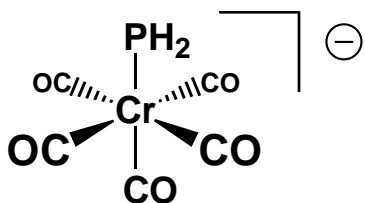


EXAM # 1 – Feb 21, 2008

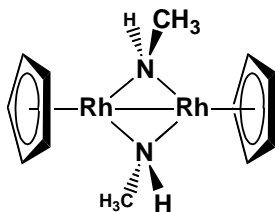
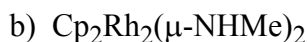
Check the box to the right if you want your graded exam to be placed in the public rack outside Prof. Stanley's office. Otherwise you will have to pick it up from Prof. Stanley in person:

Please answer all questions!

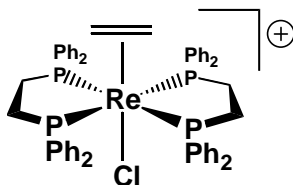
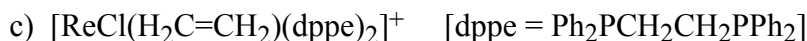
1. (40 pts) Sketch out the structure of the following transition metal complexes as accurately as possible and clearly show the electron counting for each including the metal oxidation state and ligand charges. You don't have to draw out phenyl rings on ligands (e.g., PPh₃).



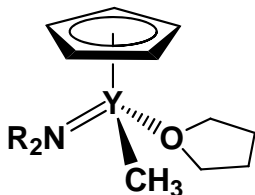
Cr(0)	6e-
PH ₂ ⁻	2e-
5 CO	10e-
Total	18 e-



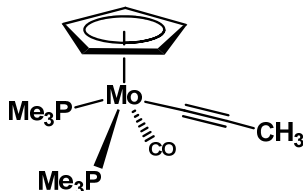
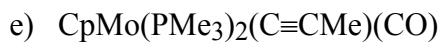
Rh(+2)	7e-
Cp ⁻	6e-
2 μ-NHMe ⁻	4e-
Rh-Rh	1e-
Total	18 e-



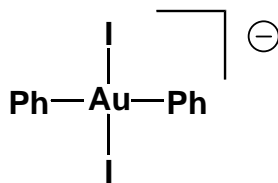
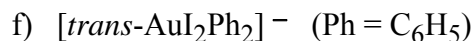
Re(+2)	5e-
Cl ⁻	2e-
C=C	2e-
2 dppe	8e-
Total	17 e-



Y(+3)	0e-
Cp ⁻	6e-
NR ₂ ⁻	4e-
CH ₃ ⁻	2e-
THF	2e-
Total	14 e-

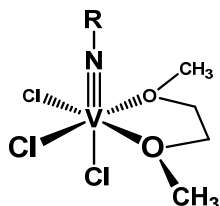


Mo(+2)	4e-
Cp ⁻	6e-
CCR ⁻	2e-
2 PR ₃	4e-
CO	2e-
Total	18 e-

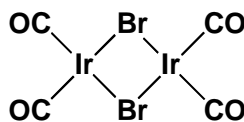
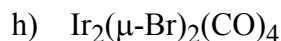


Au(+3)	8e-
2 Ph ⁻	4e-
2 I ⁻	4e-
Total	16 e-

trans means that the two Ph⁻ and I⁻ ligands should be opposite one another

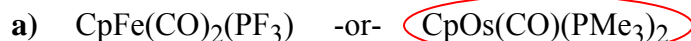


V(+5)	0e-
NR ²⁻	6e-
2 R-O-R	4e-
3 Cl ⁻	6e-
Total	16 e-



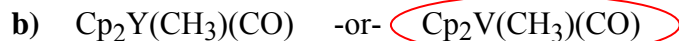
Ir(+1)	8e-
2 μ-Br ⁻	4e-
2 CO	4e-
Total	16 e-

2. (40 pts) For each of the following pairs of complexes, which will have the **lowest** average CO infrared stretching frequency? Circle your choice and briefly explain your reasoning.



The **most** electron-rich metal with **d**-electrons will **π**-backbond the **most** with the CO ligands and have the **lowest** CO stretching frequency

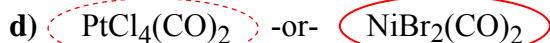
The Os complex has two strongly donating PMe₃ groups and only one π-backbonding CO, thus this one CO ligand will π-backbond more strongly with the metal center. The Os is also less electronegative and will be willing to π-backbond more strongly to the CO.



