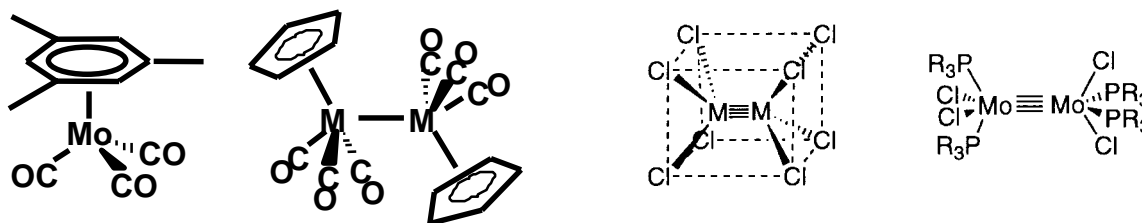


## Experiment 4: Transition-Metal Organometallic and Metal-Organic Chemistry

### Introduction

Organometallic chemistry is concerned with compounds in which one or more carbon atoms are bound to a metal. In broad terms this field may be subdivided into two recognizable areas defined by the type of metal bonded to carbon. One area involves compounds containing the main group elements such as the alkali and alkaline earth metals, and the more metallic elements in the zinc, boron, carbon, nitrogen, and oxygen vertical groups in the periodic table. In these compounds the carbon is usually bound to the metallic element by an ionic or relatively simple  $\sigma$ -bond. Examples include Grignard reagents, organolithium reagents, tetraethyllead, and other compounds used routinely in the laboratory and by the chemical industry.<sup>1</sup> The other area includes compounds containing transition metal elements in which a number of general compound classes may be recognized. Among these are the metal carbonyl, olefin, acetylene, cyclopentadienyl, arene,  $\pi$ -enyl, alkyl, and aryl groups of complexes.<sup>2,3</sup> Within this area is found a rich diversity of modes of metal-carbon bonding and types of molecular structure. The complexes which constitute these classes contain species with localized metal-carbon  $\sigma$ -bonds often accompanied by some amount of "back (or  $\pi$ -) bonding", as exemplified by the metal carbonyls, but more frequently highly delocalized bonding between a metal and two or more carbon atoms is encountered. Examples of such delocalized bonding are the interactions of metals with alkyne, alkene, and alkyl moieties, and with the aromatic ring systems  $C_5H_5^-$ ,  $C_6H_6$ , and  $C_7H_7^+$ . These interactions may generally be considered as highly covalent and rather strongly bonding.

One of the features of transition metal chemistry that is not shared by main group elements is the potential for formation of metal-metal multiple bonds with a bond order of 4.<sup>4</sup> The difference in the maximum number of bonds is due to the importance of the overlap between d orbitals in the transition metals. In addition to  $\sigma$  and  $\pi$  overlap, which is familiar from main group chemistry, all four lobes on each of two d orbitals may overlap in a face-to-face manner to form a  $\delta$  bond. The first complex containing a quadruple bond was  $[Re_2Cl_8]^{2-}$ , characterized by Cotton and co-workers by X-ray crystallography in the 1960s.<sup>4,5,6</sup> Since that time, compounds containing quadruple bonds have been characterized for Cr, Mo, W, Tc, and Re with molybdenum examples among the most numerous.<sup>5</sup> There are relatively few reactions known to cause the formation of quadruple bonds, so new compounds are usually formed by ligand substitution reactions on one of the common starting materials. The reaction to prepare dimolybdenum tetraacetate,  $[Mo_2(O_2CCH_3)_4]$ , from the reaction of molybdenum hexacarbonyl,  $Mo(CO)_6$  in glacial acetic acid and acetic anhydride,<sup>7</sup> involves the difficult formation of a quadruple bond and requires high heat and long reaction times.



