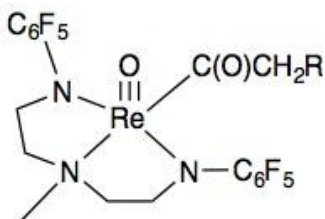


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## Building Molecular Orbitals for a Square Pyramidal Oxorhenium(V) Complex

- Consider an octahedral complex of formula  $ML_6$ . Assume for now that all ligands are  $\sigma$ -donors only.
  - Label x,y and z axes (the z axis should be the vertical axis in the plane of the page). Draw the metal  $d$  orbitals.
  - Which orbitals on the central metal will be affected by  $\sigma$  interactions with the ligands?
  - Build a MO diagram for the orbitals of metal  $d$  character in this octahedral complex. Label the orbitals on your diagram. (You should have a set of orbitals of  $e_g$  symmetry and another of  $t_{2g}$  symmetry in this  $O_h$  point group)
- Now remove a ligand L on the z axis to form a square pyramidal complex of formula  $ML_5$ .
  - How are the orbitals of metal  $d$  character affected in your MO diagram by the absence of a ligand L on the z axis?
  - Redraw your MO diagram for orbitals of metal  $d$  character in a square pyramidal complex. Label the orbitals.
- Now consider the oxorhenium(V) complex synthesized by Elon Ison's group in *Organometallics* **2015**, *34*, 3152-3158. This complex is reported to have a "distorted" square pyramidal geometry. For the purpose of this exercise, first consider the structure to be an "ideal" square pyramid of formula  $M(L)_3L'L$ , then progressively add distortions by considering the differences between ligands.



- Which ligands are also  $\pi$ -donors and/or  $\pi$ -acceptors?
- Which  $d$  orbitals on the central metal may be involved in  $\pi$  interactions with a ligand?
- Redraw a MO diagram for the square pyramidal oxorhenium(V) complex above that includes  $\pi$  interactions with the ligands. You should consider both the type of  $\pi$  interactions for the ligand (donor or acceptor) and the location of these ligands in the complex (xy plane or z axis).

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4. Rhenium has an oxidation state of (V) in the complex above.
  - a. What is the  $d^n$  configuration of rhenium?
  - b. Which  $d$  orbital(s) in your MO diagram above will contain these electrons?
  - c. Are these electrons contained in  $d$  orbital(s) of bonding, nonbonding or antibonding character?
  - d. Is the effect stabilizing or destabilizing for the complex? Explain.