

## 4.2: CO Binding

Migratory insertion involves the transfer of a hydride or alkyl group from a metal to a bound carbon monoxide. Because this reaction specifically involves bound carbon monoxide, we should take a look at how CO binds to transition metals. We should begin by reviewing the Lewis structure of carbon monoxide.



Figure 4.2.1: The Lewis structure of carbon monoxide.

Note the lone pair on carbon monoxide. It is a potential Lewis base or nucleophile. For a number of reasons, transition metals are almost always electrophiles: they are often positively charged ions, but in general they have an 18-electron octet that is difficult to fill, so they frequently need more electrons.

- Lewis: CO is a two electron donor
- Transition metals are electrophiles
- CO binds to metal atoms or ions
- The carbon is the usual donor atom; it has a lone pair and a negative formal charge

The donation of an electron pair to a metal cation is shown in figure 4.2.2.



Figure 4.2.2: Binding of CO to a metal cation.

Remember, because the 18-electron rule for transition metals makes them electrophilic, the electron pair does not need a positive charge to attract it (figure 4.2.3).



Figure 4.2.3: CO binding to a neutral metal atom.

Frequently, the formal charges and lone pairs are not even shown in the transition metal compound, because of the complexity of the picture.



Figure 4.2.4: A more commonly used picture of CO binding leaves out the formal charges.

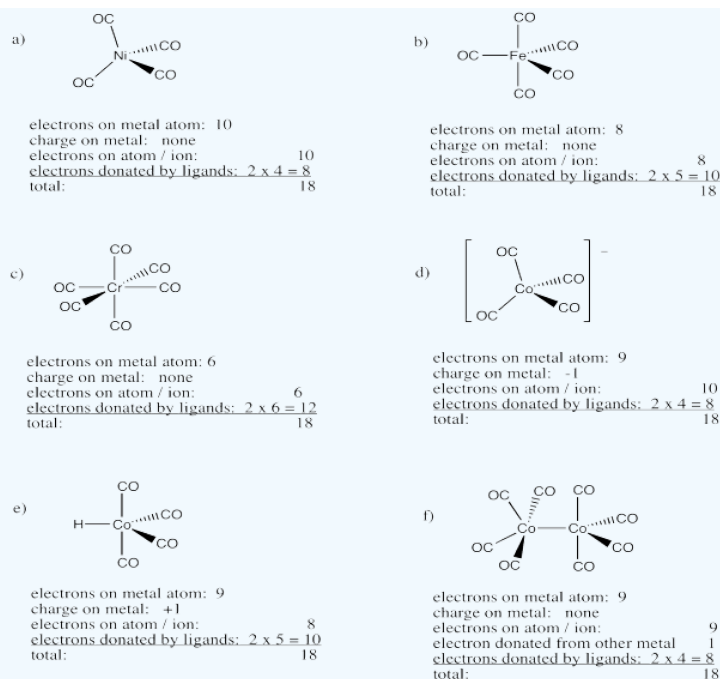
Note that CO in the context of metal complexes is often referred to as carbonyl. For example,  $\text{Cr}(\text{CO})_6$  is called hexacarbonyl chromium.

### ? Exercise 4.2.1

Draw structures for the following metal carbonyl compounds. For each compound, indicate

- the electron count at the metal in the complex (show your work)
- the geometry at the metal
  - tetracarbonyl nickel,  $\text{Ni}(\text{CO})_4$
  - pentacarbonyl iron,  $\text{Fe}(\text{CO})_5$
  - hexacarbonyl chromium,  $\text{Cr}(\text{CO})_6$
  - tetracarbonyl cobalt anion,  $\text{Co}(\text{CO})_4^-$
  - tetracarbonyl cobalt hydride,  $\text{Co}(\text{CO})_4\text{H}$
  - octacarbonyl cobalt,  $\text{Co}_2(\text{CO})_9$  (there is a bond between the two cobalt atoms)

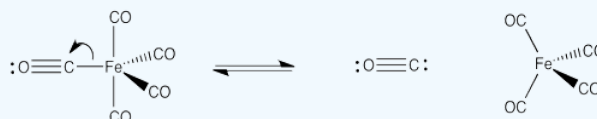
**Answer**



### ? Exercise 4.2.2

Draw, with structures and arrows, the equilibrium between pentacarbonyl iron and tetracarbonyl iron,  $\text{Fe}(\text{CO})_4$  plus carbon monoxide.

**Answer**



An important aspect of CO binding is called "back-donation". In back-donation, not only does the ligand donate electrons to the metal, but the metal also donates to the ligand. We can think of the CO as donating a pair of electrons from a carbon-based orbital into an empty orbital on the metal, such as a p orbital (figure MI2.5). The metal has d orbitals that have good symmetry overlap with the pi antibonding orbitals in the CO. Electron density can be donated from a metal d orbital into the pi\* level (figure MI2.6). Thus, binding to a metal actually weakens the CO bond because a pi\* orbital receives electron density from the metal.

- MO picture: donation from carbon-based orbital into vacant metal p orbital
- MO picture, part 2: donation from occupied metal d orbital into CO pi\* orbital
- this interaction weakens the C-O multiple bond

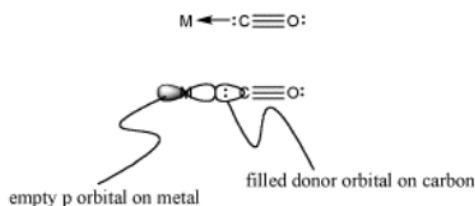


Figure 4.2.5: Donation from CO to metal in qualitative molecular orbital terms.

