

# An Advanced Inorganic Laboratory Experiment Using Synthesis and Reactivity of a Cycloheptatriene Molybdenum Complex

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Since ferrocene was first proposed as a sandwich compound in 1952, the field of organometallic chemistry has experienced explosive growth. Complexes between transition metals and unsaturated organic compounds have become ubiquitous to this area of chemistry (1). These unsaturated organic fragments bond to the transition metal such that the  $\pi$ -electrons of the organic moiety donate to an empty metal d-orbital to form a  $\sigma$ -bond. Concurrently, a set of electrons in filled metal d-orbitals donate to the empty  $\pi$ -antibonding orbitals of appropriate symmetry on the organic ligand to form  $\pi$ -bonds (Fig. 1). Because the  $\pi$ -electrons of the organic group become the  $\sigma$ -bond in the complex, these materials frequently are referred to as  $\pi$ -complexes. The notation  $\eta^x$  is used to describe the number of atoms, x, coordinated to the metal center in a  $\pi$ -complex. Organic ligands of this type are referred to as  $\sigma$ -donor and  $\pi$ -acceptor ligands. The degree of  $\sigma$ -donating and  $\pi$ -accepting ability of the ligand greatly affects the electron density (and, therefore, reactivity) at both the organic moi-

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ety and the metal center. For this reason  $\pi$ -complexes remain an intense area of study as stoichiometric reagents in organic synthesis and in catalysis applications.

There is, however, a paucity of advanced inorganic laboratory experiments that address the synthesis, characterization and reactivity of  $\pi$ -complexes and many that do exist deal with ferrocene and its derivatives. One reason for this problem is the lack of relevant experiments that can be performed within a reasonable laboratory time frame. The reactions in the laboratory experiment described herein involve the synthesis, reactivity, and characterization of ( $\eta^6$ -cycloheptatriene) molybdenum tricarbonyl, ( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub>. Isolation and characterization of all major products are designed to be accomplished within two laboratory periods (total time 7 h). The reactions involved in this experiment are summarized in Figure 2. The first reaction is the synthesis of ( $\eta^6$ -cycloheptatriene) molybdenum tricarbonyl, ( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub>, through the direct reaction of molybdenum hexacarbonyl, Mo(CO)<sub>6</sub>, with cycloheptatriene. The second reaction is the formation of

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[( $\eta^7$ -cycloheptatrienyl)molybdenum tricarbonyl] hexafluorophosphate, [( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>3</sub>][PF<sub>6</sub>]. This transformation is done by hydride abstraction using the triphenylcarbenium ion. ( $\eta^7$ -cycloheptatrienyl)iodomolybdenum dicarbonyl, ( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>2</sub>I, is synthesized in the third reaction by substitution of CO by I<sup>-</sup> in [( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>3</sub>]<sup>+</sup>. The substitution reaction is an *in situ* NMR tube reaction that increases the number of experimental techniques to which the student is exposed in this laboratory experience. The experimental procedures described herein are different from those reported in the literature (2–4) in that they are simpler to perform and take up much less time. The synthesis and characterization of the primary product are completed in the first

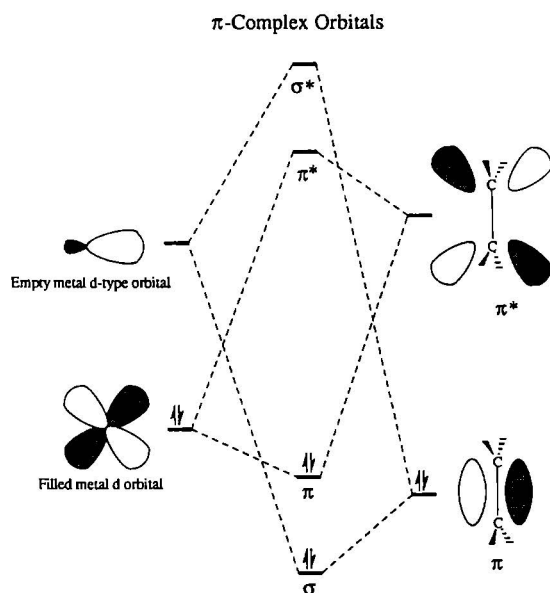


Figure 1. Molecular orbital diagram for a metal-olefin  $\pi$ -complex.