**Figure 1.** Variety of metal carbonyl and metal - metal bonded structures.

In the set of experiments we will perform, two molybdenum complexes will be synthesized from a common precursor, molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$ .  $\text{Mo}(\text{CO})_6$  is one of the triad of metal hexacarbonyls of Group 6. Its chemical and physical properties are very similar to the other group members,  $\text{Cr}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ , and are also representative of other metal carbonyls having different stoichiometries and structures.<sup>3</sup>  $\text{Mo}(\text{CO})_6$  is a colorless compound whose crystals are composed of molecular octahedral units. It is readily volatile and may be easily sublimed without decomposition in vacuo at room temperature or at atmospheric pressure at slightly higher temperatures. It is readily soluble in most common, non-polar organic solvents without decomposition. It is also stable to air in the solid phase and in solution, a property which does not extend to certain other metal carbonyls such as  $\text{Co}_2(\text{CO})_8$  and  $\text{Ni}(\text{CO})_4$ .  $\text{Mo}(\text{CO})_6$  has been selected as the starting point for this experiment because of its own air stability and that of certain of its reaction products, the convenient rate of its reactions under normal laboratory conditions, and its ready accessibility. The compound is made commercially by the reaction of a molybdenum salt, reducing agent, and carbon monoxide at elevated temperature and pressure. It should be realized that, like other metal carbonyls,  $\text{Mo}(\text{CO})_6$  is a *toxic* chemical. The compound has an appreciable vapor pressure at room temperature and above. It may be routinely handled outside a hood in the preparation of reaction mixtures, but inhalation of its vapor or of finely divided particles must be avoided. These same toxic properties extend to the CO-containing product that will be prepared in Part 1 of this experiment. All of our syntheses will be performed in the hood and CO detectors will be placed nearby.

The experiments described below will provide you with experience in organometallic chemistry by preparing, purifying molybdenum organometallic compounds and metal-metal multiple bond systems, and characterizing them by IR, UV-vis, and NMR spectroscopy. Some of the reactions, purifications, and other manipulations must be carried out in the absence of air. Compounds are to be characterized principally by melting points, NMR spectroscopy, IR, and UV-vis spectral measurements. Metal carbonyls and their derivatives display sharp, intense CO stretching vibrations in the 1700 - 2200  $\text{cm}^{-1}$  region, the number and relative intensities of which are functions of the molecular symmetry. The frequencies (energies) of CO absorptions in the infrared are often diagnostic of the type of bond that the CO forms with the metal center. The two most important units are the terminal (M-C-O) and bridging (M-C(O)-M) groups whose CO frequencies in neutral molecules usually, but not always, fall in the 1900 - 2125 and 1700 - 1850  $\text{cm}^{-1}$  regions, respectively.

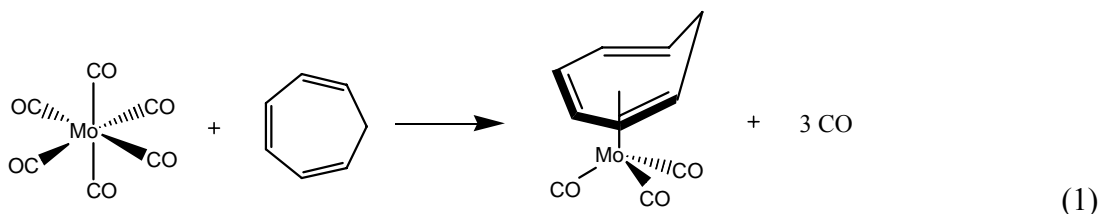
### Approximate Experimental Timeline

- Day 1:** Perform synthesis of  $(\text{C}_7\text{H}_8)\text{Mo}(\text{CO})_3$  and isolate crude product.
- Day 2:** Isolate purified Part 1 product. Start synthesis of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_3$  (2B).  
Begin characterization of Part 1 product.
- Day 3:** Isolate 2A product. Perform conversion of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_3$  to  $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9$  (Part 2B).  
Start characterization of 2A.
- Day 4:** Synthesize  $[(n\text{-Bu})_3\text{P}]_4\text{Mo}_2\text{Cl}_4$  from  $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9$  (Part 2C).  
Start characterization of 2B.
- Day 5:** Isolate 2C product and continue analysis of Part 1 and 2 products.
- Day 6:** Finish NMR experiments, if needed.

## Experimental Procedures

### Part 1. Synthesis of $\eta^6$ -cycloheptatriene molybdenum tricarbonyl $[(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3]^8$

Our first synthetic goal is to convert  $\text{Mo}(\text{CO})_6$  into a moderately air-sensitive organometallic arene complex. The molecular structure of  $(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$  has been determined by X-ray diffraction<sup>9</sup> and the compound has the structure indicated in Equation 1. Those of the closely related compounds  $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  [(benzene) chromium tricarbonyl]<sup>10</sup> and  $(\text{Me}_6\text{C}_6)\text{Cr}(\text{CO})_3$  [(hexamethylbenzene) chromium tricarbonyl]<sup>11</sup> have also been established in detail and reveal a "piano stool" structure with the arene moiety  $\pi$ -bonded to the metal (c.f., Equation 1 or Figure 1 left).



