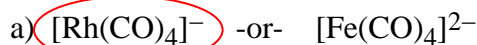


HW # 2 Due: March 13, 2008

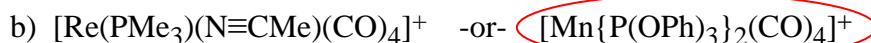
Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person:

1. (18 pts) For each of the following pairs of metal complexes, circle the one that should have the highest average carbonyl IR stretching frequency. What does this tell you about the relative electron density on the metal center (electron-rich or deficient)? Briefly discuss your reasoning for each case.



The highest CO stretching frequency corresponds to the metal that is the most electron deficient (poor) or has no d-electrons.

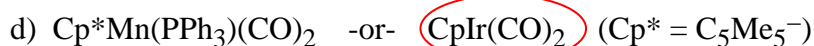
Rh and Fe have similar electronegativities and the same # of CO ligands. But Fe is in the -2 oxidation state and has an overall $2-$ charge which makes it more electron-rich than the mono-anionic Rh complex. On page 5 of your Carbonyl chapter notes the table at the bottom lists $[\text{Fe}(\text{CO})_4]^{2-}$ as having a rather low ν_{CO} of 1790 cm^{-1} , while $[\text{Co}(\text{CO})_4]^-$ has a ν_{CO} of 1890 cm^{-1} .



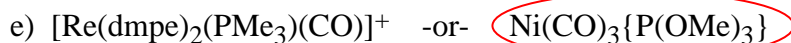
Both complexes are cationic and have the same # of CO ligands, but the phosphite ligands in the Mn complex are poorer donors than PMe_3 (about the same as $\text{N}=\text{CMe}$) and certainly better π -acceptors making the Mn center more electron-deficient. Mn is also more electronegative than Re and will hang onto its electrons a little more strongly have less tendency to π -backbond to the CO's.



The Os complex is d^0 (+8 oxidation state) and can't π -backbond effectively to the CO ligands. The Fe complex is d^6 and can.



The Ir complex is more electron-deficient due to the less donating Cp ligand (compared to the stronger donating Cp^*). The Mn complex also has an extra donating (moderately) PPh_3 ligand.

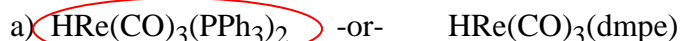


Although the Re complex is cationic, it has two sets of strongly donating alkylated dmpe ligands (the equivalent of 4 PMe_3 ligands) and a PMe_3 ligand and only one π -backbonding CO ligand. These strongly donating ligands more than compensate for the cationic charge on the Re making it more electron-rich. The Ni complex on the other hand is more electronegative and has 3 CO ligands and one poorly donating (and moderately π -accepting) phosphite ligand.



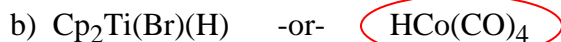
The Au complex is considerably more electronegative and will not want to π -backbond well to the CO. The vanadium complex on the other hand has a d^2 configuration and some strongly donating ligands. As I mentioned during the lectures on carbonyls, the tendency for metals to bind CO ligands drops off as one moves to the far right of the transition metal series.

2. (18 pts) For each of the following pairs of metal hydride complexes, circle the one that should have the lowest pK_a value. Briefly discuss your reasoning for each case.



The lowest pK_a value refers to the most acidic hydride, which is the most electron deficient (poor) metal complex.

The dmpe ligand is considerably more donating than the two PPh_3 ligands. Therefore, the circled complex will be the least electron-rich (most electron-deficient) and have the most acidic hydride (lowest pK_a)



The cobalt complex has 4 electron-withdrawing (π -backbonding) CO ligands that will drain electron-density from the hydride and make the hydride more acidic. The Ti complex may be d^0 , but has good donating ligands making the Ti center relatively electron-rich (though still unsaturated). The $\text{HCo}(\text{CO})_4$ complex was also clearly discussed multiple times in class and in the notes as being a strong acid.



The three strongly donating PEt_3 ligands make the Co center quite electron-rich, which will in turn make the hydride more hydridic (less protic, less acidic, higher pK_a). The Ru complex, on the other hand, is cationic and only has one weakly to moderately donating acetonitrile ligand and 4 electron-withdrawing CO ligands. This will definitely make the Ru complex the most acidic complex. The lower electronegativity and somewhat stronger second-row M-ligand bonding effects are minor compared to the ligand and charge factors in this case.



Tp is not as strongly donating as Cp and there is an extra electron-withdrawing CO ligand present on the Os complex. These will work together to make the Os complex less electron-rich and the hydride more acidic. This will over-ride stronger third-row metal-ligand bonding effect and lower electronegativity of the Os vs. Ru.



The two PCy_3 ligands are strongly donating and will make the Rh center more electron-rich and the hydride more hydridic. The COD ligand is relatively weakly donating making the Ir less electron-rich and the hydride more hydridic.

