

Organometallic Chemistry - 4571

ANSWER KEY

HW # 2 Due: March 15 (by Noon!), 2007

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

The **highest** CO stretching frequency will be the complex with the least amount of electron density that can be π -backbonded to the CO ligands.

a) $\text{CpRe}(\text{CO})_3$ -or- $\text{Cp}^*\text{Mn}(\text{PEt}_3)(\text{CO})_2$

The Mn complex is more electron-rich and will have the lower CO stretching frequency since it has the stronger donating Cp^* (pentamethyl-Cp) and PEt_3 ligands, along with one fewer electron-withdrawing CO ligand. These ligand effects easily over-ride the higher electronegativity of the Mn center.

b) $\text{W}(\text{CH})\text{Cl}_2(\text{CH}_3)(\text{PMe}_3)(\text{CO})$ -or- $\text{Ta}(\text{NR})(\text{CH}_3)(\text{CO})_2[\text{P}(\text{OMe})_3]_2$

The W complex is in the +6 oxidation state and is d^0 , while the Ta complex is in the +3 oxidation state and d^2 . Even with strong donating ligands it is safe to generally assume that a d^0 complex will have the highest CO stretching frequency. So ALWAYS electron-count.

c) $\text{PtCl}_4(\text{CO})_2$ -or- $[\text{PtBr}_3(\text{CO})]^-$

This Pt complex is in the +4 (d^6) state with 4 poorly donating chloride ligands and two CO groups. This means that the Pt center should have a reasonably high positive charge and contracted orbitals leading to less π -backbonding to the CO ligands. $[\text{PtBr}_3(\text{CO})]^-$, on the other hand, has Pt in the +2 (d^8) state with three somewhat more strongly donating bromide ligands, a formal negative charge on the complex, and only one CO ligand.

d) $[\text{Co}(\text{CO})_4]^-$ -or- $[\text{V}(\text{CO})_6]^-$

Page 5 of Carbonyls: $\nu_{\text{CO}} [\text{Co}(\text{CO})_4]^- = 1890 \text{ cm}^{-1}$, $\nu_{\text{CO}} [\text{V}(\text{CO})_6]^- = 1860 \text{ cm}^{-1}$. Important explanation: Co is considerably more electronegative. V is in a very low oxidation state (-1, relative to usual +3 or +5) meaning that it is very electron-rich. This more than compensates for the presence of two more CO ligands. Co is also in the -1 oxidation state, but this is closer to its norm of 0 to +3.

e) $\text{CoF}_3(\text{CO})_3$ -or- $\text{Cp}^*\text{Mo}(\text{NO})(\text{CO})_2$

The fluorides are very poor σ -donors and hang on to most of their negative charge. This makes the Co fairly electron-deficient and with a fair bit of the positive charge from its +3 oxidation state localized and contracting its orbitals, thus minimizing the π -backbonding to the CO ligands. Cp^* is a strong donating anionic ligand and Mo is a fair bit less electronegative than Co. These two factors out-weigh the presence of the NO^+ ligand.

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 discuss your reasoning for each case.

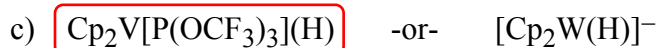
a) $\text{Cp}_2\text{Zr}(\text{H})(\text{Br})$ -or- $[\text{CpMo}(\text{H})(\text{CO})_3]^+$

The **lowest** pK_a represents the **highest** acidity and the complex with the least amount of electron density. The hydride ligand wants to donate more of its electron-pair making it more protic.

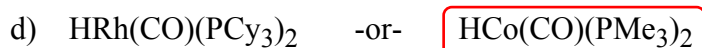
The Mo complex has only one good Cp donor, three good π -backbonding (electron-withdrawing) CO ligands, and a localized positive charge on the metal. All these work together to make the hydride the most acidic.



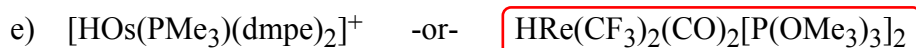
Everything is the same except for the $:\text{C}\equiv\text{NCH}_3$ (isocyanide) and $:\text{PMe}_3$ ligands (both neutral). The alkylated phosphine is the stronger σ -donor (negligible π -acceptor), while the isocyanide is not as strong a σ donor and a better π -acceptor (see homework assignment # 1). This makes the isocyanide complex less electron-rich and more acidic.



The V complex has poor σ -donating phosphites that will be fairly good π -acceptors with the electron-withdrawing CF_3 groups. This will make it easier to dissociate a proton. If the W complex loses a proton it will be dianionic and too electron-rich.



The ligands are pretty similar with the PCy_3 being a somewhat stronger σ -donator relative to PMe_3 . Co is more electronegative than Rh and this also helps make the Co complex the more acidic.



Poor donor ligands coupled with moderate (phosphite) and good π -acceptor (CO) ligands is more important here for the Re complex than the positive charge on the Os complex which has strong phosphine donor ligands. Six ligands can override a single charge.

4. (10 pts) Consider $\text{Cp}_2\text{Rh}_2[\mu-(\text{CF}_3\text{CCCF}_3)](\text{CO})(\text{CNR})$ shown on page 7 of the Alkene/Alkyne chapter. The Rh-Rh bond distance is 2.67 Å strongly indicating the presence of a covalent bond between the two rhodium atoms. (a) (5 pts) show the electron-counting for this complex including Rh oxidation state, ligand charges, # of e- donated, etc. Only one Rh center needs to be counted since both the CO and $\text{C}\equiv\text{NR}$ ligands are neutral 2e- donors making the complex electronically symmetrical from an electron counting viewpoint. (b) (5 pts) Why does the alkyne ligand orient parallel to the Rh-Rh bond? From an organic hybridization and bonding viewpoint how should the “alkyne” be considered? Draw a simple orbital picture showing how the filled “alkyne” orbitals are overlapping with the empty Rh orbitals (use the diagram below as a starting point, ignore all other ligands).

- a) The electron-withdrawing groups on the alkyne allow it to oxidize each Rh center by 1e- to put each into the +2 oxidation state (d^7) and convert the alkyne into a dianionic bridging *alkene* ligand. This is analogous to the alkene example on the first page of the alkene chapter where the electron-withdrawing cyano groups allow it to formally oxidize the Pt center and make a σ -coordinated metallocyclopropane complex.
- | | |
|---|--|
| Rh(+2) | d^7 |
| Cp- | 6e- |
| $[\text{CF}_3\text{C}=\text{CCF}_3]^{2-}$ | 2e- |
| CO (or CNR) | 2e- |
| Rh-Rh | 1e- |
| | <hr style="border: 0.5px solid black;"/> |
| | 18e- |
- b) The 2e- reduction of the alkyne changes the carbon hybridization from sp to sp^2 (double bond like). Each carbon center now has a sp^2 hybrid orbital in the plane of the double bond with a lone-pair to bond to each Rh center. By using these stronger σ -donating orbitals the “alkyne” ligand now must orient parallel to the Rh-Rh bond axis. Remember that ligands with π -systems and σ -lone pairs generally prefer bonding to the metal via the σ -lone pairs.

