

Recommended Reading: 20, 21.2-21.4, 13 (3rd edition); 19, 20.2-20.4, 13 (4th edition)

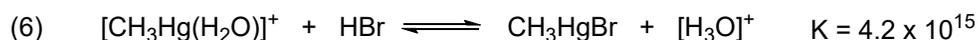
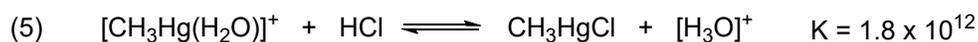
Ch 102 – Problem Set 5

Due: Thursday, May 18 – Before Class

Problem 1 (2 points)

Part A

In class we predicted whether Li^+ or Cs^+ salts of F^- or I^- were soluble based on a combination of ΔH_{solv} and lattice energies for each combination. In an analogous sense, the equilibrium constants for equations 4-6 (shown below) are the result of a combination the halide ion affinity for $[\text{CH}_3\text{Hg}(\text{H}_2\text{O})]^+$ and the dissociation constants for the hydrohalic acid.

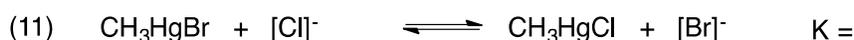
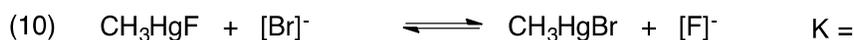


a) Using the information provided, calculate the equilibrium constants for the following reactions. Show your work.



b) Rationalize the trends in equilibrium constants for equations 7-9 using HSAB theory. Do you expect K for iodide to be larger or smaller than K for bromide? Explain.

c) Calculate K for the following reactions. Show your work. Rationalize in terms of HSAB theory.



Part B

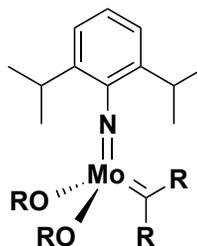
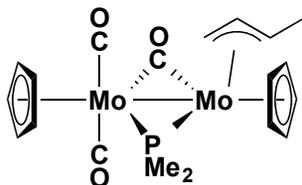
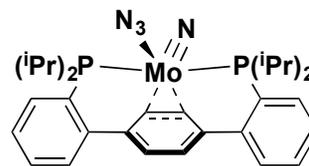
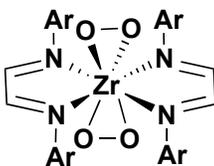
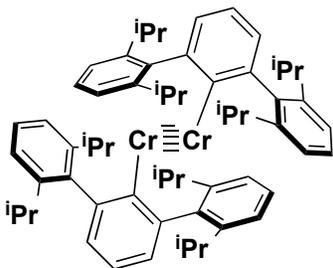
For each pair of complexes predict which has the larger $d-d$ splitting, and explain all the relevant factors in your reasoning (do not just cite the trends; explain them).

- $[\text{Cr}(\text{OH}_2)_6]^{3+}$ vs. $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- $[\text{Fe}(\text{CN})_6]^{4-}$ vs. $[\text{Ru}(\text{CN})_6]^{4-}$
- $[\text{NiCl}_4]^{2-}$ vs. $[\text{Fe}(\text{oxalate})_3]^{3-}$
- $[\text{Co}(\text{phen})_3]^{3+}$ vs. $[\text{Co}(\text{NH}_3)_6]^{3+}$
- $[\text{Fe}(\text{OH}_2)_6]^{3+}$ vs. $[\text{Fe}(\text{OH}_2)_6]^{2+}$
- $[\text{PdCl}_4]^{2-}$ vs. $[\text{PtCl}_4]^{2-}$

Problem 2 (3 points)

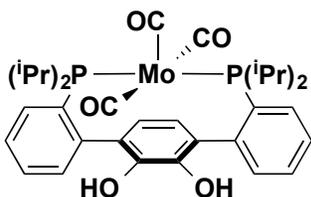
Part A

Give the oxidation state, d-electron count, and valence electron count for the following compounds:

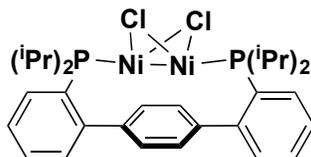


Part B

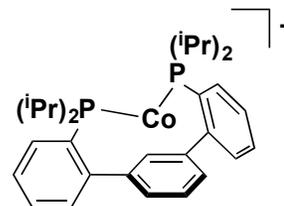
The following are all 18-electron compounds that exhibit a metal-arene interaction (with the central arene). Redraw each compound showing the metal-arene interaction and specify the hapticity (i.e. η^2 , η^3 , η^4 , η^5 or η^6). Give the oxidation state and the d-electron count.



I



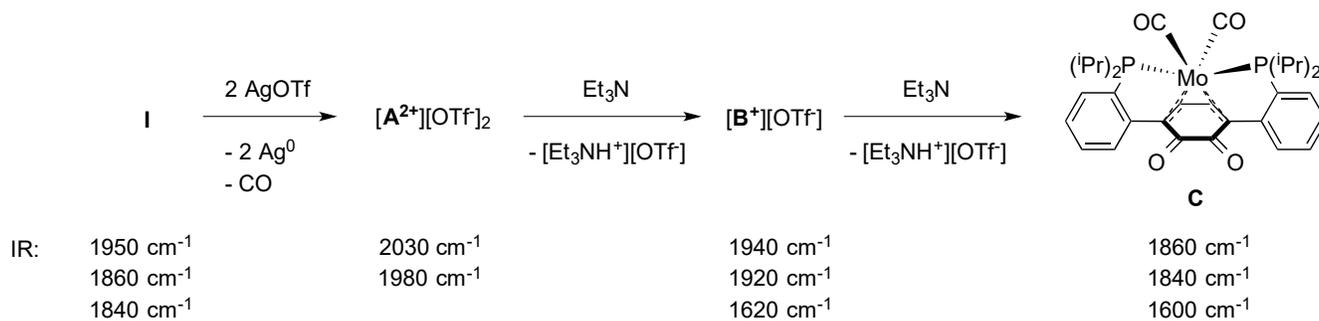
II



III

Part C

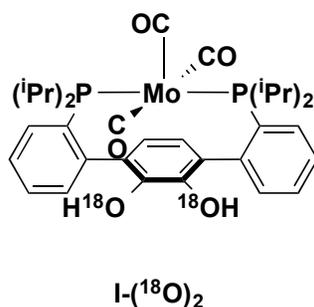
Compound **I** from above can be oxidized by 2 electrons using 2 equivalents of silver(I) trifluoromethanesulfonate (AgOTf) to yield a new 18-electron compound \mathbf{A}^{2+} . Compound \mathbf{A}^{2+} also exhibits a metal-arene interaction. Compound \mathbf{A}^{2+} can then be deprotonated with Et_3N to yield \mathbf{B}^+ , and further deprotonation with a second equivalent of Et_3N yields **C**. Relevant IR data is given for all of the compounds below. Note that the bands between $1800\text{-}2030\text{ cm}^{-1}$ are assigned to metal-carbonyl moieties and the bands between $1600\text{-}1650\text{ cm}^{-1}$ are assigned to organic $\text{C}=\text{O}$ moieties.



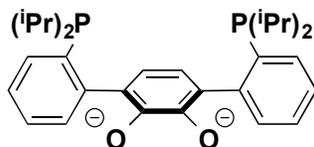
a) Draw structures for \mathbf{A}^{2+} and \mathbf{B}^+ . For \mathbf{B}^+ , draw three resonance structures, one in which the negative charge is localized on an oxygen atom of the central ring, and two in which the negative charge is localized on a carbon of the central ring.

b) Compounds \mathbf{A}^{2+} , \mathbf{B}^+ , and **C** are all 18-electron compounds. Give oxidation states and d-electron counts for the three compounds.

c) If compounds \mathbf{B}^+ were synthesized from ^{18}O labeled precursor below ($\mathbf{I}\text{-}(^{18}\text{O})_2$), estimate the new energies of the three IR bands listed above for \mathbf{B}^+ .