### General Experimental Setup Information

If any of the round-bottomed flasks do not come equipped with glass ears at the neck then copper ears must be made as anchors for rubber bands to secure glass joints together. To make copper ears, cut a length of copper wire, bend and twist it once in the center, and then wrap the two ends around the neck of the flask. There should be a loop of wire on one side of the neck from the original twist and two pieces of excess wire to be twisted together on the opposite side. Twist both sides with pliers until the wire is snug to the neck of the flask and the "ears" are 1-2 cm in length. To anchor the flask to a condenser, adapter, or stopper, bend the copper ears down toward the flask to prevent the rubber bands from slipping off, loop a rubber band around one copper ear on the flask, wrap the rubber band around the other piece of glassware and loop it around a constriction or the water port on a condenser to secure the pieces together, and fasten the rubber band in place by looping it around the other ear on the flask.

All molybdenum-containing solutions should be collected for heavy metal waste disposal.

### Part 1 – Experimental Procedures

*Caution: Molybdenum hexacarbonyl is extremely toxic and should be handled with gloves and kept in a hood. Wear gloves when dispensing this chemical.*

Combine reagent grade cycloheptatriene (8 ml, 76 mmol) and 20 ml of nonane (bp = 151 °C) in a 100 mL round-bottom flask. Add  $\text{Mo}(\text{CO})_6$  (2.0 g, 7.6 mmol) to this flask and attach a reflux condenser, connected to a Claisen adapter that is capped with a septum. Connect this assembly to a Schlenk line open to an oil bubbler and flush out the flask with a gentle stream of nitrogen for several minutes. Turn off the nitrogen flow and heat the contents of the flask to reflux with a heating mantle for 2 hours. During this time the condenser may be cooled as necessary with a

stream of air (do not use water cooling); excessive cooling is not desirable and leads to crystallization of  $\text{Mo}(\text{CO})_6$  in the condenser. Any sublimed metal carbonyl should be returned to the reaction mixture from time to time by scraping it off the condenser surface with a stiff copper wire poked through a hole in a septum in the Claisen adapter as nitrogen is slowly passed. At the end of the reflux period, cool the reaction mixture to room temperature under a nitrogen gas flow. After the flask is thoroughly flushed with  $\text{N}_2$  and closed with a gas adapter, it may be left in the hood until the next laboratory period.

Prepare a plug of neutral alumina in a fritted glass tube. Add the alumina powder to a beaker with hexane or ligroin and stir it to make a uniform slurry (no lumps). Transfer this slurry to the glass frit and repeat this until you generate a wet continuous column of alumina powder. Swirl around your red/orange/black reaction solution and place all of it on the alumina cake. Use  $\text{N}_2$  gas to push the solvent through the column. Discard this nonane/cyclopentadiene solution, unless it is strongly colored; in which case, send it through the column again. Wash the column with three 10 ml aliquots of nitrogen-purged ligroin to remove any unreacted starting materials and solvent. Finally, place a clean round bottom flask under the column and wash the orange product off the alumina using nitrogen-purged  $\text{CH}_2\text{Cl}_2$ . Attach the flask to a gas adapter and connect it to your Schlenk line. *Carefully* open the valve to vacuum and slowly reduce the volume of  $\text{CH}_2\text{Cl}_2$  (alternately there may be rotary evaporators that can assist with this). Swirl the flask gently to prevent bumping and excessive product splatter. Evacuate the powder to dryness. Quickly transfer the red solid to a pre-weighed vial and store the closed vial in a nitrogen purged plastic bag.

**Part 1 Characterization:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), IR (KBr), UV-vis ( $\text{CH}_2\text{Cl}_2$ , quartz cuvette)

## Part 2. Sequential synthesis of several complexes containing a Mo-Mo quadruple bond<sup>12</sup>

The first reaction involves the preparation of dimolybdenum tetraacetate,  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ , from the reaction of molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$ .<sup>7</sup> This insoluble product will be converted to  $[\text{Mo}_2\text{Cl}_8]^{4-}$  via a ligand substitution reaction that utilizes HCl gas and  $\text{NH}_4\text{Cl}$  and produces a complex with an unbridged quadruple bond.<sup>13</sup> The ammonium salt of the molybdenum complex has the formula,  $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9$ , but the ninth chloride ion, like the five  $\text{NH}_4^+$  cations, resides in the lattice of the solid and is not attached to either of the molybdenum centers. A similar salt using potassium has been characterized as  $\text{K}_4\text{Mo}_2\text{Cl}_8$ .<sup>14</sup> The diagram of  $[\text{Mo}_2\text{Cl}_8]^{4-}$ , presented in Figure 1, which shows the metal and ligands in a single plane is the most common way of representing structures of  $[\text{M}_2\text{L}_8]^{n-}$  compounds, although X-ray crystal structures have demonstrated that the structure is more accurately viewed with the ligands at the eight corners of a cube.<sup>6,13</sup> The dimetal unit resides within the cube so that the  $\{\text{MCl}_4\}^{n-}$  fragments are actually pyramidal rather than planar. Although steric repulsion between the ligands favors a staggered conformation between the two metals, the presence of the d bond favors an eclipsed conformation to maximize the d-d overlap.

