

Experiment 6:
The Metal-Arene Complex
 $1,3,5\text{-(CH}_3\text{)}_3\text{C}_6\text{H}_3\text{Mo(CO)}_3$

Text #16

CHEM 531

Reminders

- Due this Thursday (3/5):
 - Formal Report: Experiment 4
 - Borane-Amine Complex Synthesis
 - Report Experiment 5
 - Molecular Modeling
 - Prelab: Experiment 6
 - Metal Arene Complex
- Due next week (3/12):
 - Report: Experiment 6
 - Metal Arene Complex
 - Prelab: Experiment 7
 - Amino Acid Complexes (Text #22)
- Team Project Ideas
 - Due to Dr. Grossoehme by 5 pm Friday, March 13

Organotransition Metal Chemistry

- Organometallic compounds
 - Compounds containing a C-[M] bond
 - Grignard reagents (R-MgBr)
 - Organolithium reagents (R-Li)
- Organotransition metal compounds
 - [M] = “B” group (3 – 12) metal
 - Gilman reagents (R₂CuLi)
 - Important to common organic transformations
 - Coupling reactions (Suzuki, Heck)
 - Ring-closing metathesis (RCM)

Organotransition Metal Compounds

Structure

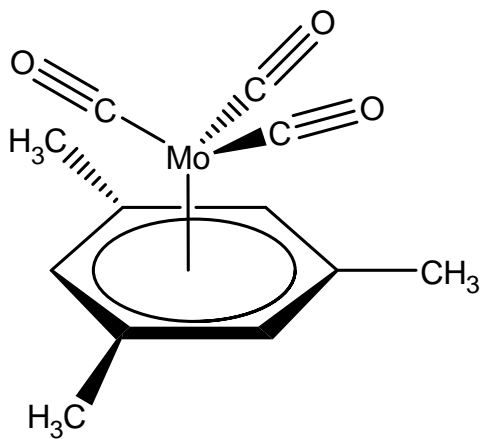
- 18 electron rule
 - Kr configuration: $[\text{Ar}] 4s^2 3d^{10} 4p^6$
 - 18 electrons in “valence” shell
 - Stable configuration for period 4 and higher elements
- Transition metal configurations
 - “Coordinatively unsaturated”
 - Zr: $[\text{Ar}] 5s^2 4d^2$ (4) (“early” TM)
 - Fe: $[\text{Ar}] 4s^2 3d^6$ (8)
 - Pd: $[\text{Ar}] 4d^{10}$ (10) (“late” TM)

Organotransition Metal Compounds

Structure

- TM achieve stable configuration by “coordination” with “ligands”
 - $\text{Fe}[\text{H}_2\text{O}]_6^{2+}$, $\text{Co}[\text{NH}_3]_6^{3+}$
 - Called a “coordination compound” or “metal complex”
- Organometallic compounds
 - Coordination compounds containing a [M]-C bond
 - Include π -bonding ligands (butadiene, cyclopentadienyl (Cp))
 - M-L bonds are more “covalent” than typical coordination compounds
 - Usually have a substantial π component
 - Perturbs the electronic structure of the ligands \rightarrow generates reactivity

Organotransition Metal Compounds



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)

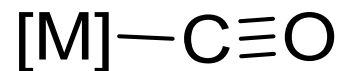
Ligands donate e⁻ to form M-L
coordinate covalent or **dative** bonds.

Organotransition Metal Compounds Structure

- Common ligands

- Neutral (L)

- PR_3 , NR_3 , CO – donate lone pair to metal

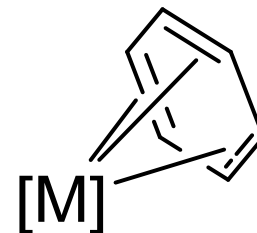
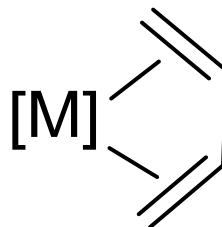
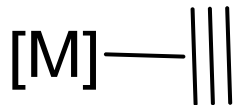
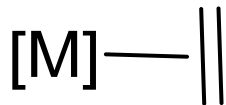


- PR_3 , NR_3 are “spectator” ligands

- » Remain unchanged during reactions

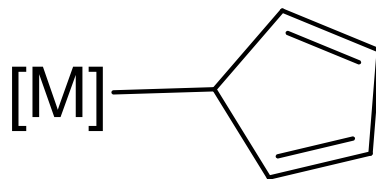
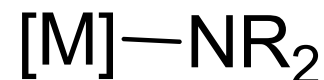
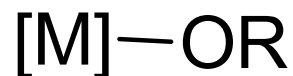
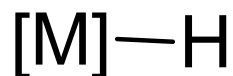
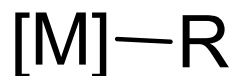
- » Influence steric and electronic properties of the complex

