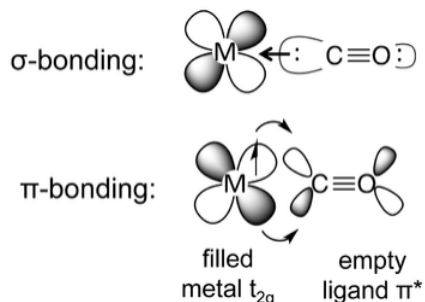


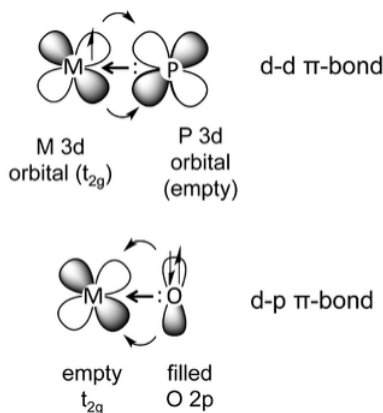
5.5: π -Bonding between Metals and Ligands

An important factor that contributes to the high ligand field strength of ligands such as CO, CN⁻, and phosphines is **π -bonding** between the metal and the ligand. There are three types of π -bonding in metal complexes:

The most common situation is when a ligand such as carbon monoxide or cyanide donates its sigma (nonbonding) electrons to the metal, while accepting electron density from the metal through overlap of a metal t_{2g} orbital and a ligand π^* orbital. This situation is called "**back-bonding**" because the ligand donates σ -electron density to the metal and the metal donates π -electron density to the ligand. The ligand is thus acting as a **σ -donor and a π -acceptor**. In π -backbonding, the metal donates π electrons to the ligand π^* orbital, adding electron density to an *antibonding* molecular orbital. This results in weakening of the C-O bond, which is experimentally observed as lengthening of the bond (relative to free CO in the gas phase) and lowering of the C-O infrared stretching frequency.



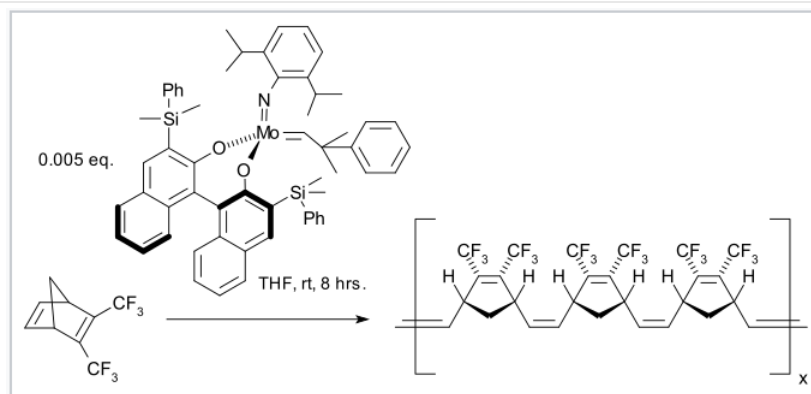
d-d π bonding occurs when an element such as phosphorus, which has a σ -symmetry lone pair and an empty metal 3d orbital, binds to a metal that has electrons in a t_{2g} orbital. This is a common situation for phosphine complexes (e.g., triphenylphosphine) bound to low-valent, late transition metals. The backbonding in this case is analogous to the CO example, except that the acceptor orbital is a phosphorus 3d orbital rather than a ligand π^* orbital. Here the phosphine ligand acts as a σ -donor and a π -acceptor, forming a $d\pi$ - $d\pi$ bond.



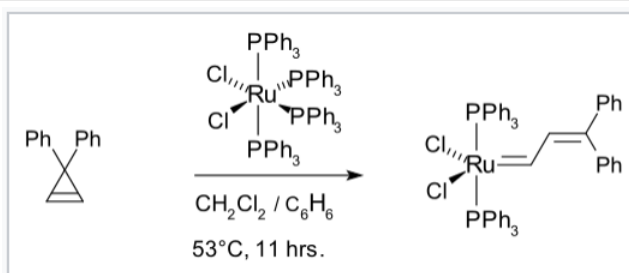
The third kind of metal-ligand π -bonding occurs when a **π -donor ligand** - an element with both a σ -symmetry electron pair and a filled orthogonal p-orbital - bonds to a metal, as shown above at the right for an O^{2-} ligand. This occurs in early transition metal complexes. In this example, O^{2-} is acting as both a **σ -donor and a π -donor**. This interaction is typically drawn as a metal-ligand multiple bond, e.g., the V=O bond in the vanadyl cation $[VO]^{2+}$. Typical π -donor ligands are oxide (O^{2-}), nitride (N^{3-}), imide (RN^{2-}), alkoxide (RO^-), amide (R_2N^-), and fluoride (F^-). For late transition metals, strong π -donors form anti-bonding interactions with the filled d-levels, with consequences for spin state, redox potentials, and ligand exchange rates. π -donor ligands are low in the spectrochemical series.^[5]

Carbon-containing ligands that are π -donors and their complexes with transition metal ions are very important in **olefin metathesis**, a reaction in which carbon-carbon double bonds are interchanged. Using these catalysts, cyclic olefins can be transformed into linear polymers in high yield through ring-opening metathesis polymerization (ROMP). Catalysts of this kind were developed by the groups of Richard Schrock and Robert Grubbs, who shared the 2005 Nobel Prize in Chemistry with Yves Chauvin for their

discoveries. The Schrock catalysts are based on early transition metals such as Mo; they are more reactive but less tolerant of different organic functional groups and protic solvents than the Grubbs catalysts, which are based on Ru complexes.



A chiral Schrock catalyst polymerizes a norbornadiene derivative to a highly stereoregular isotactic polymer.^[6]



Synthesis of a Grubbs olefin metathesis catalyst.^[7]

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