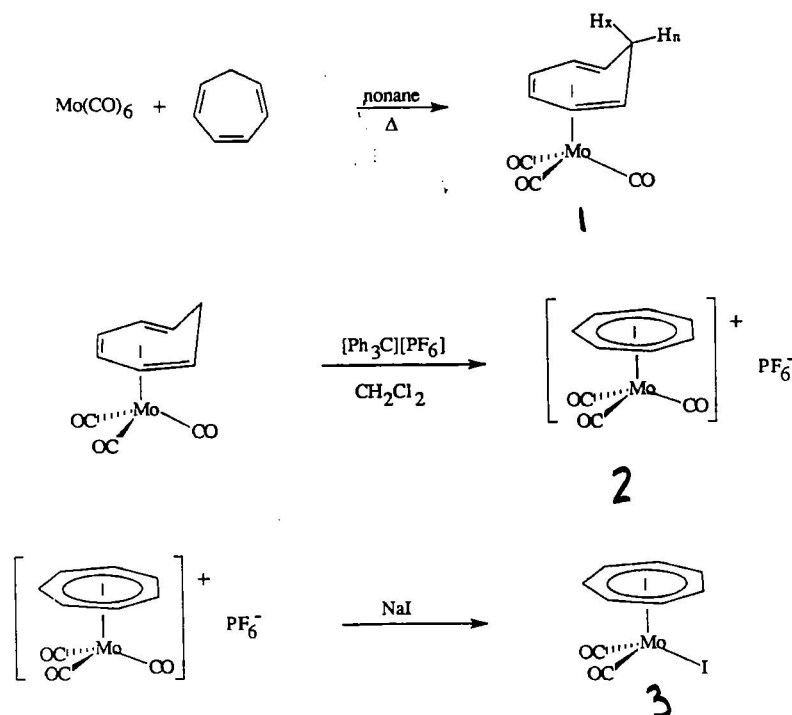


Figure 2. Reactions of the cycloheptatriene molybdenum complexes.

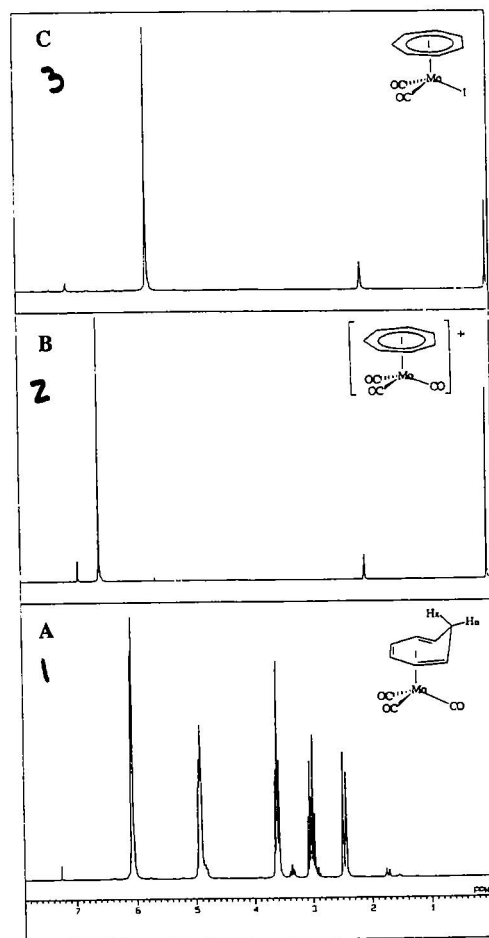


Figure 3. <sup>1</sup>H NMR spectra for ( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub> (A), [( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>3</sub>][PF<sub>6</sub>] (B), ( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>2</sub>I (C). Note: Peaks observed at 2.2 ppm in B and C, and at 7.2 in A are due to residual protons in the acetone-d<sub>6</sub> and chloroform-d<sub>3</sub>, respectively. Other peaks in the spectrum are due to a small amount of free cycloheptatriene.

laboratory period with the remainder of the experiment finished in the second period. These experiments involve inert atmosphere techniques including “flash” column chromatography under nitrogen, and the use of IR, <sup>1</sup>H and <sup>13</sup>C NMR spectral analysis to characterize the products. These experiments also can help to launch a discussion on concepts developed in lecture. These include substitution mechanisms, aromaticity, assignment of oxidation states, electron density changes at the metal, coupling in <sup>1</sup>H NMR and 2-D NMR techniques and the use of group theory to explain the number of observed bands in the IR spectra.

