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 17 – *Before Class*

Problem 1 (2 points)

Part A

Hard and soft acids and bases (HSAB) theory can be used to explain the precipitation of metal sulfides.

An aqueous solution of Na_2S (1 mM) was acidified to pH=2 (H_2S: $pKa_1=7.4$, $pKa_2=19$).

a) Determine the minimum concentration of Hg^{2+} that will cause precipitation of HgS ($K_{sp}=2\text{x}10^{-54}$). How many grams Hg does this correspond to in a liter of solution?

b) Determine the minimum concentration of Zn^{2+} that will cause precipitation of ZnS ($K_{sp}=2\text{x}10^{-25}$). How many grams Zn does this correspond to in a liter of solution?

A solution of Na_2S (1 mM) was buffered to pH=10.

c) Determine the minimum concentration of Zn^{2+} that will cause precipitation of ZnS at pH=10. How many grams Zn does this correspond to in a liter of solution?

d) Explain the difference in solubility between ZnS and HgS using the HSAB theory and referring to the appropriate chemical equations.

Part B

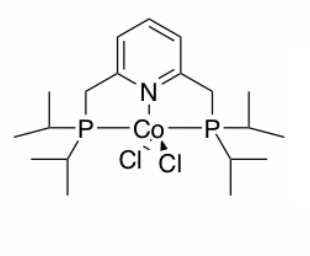
For each pair of complexes predict which has the larger *d*-*d* splitting, and explain all the relevant factors in your reasoning (do not just cite the trends; explain them).

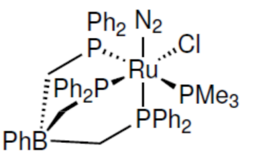
a) $[Cr(OH_2)_6]^{3+}$ vs. $[Cr(NH_3)_6]^{3+}$
b) $[Fe(CN)_6]^{4-}$ vs. $[Ru(CN)_6]^{4-}$
c) $[NiCl_4]^{2-}$ vs. $[Fe(oxalate)_3]^{3-}$
d) $[Co(phen)_3]^{3+}$ vs. $[Co(NH_3)_6]^{3+}$
e) $[Fe(OH_2)_6]^{3+}$ vs. $[Fe(OH_2)_6]^{2+}$
f) $[PdCl_4]^{2-}$ vs. $[PtCl_4]^{2-}$

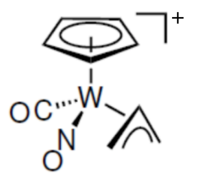
Problem 2 (3 points)

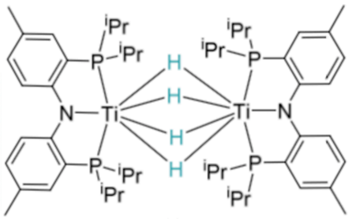
Part A

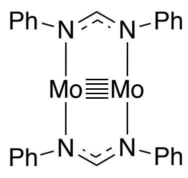
Give the oxidation state, d-electron count, and valence electron count for compounds below. If there is ambiguity regarding the ligand binding mode, sketch all reasonable possibilities and indicate the preferred isomer.





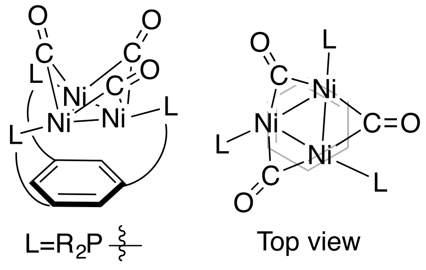




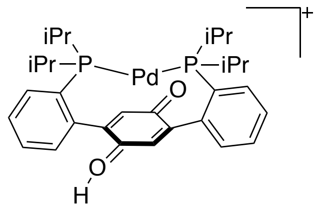


Part B

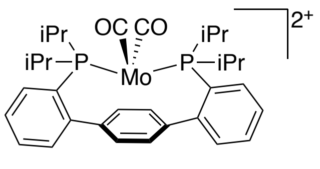
The following are all 18-electron compounds that exhibit a metal-arene interaction (with the central arene). Redraw each compound showing the metal-arene interaction and specify the hapticity (i.e. η^2, η^3, η^4, η^5 or η^6). Give the oxidation state and the d-electron count.



