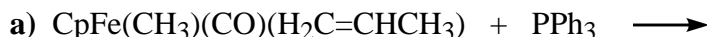


HW # 3 Due: April 10, 2008

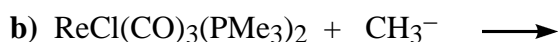
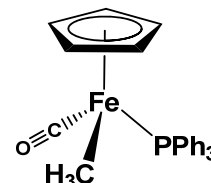
Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person:



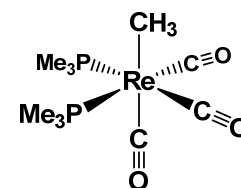
1. (30 pts) Predict and sketch out the structure for the transition-metal containing product for the following substitution reactions using one equivalent of each the reactants. State whether the mechanism is most likely **associative** or **dissociative** and reason(s) for your choice.



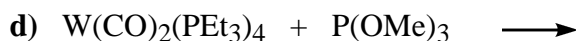
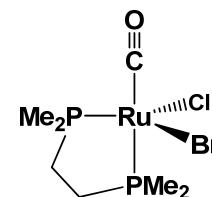
Dissociative: The Fe complex is 18e-, so it needs to lose the weakest coordinated ligand to open up a coordination site to bind the new ligand. Propylene will definitely be the most labile ligand.



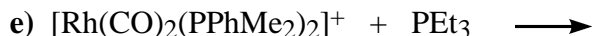
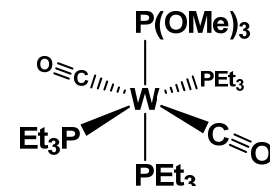
Dissociative: The Re complex is 18e-, so it needs to lose the weakest coordinated ligand to open up a coordination site to bind the new ligand. Chloride is the most likely candidate to dissociate first.



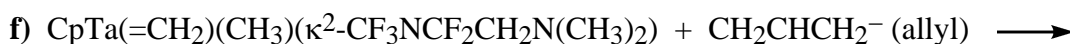
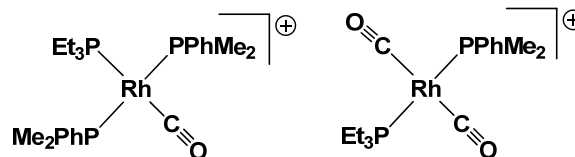
Associative: The Ru complex is 16e-, so it already has an empty orbital and has fairly small ligands to allow an associative substitution by bromide to replace one of the more weakly bound chloride ligands. Ru has a moderate tendency for 16e- d^6 complexes.



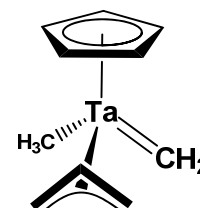
Dissociative: The W complex is 18e-, so it needs to lose the weakest coordinated ligand to open up a coordination site to bind the new ligand. Since the CO's are very strongly π -backbonding, one of the bulkier, electron-donating PEt_3 ligands should dissociate first. 4-strongly donating alkylated phosphine ligands makes the metal too electron-rich so this (and sterics) will favor PEt_3 dissociation to allow a poorer σ -donor, better π -acceptor, and smaller phosphite ligand to coordinate.



Associative or dissociative: The Rh complex is 16e-, so it has an empty orbital to allow an associative substitution by PEt_3 to replace one of the other ligands. But if you judge the PPhMe_2 ligands as being too bulky, proposing the dissociation of one of them is reasonable. Alternatively, the cationic charge will favor dissociation of one of the CO ligands over the electron-donating phosphine. So that would be a reasonable choice. So this can lead to two reasonable possible substitution products.

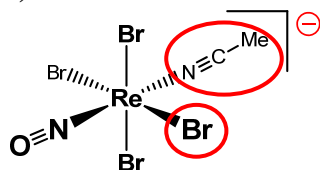


Associative: The Ta complex is 16e- (counting the amide as a 2e- donor) so it has an empty orbital and has fairly small ligands to allow an associative substitution by allyl to replace the more weakly chelating amine-amide ligand. The electron-withdrawing CF_3 - and CF_2 -groups on the amide nitrogen will weaken its donor ability considerably, favoring complete substitution by the stronger donor allyl. The η^3 -coordination mode is the most common for allyl.



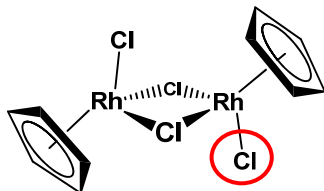
2. (25 pts) Circle the ligand on the following complexes that will most easily dissociate. Briefly state the reason(s) for your choice.

a)



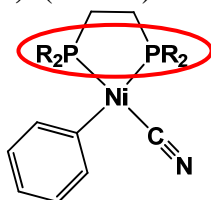
The two acceptable choices are Br^- and $\text{N}\equiv\text{CMe}$ (acetonitrile). The negative charge on the complex makes dissociation by a halide somewhat easier. On the other hand, acetonitrile is a neutral ligand and typically doesn't coordinate too strongly.

c)



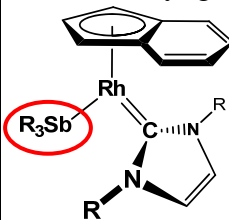
The terminal chloride is the weakest ligand and the easiest to dissociate. A bridging chloride ligand is bonding to two metal centers and has to break both bonds before dissociating, which is usually harder to do relative to a terminal ligand.

e) (R = Ph)



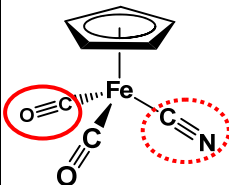
The dppe ligand is not that strong a coordinating ligand, even with the chelate effect. Both Ph^- and CN^- are considerably stronger σ -donors and will help to labilize (weaken) the dppe ligand for dissociation. For example, cyanide is used by my group to displace alkylated phosphines from transition metal centers.

