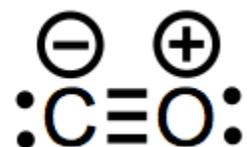


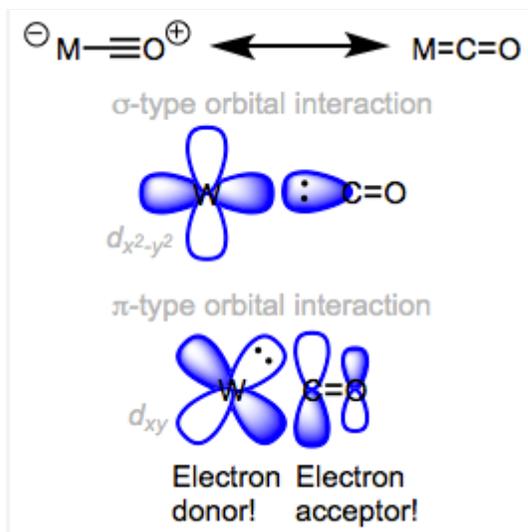
EPIC LIGAND SURVEY: CARBON MONOXIDE



As a young, growing field, organometallic chemistry may be taught in many ways. Some professors (e.g., [Shaugnessy](#)) spend a significant chunk of time discussing ligands, while others forego ligand surveys (e.g., [White](#)) to dive right in to reactions and mechanisms. I like the ligand survey approach because it lays out many of the general concerns associated with certain ligand sets before organometallic intermediates pop up. With the general concerns in hand, it becomes easier to generate explanations for certain observed effects on reactions that depend on ligands. Instead of generalizing from complex, specific examples in the context of reaction mechanisms, we'll look at general trends first and apply these to reaction intermediates and mechanisms later. This post kicks off our epic ligand survey with carbon monoxide, a simple but fascinating ligand.

General Properties

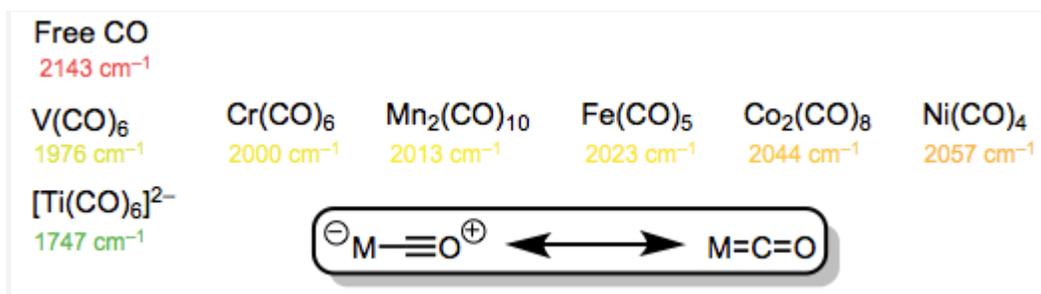
CO is a dative, L-type ligand that does not affect the oxidation state of the metal center upon binding, but does increase the total electron count by two units. We've recently seen that there are really two bonding interactions at play in the carbonyl ligand: a ligand-to-metal $n \rightarrow d_\sigma$ interaction and a metal-to-ligand $d_\pi \rightarrow \pi^*$ interaction. The latter interaction is called **backbonding**, because the metal donates electron density back to the ligand. To remind myself of the existence of backbonding, I like to use the right-hand resonance structure whenever possible; however, it's important to remember to treat CO as an L-type ligand no matter what resonance form is drawn.



Orbital interactions in $\text{M}=\text{C}=\text{O}$.

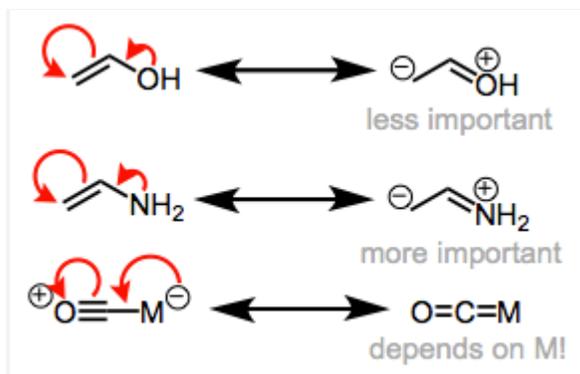
CO is a strong σ -donor (or σ -base) and a good π -acceptor (or π -acid). The properties of ligated CO depend profoundly upon the identity of the metal center. More specifically, the electronic properties of the metal center dictate the importance of backbonding in metal carbonyl complexes. Most bluntly, *more electron-rich metal centers are better at backbonding to CO*. Why is it important to ascertain the strength of backbonding? I'll leave that question hanging for the moment, but we'll have an answer very soon. Read on!

Infrared spectroscopy has famously been used to empirically support the idea of backbonding. The table below arranges some metal carbonyl complexes in "periodic" order and provides the frequency corresponding to the C=O stretching mode. Notice that without exception, every complexed CO has a stretching frequency lower than that of free CO. Backbonding is to blame! The C–O bond order in complexed carbon monoxide is (almost always) lower than that of free CO.



C=O stretching frequencies in metal-carbonyl complexes. Does something seem off here?