I



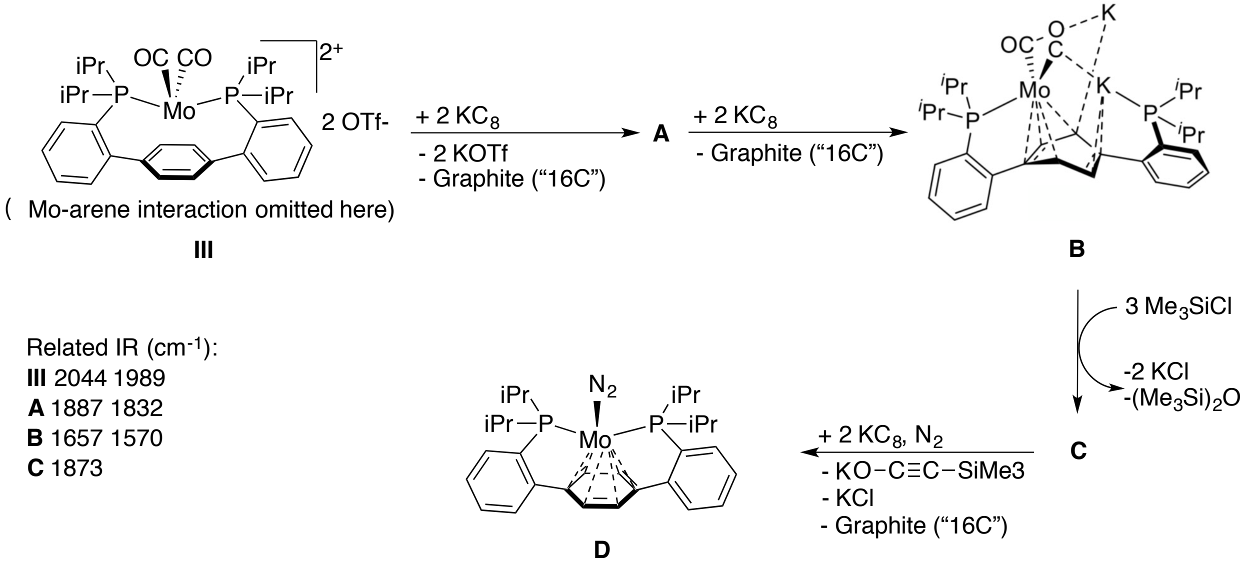
II



III

Part C

Compound **III** from above can be reduced by two electrons using two equivalents of KC_8 to yield a new 18-electron neutral compound **A**. Compound **A** also exhibits a metal-arene interaction. Compound **A** can then be reduced again by two electrons using two equivalents of KC_8 to yield **B**. Further reaction with excess Me_3SiCl (more than 3 equivalents) yields 18-electron compound **C** with two equivalents of KCl and one equivalent of $(Me_3Si)_2O$ as byproducts. **C** can be reduced by two equivalents of KC_8 under a nitrogen atmosphere to form **D**, KCl, and an alkyne product. IR data corresponding to stretches of CO ligands are given below.



Related IR (cm^{-1}):
III 2044 1989
A 1887 1832
B 1657 1570
C 1873

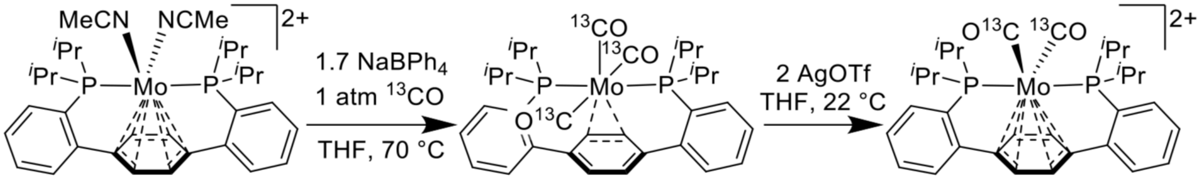
a) Draw two possible structures for **A** (one is η^4-type and one is η^6-type), then give the oxidation state, d-electron count, and valence electron count of each compound. Given the ^{31}P NMR of related compounds (see below), which structure is most consistent with the data and why? Hint: Chemical shifts downfield of 30 ppm are typical of coordination to Mo.

