**Introduction to Organometallic Ligands – Carbon Monoxide**

**Part I. Bonding**

|  |  |
| --- | --- |
| 1a | 1b |

Figure 1. Metal-ligand orbital overlap in a carbonyl complex.

1. Draw a Lewis structure for CO.
2. In a metal carbonyl complex, the metal *d* orbitals interact with the frontier orbitals of CO. Circle these on the attached MO diagram of CO and label them HOMO and LUMO.

In Fig. 1a, what type of overlap occurs (sigma, pi, etc.)? \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

In Fig. 1b, what type of overlap occurs (sigma, pi, etc.)? \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

In Fig. 1a, is the CO ligand and electron donor or acceptor? \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

In Fig. 1b, is the CO ligand and electron donor or acceptor? \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

1. On Figure 1, draw arrows from each donor orbital into each acceptor orbital, to show these interactions.
2. Summarize the bonding interactions, filling in the blanks with one of the following: *filled*, *empty*, *donates,* or *accepts*. Circle *to* or *from* as appropriate.

In a metal carbonyl complex, a(n) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ metal orbital \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ ***sigma*** electron density to/from a(n) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ carbonyl orbital, and a(n) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ carbonyl orbital \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ ***pi*** electron density to/from a(n) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ metal orbital.

1. This type of give and take of electron density is called *synergism*. The donation from metal to ligand is referred to as *backbonding* or *backdonation*.

Briefly explain why you think these particular terms are used.

**Part II. M-C and C-O bond strength**

1. Use the MO diagram of CO to determine the bond order of the molecule. Does it match your Lewis structure above?

Bond order =

1. When CO binds to the metal, it donates electron density from a particular orbital (*which one?)*, making a M-C bond. How, if at all, does this affect the strength of the **C-O** bond? (Think about how bond order would be affected.) Explain.
2. When CO binds to the metal, it also accepts electron density into a particular orbital (*which one?)*, strengthening the M-C bond. How, if at all, does this affect the strength of the **C-O** bond? (Think about how bond order would be affected.) Explain.
3. Summarize this relationship, filling in the blanks with *weaker* and/or *stronger.*

In a metal carbonyl complex, the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ the M-C bond, the \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ the C-O bond.

1. Typically we draw a carbonyl ligand as in Figure 2 below. Consider a case in which the backbonding from the metal is very strong. Can you draw a resonance structure that more accurately depicts this interaction?

$$M-C≡O$$

Figure 2. Weak backbonding Strong backbonding

**Part III. Infrared spectroscopy**

IR spectroscopy is a useful technique for assessing the C-O bond strength of organic carbonyl compounds. The same is true for metal carbonyls. Recall that IR spectroscopy assesses the frequency of vibrational motions (stretching and bending) in a molecule. Frequencies are reported in wavenumbers (cm-1).

1. Summarize, filling in the blanks with *increases* or *decreases*.

The frequency of stretching **increases** as

* the size/mass of an atom \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ and
* the strength of the bond \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.
1. The observed stretching band in free CO is 2143 cm-1. Do you expect the CO stretching band in a carbonyl complex to be higher or lower? Explain.
2. Consider the data provided in the table below.

|  |  |  |
| --- | --- | --- |
| Compound | Frequency (cm-1) | Rationalize the trend observed for νCO in the first five complexes. |
| [Ti(CO)6]2- | 1748 |
| [V(CO)6]- | 1859 |
| V(CO)6 | 1976 |
| Cr(CO)6 | 2000 |
| [Mn(CO)6]+ | 2100 |
| free CO | 2143 |
| [Fe(CO)6]2+ | 2204 |

1. Challenge: The iron complex has a stretching band *higher* than that of free CO. How might this be possible?

**Part IV. Binding Modes of CO**

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Figure 3. Binding modes of CO.

Figure 3 shows multiple binding modes of CO. The first depiction is called a *terminal* CO; the others are referred to as *bridging*. Bridging carbonyl ligands can be symmetric or asymmetric, and are named by the number of metals they bridge, i.e. μ2-CO, μ3-CO, etc.

1. Consider the generic μ2-CO picture in Fig 3.

Draw an orbital picture of a sigma interaction between the metals and the CO ligand.

Draw an orbital picture of a pi interaction between the metals and CO ligand.

1. Make a prediction, filling in the blanks with *increases* or *decreases.*

As the number of metal centers attached to each CO ligand increases, the CO stretching frequency \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ .

Explain your prediction.

MO diagram of carbon monoxide

