CH_2 \longrightarrow HRu(CH_2CH_3)(CO)_3 + CO$

1) ligand dissociation
2) alkene ligand coordination
3) migratory insertion of hydride with alkene

The product is 16e- and would probably need to re-coordinate the dissociated CO (or another ligand) to get back to 18e-.

For each pair of complexes shown below, circle the one that should be the most reactive towards the oxidative addition the substrate shown. Give a brief but clear explanation for your choice.

We are looking for the most electron-rich complex that has an empty orbital and at least 2 d electrons. For non-electrophillic reactants we also need an empty orbital to pre-coordinate the reactant.

a) $[Co(dmpe)_2]^+$ -or- $[Rh(dppe)_2]^+$ Substrate = H_2

The dmpe ligands are considerably stronger donors compared to dppe, so the Co complex will be easier to oxidize. This over-rides the higher electronegativity of the Co center. Both complexes have a 16e- count.

b) $RhCl(PPh_3)_3$ -or- $RhCl(CO)(PPh_3)_2$ Substrate = CH_3CH_2Br

Although the three PPh_3 ligands make the first Rh complex more electron-rich, the steric bulk of the three PPh_3 ligands is more important for the more sterically hindered CH_3CH_2Br substrate.

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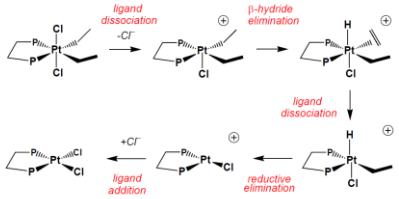
c) $Co(CO)(PEt_3)_2Cl$ -or- $Ir(CO)(PMe_3)_2Br$ Substrate = $HSiMe_3$

The Ir is less electronegative and the Br^- is a stronger donating ligand relative to Cl^-. PEt_3 is a slightly stronger donating ligand, but this probably would not compensate for the bromide ligand and lower electronegativity of the Ir center. Sterics is also important here due to the shorter Co-ligand bonds and the larger PEt_3 ligand. Both complexes have a 16 e- count.

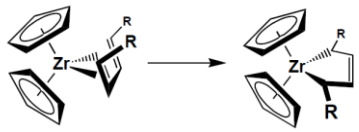
d) $Cr(CO)_6$ -or- $W(CH)(CH_3)_3(dmpe)$ Substrate = CH_3Cl

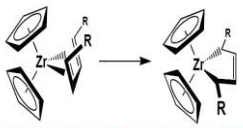
The W complex is d^0 and can't do an oxidative addition reaction. CH_3Cl is an electrophillic substrate and does not need an empty orbital on the Cr center.

Consider the following reaction:
$PtCl_2(CH_2CH_3)_2(dmpe) \rightarrow PtCl_2(dmpe) + CH_2{=}CH_2 + CH_3CH_3$
Show in detail each mechanistic step in the conversion to the product species shown. Label and clearly identify each step. The order of the steps may be important – if so list them in the correct order when necessary.



Consider the reaction shown below. Clearly describe what is happening from a reaction viewpoint. What kind of electronic effect R groups (electron-withdrawing or electron-donating) on the diene ligand will favor formation of the product? Why?





Oxidative Addition

Zr(+2, d^2) is being oxidized to Zr(+4, d^0). The diene ligand is accepting the two electrons from the Zr to become a dianionic ligand. Note that we have broken a bond in the diene (two double bonds down to one double bond).

*Electron-withdrawing R-groups on the diene will **favor** the oxidative addition by helping the not very electronegative diene to attract the electrons from the metal. Normally one does want to have electron-donating ligands on the metal to help favor oxidative addition reactions and putting electron-donating groups on the Cp- rings will help make the metal more electron-rich and make the oxidative addition more facile.*

b) Why won't the following complex undergo the same transformation?

The Ti is in the +4 oxidation state and is already d^0. A d^0 metal center can NOT do an oxidative addition reaction.

Which of the following products will be the most likely formed from the reaction shown. Circle the best choice and give a brief explanation/justification for your choice.

a) $OsO_2Me_4 + I_2 \rightarrow OsO_2Me_4I_2$ -or- no reaction

b) $[Re(CO)_5]^- + CH_2{=}CHCH_2Br \rightarrow [(\eta^2\text{-}CH_2{=}CHCH_2Br)Re(CO)_5]^-$ or $(\eta^3\text{-allyl})Re(CO)_4 + Br^-$

a) $OsO_2Me_4 + I_2 \longrightarrow OsO_2Me_4I_2$ -or- no reaction

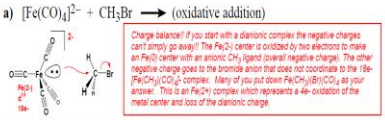
The starting Os complex is d^0 and can NOT do an oxidative addition reaction. So there is no reaction.

b) $[Re(CO)_5]^- + CH_2{=}CHCH_2Br \longrightarrow [(\eta^2\text{-}CH_2{=}CHCH_2Br)Re(CO)_5]^-$ or $(\eta^3\text{-allyl})Re(CO)_4 + Br^-$

The 18e- Re complex is d^8 and can do a direct oxidative addition reaction with alkyl bromides, which are reactive polar substrates. No empty orbital is needed for this initial rxn. Once the oxidative addition occurs and forms the η^1-allyl, one gets CO dissociation and a hapticity change from η^1- to η^3-allyl.

