

**Recommended reading:** 20, 21.2-21.4, 13, 22.1-22.6

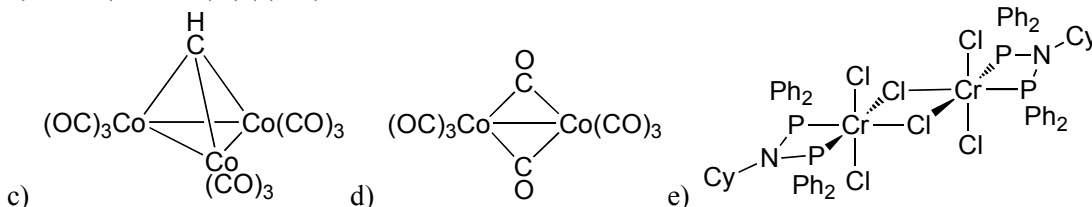
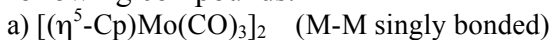
**Ch 102 Problem Set 5**

**Due: Tuesday, May 10, before class**

**Problem 1 (20 points)**

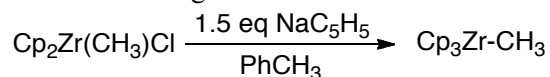
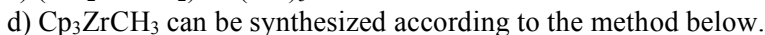
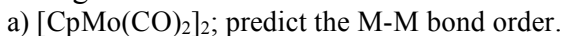
**Part A**

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



**Part B**

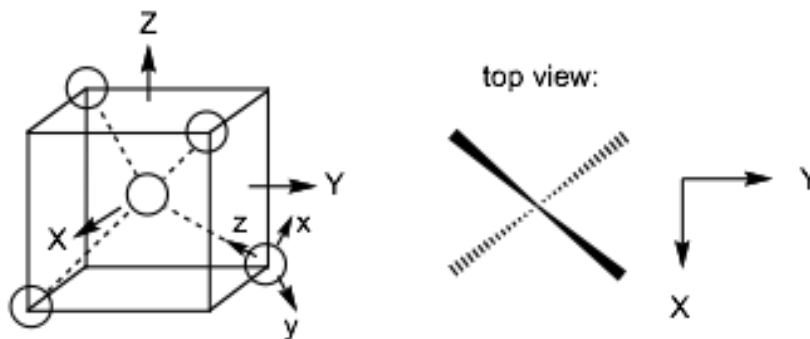
The following are all 18-electron compounds. Draw them. Give the oxidation state, d-electron configuration.



Draw the Zr complexes above showing the binding mode of Cp ligands. What are the oxidation state, d-electron configuration, and valence electron count for these Zr complexes?

**Problem 2 (20 Points)**

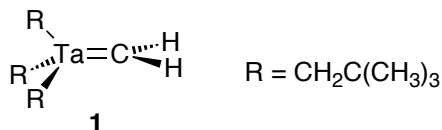
Permanganate  $\text{MnO}_4^-$  is a tetrahedral ion with an intense purple color that is widely used as an oxidizing agent. The figure below shows a convenient coordinate system for a tetrahedral complex that will be useful for generating a molecular orbital diagram for permanganate.



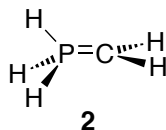
- a) Give the total electron count and d-electron count for Mn. Note that  $O^{2-}$  is a strong  $\pi$  donor and the donated  $\pi$ -lone pairs are considered in electron count. For now do not consider the availability of appropriate orbitals on Mn to accept these electrons and include them in electron count.
- b) Using the coordinate system shown above, generate the reducible and irreducible representations for the ligand  $\sigma$ -bonding interactions (note that there are two orbitals on oxygen that have  $\sigma$ -symmetry with respect to the Mn-O interaction; for this problem consider only one  $\sigma$ -orbital per oxygen, the second will formally constitute a low energy lone pair on oxygen that should not be included in your analysis).
- c) Draw an MO diagram incorporating the ligand  $\sigma$ -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
  - Label ligand orbitals with the appropriate Mulliken symbol
  - Draw the metal and ligand orbitals at the appropriate relative energies (remember that due to oxygen's high electronegativity all 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  $\sigma$ ,  $\sigma^*$ , or nb
  - Fill in the correct number of electrons
  - Draw the LUMO
- d) Generate the reducible and irreducible representations for the ligand  $\pi$ -bonding interactions (two  $\pi$ -interactions per ligand)
- e) Draw a complete MO diagram incorporating both  $\sigma$ - and  $\pi$ -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  $\sigma$  or  $\pi$
  - 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  $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$ , or nb
  - Fill in the correct number of electrons
  - Draw the HOMO and LUMO.
- f) Based on the MO diagram derived at e), what is the correct electron count for Mn?
- g) Is the electronic transition from the HOMO to the LUMO Laporte allowed? Depict this spin allowed excited state in the terms of a new electron configuration on the above MO diagram (only redraw the levels involved in the transition). Clearly show the spins of the electrons populating the frontier orbitals.
- h) Use the file on the class website to look at the  $[MnO_4]^-$  frontier orbitals. Attach pictures of the LUMO and HOMO. How do they compare with your derivation?