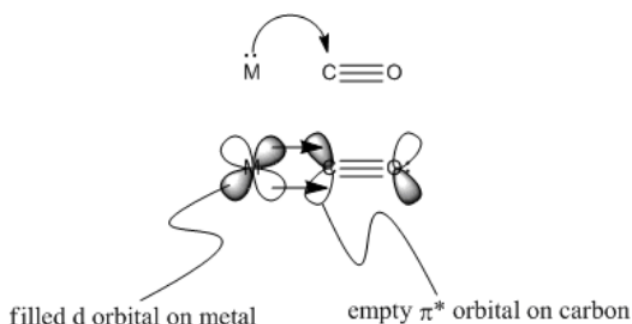
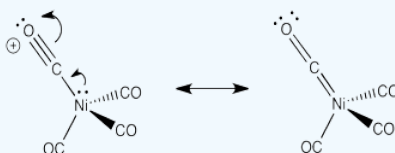


Figure 4.2.6: Donation from metal to CO in qualitative molecular orbital terms.

### ? Exercise 4.2.3

Draw a Lewis structure that takes into account the effect of metal-to-carbonyl electron donation in tetracarbonyl nickel.

**Answer**



### ? Exercise 4.2.4

Infrared spectroscopy is often used to assess bond order between specific atoms within a molecule. Because stretching frequencies are proportional to bond strength, a comparison of frequencies from a bond one molecule to a similar bond in another can give insight into the bond orders in each case.

- A C-O bond in organic compounds shows up between  $1000\text{--}1200\text{ cm}^{-1}$  in most cases. A C=O bond normally shows up near  $1600\text{--}1700\text{ cm}^{-1}$ . Explain why these two bonds give rise to two different stretching frequencies.
- Based on the Lewis structure, what do you predict for this bond frequency in a CO molecule?
- What will happen to the CO stretching frequency in carbon monoxide if the molecule binds to a palladium atom?

### ? Exercise 4.2.5

Explain the differences in CO stretching frequencies in the following pairs of compounds. (Note: the *number* of peaks is related to molecular symmetry and group theory; focus only on the difference in magnitude of the frequency.)

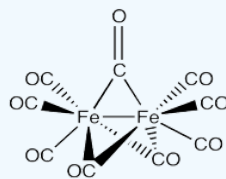
- CO at  $2143\text{ cm}^{-1}$  vs.  $\text{Mo(CO)}_6$  at  $2004\text{ cm}^{-1}$ .
- $\text{Ni(CO)}_4$  at  $2060\text{ cm}^{-1}$  vs.  $\text{Fe(CO)}_4^{2-}$  at  $1790\text{ cm}^{-1}$ .
- $\text{Cr(CO)}_6$  at  $2000\text{ cm}^{-1}$  vs.  $\text{Mn(CO)}_6^+$  at  $2090\text{ cm}^{-1}$ .
- $(\text{PF}_3)\text{Mo(CO)}_3$  at  $2055$  &  $2090\text{ cm}^{-1}$  vs.  $(\text{PPh}_3)\text{Mo(CO)}_3$  at  $1835$  &  $1934\text{ cm}^{-1}$ .
- $\text{Cr(CO)}_6$  at  $2000\text{ cm}^{-1}$  vs.  $(\text{C}_6\text{H}_5\text{CH}_3)\text{Cr(CO)}_3$  at  $1963$  and  $1869\text{ cm}^{-1}$ .

### ? Exercise 4.2.6

Sometimes, carbonyls can bridge between two metals. For example, the iron cluster  $\text{Fe}_2(\text{CO})_9$  contains six "terminal" carbonyls, bound to only one iron each, and three "bridging" carbonyls, each of which is bound to both iron atoms. This complex also features a metal-metal bond.

- draw a structure for this compound.
- explain why the terminal carbonyls display stretching frequencies of  $2082$  and  $2019\text{ cm}^{-1}$ , but the bridging carbonyls display a stretching frequency of  $1829\text{ cm}^{-1}$ .

## Answer



"Organic" carbonyls, such as aldehydes and ketones, can also bind to transition metals, as you may have seen before. These compounds bind to transition metals in a very different way than carbon monoxide. Normally, we think of them as simple lone pair donors. The oxygen lone pair donates to the metal atom or ion. The resulting complexes are important because the carbonyl becomes "activated" or ready to accept nucleophiles.

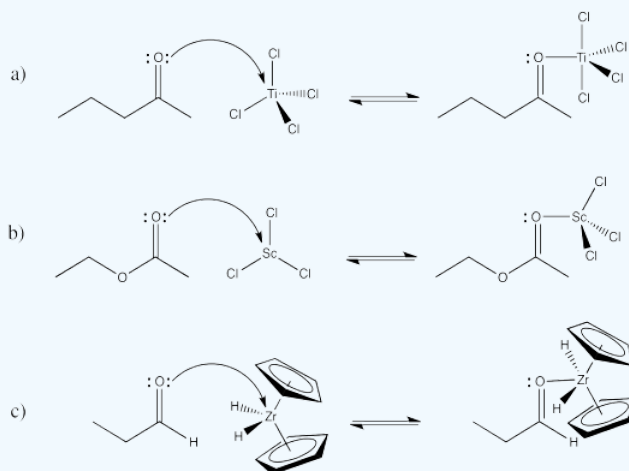
- Organic carbonyls can also bind to metal atoms or ions.
- Binding is usually via the heteroatom.

### ? Exercise 4.2.7

Draw, with arrows, the coordination of the following organic carbonyl compounds to metal complexes.

- 2-pentanone with  $\text{TiCl}_4$ .
- ethyl acetate with  $\text{ScCl}_3$ .
- propanal with  $\text{Cp}_2\text{ZrH}_2$  ( $\text{Cp}$  = cyclopentadienyl anion,  $\text{C}_5\text{H}_5^-$ ).

## Answer



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