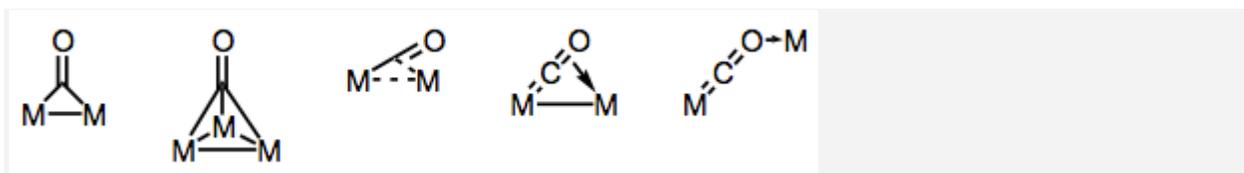
The figure above depicts a clear increase in frequency (an increase in C–O bond order) as we move left to right across the periodic table. This finding may seem odd if we consider that the number of *d* electrons in the neutral metal increases as we move left to right. Shouldn't metal centers with more *d* electrons be better at backbonding (and more “electron rich”)? What's going on here? Recall the periodic trend in *orbital energy*. As we move left to right, the *d* orbital energies decrease and the energies of the *d*_π and π* orbitals separate. As a result, the backbonding orbital interaction becomes worse (remember that strong orbital interactions require well-matched orbital energies) as we move toward the more electronegative late transition metals! We can draw an analogy to enamines and enol ethers from organic chemistry. The more electronegative oxygen atom in enol ethers is a worse electron donor than the enamine's nitrogen atom.



The importance of backbonding depends on the electronegativity of the metal and its electron density.

Of course, the contribution of other ligands on the metal center to backbonding cannot be forgotten, either. Logically, electron-donating ligands will tend to make the backbond stronger (they make the metal a better electron donor), while electron-withdrawing ligands will worsen backbonding. Adding electron-rich phosphine ligands to a metal center, for instance, *decreases* the CO stretching frequency due to *improved* backbonding.

Carbonyl ligands are famously able to **bridge** multiple metal centers. Bonding in bridged carbonyl complexes may be either “traditional” or delocalized, depending on the structure of the complex and the bridging mode. The variety of bridging modes stems from the different electron donors and acceptors present on the CO ligand (and the possibility of delocalized bonding). Known bridging modes are shown in the figure below.



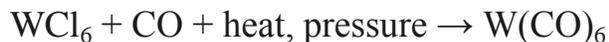
Building bridges with carbonyl ligands!

Synthesis

Metal carbonyl complexes containing only CO ligands abound, but most cannot be synthesized by the method we all wish worked, bathing the elemental metal in an atmosphere of carbon monoxide (entropy is a problem, as we already discussed for $\text{W}(\text{CO})_6$). This method does work for nickel(0) and iron(0) carbonyls, however.



Other metal carbonyl complexes can be prepared by **reductive carbonylation**, the treatment of a high-oxidation-state complex with CO. These methods usually require significant heat and pressure. One example:



Still other methods employ **deinsertion** from organic carbonyl compounds like dimethylformamide. These methods are particularly useful for preparing mixed carbonyl complexes in the presence of reducing ligands like phosphines.

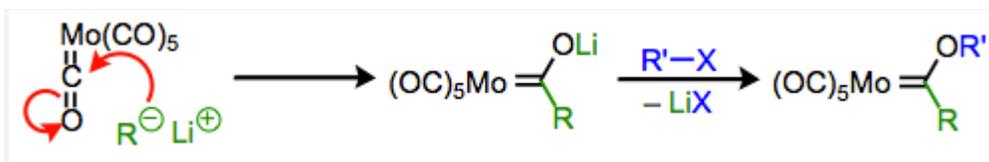


The key thing to notice about the reaction above is that the CO ligand is derived from dimethylformamide (DMF).

Reactions

The dissociation of carbonyl ligands is common in reactions that require an open coordination site at the metal. Naturally, the favorability of dissociation is governed by electron density at the metal—weaker backbonding metals lose CO more easily. This is one reason understanding trends in backbonding strength is important!

Like the carbonyl carbon in organic compounds, the carbon of ligated CO is often an exquisite electrophile—particularly when the metal is a poor π -base, leaving the carbonyl carbon starved of electrons. CO ligands are susceptible to nucleophilic attack at the carbonyl carbon in the presence of strong nucleophiles. Treating the adduct with an electrophile yields a Fischer carbene complex. If we imagine $\text{M}=\text{C}=\text{O}$ as an analogue of ketene, this reactivity just corresponds to classic nucleophilic addition across the $\text{C}=\text{O}$ bond.



Metal carbene complexes from metal carbonyls via nucleophilic addition.

Perhaps the most important elementary step in which the CO ligand participates is **migratory insertion**, a step typical of oxidized organic ligands (CO, alkenes, alkynes, etc.). The net result of the process is the insertion of the carbonyl carbon into an M–X bond (X is most commonly C or H, but can be any X-type ligand). An empty coordination site—the strange-looking box in the figure below—is left behind after migration. The **hydroformylation** reaction involves the insertion of CO into an M–C bond as a key step. We'll talk about this fascinating processes in more detail in a later post.



Migratory insertion, a powerful method for C–C bond construction on transition metal centers.

For CO, it's useful to think about migratory insertion as a sort of intramolecular nucleophilic attack by the X-type ligand on coordinated CO. In this respect its similar to the intermolecular nucleophilic addition process leading to carbenes described above. Just view the carbonyl carbon as an electrophile (as if you don't already!) and it becomes easy to keep these ideas in mind. We'll see migratory insertion in more detail in a future post as well.

Source : <http://organometallicchem.wordpress.com/2012/01/17/epic-ligand-survey-carbon-monoxide/>