### Experimental

The reagents for this experiment are priced reasonably depending on quantities purchased. Cycloheptatriene (Aldrich, ≈\$15.00/100mL) should be freshly distilled prior to the laboratory for best results. Molybdenum hexacarbonyl (Aldrich, ≈\$22.00/10 g) and triphenylcarbenium hexafluorophosphate (Aldrich, ≈\$30.00/10 g) can be used as received. All other reagents and solvents were used as received. All reactions were carried out under a blanket of nitrogen. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a JEOL GSX270 spectrometer at am-

bient temperatures. Chemical shifts are expressed as ppm downfield of internal TMS followed by multiplicity. IR spectra were obtained on a Mattson Polaris Fourier Transform Infrared spectrometer using either KBr solution cells, or CaF<sub>2</sub> solution cells whenever hexafluorophosphate salts were present. Isolated products are only moderately air sensitive. They can be handled briefly in air or under a nitrogen blanket but they should be stored under nitrogen.

( $\eta^6$ -Cycloheptatriene)molybdenum tricarbonyl,  
( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub>

Mo(CO)<sub>6</sub> (1.0 g, 3.8 mmole) was added to cycloheptatriene (4.0 mL, 38 mmole) in 10 mL of nonane and heated to reflux for 2 h with stirring. (The limit to higher yields in this reaction is believed to be due to the sublimation of the Mo(CO)<sub>6</sub> away from the reaction mixture. As noted in other published syntheses (5), this unreacted Mo(CO)<sub>6</sub> sublimes into the condenser and must be pushed back manually into the reaction mixture to maximize the yield over shorter reaction times. We use a long spatula for this purpose. An alternative method that also produces an increase in the yields is to wrap the hose that feeds cold water to the condenser around the unheated top of the reaction flask. This leads to the subliming of the Mo(CO)<sub>6</sub> to occur at the upper surface of the round-bottomed flask rather than in the condenser. Agitation of the reaction mixture easily washes the sublimed material back into the reaction solution.) The solution was then cooled to room temperature under nitrogen. The reaction mixture was passed through a 3 in. × 1 in. dry plug of neutral alumina using nitrogen gas to push the solvent quickly through the plug. The column was then washed with 3 × 10 mL of nitrogen-saturated ligroin to elute nonane, unreacted cycloheptatriene, and unreacted Mo(CO)<sub>6</sub>. The orange product was removed from the col-

umn by the addition of nitrogen-saturated dichloromethane, CH<sub>2</sub>Cl<sub>2</sub>. The product was collected in a pre-weighed 100-mL round-bottomed flask. The solution was concentrated on a rotary evaporator under reduced pressure with the last traces of solvents being removed in vacuo. The typical yield for students in our experiences is approximately 30–45%. The red solid was stored under nitrogen. No more than 25% of the isolated solid should be used for NMR and IR analyses. Solvent choices include benzene-d<sub>6</sub>, chloroform-d<sub>3</sub>, CCl<sub>4</sub>, and CS<sub>2</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 2.45 (m), 3.00 (m), 3.60 (μ), 4.92 (m), and 5.2 (m) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 102.7, 97.2, 60.2, 27.2 ppm. CO carbons are observed at 216.1 ppm as a very small broad peak. IR (benzene) ν<sub>CO</sub> 1984, 1915, and 1887 cm<sup>-1</sup>.

[( $\eta^7$ -Cycloheptatrienyl)molybdenum tricarbonyl]hexafluorophosphate, [( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>3</sub>][PF<sub>6</sub>]

Approximately 75% of the product obtained in the first synthesis was weighed and then dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub>. To this solution was added an equimolar quantity of triphenylcarbenium hexafluorophosphate, [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C][PF<sub>6</sub>].

• **Caution:** Handle this solid and solutions with the triphenylcarbenium ion present with gloves.

The solution was stirred at room temperature for 30 minutes. The solution was vacuum filtered, washed with 3 × 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, dried in vacuo, and collected (80–90% yield). <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 6.6 (s) ppm. <sup>13</sup>C NMR (acetone-d<sub>6</sub>) δ 101.8 ppm (CO carbons not observed). IR (acetone) ν<sub>CO</sub> 2076 and 2028 cm<sup>-1</sup>.

( $\eta^7$ -Cycloheptatrienyl)iodomolybdenum dicarbonyl,  
( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>2</sub>I

This preparation was carried out in situ in an NMR tube. Approximately 25% of the product from the previous reaction, [( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>3</sub>][PF<sub>6</sub>], was placed in an NMR tube and dissolved in acetone-d<sub>6</sub>. A <sup>1</sup>H NMR spectrum was obtained. To the NMR tube a few small crystals of sodium iodide were added. The solution turned dark green quickly and gas evolution was observed. A <sup>1</sup>H NMR spectrum was obtained. Several drops of the solution from the NMR tube were removed and diluted with acetone. The IR spectrum was obtained on the resulting solution using acetone as the reference. Yield is quantitative by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 5.7 (s) ppm. <sup>13</sup>C NMR (acetone-d<sub>6</sub>) δ 95.7 ppm (CO carbons not observed). IR (acetone) ν<sub>CO</sub> 2011 and 1963 cm<sup>-1</sup>.

