Questions on the Bercaw paper:

*J. Am. Chem. Soc.*, **1987**, *109(5)*, 1435-1444

1. Define heterolytic/homolytic bond energies
2. What is s a “well defined compound?” A “group 8 metal?” “Thermoneutral?”
3. "Early transition metal-oxygen and -nitrogen bonds are quite robust, presumably due to ligand-to-metal pi-donation of an oxygen or nitrogen lone electron pair to an empty orbital of the electrophillic metal center. In contrast, there has been a common perception that late transition metal-nitrogen and -oxygen linkages are intrinsically weak due to the mismatch of hard ligand base with soft metal acid, thus explaining the relative scarcity of such complexes in the literature." What do these statements mean? What does the paper argue for?
4. Using the CBC method, classify the following two complexes: (dppe)MePtX and Cp\*(PMe)2RuX (compounds 2 and 4) and describe the type of reaction occuring.
5. What is scheme I doing in the paper? What are they trying to do with it? Derive the Keq (line 7 in Scheme I) from 1-6 using Hess's Law.
6. Write an anlagous scheme showing the homolytic bond dissassociation relationship
7. Why in Figure 5 are SH and CN such outliers?
8. In 1987, Bryndza and Bercaw demonstrated that M-X bond strengths tend to track H-X bond strenghts (Fig. 5, p. 1451).
   1. Given what you know about M-L bonding, provide a rationalization for the unusual observation for the thiol.
   2. CN- also has an anomoloulsy strong bond to metals. Given what you know about M-L bonding, provide a rationalization. A picture or sketch may be useful in your answer. (Hint: This cannot be explained in the same way as the thiol.)

Questions on the Bergman paper:

*J. Am. Chem. Soc.*, **1997**, *119(52)*, 12800 -12814

1. Look at Figures 6 and 7. What would the expected behavior be in these Figures if the Bercaw paper was correct?
2. Propose an explanation for why Ni behaves differently than Ru and Pt as you change X. Hint: what are the electronegativity values of the metals involved?
3. In Scheme 1:
   1. Classify each complex using the CBC method and provide a d-electron count for each complex
   2. break down the mechanism into elemtary reaction steps and name the reaction types.
4. Read footnote 101:
   1. The reviewer argues for loose ionic bonding and a slipped Cp\* ring. Explain or draw what these are.
   2. Why was the reviewer making this argument?
   3. Draw all three intermediates - the one proposed by Bergman and the two proposed by the reviewer - and indicate which is which. What are two possible mechanisms for the exchange of X and Y?
   4. What factors would favor the 16 , 18, and 20 electron mechanisms.
   5. The reviewers discuss characterization of Cp\*Ni(η2-acac)(PEt3) as a three-legged piano stool with a symmetric, η5-Cp. Draw this complex.