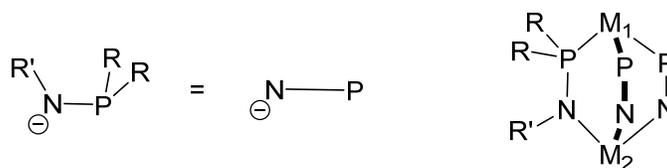


d) Consider the ligand below. How do you expect Pd^0 and Al^{3+} to bind based on HSAB theory?



Problem 3 (2 points)

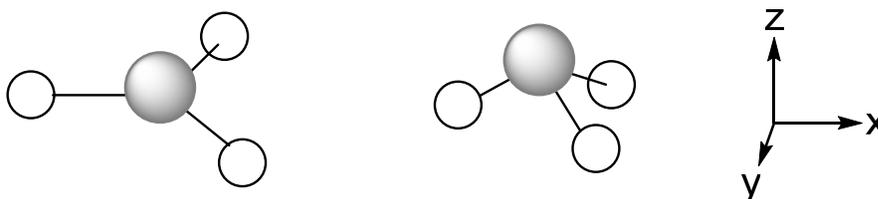
Early-late heterobimetallic complexes are of interest due to the unusual cooperative reactivity that can be observed that neither metal individually would be capable of doing. A ligand that has been employed to support this type of metal complex is the phosphine-amide ligand shown below. Three-fold symmetric complexes can be synthesized as shown on the right.



- a) For the following metal combinations, which metal binding site (M₁ or M₂) do you expect each to occupy?



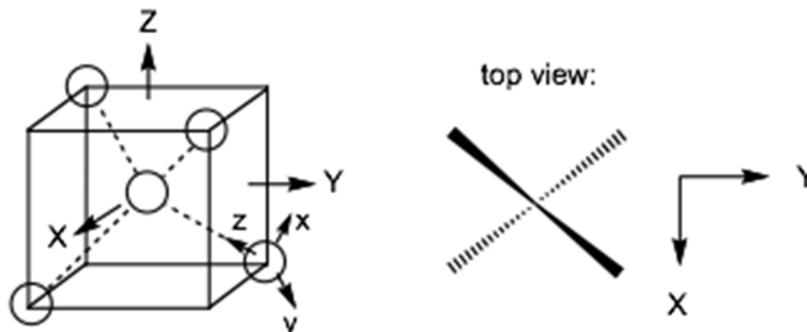
- b) For a complex that contains an Fe center at both M₁ and M₂ sites, which metal center would you expect to be more likely to bind [F]⁻? Which metal center would you expect to be more likely to bind CO? Explain.
- c) Considering the σ -only picture for one of the metal centers (i.e. ignoring any M-M bonding), construct a d-orbital splitting diagram (use only the five d orbitals for the metal) for a trigonal planar (D_{3h}) and trigonal pyramidal (C_{3v}) geometry using the axes shown below. Label with Mulliken symbols and show the d-parentage (d_{z^2} , d_{xy} , etc)



- d) For each of the MO diagrams from part (c), derive a new MO diagram for cases where the white circles correspond to the **amide** portion of the “PN” ligand and are capable of π -donation (take into account the directionality of the π -donation relevant orbitals!). Label with Mulliken symbols, show the d-parentage (d_{z^2} , d_{xy} , etc), and indicate whether the MOs are σ , σ^* , π , π^* , or nb.
- e) For each of the MO diagrams from part (c), derive a new MO diagram for cases where the white circles correspond to the **phosphine** portion of the “PN” ligand and are capable of π -backbonding (take into account the directionality of the π -backbonding relevant orbitals!). Label with Mulliken symbols, show the d-parentage (d_{z^2} , d_{xy} , etc), and indicate whether the MOs are σ , σ^* , π , π^* , or nb.

