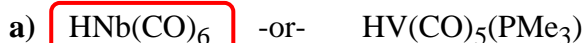


EXAM # 2 - March 29, 2007

Please answer all questions!

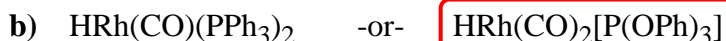
Check this box if you want your graded test put out
in the public boxes outside Prof. Stanley's office:

1. (20 pts) Which of the following metal hydrides should be the *most acidic*? Clearly explain your reasoning.

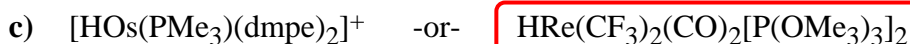


The most electron-poor metal center will have the most acidic hydride ligand.

The V complex has a strong donor alkylated phosphine ligand, thus making it more electron-rich than the Nb complex.



The circled complex has the most and best π -acceptor (electron-withdrawing) ligands (2 carbonyls & one phosphite). This makes it more electron-deficient and most able to handle the negative charge and lower Rh oxidation state after H^+ loss.

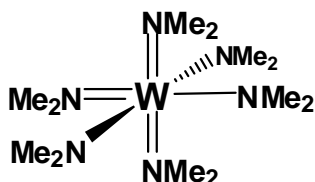


This was from homework # 2. The circled complex has the best π -acceptor (electron-withdrawing) ligands (2 carbonyls & 2 phosphites) and worst donor ligands. This makes it more electron-deficient and most able to handle the negative charge and lower Re oxidation state after H^+ loss. The Os complex, despite its positive charge, has all strongly donating alkylated phosphine ligands.



The circled complex has a Co(+3) center, poor σ -donors (amines & chloride), and a positive charge. This makes it more electron-deficient and most able to handle the negative charge and lower Co oxidation state after H^+ loss. The Fe complex has a good Cp^- donor and a medium donor dppe bisphosphine.

2. (10 pts) a) (5 pts) Electron-count $\text{W}(\text{NMe}_2)_6$ clearly showing the W oxidation state, ligand charges, and # of electrons donated from the ligands to the metal center.

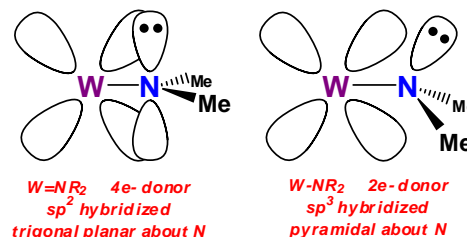


W(+6)	d0
3 $\text{M}=\text{NMe}_2^-$	12e-
3 $\text{M}-\text{NMe}_2^-$	6e-
Total	18e-

Use three amides that are 4e- donors and three that are 2e- donors to get to 18e-. Using all six as 2e- donors only gives you a very unsaturated 12e- count that is too low considering that the amide ligands can potentially donate 4e-.

b) (5 pts) Based on your electron-counting, what feature(s) about the $\text{W}-\text{NMe}_2$ bonding/geometry might you expect to show up in an X-Ray structure of this complex?

You might expect to see the three double bonded $\text{W}=\text{NMe}_2$ ligands with shorter $\text{W}-\text{N}$ bond distances, while the three with single bonds should have longer bond distances. The geometry of the W -amide will also change with the bonding: the double bonded amides will be sp^2 hybridized and have trigonal planar geometry, while the singly bonded amides will have pyramidal geometry with an uncoordinated lone pair of electrons.

