

HW # 2 Due: October 30, 2008 (by 2 PM)

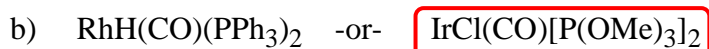
Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person:

1. (15 pts) For each of the following pairs of metal complexes, circle the one that will have the highest CO stretching frequency. Briefly and clearly discuss your reasoning for each case.

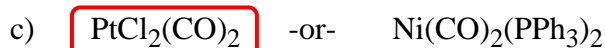
The metal complex that has the least amount of electron density on the metal center (most electron deficient) will be the one with the highest IR CO stretching frequency.



Although both complexes can be counted as 18 e- systems, the first Ti complex is d^0 and has no d electrons to π -backbond to the CO ligand. It is, therefore, the most electron deficient and will have the highest IR CO stretching frequency (and the most labile CO ligand). The second Ti complex is in the +2 oxidation state and has a rather electron-rich d^2 configuration.



The Ir complex is more electron-deficient due to the poorly donating Cl^- and $\text{P}(\text{OMe})_3$ ligands. The $\text{P}(\text{OMe})_3$ ligands are also moderately good π -backbonders. The Ir complex, therefore will have the higher CO stretching frequency. The Rh complex, on the other hand, has a strongly donating hydride and better donating PPh_3 ligands. The Ir is less electronegative than Rh and as a 3rd row metal will bind more strongly to the CO, but these are relatively minor factors compared to the more dominate ligand effects.



The Pt complex is more electron-deficient due to the poorly donating Cl^- ligands, the +2 oxidation state, and d^8 electron configuration. The Ni complex is in the zero oxidation state (d^{10}) and has moderately good donor PPh_3 ligands. Pt is less electronegative than Ni and as a 3rd row metal will bind more strongly to the CO, but these are relatively minor factors compared to the stronger ligand effects.



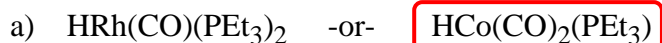
The Co complex is less electron-rich due to the fact that it is more electronegative, and thus willing to hang onto its d electron density and not π -backbond to the CO ligands. Secondly it only has a single anionic charge while the Fe complex is dianionic. This will overload the Fe complex and make it considerably more electron-rich. The ν_{CO} stretching frequency for each complex is given in your notes.



The Mn complex is less electron-rich due to the fact that it has a very poorly donating F^- ligand and one extra CO ligand relative to the W complex. Secondly, it is more electronegative and will hang onto its d electron density and not π -backbond to the CO ligands as well.

2. (20 pts) For each of the following pairs of metal hydride complexes, circle the one that should have the lowest pK_a value. Briefly and clearly discuss your reasoning for each case.

The metal complex that has the least amount of electron density on the metal center (most electron deficient) will be the one with the lowest pK_a value (most acidic).



The Co complex is less electron-rich due to the fact that it has two electron-withdrawing CO ligands and only one strongly donating PEt_3 ligand. It is also more electronegative than the Rh center.



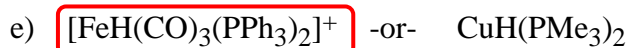
The Fe complex is less electron-rich due to the fact that it has four electron-withdrawing CO ligands. It is also more electronegative than the Os center. The bipy ligands on the Os are poor π -backbonding ligands.



The Ta complex is less electron-rich due to the fact that it has two very poorly donating F^- ligands. This will make the Ta center more cationic and likely to dissociate an H^+ .

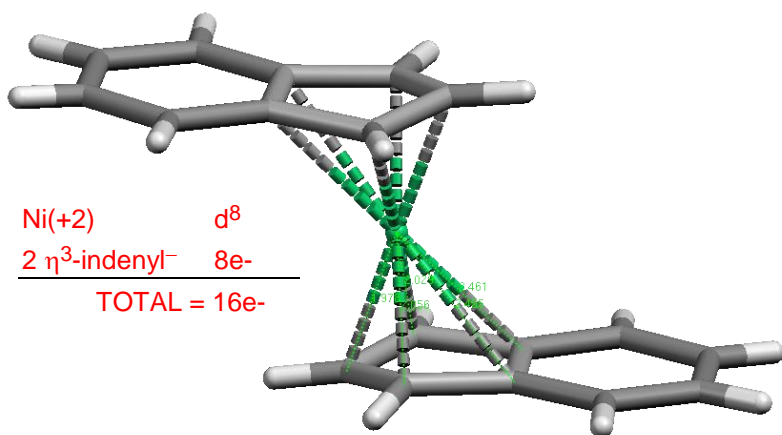


The second Re complex is less electron-rich due to the fact that it has three electron-withdrawing CO ligands and two poorly donating $\text{P}(\text{OMe})_3$ ligands. The first Re complex has four strongly donating PEt_3 ligands and three very strongly donating hydrides. It is true that the second Re complex is d^6 , while the first one is d^4 , but the ligand donor properties dominate.



The Fe complex is more electron deficient due to the fact that it is cationic, has three electron-withdrawing CO ligands, and two moderately donating PPh_3 ligands. The Cu complex has two strongly donating phosphine ligands. Although the Cu is more electronegative, the cationic charge and ligand factors on the Fe complex dominate.

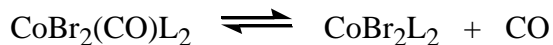
3. (5 pts) $(\eta^x\text{-indenyl})_2\text{Ni}$ has the structure shown below. Three of the Cp-ring to Ni distances average 2.0 Å, while the other two average 2.46 Å. Describe the indenyl-Ni bonding and show the electron-counting for this complex. For more info on the indenyl ligand see your notes (Cp & ligand substitution chapters).



The complex should be formulated as $(\eta^3\text{-indenyl})_2\text{Ni}$, a Ni(+2), d^8 , 16e- complex. Both indenyl ligands are coordinating in an η^3 -allylic fashion and each is acting as 4e- donors. Thus, we see two long Ni-C distances that are not bonds, and 3 shorter Ni-C distances that represent the η^3 -indenyl allylic bonding to the Ni center.

The Ni can then be considered a typical d^8 square-planar 16e- complex.

4. (10 pts) Consider the following equilibrium:



The equilibrium constants for the reaction with various L ligands are given in the table below. Explain the trends in K_d .

L	K_d	ν_{CO} (cm^{-1})	cone angle
PEt ₃	1	1985	132°
PPr ₃	1.1	1980	135°
PEt ₂ Ph	2.5	1990	135°
PEtPh ₂	24	1990	140°
PPh ₃	750	1995	145°

Generally, the more electron-donating the phosphine the lower the ν_{CO} stretching frequency. This means stronger π -backbonding to the CO and stronger M-CO bonding. Thus, a lower K_d dissociation value. Steric effects, however, can over-ride the electronic effects. PPr₃, for example, is a stronger donor than PEt₃, but the K_d value actually increases slightly. This is due to the larger cone angle of the PPr₃ ligand. This causes more steric crowding around the metal favoring CO dissociation.

In going from PPr₃ to PEt₂Ph, the cone angle is the same, but the PEt₂Ph ligand is not as strong a donor, so we see an increase in the ν_{CO} stretching frequency (weaker M-CO bonding) and more dissociation. The increased steric size of the PEtPh₂ ligand causes a ten-fold increase in the dissociation, even though the ν_{CO} stays about the same. PPh₃ is the biggest ligand and poorest donor so we see the largest increase in the CO dissociation.