- π -Bonds – donate π -electrons to metal



Organotransition Metal Compounds Structure

- Common ligands
 - Negative (X)
 - R^- , H^- , RO^- , R_2N^- – donate lone pair to metal

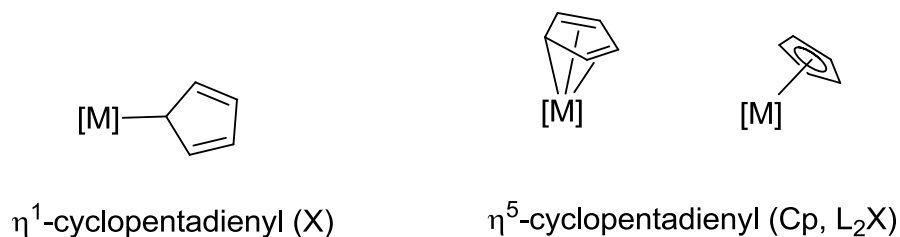
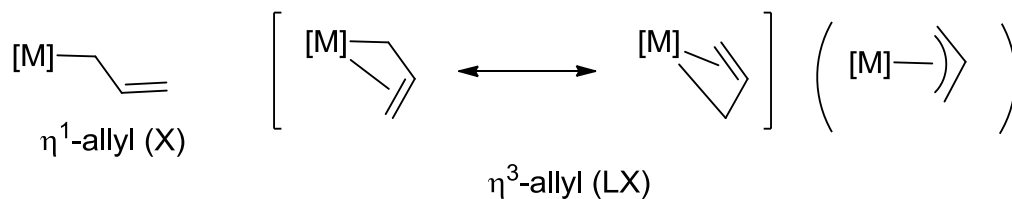
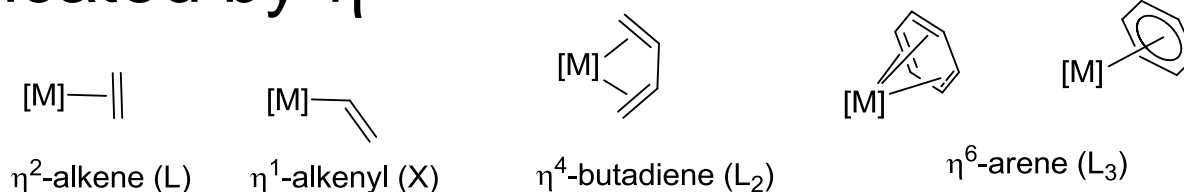


Organotransition Metal Compounds Structure

- Hapticity

- No. of atoms in a single ligand bound to metal

- Indicated by η^x



Organotransition Metal Compounds

Structure – 18 Electron Rule

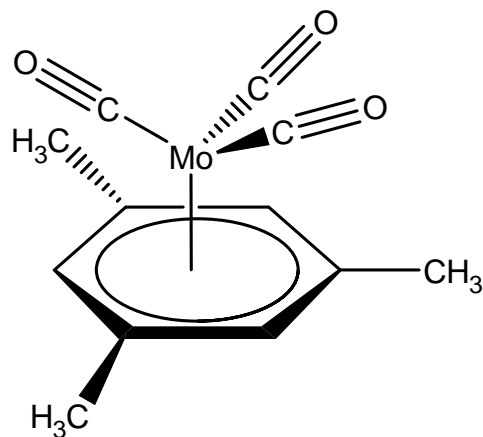
- Octet Rule
 - Applies to main group compounds
- 18 Electron Rule
 - Applies to metal complexes
 - Metal valence e⁻ (“d-count”) + ligand e⁻
- Electron-counting
 - Ionic Model
 - Metal “d-count” = (group # - oxidation #)_{Metal}
 - X ligands = (-) charge, 2 e donors
 - L ligands = (0) charge, 2 e donors

Organotransition Metal Compounds

Structure – 18 Electron Rule

- $(\text{CH}_3)\text{Mn}(\text{CO})_5$
 - Mn oxidation state
 - 1 'X' ligand = -1 charge
 - 5 'L' ligands = 0 charge
 - Oxidation state of Mn = +1
 - Mn d-Electron count
 - Neutral Mn: d^7 (determined from periodic table group number)
 - Mn^{+1} : d^6
 - Total electron count
 - Mn^{+1} : d^6
 - 1 'X' ligand = $2e$
 - 5 'L' ligands = $10e$
 - Total $e = 18e$

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. . . .

