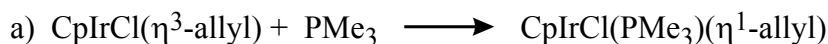


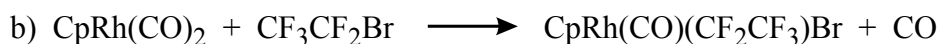
## HW # 3 Due: April 19 (by Noon), 2007

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:

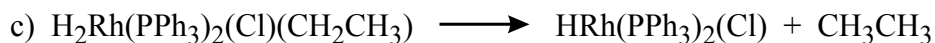
1. (30 pts) Identify the following reactions by their type (migratory insertion, elimination,  $\beta$ -hydride elimination, oxidative addition, reductive elimination, ligand addition, ligand dissociation, ligand coordination change, etc.). Note that in some cases you will have to use more than one description for a reaction that has several steps. Note also that the order may be important! No discussion is needed.



1. Ligand coordination change ( $\eta^3$ -allyl to  $\eta^1$ -allyl)
2.  $\text{PMe}_3$  ligand addition.



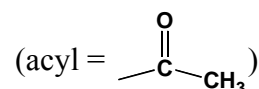
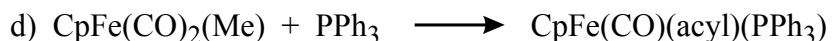
1. oxidative addition to produce  $[\text{CpRh}(\text{CO})_2(\text{CF}_2\text{CF}_3)]^+$  (18e-) +  $\text{Br}^-$
2. CO ligand dissociation (favored by higher oxidation state and cationic charge on Rh)
3. bromide ligand addition



reduction elimination of H and  $\text{CH}_2\text{CH}_3$

- or -

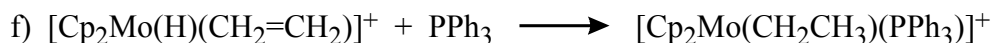
1.  $\text{PPh}_3$  ligand dissociation (makes 16e- metal that is more likely to reductively eliminate)
2. reduction elimination of H and  $\text{CH}_2\text{CH}_3$
3.  $\text{PPh}_3$  ligand addition



1. migratory insertion of CO and Me ligands to make acyl
2.  $\text{PPh}_3$  ligand addition



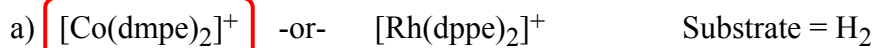
1.  $\text{Cl}^-$  ligand dissociation (must make empty orbital for  $\beta$ -hydride elimination,  $\text{Cl}^-$  is weakest binding ligand)
2.  $\beta$ -hydride elimination to make Pt-H(ethylene) complex
3.  $\text{CH}_2=\text{CH}_2$  ligand dissociation
4. reduction elimination of H and  $\text{CH}_2\text{CH}_3$  (steps 3 and 4 in either order)
5.  $\text{Cl}^-$  ligand addition



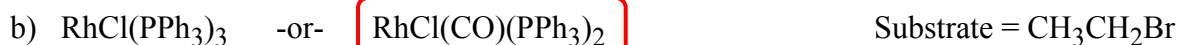
1. migratory insertion of H and ethylene ligand to make Mo- $\text{CH}_2\text{CH}_3$
2.  $\text{PPh}_3$  ligand addition

2. (20 pts) 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-electrophilic reactants we also need an empty orbital to pre-coordinate the reactant.*



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.



Although the three  $\text{PPh}_3$  ligands make the first Rh complex more electron-rich, the steric bulk of the three  $\text{PPh}_3$  ligands is more important for the more sterically hindered  $\text{CH}_3\text{CH}_2\text{Br}$  substrate.



The Ir is less electronegative and the  $\text{Br}^-$  is a stronger donating ligand relative to  $\text{Cl}^-$ .  $\text{PEt}_3$  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  $\text{PEt}_3$  ligand. Both complexes have a 16 e- count.



The W complex is  $d^0$  and can't do an oxidative addition reaction.  $\text{CH}_3\text{Cl}$  is an electrophilic substrate and does not need an empty orbital on the Cr center.

3. (10 pts)  $(\eta^3\text{-allyl})\text{Co}[\text{P}(\text{OMe})_3]_3$  is an arene hydrogenation catalyst that can cleanly hydrogenate benzene to cyclohexane.

a) (5 pts) It is known that the first reaction step in the hydrogenation mechanism is  $\text{H}_2$  oxidative addition to the complex. It is also known that there is **no** phosphine dissociation for this step. How does  $\text{H}_2$  add to the complex? Discuss.

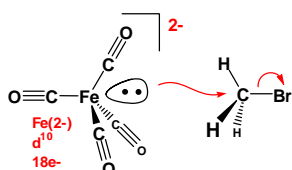
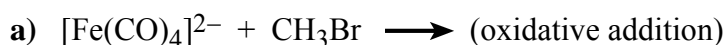
The  $\eta^3\text{-allyl}$  ligand changes its coordination mode from  $\eta^3$  to  $\eta^1$ , and this opens up an empty orbital to allow the  $\text{H}_2$  to bind and do the oxidative addition.