b) (R = alkyl groups)



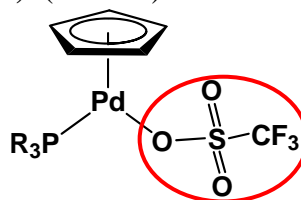
The antimony ligand coordinates the weakest due to the poor σ -orbital overlap efficiency (large diffuse lone pair orbital on the Sb) and the lower energy (poor donor ability) of the lone pair orbital. The hapticity changing ability of the indenyl ligand does not play a role here. The N-heterocyclic carbene ligand is a very strong donor and very unlikely to dissociate.

d)



My first choice would be the CO ligand, since an anionic cyanide is a fairly strong σ -donor (and usually a poor π -acceptor). But I will accept the reasoning that the CO ligands are π -backbonding strongly enough to make the cyanide more likely to dissociate.

f) (R = Me)



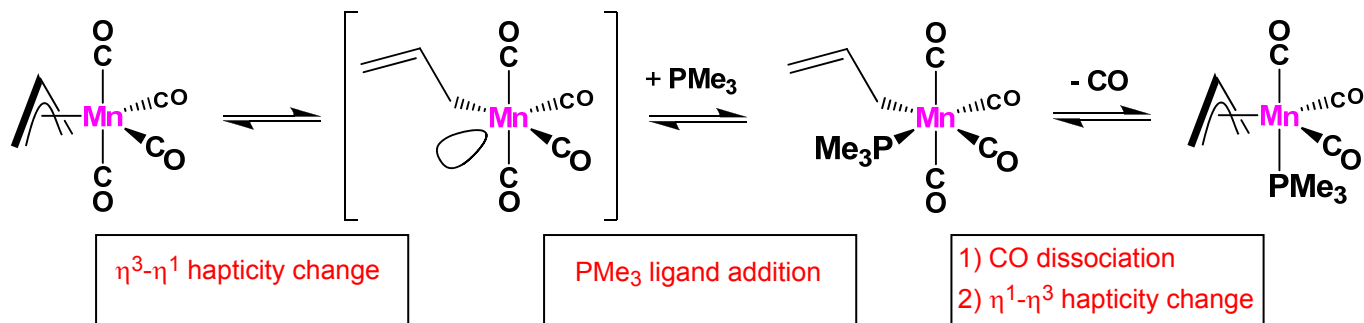
The SO_2CF_3 group is very electron-withdrawing, making the anionic oxygen a very poor donor, especially for late transition metals that aren't oxophilic in the first place. This group is called a triflate anion and is considered a non-coordinating anion due to its very weak bonding interactions with most metal centers.

3. (10 pts) $\text{Re}(\text{O})(\text{CO})_4[\text{P}(\text{OMe})_3]$ reacts extremely quickly with one equivalent of PMe_3 to do a CO ligand substitution. $\text{Mn}(\text{OMe})(\text{CO})_3(\text{dmpe})$, however, reacts far more slowly with PMe_3 to do a CO ligand substitution. Clearly state the reason(s) for this.

$\text{Re}(\text{O})(\text{CO})_4[\text{P}(\text{OMe})_3]$ is a 19e- complex and the one extra electron is in a metal-ligand antibonding orbital that will favor dissociation by one of the existing ligands. CO substitution is favored in order to give stronger π -backbonding for the remaining CO ligands after substitution. [I actually wanted this to be a 17e- system, but put one too many CO ligands on the complex, but the answer is the same either way]

$\text{Mn}(\text{OMe})(\text{CO})_3(\text{dmpe})$ is 18e- and has a good balance of σ -donating and π -backbonding ligands. This more than compensates for the "third row" stronger M-L bonding effect.

4. (15 pts) Consider the following allyl-mediated substitution reaction:

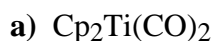


- a) (8 pts) Label each forward-going reaction step in the boxes provided below the reaction (there may be more than one fundamental reaction occurring in each step, if so, label in the correct order).
- b) (7 pts) Of the last two compounds, the final product is the most stable. Clearly state the reason(s) for this.

The anionic η^3 -allyl ligand (and PMe₃) donates more electron-density to the Mn atom making it more electron-rich so it can engage in more π -backbonding to the 3 remaining CO ligands. This is a more stable situation than 4 CO ligands competing for π -backbonding with an η^1 -allyl and one PMe₃ ligand.

5. (20 pts) To which of the following intact (no ligand dissociations) complexes can H₂ do an oxidative addition reaction to make a dihydride complex. Please circle **Yes** or **No** for each complex and clearly state the reason(s) for this.

You need at least a d² metal center and an empty orbital (17e⁻ or lower) for H₂ to be able to coordinate and do an oxidative addition.



Yes -or- **No**

18e⁻ Ti(+2) d² complex with no empty orbitals



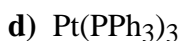
Yes -or- **No**

15e⁻ Cr(+5) d¹ complex, not enough d electrons for a 2e⁻ oxidative addition.



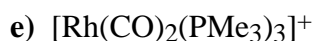
Yes -or- No

16e⁻ Fe(+2) d⁶ complex; OK for H₂ oxidative addition



Yes -or- No

16e⁻ Pt(0) d¹⁰ complex; OK for H₂ oxidative addition. Note that d¹⁰ Pt is very different from a square-planar d⁸ Pt(+2) center.



Yes -or- **No**

18e⁻ Rh(+1) d⁸ center with no empty orbitals (CO ligands, however, are probably quite labile due to the cationic charge).