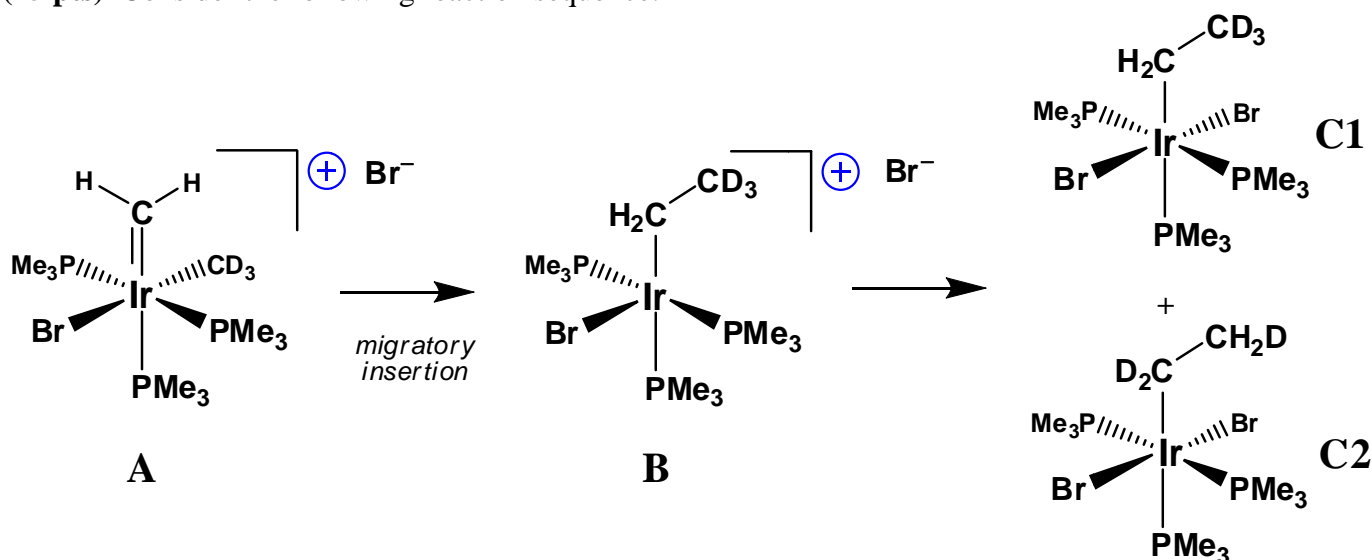


c) (5 pts BONUS) How would you explain the structure of $W(NMe_2)_6$ if it showed all approximately planar W-NMe₂ ligands (trigonal planar geometry about the nitrogen center)?

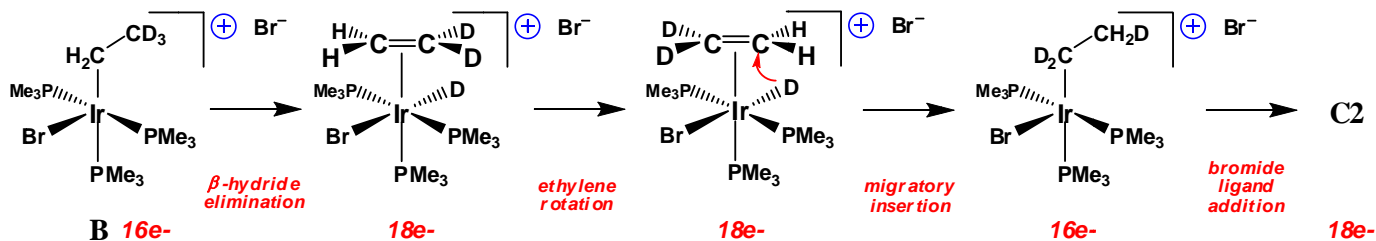
There are several possible explanations:

- 1) Delocalized bonding would result in an average W-N bond order of 1.5, a bond length intermediate between a localized single and double bond, and a structural geometry about the N of the amide ligand that is in between trigonal planar and pyramidal. This would look approximately trigonal planar.
- 2) N atoms occasionally prefer a trigonal planar sp^2 hybridized geometry with the lone pair residing in a pure p-type orbital. Only three of these would donate 4e⁻ to the metal, while the other three amides would act as 2e⁻ donors. One might then expect to see different W-N bond distances unless delocalized bonding is occurring (likely).

