

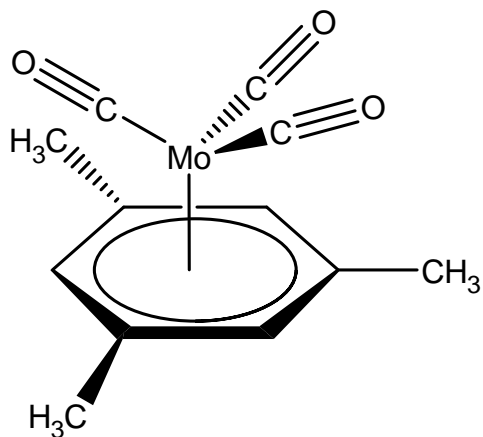
Upcoming Deadlines

Due 3/13: Borane-Amine formal report

AND

Team Project Idea

Exp. 6: Metal-Arene $[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]\text{Mo}(\text{CO})_3$ (Text #16)



An **organometallic** compound:

contains **metal-carbon bonds**

Metal-ligand complexes can be viewed as **Lewis acid-base adducts**:

Metal: Lewis acid (e- acceptor)

Ligands: Lewis bases (e- donors)

Ligands donate e- to form M-L
coordinate covalent or **dative** bonds.

“Electron Counting” in Organometallic Compounds

The 18-electron “Rule:” Many stable organometallic compounds have 18 total valence electrons around the metal.

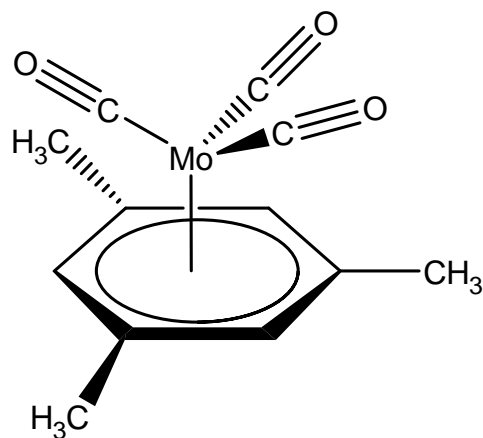
– counting metal valence e- and e- donated by ligands

What is “special” about 18 electrons?

Counting electrons:

- 1) Determine the charge on the metal and its total number of valence electrons
- 2) Add up the number of electrons donated by the ligands
 - a. Lone-pair and/or π electrons can be donated

Counting Electrons in $[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]\text{Mo}(\text{CO})_3$



- 1) Determine the charge on Mo and its total # of ve-
 - a. Consider **charges on ligands**: CO and mesitylene are both neutral molecules. . . .
 - b. Determine total # of Mo valence e-

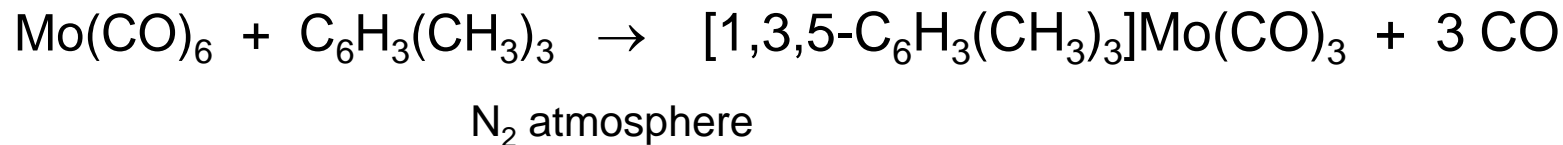
2) Add up the number of e- donated by the ligands:

CO ligands:

$\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3$:

6 Mo valence e- + 6 + 3(2) e- donated by ligands = 18 e- total

Synthesis of $[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]\text{Mo}(\text{CO})_3$



A few questions to consider:

- 1) This reaction is more successful in mesitylene than it is in benzene. Why?
- 2) Why do you think this reaction is thermodynamically favorable?
- 3) Why do you think the reaction must be performed under N_2 ?

Characterization of $[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]\text{Mo}(\text{CO})_3$

We will use IR spectroscopy to characterize the product, focusing specifically on the **CO stretches**.

CO peaks are distinctive in IR spectra of organometallic compounds, occurring in a fairly empty region of the spectrum.

~1850-2125 cm^{-1}

How many total CO stretches does this molecule have?

3

can use Group Theory to determine how many are IR-active, how many peaks are expected in IR spectrum

Observed CO stretches (intensity, frequency) are sensitive to molecular geometry and **ligand-metal electronic interactions**.

You will see in lecture (Ch. 10) that CO ligands can accept e- density from the metal (π -acceptor ligands), stabilizing metals in low ox. states [Mo(0)]

As CO accepts e- density, bond strength decreases

As CO bond weakens, observed peak shifts to lower freq./energy

Using CO Peaks to Probe Molecular Geometry

By comparing intensities of CO peaks in the IR spectrum, we can estimate the OC-Mo-CO bond angle (θ) between carbonyls:

$$\frac{I_{sym}}{I_{anti}} = \frac{3 \cot^2\left(\frac{\theta}{2}\right) - 1}{4}$$

- Plot **absorbance (not %T)** versus wavenumbers
- Identify symmetric and antisymmetric peaks (Which is which?)
- Estimate integrated areas to use as intensities and solve for θ .

[Theoretical Study of $[1,3,5\text{-C}_6\text{H}_3(\text{CH}_3)_3]\text{Mo}(\text{CO})_3$ (3/10)]

Additional Exercises Related to this Experiment:

- 1) Use Group Theory to predict/justify the number of CO peaks expected in the IR spectrum
- 2) Use Spartan (molecular mechanics and semi-empirical PM3 calculations) to optimize the geometry of the product
 - a. Calculate the OC-Mo-CO bond angles; compare to estimate from IR spectrum
 - b. Predict the IR spectrum, identify CO stretches and determine their frequencies (cm^{-1}); compare to your measured spectrum

Procedural Notes

1. **SAFETY:** Metal carbonyl compounds (and CO, itself) are toxic. **Wear gloves and keep all materials under your benchtop hood.**
2. You will use a Variac (rheostat) for temperature control on **120-V setting**.
 - Turning the large knob on top of the Variac changes the voltage sent to the heating mantle (“100” means 100% of 120 V).
 - I suggest that you start at a setting of ~60-70%.
 - If you put a little sand in your heating mantle, you can check the temperature of the sand with a thermometer.
 - You want to achieve reflux (at ~165 °C) quickly, but not overshoot it.
3. You will connect the N₂ tank directly to the top of your condenser (no bubbler), using the gas to flush the apparatus before and after reaction.
4. To recover the product, use a Pasteur pipet to add the reaction mixture (avoiding undissolved starting material, etc.) to **cold** hexane. **[This is a change from your manual.]** Then proceed with filtration, washing with hexane.
 - a) Set aside a few crude yellow crystals for IR analysis; then, do recrystallization. (A significant amount of crude product will be lost.)
 - a) Acquire IR spectra of crude and “pure” products.

Formal Report Due 3/27

Be sure to include:

- A sketch and description of the apparatus
- Your yield and calculations of percent yield, as well as a discussion of likely causes for low yield, if necessary.
- **Group Theory analysis** showing the number of predicted IR-active CO vibrations and the number of CO bands expected in the spectrum
- Your measured IR spectrum and calculations of C-Mo-C bond angles between CO groups
- **Comparison of your experimentally determined IR spectrum and C-Mo-C angles with those obtained from modeling**
 - Also include some description of modeling throughout (methods used, etc.)