	III	**A**	**B**	**C**	**D**
^{31}P NMR δ (ppm)	75.1	92.3 -7.3	104.6 -2.7	36.6	76.7

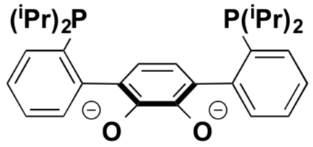
b) Based on the characterization data shown above, draw a structure for **C** that corresponds to an 18-electron count. Give the oxidation state and d-electron count.

c) Give the oxidation state, d-electron count, and valence electron count for **D**.

d) Compound **III** can be synthesized with ^{13}C labeled CO as shown below. Calculate the new energies of the two IR bands listed above for **III**.

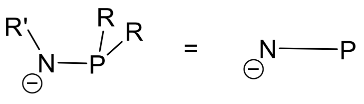


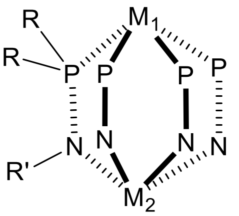
e) Consider the ligand below. How do you expect Pd^0 and Al^{3+} to bind based on HSAB theory?



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. A hypothetical four-fold symmetric complex from this type of ligand is shown on the right.



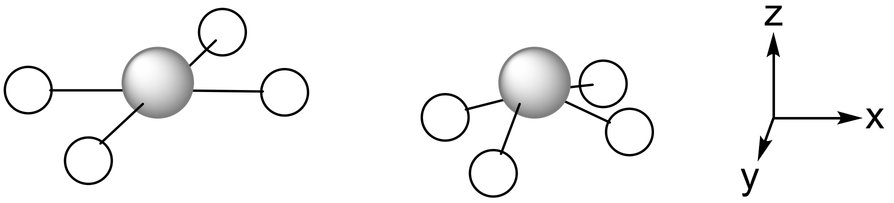


a) For the following metal combinations, which metal binding site (M$_1$ or M$_2$) do you expect each to occupy?

Hf(IV)	Co(II)
Cu(I)	Zr(IV)

b) For a complex that contains an Fe center at both M_1 and M_2 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 square planar (D_{4h}) and trigonal pyramidal (C_{4v}) geometry using the axes shown below. Label with Mulliken symbols and show the d-parentage (d_{z2}, d_{xy}, etc).

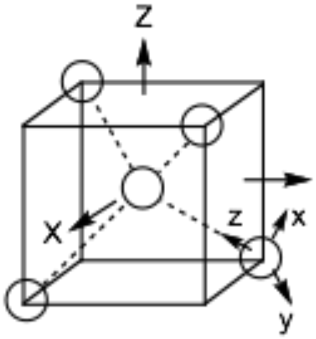


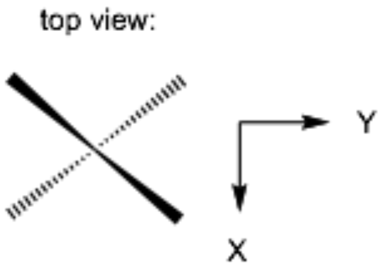
d) For each of the MO diagrams from part (c), derive a new MO diagram for cases where the white circles correspond to the **amide** portion of the "PN" ligand and are capable of π-donation (take into account the directionality of the π-donation relevant orbitals!). Label with Mulliken symbols, show the d-parentage (d_{z2}, 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_{z2}, 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-}.





a) 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).

b) 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)

c) Generate the reducible and irreducible representations for the ligand π-bonding interactions (two π-interactions per ligand)

d) 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)

e) 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.