3. (15 pts) Consider the following reaction sequence:

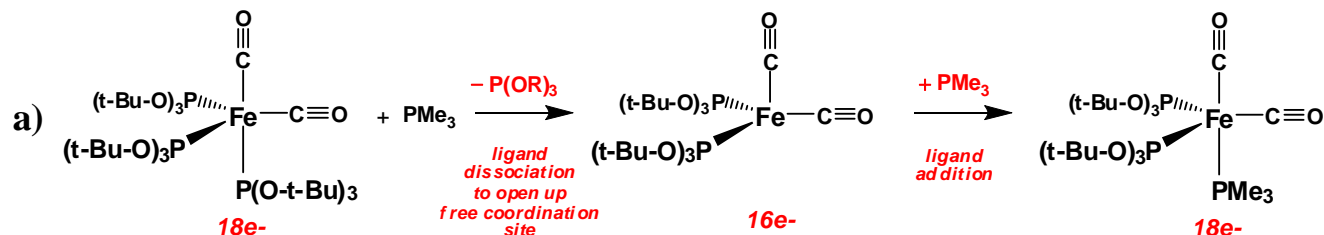


The deuterated methyl group in the complex **A** does a migratory insertion with the carbene ligand to form the ethyl group in **B**. Migratory insertion is the reaction of an anionic ligand with a neutral ligand to produce a new anionic ligand (examples: $M\text{-carbene} + M\text{-}CD_3 \longrightarrow M\text{-}CH_2CD_3$; $M\text{-ethylene} + M\text{-}H \longrightarrow M\text{-Et}$). The product **C2**, however, shows that one can get some scrambling of the deuterium labels from the original CD_3 methyl group. Clearly explain and show the properly labeled reaction steps that convert **B** to **C2**. Don't worry about bromide coordination till the last step. [Hint: an ethylene ligand can freely rotate about the metal-ethylene bond]

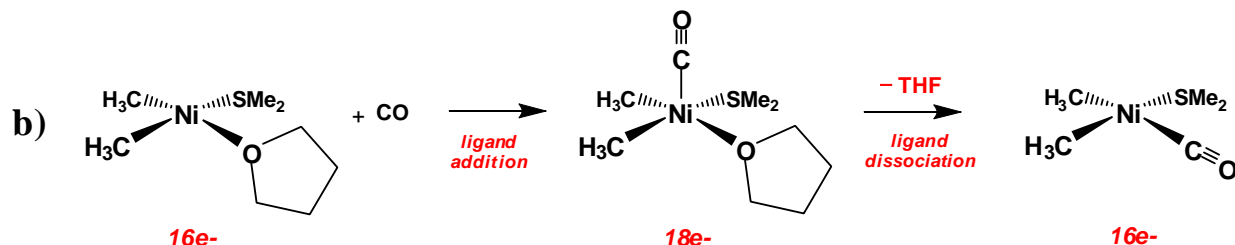


B is a 16e⁻ complex that has an empty orbital next to the ethyl (CH_2CD_3) group. This allows a β -hydride elimination to make the 18e⁻ ethylene-Ir-deuteride complex. Rotation of the ethylene group to place the CH_2 portion in proximity to the Ir-D bond then leads to a migratory insertion to make the 16e⁻ Ir- CD_2 - CH_2D complex, followed by bromide ligand addition to make **C2**.

4. (20 pts) 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.



Since we are starting with an 18e- complex, we have 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.

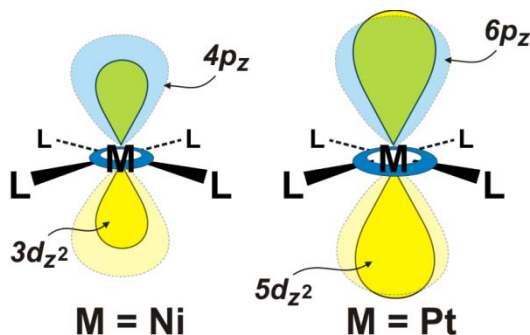


Since we are starting with a 16e- Ni complex without any steric problems we can proceed by an associative substitution reaction. Once the CO ligand coordinates, the weakest ligand that should fall off is the THF. Late transition metals have a far stronger preference for S over O-based ligands.

5. (10 pts) Explain why square-planar d^8 complexes of Rh(+1), Ir(+1), Ni(+2), Pd(+2), Pt(+2), and Au(+3) are stable with 16e- configurations and why they only bind a fifth ligand weakly (to moderately).

Square-planar d^8 complexes have an empty p_z orbital (p_z) perpendicular to the ligand plane (xy plane). This is what incoming ligands would like to coordinate to. BUT, there is also a filled d -orbital (d_{z^2}) in the same exact region of space. This filled orbital will repel the incoming ligand lone pair orbital. This results in a reasonably stable 16e- configuration and generally weak coordination to a fifth ligand.