- b) (5 pts) The use of bulkier phosphite ligands such as  $\text{P}(\text{OEt})_3$  or  $\text{P}(\text{O}^i\text{Pr})_3$  speeds up the rate of arene hydrogenation. Discuss the reason(s) for this observation. The statement in part a) does not necessarily apply.

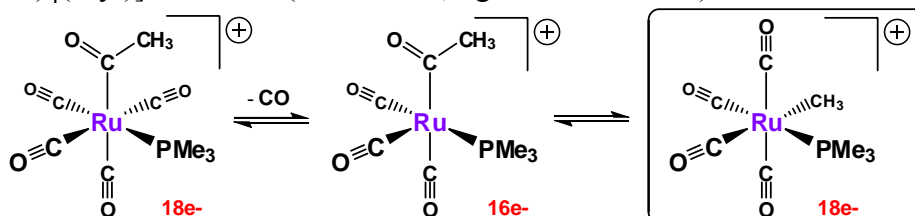
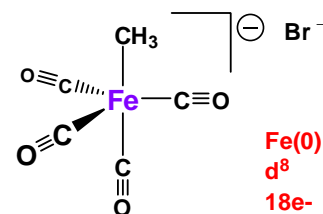
Two good reasons (either will do):

- 1) The bulkier phosphites can dissociate more easily due to increased steric hindrance. This opens up a coordination site to allow the arene substrate to bind and start the hydrogenation. Remember that phosphites do not bind that strongly.
- 2) The bulkier phosphite ligand cause more steric hindrance, which favors and speeds up the  $\eta^3$ - to  $\eta^1$ -allyl coordination mode change. The faster this occurs the faster the reaction of  $\text{H}_2$  with the catalyst.

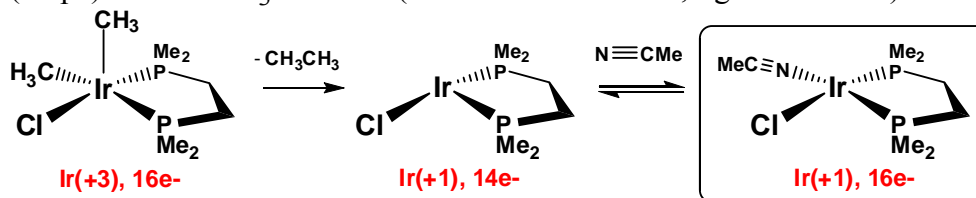
4. (20 pts) Consider the following reactions. Sketch out the final product clearly showing the structure and geometry. The rxn steps listed may not be in the correct order. If they are NOT in the correct order please include a brief and clear explanation of the correct order of steps and why they go in that order.



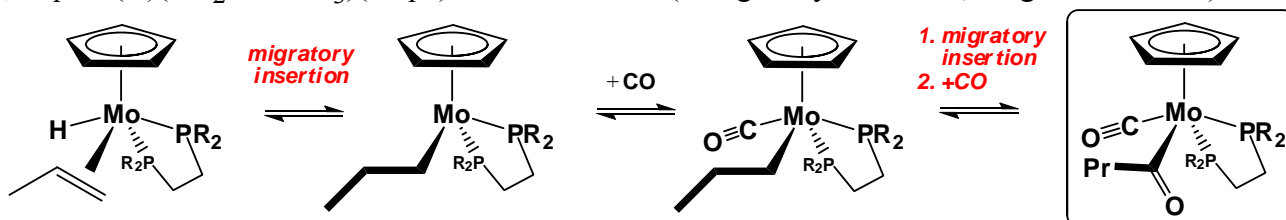
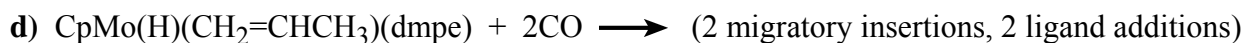
Charge balance!! If you start with a dianionic complex the negative charges can't simply go away!! The  $\text{Fe}(2-)$  center is oxidized by two electrons to make an  $\text{Fe}(0)$  center with an anionic  $\text{CH}_3$  ligand (overall negative charge). The other negative charge goes to the bromide anion that does not coordinate to the  $18e^-$   $[\text{Fe}(\text{CH}_3)(\text{CO})_4]^-$  complex. Many of you put down  $\text{Fe}(\text{CH}_3)(\text{Br})(\text{CO})_4$  as your answer. This is an  $\text{Fe}(2+)$  complex which represents a  $4e^-$  oxidation of the metal center and loss of the dianionic charge.



Ligand dissociation has to be the first step in order to make an empty orbital cisoidal to the acyl group for the carbonyl elimination.