### Problem 3 (20 points)

The three chemists responsible for the discovery of the olefin metathesis reaction (Robert Grubbs, Richard Schrock, and Yves Chauvin) were awarded the 2005 Nobel Prize in Chemistry for their work in this field. One of the key species involved in the catalytic olefin metathesis reaction is an alkylidene complex such as tantalum species **1**.



Transition metal methyldene complexes have a main group counterpart in phosphonium ylides such as phosphonium ylide (**2**, shown as a resonance structure that does not obey the octet rule).



MO theory can be used to determine the similarities and differences in bonding between these two kinds of complexes. The MO diagram for each species can be obtained by interacting the frontier molecular orbitals of the  $\text{:CH}_2$  fragment with the frontier MOs of  $\text{TaR}_3$  and  $\text{PH}_3$ , respectively

- Consider the  $C_{3v}$ -symmetric  $\text{:PH}_3$  fragment; determine the reducible representation for the 3 H 1s orbitals, then reduce it to a sum of irreducible representations. Sketch the three SALCs for this basis set, and label each with its Mulliken symbol. Given that the d-orbitals of phosphorous are too high in energy to be involved in bonding, the P basis set will comprise the 3s and 3p orbitals only. Assign Mulliken symbols to the orbitals in the basis set, then interact them with the three H SALCs to obtain an MO diagram for  $\text{:PH}_3$ . Fill in the appropriate number of electrons, and identify HOMO and LUMO.
- Follow the same guidelines in part (a) to derive an MO diagram for the  $\text{TaR}_3$  fragment (use  $C_{3v}$ -symmetric  $\text{:TaH}_3$  as a model). You can use the SALC derivations from part a, since these will be the same. Remember that unlike phosphorous, tantalum has accessible d-orbitals, which will be involved in bonding. Remember to fill in the MO diagram with the appropriate number of electrons and to identify the HOMO and the LUMO.
- Consider now the  $C_{2v}$ -symmetric  $\text{:CH}_2$  fragment. Draw an MO diagram for  $\text{:CH}_2$  (use of class notes is allowed) Although normally methylene has a triplet ground state, consider it here as a singlet, with all electrons paired. Remember to fill in the MO diagram with the appropriate number of electrons and to identify the HOMO and the LUMO.
- Derive the MO diagram for the phosphonium ylide **2** by interacting the frontier orbitals (only HOMO and LUMO) of phosphine and methylene. Only take into account axial symmetry (ignore Mulliken symbols). Sketch the MOs for the HOMOs and LUMOs of

the :PH<sub>3</sub> and :CH<sub>2</sub> fragments. Based on these sketches and their respective axial symmetries (down the P-C axis), interact the orbitals of appropriate symmetry and derive the frontier MO diagram for **2**. Fill in the correct number of electrons. Sketch the resulting MOs and label HOMO and LUMO for **2**.

e) Repeat part (d) using the TaR<sub>3</sub> and :CH<sub>2</sub> fragments. For Ta use all 5 d-based frontier orbitals.

f) Comment on the character of the HOMO of H<sub>3</sub>PCH<sub>2</sub> (as derived in d). In this MO, what is the nature of the bonding between P and C (bonding vs antibonding, σ vs π)? Between P and H? How does the HOMO of H<sub>3</sub>TaCH<sub>2</sub> compare to the P analog?

g) Which species has a higher bond order for the E-CH<sub>2</sub> interactions (E=P or Ta)?

#### Problem 4 (20 points)

##### Part A

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).

- [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> vs. [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>
- [Fe(CN)<sub>6</sub>]<sup>4-</sup> vs. [Ru(CN)<sub>6</sub>]<sup>4-</sup>
- [NiCl<sub>4</sub>]<sup>2-</sup> vs. [Fe(oxalate)<sub>3</sub>]<sup>3-</sup>
- [Co(phen)<sub>3</sub>]<sup>3+</sup> vs. [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>
- [Fe(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> vs. [Fe(OH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup>
- [PdCl<sub>4</sub>]<sup>2-</sup> vs. [PtCl<sub>4</sub>]<sup>2-</sup>

##### Part B

As discussed in class, thiocyanate (NCS-) and cyanide (CN-) ligands can bind to metal centers through either the N or the S.

- What would expect the binding mode of Co(py)<sub>2</sub>(NCS)<sub>2</sub> to be based on your knowledge of hard-soft acid base theory?
- Prussian blue is a dark blue pigment with the formula Fe<sub>7</sub>(CN)<sub>18</sub>·14H<sub>2</sub>O and is known to contain bridging cyano groups between the Fe(II) and Fe(III) centers. Which oxidation state of Fe would you expect to bind to the C and to the N?

#### Problem 5 (20 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).