The final product of this experiment is  $\text{Mo}_2\text{Cl}_4[\text{P}(n\text{-Bu})_3]_4$ . Replacing four anionic chloride ligands from  $[\text{Mo}_2\text{Cl}_8]^{4-}$  with neutral phosphines removes the charge on the overall complex.<sup>15</sup>

X-ray crystallography has shown that the phosphines occupy *trans* positions on each metal with the phosphines staggered from one metal to the other as seen in Figure 1 right.

The molecular orbital diagram of the orbitals involved in the metal-metal bond shows that the highest occupied molecular orbital (HOMO) is the  $\delta$  orbital and the lowest unoccupied molecular orbital (LUMO) is the  $\delta^*$  orbital. The energy difference between the frontier orbitals (HOMO and LUMO) corresponds to an electronic transition with the wavelength of visible light. Therefore, compounds containing quadruple bonds are often brilliantly colored. The exact energies of the orbitals are influenced by the nature of the ligands in the complex. Thus  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ , which has ligands of intermediate field strength, will have a different color from  $[\text{Mo}_2\text{Cl}_8]^{4-}$ , which has weak field p-donors. The final compound,  $\text{Mo}_2\text{Cl}_4[\text{P}(n\text{-Bu})_3]_4$ , has yet a third color caused by the mixture of  $\sigma$ -donor and  $\pi$ -acceptor ligands.

## Part 2 - Experimental Procedures

### Part 2A: Preparation of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$

*Caution: Molybdenum hexacarbonyl is extremely toxic and should be handled with gloves and kept in a hood. Acetic acid causes severe burns to skin and eyes, and acetic anhydride is also a skin and severe eye irritant. Wear gloves when dispensing these chemicals.*

Place 3.0 g of molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$ , in a 500 mL round-bottomed flask. Add 20 mL of acetic anhydride, 100 mL of glacial acetic acid and several boiling chips or a stir bar to the flask. Attach a reflux condenser to the flask and a gas inlet to the top of the condenser. The gas inlet is used to supply an inert atmosphere of  $\text{N}_2$  for the duration of the reaction. Turn on the gas tank and adjust the flow rate to have a gas bubble escape the mineral oil approximately every second. Reflux the reaction for approximately 20 hours using glass wool around the flask to insulate the reaction and improve heating efficiency. When cooling the solution, the gas flow rate must be increased slightly to avoid creating a vacuum in the flask, which siphons the bubbler oil back into the reaction solution. After cooling the system to room temperature, turn off the gas. The solution can be filtered in air after cooling although waiting several days before isolating the product does not affect the yield. Isolate the bright yellow crystals by suction filtration in the hood and wash the crystals with approximately 10 mL of ethanol. Use a freshly prepared sample for characterization because within two days of isolating the crystals or powder, the color becomes brown instead of the original bright yellow. A greenish or brownish sample does not affect the next reaction, but the yield is reduced slightly. The solid is insoluble in all common solvents and is therefore not suitable for characterization by solution methods.

**Part 2A Characterization:** IR (KBR), magnetic susceptibility

**Part 2B: Preparation of  $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9$** 

*Caution: Concentrated HCl and  $\text{H}_2\text{SO}_4$  will cause severe burns upon contact with skin. HCl is also volatile and is therefore a severe irritant if inhaled. Handle both chemicals with proper gloves and generate HCl gas in the hood.*

*Generation of HCl gas.* A convenient source of HCl gas may be generated by the reaction of  $\text{H}_2\text{SO}_4$  with HCl. The gas generation and the reaction itself should be carried out in the hood. Attach one end of an approximately 2 ft. length of rubber tubing to the side arm of a 500 mL round bottomed side arm flask and the other end of the tubing to a disposable Pasteur pipette. Use copper wire to secure the tubing to the glass pieces to prevent leakage of the gas. Fill the flask a little less than half way full with concentrated hydrochloric acid and clamp it upright to a ring stand or lattice. Attach the pressure equalizing dropping funnel to the flask, remembering to grease the joint between the two pieces of glassware using vacuum grease and secure it with copper ears and rubber bands. Add concentrated sulfuric acid to the dropping funnel, and close the top with a stopper. When the  $\text{H}_2\text{SO}_4$  comes in contact with the HCl, gas will be produced. When the reaction is to be started, adjust the dropping rate of the  $\text{H}_2\text{SO}_4$  into the HCl using the stopcock of the funnel. If no bubbles form in the reaction solution, check all connections for any leaks.