For Ni, Rh, and Pd the empty p_z orbital is more spatially extended than the more contracted d_{z^2} orbital and favors weak bonding of the fifth ligand.



For Ir, Pt, and Au, the empty p_z orbital is more contracted and the filled d_{z^2} orbital more spatially expanded. This leads to the filled orbital having a considerably stronger blocking effect on incoming ligands and a far lower propensity for coordinating a fifth ligand.

6. (15 pts) Circle the complex that should have the *weakest* M-CO bonding. Clearly explain your answer.



-or-

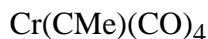


The most electron-poor metal center will have the least π -backbonding and the weakest M-CO bond.

The very poorly donating F^- ligand will increase the amount of positive charge on the metal and reduce the amount of π -backbonding to the carbonyls, weakening their bonding to the metal. This is a larger factor than the third-row effect. The CH_3^- ligand in the Tc complex is strongly donating and will increase the amount of π -backbonding to the Tc increasing the Tc-CO bond strength.



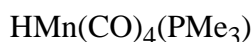
-or-



The W(+6) complex is d^0 , so there will be minimal π -backbonding to the carbonyls, thus giving the weakest bonding to the metal. The Cr(+3) complex is d^3 and has a very strongly donating trianionic $6e^-$ donor carbyne ligand.



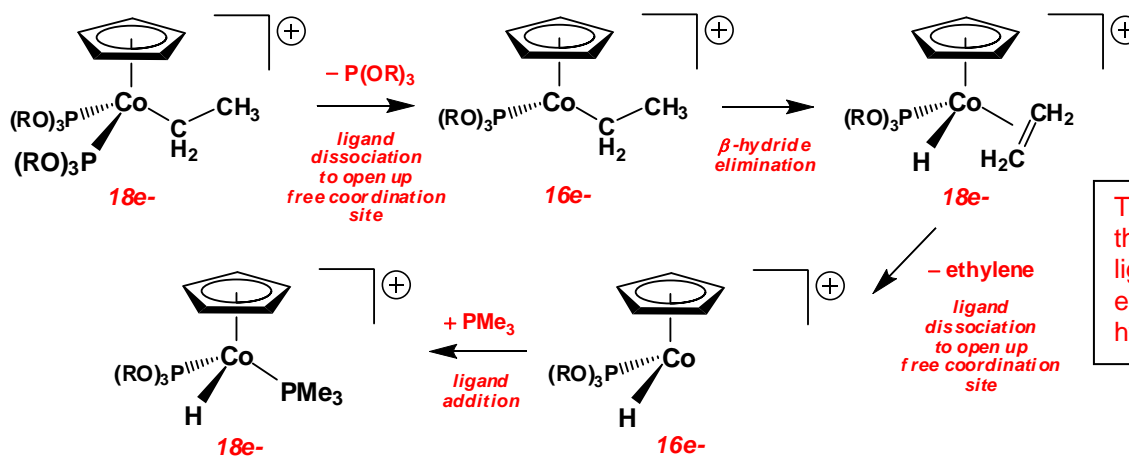
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The Mn(+1) complex has a strong donor alkylated phosphine ligand, a d^6 configuration, and the Mn is less electronegative relative to Co. Thus, it should have more π -backbonding and stronger Mn-CO bonds.

7. (10 pts) $[\text{CpIr}(\text{dmpe})(\text{Et})]^+$ is quite stable while $[\text{CpCo}[\text{P}(\text{OMe})_3]_2(\text{Et})]^+$ readily reacts with one equivalent of PMe_3 to produce $\{\text{CpCo}(\text{H})(\text{PMe}_3)[\text{P}(\text{OMe})_3]\}^+$ plus a gas that bubbles off the solution.

a) (5 pts) Write out a mechanism for the reaction of $[\text{CpCo}[\text{P}(\text{OMe})_3]_2(\text{Et})]^+$ to form $\{\text{CpCo}(\text{H})(\text{PMe}_3)[\text{P}(\text{OMe})_3]\}^+$.



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

b) (5 pts) Why is $[\text{CpIr}(\text{dmpe})(\text{Et})]^+$ considerably more stable?

The strong chelating dmpe ($\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) 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.