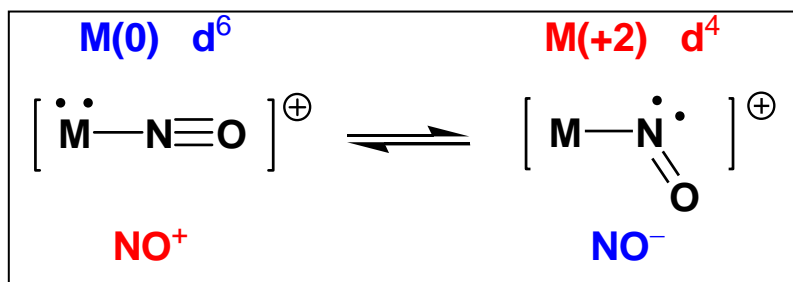


The strongly electron-withdrawing (π -backbonding) NO^+ and CO ligands will dramatically stabilize the anionic complex, $[\text{Fe}(\text{NO})(\text{CO})_3]^-$ left after a proton dissociates. This will, therefore, be far and away the most acidic complex.

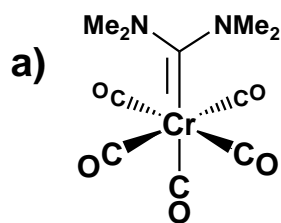
3. (8 points) The nitrosyl ligand usually coordinates as a cationic ligand, NO^+ . It can, however, occasionally act as an anionic NO^- ligand. When it is behaving as an anionic ligand it adopts a bent coordination geometry. Discuss (using Lewis dot-like figures) the distribution of electrons in both kinds of M-NO complexes and how these affect the structures (linear vs. bent). Assume in both cases that you are dealing with a $[\text{M-NO}]^+$ unit (positive charge on the overall complex) where the metal has 2 or more d electrons. Clearly show the relative oxidation states of the metal and the relative d electron count for each bonding case (linear vs. bent). I mentioned briefly in class that in some ways NO^- is the extreme case of NO^+ acting as a hyper π -backbonding ligand. Explain what I meant by that statement.

NO^+ is isoelectronic with CO, that is, it has the same bonding and electronic structure. The difference is that the more electronegative nitrogen atom combined with the net positive charge work together to make NO^+ the strongest π -backbonding ligand known. In fact, it can backbond enough to formally oxidize the metal center by two electrons to transform the NO^+ ligand into a NO^- ligand. This is shown below in the transfer of a pair of electrons from the metal to the NO^+ ligand to produce the bent NO^- ligand. The lone pair that used to be on the metal center is now on the nitrogen of the NO^- ligand.

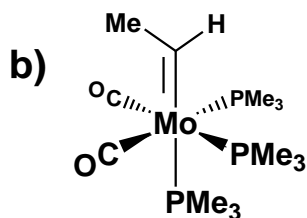
This is what I was referring to as hyper- π -backbonding. When the NO^+ ligand turns into a NO^- ligand it has formally oxidized the metal center by 2 electrons. That represents the "ultimate" in π -backbonding.



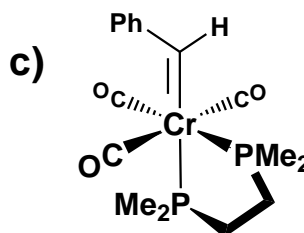
4. (6 points) Circle the correct ordering of the following group of Fischer carbenes from the strongest $\text{M}=\text{CR}_2$ bond to weakest. Explain your reasoning.



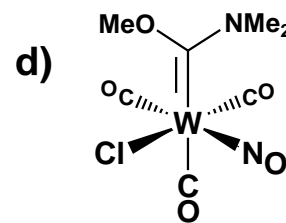
a > b > c > d



b > c > d > a



d > c > b > a



c > a > d > b

b) has the strongest carbene bond because it has the poorest π -donating groups on the carbene carbon atom – this will allow the empty p-orbital on the carbene to be fully available to π -backbond to the filled d-orbitals on the metal. The Mo center is also the most electron-rich due to the strong donating alkylated phosphine ligands and the lower electronegativity of the Mo center. The Cr center in c) also has strong donating phosphine ligands, but the Cr is a little more electronegative than the Mo and can hang onto its electrons better and not π -backbond as much. The Mo center also has the second-row stronger M-L bonding effect to help it. The Cr complex c) also has a phenyl group on the carbene carbon that can π -donate to the empty p-orbital and weaken the ability of the carbene to π -backbond to the metal center. d) has the next weakest carbene-M bonding due to the strong π -donating OMe and NMe_2 groups on the carbene filling up that empty p-orbital and the very strong π -backbonding of the NO^+ ligand that drains electron-density off the W atom. a) has the very weakest M-carbene bond due to the two strong π -donating NMe_2 groups on the carbene and the lack of any good donor groups on the metal.