*Assembling the reaction.* To prepare the molybdenum complex,  $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9$ , place 1.0 g of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ , 1.12 g of  $\text{NH}_4\text{Cl}$  (9 equiv.), 75 mL of HCl, and a stir bar in a 150 mL beaker. Place the beaker in an ice bath on a stir plate and stir for fifteen minutes before initiating the gas flow. Bubble HCl gas through the solution with continuous stirring by placing the pipette from the gas generator in the solution but not near the stir bar. After 30 minutes, stop the addition of HCl gas, gradually warm the solution to room temperature, and filter. The purple product is stable indefinitely. The solid is insoluble in most common organic solvents, and although soluble in water, it decomposes immediately to form a brown solution.

**Part 2B Characterization: IR (KBr)****Part 2C: Preparation of the Tertiary Phosphine complex,  $\text{Mo}_2\text{Cl}_4[\text{P}(n\text{-Bu})_3]_4$** 

*Caution: Phosphines are toxic and are significant irritants; avoid physical contact with these substances through skin contact or inhalation. All liquid phosphines have an unpleasant stench, which is rapidly spread through the lab by hand contact with the phosphine bottle or reaction flask followed by touching other equipment. Phosphines are air-sensitive, so they must be dispensed under  $\text{N}_2$  or Ar gas. Any equipment, gloves, glove bags, glassware, etc. which have been contaminated with phosphines should be placed in a hood to minimize the amount of the compounds released into the laboratory atmosphere.*

*Solvent Preparation.* The methanol solvent should be deoxygenated by purging with  $\text{N}_2$  for a minimum of 20 minutes before use. Deoxygenate a larger sample of methanol than needed since evaporation will occur during the purging process. To remove the oxygen from the solvent, place the liquid in an Erlenmeyer flask and bubble gas through the solvent by using a metal needle attached with tubing to an inert gas source.

*Assembling the Reaction.* Prior to assembling the apparatus, place 0.3 g of  $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9$  and a small stir bar in a 50 mL round bottomed flask. From this point until filtration of the final product, an air-free atmosphere should be maintained. Cap the flask with a Suba septa or gas adapter then evacuate and purge the flask with  $\text{N}_2$  for 10 minutes. Add 25 mL of freshly distilled or deoxygenated methanol to the flask. At this point, get your TAs attention and he/she will quickly syringe 1.5 mL of  $\text{P}(n\text{-Bu})_3$  into your reaction flask. The addition should be done quickly, since the syringe plunger tends to freeze after exposure to the phosphine. Poke the needle back into the phosphine bottle after use. Attach a reflux condenser to your Schlenk line, purge it out with  $\text{N}_2$ , then grease the joint and quickly connect it to the purged flask. Keep  $\text{N}_2$  flowing during this connection and work to minimize the amount of air that enters the system. Any glassware that was exposed to the phosphine must be rinsed thoroughly with a dilute solution of bleach, followed by a rinse with water then acetone to remove the stench.

Turn on the cooling water for the condenser before heating the reaction with a heating mantle to avoid a sudden buildup of pressure within the system. Reflux the solution for two hours before cooling to room temperature. As in Reaction 2A, remember to increase the gas flow while cooling the system to avoid pulling oil from the bubbler into the system. Once the system is cool, the gas flow may be turned off. The solution can then sit for several days or be filtered immediately in air. After isolating the blue product by suction filtration and washing it with distilled water and methanol, store the solid under inert atmosphere in a sealed container. After putting the sample in a wide mouth vial, cover it with a septa and purge the vial with  $\text{N}_2$  then quickly cap it. You can put it in an  $\text{N}_2$ -purged zip lock plastic bag.

The  $\text{Mo}_2\text{Cl}_4[\text{P}(n\text{-Bu})_3]_4$  product is extremely oxygen sensitive in solution, so preparation of samples for characterization by solution methods such as electronic spectroscopy or NMR should be carried out under an inert atmosphere using deoxygenated solvent. The sample holders should be tightly sealed to prevent leakage of oxygen. All of the phosphine complexes are soluble in dichloromethane. When preparing for IR spectroscopy, work quickly and use a dry mortar and pestle.

**Part 2C Characterization:** IR(KBr), UV-vis ( $\text{CH}_2\text{Cl}_2$  quartz cuvette),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )

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