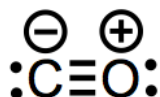


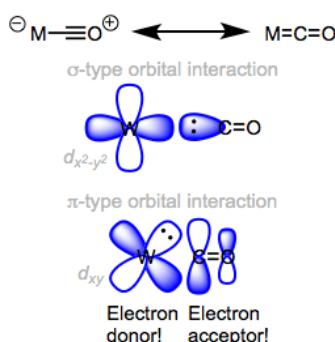
# CARBON MONOXIDE AND BACKBONDING

Carbon monoxide is a simple but fascinating ligand. We have previously noted that carbon monoxide, although a very poor base, is a strong field ligand due to the presence of  $\pi$  backbonding.



## 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 is important to remember to treat CO as an L-type ligand no matter what resonance form is drawn.



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

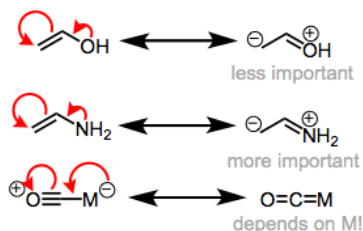
CO is a strong  $\sigma$ -donor (or  $\sigma$ -base) and a good  $\pi$ -acceptor (or  $\pi$ -acid). The properties of ligated CO depend profoundly upon the identity of the metal center. More specifically, the electronic properties of the metal center dictate the importance of backbonding in metal carbonyl complexes. Most bluntly, more electron-rich metal centers are better at backbonding to CO. Why is it important to ascertain the strength of backbonding?

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.

Free CO 2143 $\text{cm}^{-1}$					
$\text{V}(\text{CO})_6$ 1976 $\text{cm}^{-1}$	$\text{Cr}(\text{CO})_6$ 2000 $\text{cm}^{-1}$	$\text{Mn}_2(\text{CO})_{10}$ 2013 $\text{cm}^{-1}$	$\text{Fe}(\text{CO})_5$ 2023 $\text{cm}^{-1}$	$\text{Co}_2(\text{CO})_8$ 2044 $\text{cm}^{-1}$	$\text{Ni}(\text{CO})_4$ 2057 $\text{cm}^{-1}$
$[\text{Ti}(\text{CO})_6]^{2-}$ 1747 $\text{cm}^{-1}$	$\ominus \text{M} \equiv \text{O}^{\oplus} \longleftrightarrow \text{M} = \text{C} = \text{O}$				

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

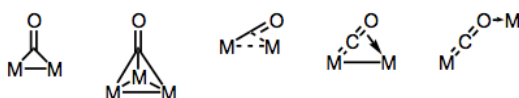
The figure above depicts a clear increase in frequency (an increase in C-O bond order) as we move left to right across the periodic table. This finding may seem odd if we consider that the number of d electrons in the neutral metal increases as we move left to right. Shouldn't metal centers with more 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  $d\pi$  and  $\pi^*$  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!

## CONTRIBUTORS

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