2.5: Problem Set 5

1. Chatt prepared the dinitrogen complexes, trans $-\mathrm{Mo(N_2)_2(PR_3)_4}$ in which the surprising result of two π-acid ligands coordinate trans to each other. Build the MO diagram for the complex. Draw the frontier d-orbital MOs and indicate the HOMO and LUMO orbitals.

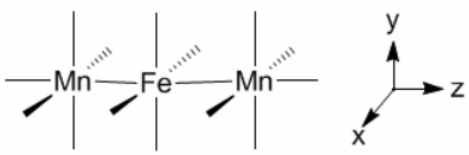
2. Shown below are two electronically different metal carbides. Use MO arguments to address the following:

a. Draw the HOMO for each complex.

b. Explain the vacant site trans to the carbide atom in the square pyramidal, Ru complex.

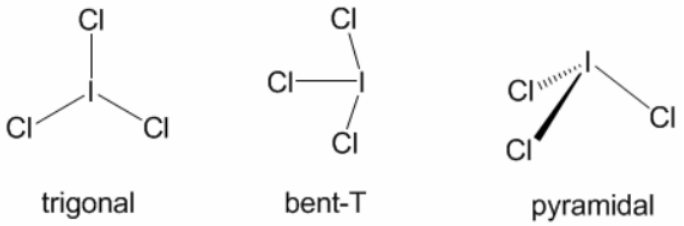
c. How many pi electrons are donated from the anilides into the metal in the moly complex (assume that for each $\mathrm{sp^2}$ hybirdized N-atom the tert-butly group point up, towards the apical carbide, and the aryl groups point down). Do the anilides and carbide compete for π symmetry orbitals on moly?

d. Estimate the relative acidity of both carbide-carbon atoms. Which of these acids will protonate the carbide: $\mathrm{MeC_6H_5}, \mathrm{HCPh_3}, \mathrm{H_3CCOOH}, \mathrm{H\,(OEt_2)\,B\,[3,5-C_6H_3(CF_3)_2]}$ (answer yes or no for each acid/carbide combination)?



3. The synthesis of uranocene, $\left[\left(\eta^8-\mathrm{C_8H_8}\right)_2\mathrm{U}\right]$, is considered as the beginning of modern organoactinide chemistry. Organoactinides are distinguished by covalent interactions between the 5f orbitals of the actinoids as well as the 6 d orbitals. Uranocene is paramagnetic, consisting of two planar $\mathrm{C_8H_8}^{2-}$ rings which are oriented in an eclipsed conformation, giving rise to its $\mathrm{D_{8\,h}}$ Symmetry.

Create an MO diagram for $(\mathrm{COT})_2\mathrm{U}$. Be careful to consider both the d and f for U. Comment on the predicted stability of this compound. What is the oxidation state of U? How many unpaired electrons are expected? What is the electron count at U?



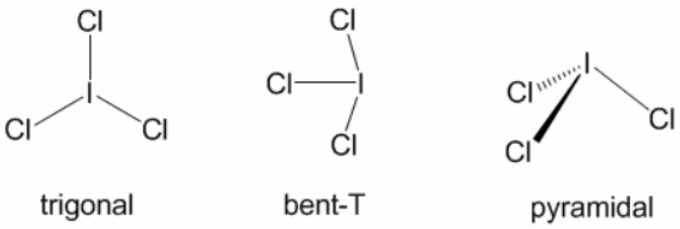
4. What is the barrier to rotation about the $\mathrm{M-N}$ bond in a $\mathrm{d^0}$ linear imido complex? What about in $\mathrm{Cp_2Zr\,(NMe_2)\,Me}$?

5. The $\mathrm{D_{4\,h}}$ linear metal-metal bonded cluster, $\mathrm{Mn_2Fe(CO)_{14}}$, shown below, is produced upon photolysis of solutions containing $\mathrm{Mn_2(CO)_{10}}$ and $\mathrm{Fe(CO)_5}$.

a. Construct the MO diagram (again, label the levels) of the cluster, considering the metal d-orbitals. Include in the MO diagram, the interaction arising from the $\mathrm{p_z}$ orbital of $\mathrm{Fe(CO)_4}$ with the $\mathrm{d_{z^2}}$ orbitals of the $\mathrm{Mn(CO)_5}$ fragments.

b. Predict the lowest energy allowed transition of this cluster and give the spectroscopic notation for the transition.

6. The interhalogen compounds have the formula $X'X_3$ $(e.g. ICl_3)$. One atom surrounded by three others can presumably occur in three symmetrically different shapes: trigonal planar, pyramidal, or Tshaped. The structure of interhalogen molecules can be deduced immediately from Lewis dot structures and the VSEPR model.



Assume that you are teaching $5.11x$ and a student challenges you to prove that VSEPR is indeed predicting the correct structure of ICl_3. With access to a Raman and IR instrument you can verify the structure of the molecule.

a. Analyze all three molecular shapes to find the number and symmetries of their vibrations and the number and symmetries of their IR and Raman allowed vibrations.

b. How many IR bands and Raman peaks will be observed for each shape?

c. The Raman and infrared spectra of ICl_3 each exhibit 6 active molecular vibrations. Which shape fits these IR and Raman data?

d. Determine the SALC's of the $I-Cl$ stretching vibrations of the molecular shape that fits the spectroscopic data above (i.e. a basis set of only three $I-Cl$ stretching vibrations is needed; not every molecular vibration in the molecule).

e. Sketch pictures of the symmetry coordinates and identify the irreducible representation to which the picture belongs.

The infrared spectrum of gaseous and the Raman spectrum of liquid WF_4O are set out below. Use them to decide the probable molecular geometry.

IR (in \left.\mathrm{cm}^{-1}\right)	Raman (in \mathrm{cm}^{-1})
1055 \mathrm{~m}	1057 s, pol
733 \mathrm{~m}	732 \mathrm{vs}, pol
698 \mathrm{vs}	
298 \mathrm{vw}	631 \mathrm{vw} \mathrm{br}
	328 br sh
	301
	298
248 \mathrm{w}	248 w, pol
236 \mathrm{~m}	234

(s = strong, m = medium, w = weak, v = very, br = broad, sh = should, pol = polarized)