Consider the following reactions. Sketch out the final product clearly showing the structure and geometry. The rxn steps listed may not be in the correct order. If they are NOT in the correct order please include a brief and clear explanation of the correct order of steps and why they go in that order.

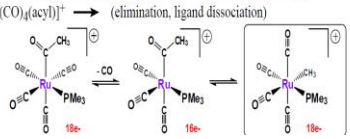
a) $[Fe(CO)_4]^{2-} + CH_3Br \longrightarrow$ (oxidative addition)



Charge balance! If you start with a dianionic complex the negative charges can't simply go away!! The Fe(-2) center is oxidized by two electrons to make an Fe(0) center with an anionic CH_3 ligand (overall negative charge). The other negative charge goes to the bromide anion that does not coordinate to the 18e- $[Fe(CH_3)(CO)_4]^-$ complex. Many of you put down $Fe(CH_3)(Br)(CO)_4$ as your answer. This is an Fe(2+) complex which represents a 4e- oxidation of the metal center and loss of the dianionic charge.

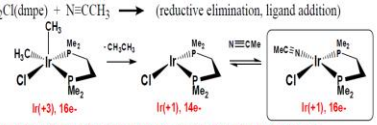
Fe(0) d^8 18e-

b) $[Ru(PMe_3)(CO)_4(acyl)]^+ \longrightarrow$ (elimination, ligand dissociation)



18e- 16e- 18e-

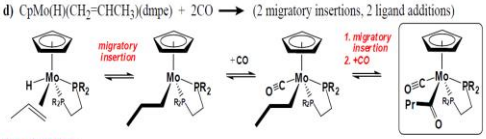
c) $Ir(CH_3)_2Cl(dmpe) + N{\equiv}CCH_3 \longrightarrow$ (reductive elimination, ligand addition)



Ir(+3), 16e- Ir(+1), 14e- Ir(+1), 16e-

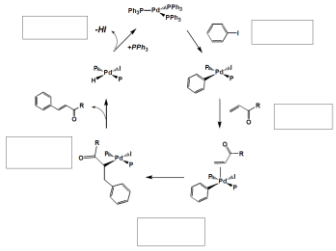
Reductive elimination is OK as a first step due to the unsaturation of the Ir(+3) complex.

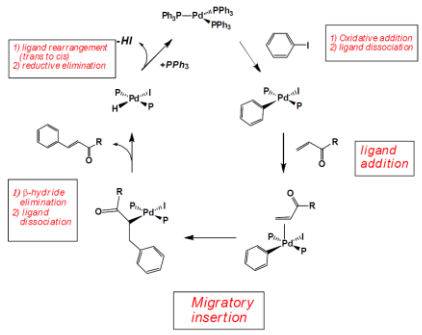
d) $CpMo(H)(CH_2{=}CHCH_3)(dmpe) + 2CO \longrightarrow$ (2 migratory insertions, 2 ligand additions)

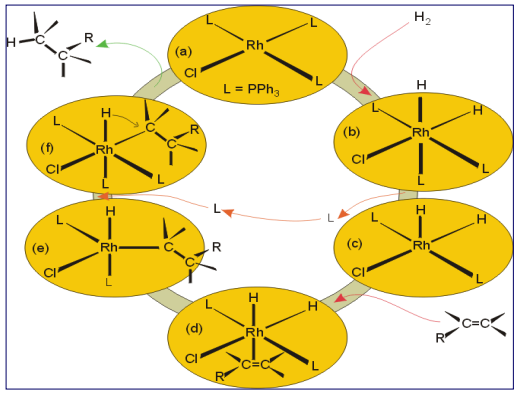


Steps shown above.

Label and clearly identify each step (i.e., migratory insertion, elimination, oxidative addition, reductive elimination, substitution, ligand addition, ligand dissociation, B-elimination, etc.) in the following catalytic reaction (called a Heck arene-alkene coupling reaction). Please write your answer(s) in the box next to the step. If there is more than one step occurring, please list them in the correct order if important. PPh3 is abbreviated as P for most of the complexes in the diagram.







Catalysis (homogeneous)
Reduction of alkenes *etc.*