## Results and Discussion

<sup>1</sup>H NMR spectra for the π-complexes synthesized in this experiment are shown in Figure 3. ( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub> exhibits five distinct complex multiplets centered at 2.45, 3.00, 3.60, 4.92, and 6.05 ppm, all exhibiting the proper integration. These are associated with the five unique type of hydrogens on the  $\eta^6$ -cycloheptatriene ligand. The endo and exo hydrogens on the sp<sup>3</sup> carbon atom of the ligand have similar chemical shifts and cannot be resolved on lower field instruments but are observable on the 270 MHz JEOL NMR. The homonuclear correlated 2-D <sup>1</sup>H spectrum of

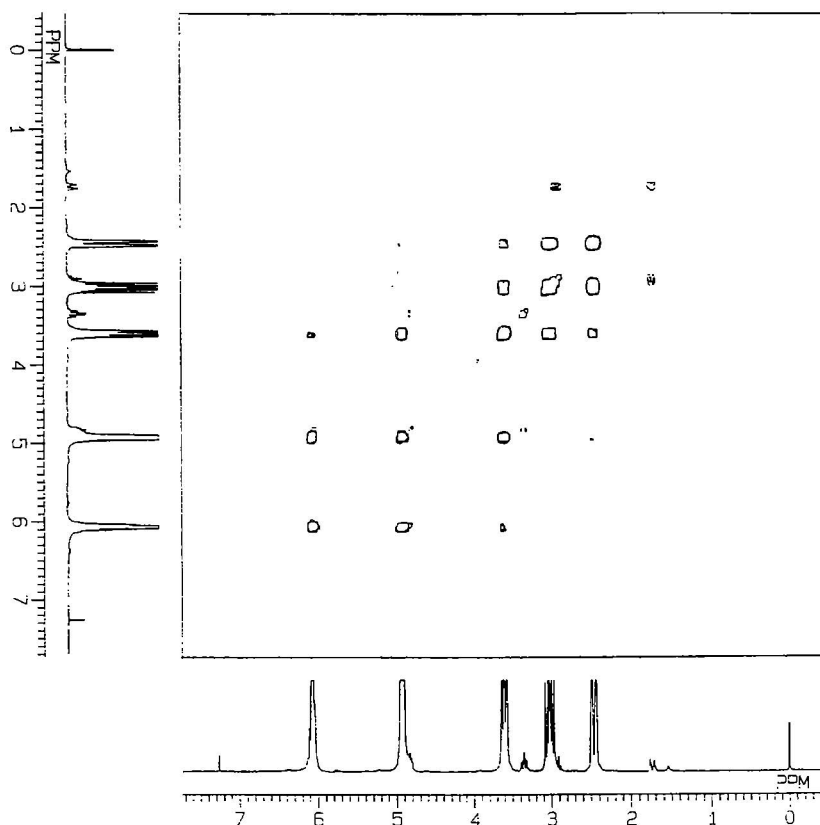


Figure 4. 2-D NMR <sup>1</sup>H-<sup>1</sup>H COSY for ( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub>.

