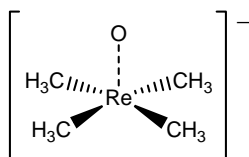
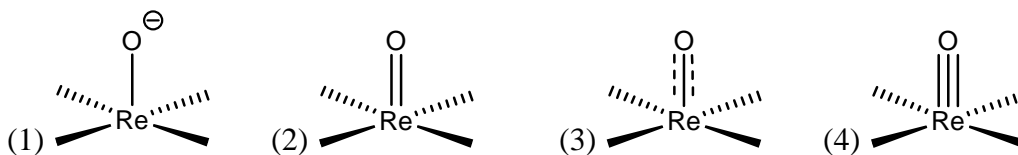


Recommended Reading: M&T pg 342-370 (Sections 10-2, 10-3, 10-4)

I. The square pyramidal anion $[\text{ReO}(\text{CH}_3)_4]^-$ was synthesized by Nobel Laureate Geoffrey Wilkinson in 1975. To generate the full ($\sigma + \pi$) MO diagram of this complex, it is often easier to start with the σ -only MO diagram and then perturb it by incorporating the π orbitals.



- What is the point group of this molecule?
- Generate the reducible representation for the ligand σ -orbitals (assume that all ligands are the same, i.e. $\text{Re}(\text{CH}_3)_5$, for the σ -only MO), and decompose it into the irreducible representations.
- Sketch the SALC's for the ligand σ -orbitals, and label with the appropriate Mulliken symbols.
- Draw the relevant atomic orbitals (5d, 6s, and 6p) for rhenium and label with the appropriate Mulliken symbols.
- Construct a σ -only MO diagram for $\text{Re}(\text{CH}_3)_5$ by interacting the SALCs with the metal orbitals. Label each MO with the appropriate Mulliken symbol. Indicate whether the MO is bonding, non-bonding, or anti-bonding. Sketch the bonding and anti-bonding MOs. Add electrons.
- Now consider the anion $[\text{ReO}(\text{CH}_3)_4]^-$. Explain how incorporating the π orbitals will change the σ -only MO diagram?
- Add π -effects from the two oxygen 2p orbitals by first determining Γ_{2O2p} .
- Draw the MO diagram containing both σ and π effects.
- What is the Re-O bond order?
- The Re-O bond is best represented by which of the following drawings? (#3 is a representation of one σ bond and 2 half π bonds)



II. Continue to practice drawing full ($\sigma + \pi$) MO diagrams by using $\Gamma_{\sigma+\pi}$ as was done in class to analyze the bonding in the following complexes:

- $[\text{MnO}_4]^-$ (tetrahedral)
- $[\text{PtCl}_4]^{2-}$ (square planar)

A complete answer will include the correct Mulliken symbol on each MO; the bonding, non-bonding, or anti-bonding designation; a sketch of each MO; and the correct number of electrons.

III. Predict which complex in each of the following pairs will have the lower energy d-d transition (give a brief explanation of your reasoning):

- a. $[\text{V}(\text{CO})_6]^-$ or $[\text{Ta}(\text{CO})_6]^-$
- b. $\text{W}(\text{PF}_3)_6$ or $\text{W}(\text{P}(\text{CH}_3)_3)_6$
- c. $[\text{Fe}(\text{CN})_6]^{4-}$ or $[\text{Co}(\text{CN})_6]^{3-}$
- d. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
- e. $[\text{RhF}_6]^{2-}$ or IrF_6
- f. $[\text{Pt}(\text{NH}_3)_6]^{4+}$ or $[\text{NiF}_6]^{2-}$