Upcoming Deadlines
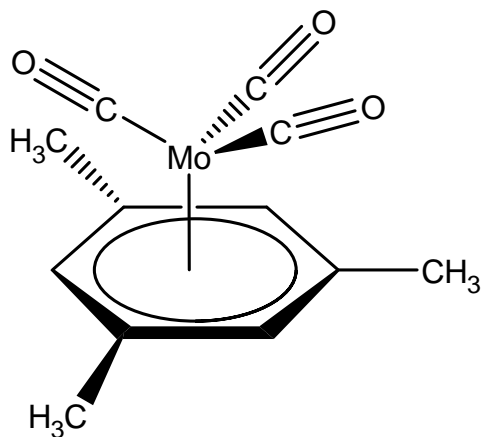**Due 3/7:** Borane-Amine formal report

Exp. 6: Metal-Arene $[1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$ (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.
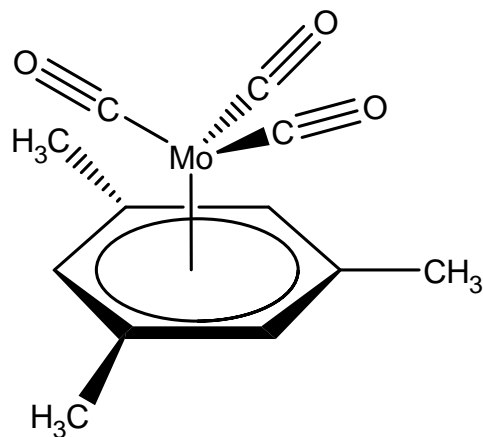
– counting metal valence e- and e- donated by ligands

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 $[1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$

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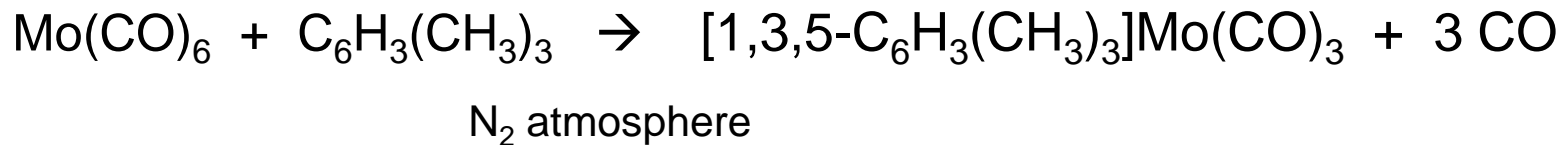
2) Add up the number of e- donated by the ligands:

   CO ligands:

   $\eta^6\text{-}$ $C_6H_3(CH_3)_3$:

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

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

Mo(CO)$_6$ + C$_6$H$_3$(CH$_3$)$_3$ → [1,3,5-C$_6$H$_3$(CH$_3$)$_3$]Mo(CO)$_3$ + 3 CO

N$_2$ atmosphere

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 $[1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$

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.

$\sim 1850\text{-}2125 \text{ cm}^{-1}$

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:

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

- 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.

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. Calcluate 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 N_2 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 3/21/12

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.)