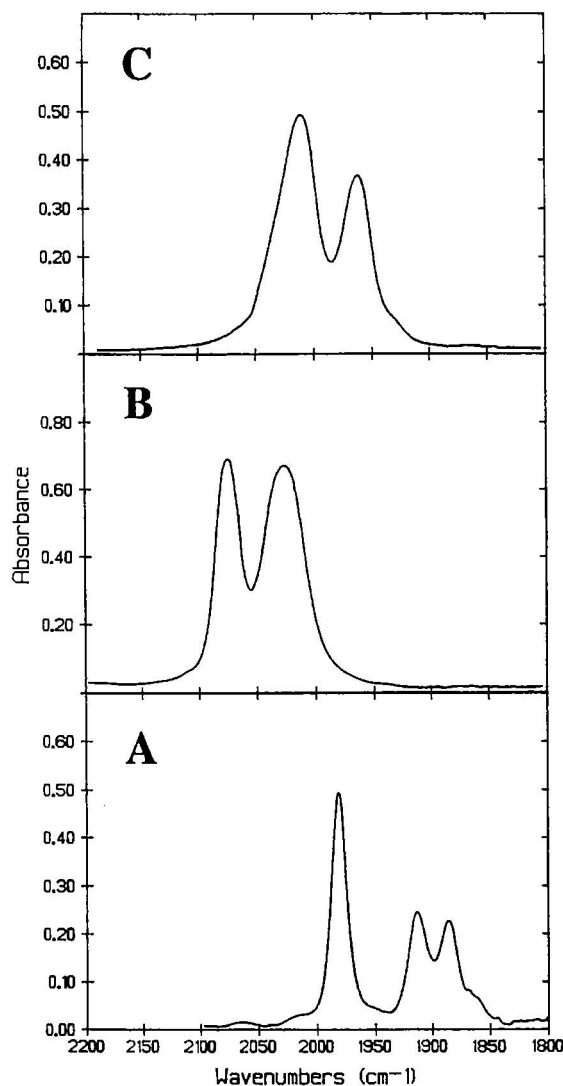


Figure 5. IR spectra for  $(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$  (A),  $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3][\text{PF}_6]$  (B),  $(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{I}$  (C).

$(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$ , Figure 4, is useful in identifying coupling between the various protons. There are several good references outlining the interpretation of 2D NMR results (6), which will not be elaborated on here.

When the hydrogen atom is abstracted from  $(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$ , the aromatic tropylium ligand is generated and all sites become chemically equivalent on the NMR time scale at room temperature. This results in a singlet at 6.6 ppm for the  $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  cation. The observed chemical shift and multiplicity demonstrates the aromatic nature of the ligand. When an  $\text{I}^-$  replaces a CO, the neutral complex  $(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{I}$  is formed. The singlet at 5.7 ppm confirms that the aromatic nature of the  $\pi$ -ligand is retained. The fact that the signal moves upfield as a result of this substitution is consistent with more electron density being available at both the metal and  $\pi$ -ligand in this complex. (The anionic iodide is a  $\pi$ -donor and replaces the neutral CO, a  $\pi$ -acceptor.)

The number and frequency of the CO-stretching bands observed in the IR spectra of the complexes demonstrate the changes in symmetry and electron density at the metal center as a result of the various transformations. The IR

spectra (Fig. 5) allow for analysis of the number of observed stretches as related to their simplified symmetry.  $(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$  has pseudo  $C_s$  symmetry and, employing group theory (7), is predicted to exhibit three bands as is observed at 1984, 1915, 1887  $\text{cm}^{-1}$ . The  $(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3$  cation has pseudo  $C_{3v}$  symmetry if the tropylium cation is treated as a flat circular plate. Theory predicts that two CO stretches should be observed and two bands are observed at 2076 and 2028  $\text{cm}^{-1}$ . Finally,  $(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{I}$  has pseudo  $C_s$  symmetry and group theory predicts two CO stretches. Two stretches are observed at 2011 and 1963  $\text{cm}^{-1}$ .

The change in frequency of the CO stretches also reflects the change in electron density at the metal. Like  $\pi$ -ligands, CO is a  $\sigma$ -donor and a  $\pi$ -acceptor. The CO bond order is reduced when the metal can  $\pi$ -donate into a  $\text{C}\equiv\text{O}$   $\pi$ -antibonding orbital; since the CO-stretching frequency reflects the CO bond order, the  $\nu_{\text{CO}}$  is reduced. Although hydride abstraction from the cycloheptatriene ligand in  $(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$  is not a formal oxidation of the metal, the CO stretches in the product,  $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$ , move to higher frequencies. This fact reflects that the tropylium ligand is a poorer  $\sigma$ -donor and a better  $\pi$ -acceptor than the cycloheptatriene ligand, thereby either pushing less electron density to the metal or pulling more electron density away from the metal. Once again, when  $\text{I}^-$  substitutes CO in  $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  to give  $(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{I}$ , no formal reduction of the metal occurs. However,  $\nu_{\text{CO}}$  moves to lower frequencies. It was pointed out above that the anionic iodide, a  $\pi$ -donor, replaces the neutral CO, a  $\pi$ -acceptor. Not only is there less competition for  $\pi$ -electron density from the metal (two CO ligands rather than three), a  $\pi$ -donor ligand is now present as well.

#### Discussion Questions

1. Why was nonane chosen as the solvent for the first reaction rather than hexane, for example?
2. What features about the triphenylcarbenium cation lead to its observed reactivity?
3. Write out balanced reactions that show how you could remake  $(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$  from  $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$ .
4. What is the oxidation state of molybdenum (Mo) in each complex?
5. Design a set of experiments (with balanced equations) that would allow you to determine whether it is the exo or endo hydrogen that is abstracted in the first reaction. Assume that the most upfield signal in the  $^1\text{H}$  NMR spectrum of  $(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$  is the exo hydrogen.

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