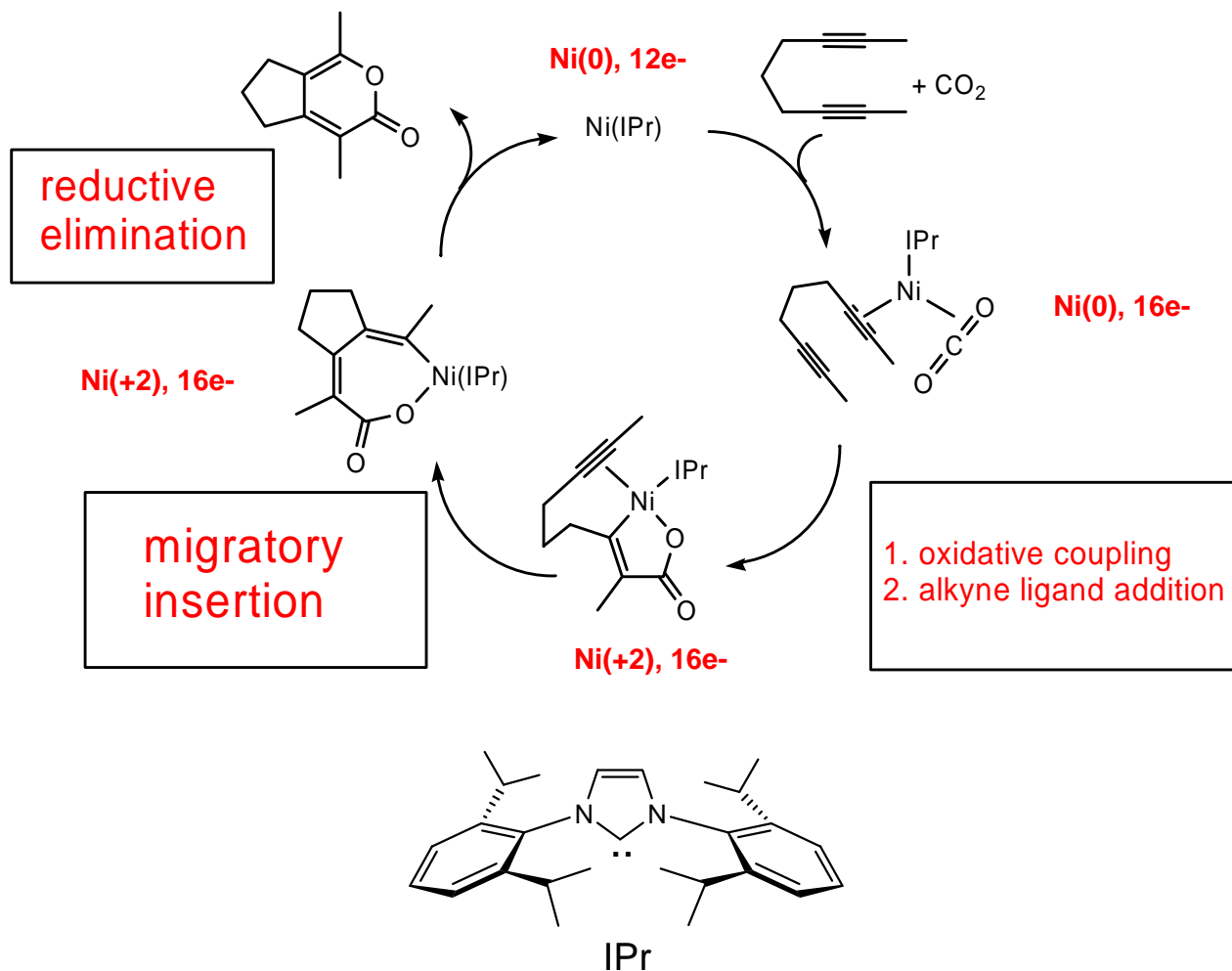
Reductive elimination is OK as a first step due to the unsaturation of the  $\text{Ir}(+3)$  complex.



Steps shown above.

5. (20 pts) Shown below is a catalytic cycle for the cyclocoupling of CO<sub>2</sub> and diynes developed by Prof. Janis Louie at the University of Utah (*JACS*, 2002, 124, 15188).

a) (15 pts) Label the steps with boxes next to them. There may be more than one step shown in each transformation. IPr ligand shown below.



b) (5 pts) The ligand is shown as a neutral ligand and Prof. Louie draws the bond from the IPr to the Ni as a single bond. Is this correct? Clearly discuss.

The Ni complex is a late transition metal carbene that should act as a Fischer carbene, which one typically considers as a neutral 2e<sup>-</sup> donor. The empty carbene p-orbital is not going to do much π-backbonding to the metal due to the presence of the two strongly π-donating N atoms flanking the carbene carbon. As was discussed in the notes the more π-donating the organic groups next to the carbene carbon, the less π-backbonding to the metal center. This effectively makes the carbene to Ni bond a single bond. See the "Hot New Carbene" ligand discussion in your Alkyl Chapter page 14.