

## 2.4: $\sigma$ , $\pi$ , and $\delta$ orbitals

Inorganic compounds use s, p, and d orbitals (and more rarely f orbitals) to make bonding and antibonding combinations. These combinations result in  $\sigma$ ,  $\pi$ , and  $\delta$  bonds (and antibonds).

You are already familiar with  $\sigma$  and  $\pi$  bonding in organic compounds. In inorganic chemistry,  $\pi$  bonds can be made from p- and/or d-orbitals.  $\delta$  bonds are more rare and occur by face-to-face overlap of d-orbitals, as in the ion  $\text{Re}_2\text{Cl}_8^{2-}$ . The fact that the Cl atoms are eclipsed in this anion is evidence of  $\delta$  bonding.

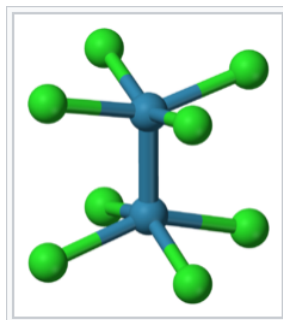
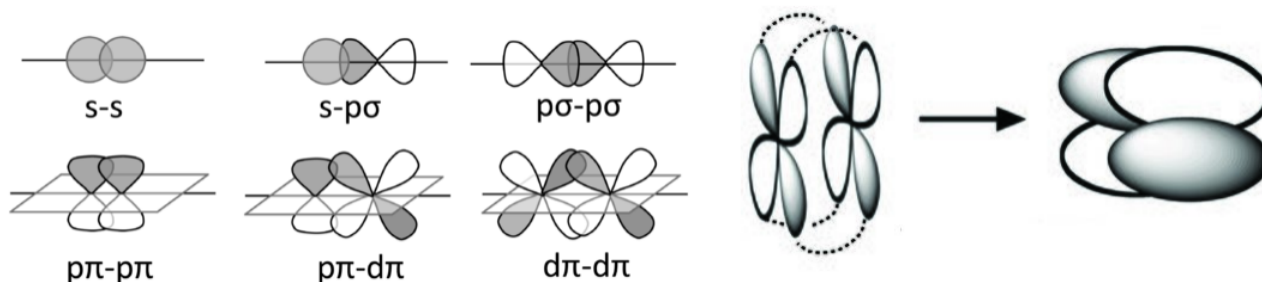
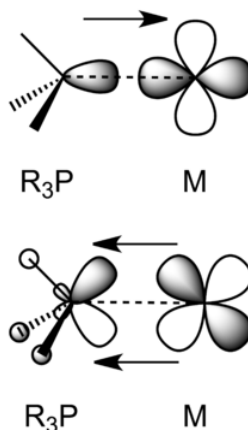


Figure 2.4.1: The octachlorodirhenate(III) anion,  $[\text{Re}_2\text{Cl}_8]^{2-}$ , which has a quadruple Re-Re bond.<sup>[3]</sup>

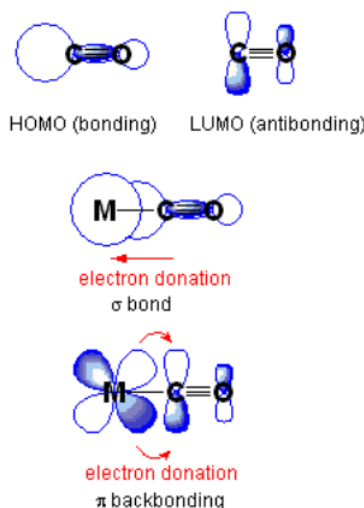
Some possible  $\sigma$  (top row),  $\pi$  (bottom row), and  $\delta$  bonding combinations (right) of s, p, and d orbitals are sketched below. In each case, we can make bonding or antibonding combinations, depending on the signs of the AO wavefunctions. Because  $\pi\pi$ - $\pi\pi$  bonding involves sideways overlap of p-orbitals, it is most commonly observed with second-row elements (C, N, O).  $\pi$ -bonded compounds of heavier elements are rare because the larger cores of the atoms prevent good  $\pi$ -overlap. For this reason, compounds containing C=C double bonds are very common, but those with Si=Si bonds are rare.  $\delta$  bonds are generally quite weak compared to  $\sigma$  and  $\pi$  bonds. Compounds with metal-metal  $\delta$  bonds occur in the middle of the transition series.



Transition metal d-orbitals can also form  $\sigma$  bonds, typically with s-p hybrid orbitals of appropriate symmetry on ligands. For example, phosphines ( $\text{R}_3\text{P}$ ) are good  $\sigma$  donors in complexes with transition metals, as shown below.



$\pi$ - $d\pi$  bonding is also important in transition metal complexes. In metal carbonyl complexes such as  $\text{Ni(CO)}_4$  and  $\text{Mo(CO)}_6$ , there is sideways overlap between filled metal d-orbitals and the empty  $\pi$ -antibonding orbitals (the LUMO) of the CO molecule, as shown in the figure below. This interaction strengthens the metal-carbon bond but weakens the carbon-oxygen bond. The C-O infrared stretching frequency is diagnostic of the strength of the bond and can be used to estimate the degree to which electrons are transferred from the metal d-orbital to the CO  $\pi$ -antibonding orbital.



The same kind of backbonding occurs with phosphine complexes, which have empty  $\pi$  orbitals, as shown at the right. Transition metal complexes containing halide ligands can also have significant  $\pi$ - $d\pi$  bonding, in which a filled  $p\pi$  orbital on the ligand donates electron density to an unfilled metal  $d\pi$  orbital. We will encounter these bonding situations in Chapter 5.

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