Mo is neutral (0 oxidation state)

b. Determine total # of Mo valence e-

$[\text{Kr}] 5s^2 4d^4 - 6$ valence e- (“d⁶”)

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

CO ligands: Each donates 2 electrons

$\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3$: Donates 6 electrons (from 3 π bonds)

Coordinated
through 6 atoms

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

Organotransition Metal Compounds Structure

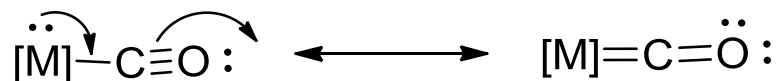
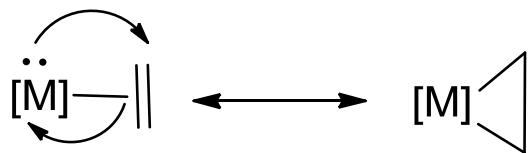
- Back-Bonding

- Electron-donation from metal to ligand

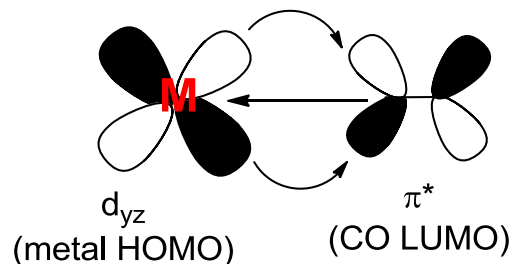
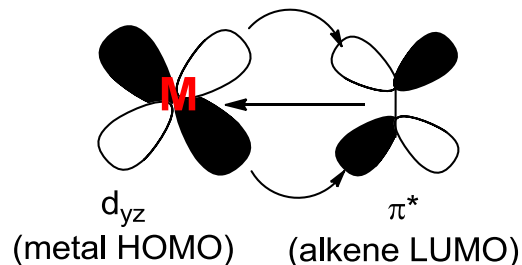
- Usually $d \rightarrow \pi^*$

- Stabilizes metals in low oxidation states

- VB model

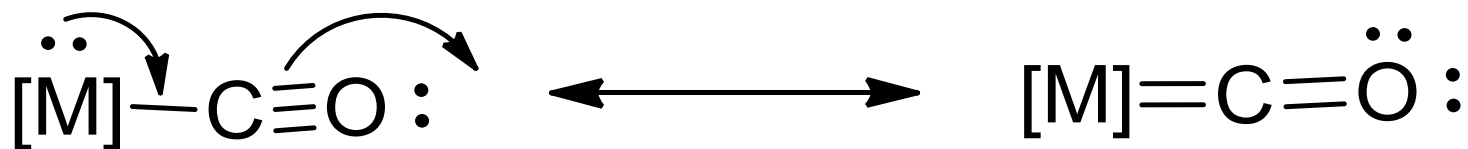


- MO model



Organotransition Metal Compounds Structure

- Evidence for Back-Bonding
 - IR stretching frequency of CO
 - “Free” CO: 2154 cm⁻¹



- Lower ν_{CO} , more backbonding
 - Stronger M-CO bond

Organotransition Metal Compounds

Structure

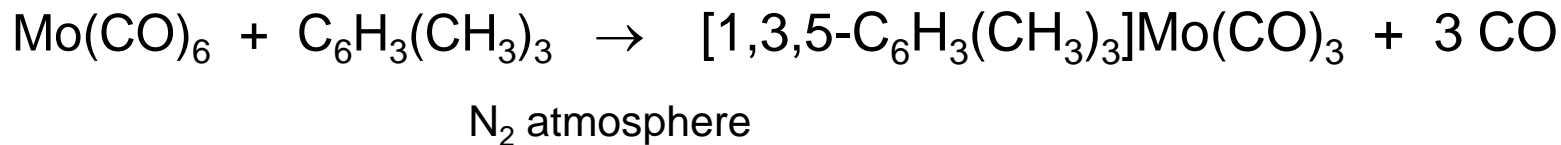
- Evidence for Back-Bonding
 - IR stretching frequency of CO

- “Free” CO: 2154 cm^{-1}



- Greater anionic charge on metal in an isoelectronic series \rightarrow more back-bonding
- *Generally: more electron density on metal \rightarrow more back-bonding*

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



A few questions to consider:

- 1) This reaction is more successful in mesitylene than it is in benzene. Please suggest an explanation.

Mesitylene is a better Lewis base. Methyl groups are electron-donating substituents.

- 2) Why do you think this reaction is thermodynamically favorable?

- Entropically favored: products are more disordered (3 mol gas)
- Product is expected to be stable (but so is $\text{Mo}(\text{CO})_6$. . .)

- 3) Why do you think the reaction must be performed under N_2 ?

O_2 in air reacts with CO (forming CO_2)

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

- IR spectroscopy
 - Focus on CO stretches near 2000 cm^{-1}
 - $1750 - 2150\text{ cm}^{-1}$
- Total CO stretches? 3 (1 ν_{sym} , 2 ν_{anti})
- Observable CO stretches? 2 ($\nu_{\text{sym}} > \nu_{\text{anti}}$)

Determining Molecular Geometry

- OC-Mo-CO bond angle (θ):

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

- Use absorbance (not %T)
- Symmetric vs. antisymmetric stretch
 - Which is which?
- Intensity = peak area

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).
 - Start at a setting of ~60-70%.
 - You want to achieve reflux (at ~165 °C) quickly, but not overshoot it.
3. 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.

Formal Report Due 3/12/15

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.)