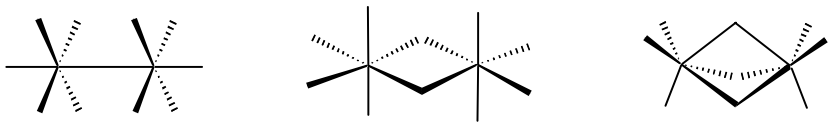
Chemistry 5.04 (F04)
Problem Set 7

Practice Problems

1. Two octahedra can be joined at a common vertex (A), at a common edge (B) or at a common face (C). Binuclear complexes possessing a confacial bioctahedral framework are prevalent in metal halide chemistry. We will construct the MO diagram for $Mo_2Cl_9^{3-}$ from a $MoCl_3$ fragment.



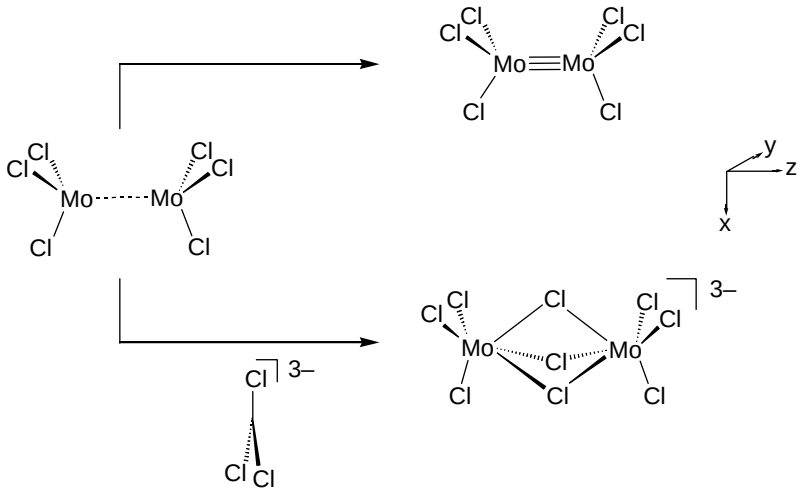
A **B** **C**

(a) Develop Mo_2Cl_6 fragment from two pyramidal $MoCl_3$ fragments using 5d orbitals and p_z orbitals of the metal.

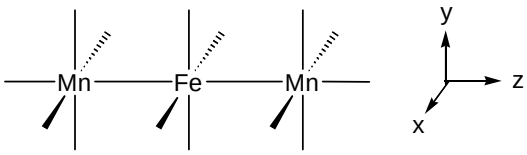
(b) Dimerization of two $MoCl_3$ fragments leads to the formation of a triply bonded metal metal dimer. Show the MO diagram for the multiply bonded species. Show orbital symmetries and pictures of the MOs formed from the frontier orbitals of the fragments.

(c) Construct the bridging ligand Cl_3^{3-} using p-orbitals of the chlorine.

(d) Combine the two fragments Mo_2Cl_6 and Cl_3^{3-} to yield the $Mo_2Cl_9^{3-}$ complex. Again show orbital symmetries and label the MOs.

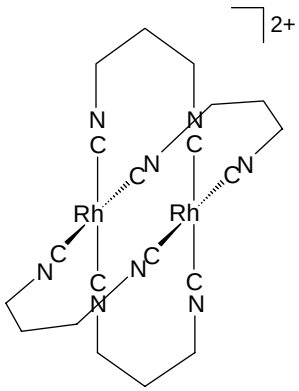


2. The D_{4h} linear metal-metal bonded cluster, $Mn_2Fe(CO)_{14}$, shown below, is produced upon photolysis of solutions containing $Mn_2(CO)_{10}$ and $Fe(CO)_5$.

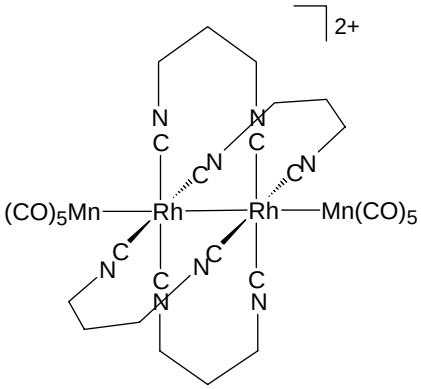


Construct the MO diagram (again, label the levels) of the cluster, considering the metal d-orbitals. Include in the MO diagram, the interaction arising from the p_z orbital of $Fe(CO)_4$ with the d_{z^2} orbitals of the $Mn(CO)_5$ fragments.

3. The d^8—d^8 metal complexes, such as Rh_2(diisocyanoalkane)$_2$, feature a long lived and highly reactive lowest energy excited state. The photochemistry of these complexes can only be understood in the context of their electronic structure. Construct the MO diagram of the ruthenium bimetallic complex **D** and identify the lowest energy excited state. Predict whether the Rh—Rh distance will decrease or increase upon excitation.



D



E

Photolysis of $Mn_2(CO)_{10}$ in the presence of **D** affords a new compound $\{[Rh(CNCH_2CH_2CH_2NC)_4Rh]Mn_2(CO)_{10}\}^{2+}$, **E**. Describe the s-bonding using frontier Mn and Rh dimer orbitals for this product.