Problem 4 (2 points)

Permanganate MnO_4^- is a tetrahedral ion with an intense purple color that is widely used as an oxidizing agent. The figure below shows a convenient coordinate system for a tetrahedral complex that will be useful for generating a molecular orbital diagram for permanganate. You are asked to first examine the structurally similar PO_4^{3-} .



- Using the coordinate system shown above, generate the reducible and irreducible representations for the ligand σ -bonding interactions (note that there are two orbitals on oxygen that have σ -symmetry with respect to the P-O and Mn-O interaction; for this problem consider only one σ -orbital per oxygen, the second will formally constitute a low energy lone pair on oxygen that should not be included in your analysis).
- For PO_4^{3-} : Draw an MO diagram incorporating the ligand σ -bonding framework and s and p orbitals on P. For full credit, be sure to do all of the following:
 - Label the generated molecular orbitals with the appropriate Mulliken symbols and indicate whether they are σ , σ^* , or nb
 - Fill in the correct number of electrons
 - Draw the HOMO and LUMO (if degenerate sets, only draw one MO per set)
- Generate the reducible and irreducible representations for the ligand π -bonding interactions (two π -interactions per ligand)
- Draw a complete MO diagram incorporating both σ - and π -bonding ligand orbitals and s and p orbitals on P. For full credit, be sure to do all of the following:
 - Label the generated molecular orbitals with the appropriate Mulliken symbols and indicate whether they are σ , σ^* , π , π^* , or nb
 - Fill in the correct number of electrons
 - Draw the HOMO and LUMO (if degenerate sets, only draw one MO per set)
- For MnO_4^- : Draw an MO diagram incorporating the ligand σ -bonding framework and d, s, and p orbitals on Mn. For full credit, be sure to do all of the following:
 - Label metal orbitals with the appropriate Mulliken symbol and designate them as d, s, or p
 - Draw the metal and ligand orbitals at the appropriate relative energies (remember that due to oxygen's high electronegativity all of its orbitals will be lower in energy than the manganese orbitals).
 - Label the generated molecular orbitals with the appropriate Mulliken symbols and indicate whether they are σ , σ^* , or nb
 - Fill in the correct number of electrons
 - Draw the HOMO and LUMO (if degenerate sets, only draw one MO per set)

- f) Draw a complete MO diagram incorporating both σ - and π -bonding ligand orbitals and d, s, and p orbitals on Mn. For full credit, be sure to do all of the following:
- Label metal orbitals with the appropriate Mulliken symbol and designate them as d, s, or p
 - Label ligand orbitals with the appropriate Mulliken symbol and designate them as σ or π
 - Draw the metal and ligand orbitals at the appropriate relative energies
 - Label the generated molecular orbitals with the appropriate Mulliken symbols and indicate whether they are σ , σ^* , π , π^* , or nb
 - Fill in the correct number of electrons
 - Draw the HOMO and LUMO (if degenerate sets, only draw one MO per set)
- g) Based on the MO diagrams derived at f) and d) what is the correct valence electron count for Mn and P, respectively?

Problem 5 (2 points)

Pick a topic of interest from the recommended reading (descriptive chemistry) in bold at the beginning of this problem set. Prepare two power point slides including relevant *descriptive chemistry* (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (oxidation states, electron count, symmetry, MO theory, vibrational spectroscopy, etc.) and some application of the provided software (since MO theory and vibrational spectroscopy were covered in class, *you are now expected to include some molecular orbital pictures / MO diagram analysis / IR/Raman analysis using the provided software*). **Turn in a printout of the slides with your problem set,** and email the TAs the slides in pdf format by 12:00 noon on the due date. Please format file names as "**FirstName LastName PSET#**" and include your name on the first slide.