The Y complex is a *d*⁰ system and can not π-backbond to the CO. The V complex, on the other hand, is a *d*² complex and has strongly donating Cp⁻ and CH₃⁻ groups

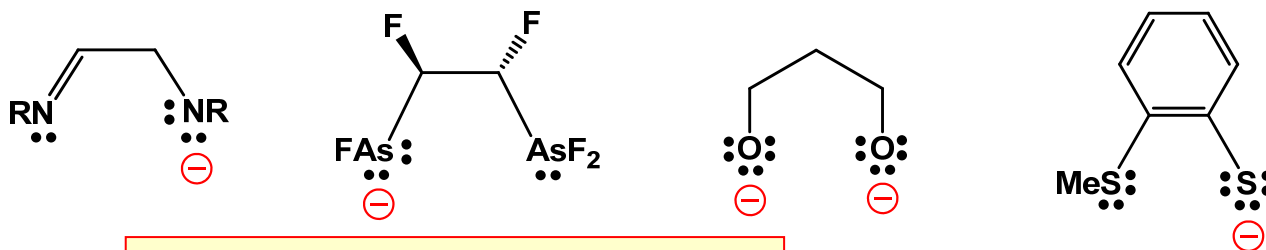


The two PEt₃ ligands on the Cr complex are strongly σ donating, considerably more so than the PPh₃ ligands. This more than compensates for the higher electronegativity of Cr vs. W.



The Ni(+2) complex is more electron-rich than the Pt(+4) complex since it has a lower oxidation state (more *d* electrons) and better donor ligands (Br⁻ vs. Cl⁻). The Pt is less electronegative and has 4 donor ligands vs. just two for the Ni complex, so that tends to compensate and make them closer together. Since they could be considered reasonably close to one another based on these two different lines of reasoning, we will give full credit for either answer so long as the justification is OK.

3. (30 points) a) (20 pts) Show the charges (may be 0) and number of electron pairs (may be zero) on the donor atoms that will coordinate to the metal center for the following chelating ligands:



F atoms attached to C or As are too electronegative to act as ligands. The As lone pairs are much higher in energy and better donors.

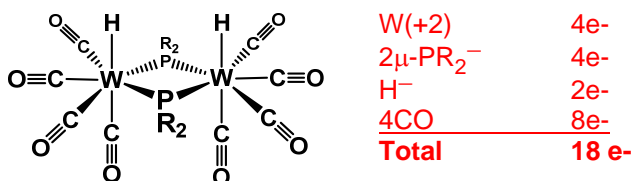
- b) (10 pts) Order the ligands above from strongest to weakest donor for a Zr(+4) metal center and include your reasoning. You can refer to the ligands by their primary donor atom type (e.g., S, O, N, etc) and do not have to sketch them out.



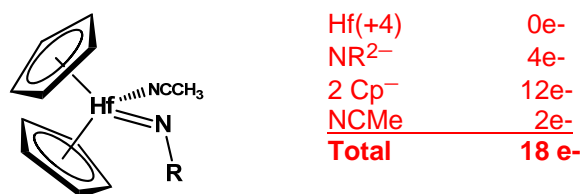
Zr(+4) is a "hard" early transition metal center that is highly oxophilic (oxygen-loving), especially for anionic "harder" ligands like O, N, C, or Cl. So the O (two anionic donors) > N (one anionic, one neutral donor) ranking is fairly straightforward based on this. S and As are both "softer" ligands, but S is less polarizable than As (fewer core electrons) so it should bind more strongly relative to As-based ligands.

4. (40 pts) Sketch out a **neutral** 18-electron structure showing the geometry about the metal center as accurately as you can at this point in the course for the following metals and ligands. Use **at least one metal and each type of ligand shown**. Try to keep your structure as simple as possible (bimetallic complexes are OK, nothing higher). Show your electron counting. Ligands are shown without charges, please indicate the proper ligand charge and metal oxidation state in your electron counting.

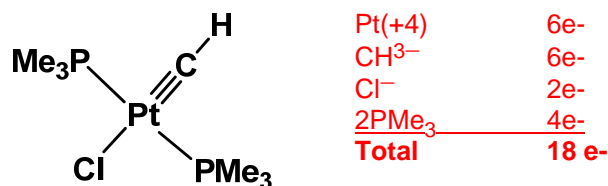
- a) W, μ -PR₂, CO, H



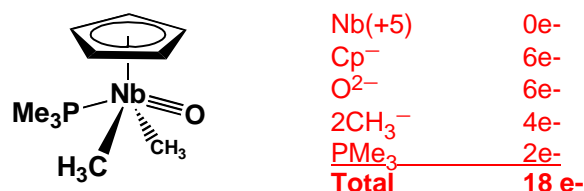
- b) Hf, Cp, N≡CCH₃, NCH₃



- c) Pt, CH, Cl, PMe₃



- d) Nb, O, CH₃, Cp, PMe₃



Bonus (10 pts): Why is C≡NMe a weaker π -acceptor than C≡O? There are two primary reasons.

Nitrogen is less electronegative (electron-withdrawing) than oxygen and the methyl group on the nitrogen is a sigma donor making the N more electron-rich and a poorer electron acceptor.