

## Chapter Three

# COMPOUNDS WITH METAL–METAL BONDS

### 16. TETRA(ACETATO)DIMOLYBDENUM(II)

Submitted by RICHARD A. WALTON,<sup>\*</sup> PHILLIP E. FANWICK,<sup>\*</sup> and  
GREGORY S. GIROLAMI<sup>†</sup>

Checked by CARLOS A. MURILLO<sup>‡</sup> and ERIK V. JOHNSTONE<sup>§</sup>



In 1960, Wilkinson discovered that several carboxylic acids,  $\text{HO}_2\text{CR}$ , react with molybdenum hexacarbonyl,  $\text{Mo}(\text{CO})_6$ , at elevated temperatures to form complexes of the type “ $\text{Mo}(\text{O}_2\text{CR})_2$ ”. The true nature of these bright yellow molybdenum(II) complexes was established in 1964 with the publication by Lawton and Mason of the X-ray crystal structure of tetra(acetato)dimolybdenum, which is depicted schematically in Fig. 1.<sup>1</sup> The Mo–Mo distance of 2.11 Å is considerably shorter than the Mo–Mo distance of 2.78 Å in molybdenum metal, and this fact is evidence that the Mo–Mo bond in  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  has considerable multiple bond character.

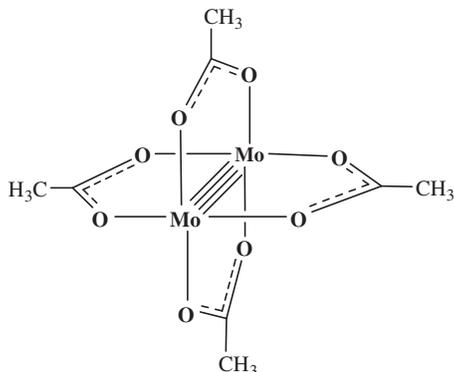
In fact, because Mo(II) is isoelectronic with Re(III), Cotton proposed that  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  contains a molybdenum–molybdenum quadruple bond. A vast

<sup>\*</sup>Department of Chemistry, Purdue University, West Lafayette, IN 47907.

<sup>†</sup>Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

<sup>‡</sup>Department of Chemistry, Texas A&M University, College Station, TX 77842.

<sup>§</sup>Department of Chemistry, University of Nevada-Las Vegas, Las Vegas, NV 89154.



**Figure 1.** Structure of tetra(acetato)dimolybdenum(II).

body of experimental data has confirmed this proposal and  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  has provided access to a large number of derivatives with a  $\text{Mo}_2^{4+}$  core. The reaction of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  with hydrochloric acid in the presence of inorganic cations was elaborated initially by Sheldon and later by Brencic and Cotton;<sup>2</sup> the products are red-colored salts containing the  $[\text{Mo}_2\text{Cl}_8]^{4-}$  ion, which is isostructural and isoelectronic with  $[\text{Re}_2\text{Cl}_8]^{2-}$ . The preparation of molybdenum(II) acetate has been described in a previous volume of this series,<sup>3</sup> but the synthesis described here gives a much higher yield of the desired complex.

### *Procedure*

■ **Caution.** *Molybdenum hexacarbonyl is highly toxic. When heated, it sublimes and partly decomposes to carbon monoxide and molybdenum. Never allow  $\text{Mo}(\text{CO})_6$  dust to form; never let any solution containing  $\text{Mo}(\text{CO})_6$  touch any part of the skin; keep the material away from any source of heat. Acetic acid and acetic anhydride are toxic and corrosive. 1,2-Dichlorobenzene is a suspected carcinogen. Do not let these chemicals come into contact with the skin; if they do, wash off the affected area with copious quantities of water. Follow local guidance/protocols for the safe disposal of chlorinated waste.*

The following reaction should be performed in a well-ventilated fume hood. An oven-dried 1 L three-necked (24/40) round-bottomed flask equipped with a condenser (topped with a nitrogen gas inlet), stopper, nitrogen gas inlet, and a large Teflon<sup>®</sup>-coated stir bar is charged with 1,2-dichlorobenzene (300 mL). All joints are either greased with Apiezon-H or fitted with Teflon sleeves. The gas inlet

atop the condenser is connected via a glass “tee” to a source of nitrogen gas and a mineral oil bubbler. Next,  $\text{Mo}(\text{CO})_6$  (14.0 g, 53 mmol), a 10:1 (v/v) mixture of acetic acid/acetic anhydride (35 mL), hexanes (35 mL),\* and trimethylamine *N*-oxide<sup>†</sup> (about 0.3 g, 4 mmol) are added.

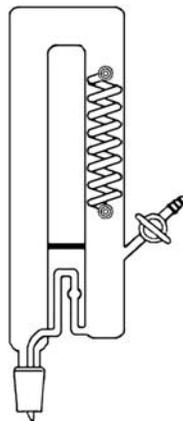
■ **Caution.** *The added hexanes prevent molybdenum carbonyl from subliming into and clogging the condenser. A solid plug of  $\text{Mo}(\text{CO})_6$  is very dangerous because the gases ( $\text{H}_2$  and  $\text{CO}$ ) that are generated during the course of the reaction could build up pressure and lead to an explosion. It is equally important to ensure that the stopcock atop the condenser is open during the reflux. Even with the addition of hexanes, the authors recommend careful monitoring of the reaction over the first few hours. Should any  $\text{Mo}(\text{CO})_6$  sublime into the condenser during the early stages of the reaction, it should be carefully pushed back into the flask with a glass rod.*

The stopcock atop the condenser is closed and the flask is quickly evacuated and backfilled with nitrogen several times to remove dissolved air. The lower stopcock is closed, the stopcock atop the condenser is opened, and a slow flow of nitrogen is started to the bubbler. A heating mantle is placed around the flask and the mixture is refluxed overnight (12 h), during which period the solution darkens and a fine yellow crystalline solid precipitates. Stirring is stopped and the suspension is slowly cooled to room temperature (the power to the heating mantle is turned off, but it is kept wrapped around the round-bottomed flask to slow the cooling). The cooled mixture is filtered in air through a 60 mL medium- or coarse porosity

\*An alternative to using hexanes to wash down the sublimed  $\text{Mo}(\text{CO})_6$  is to use a specialized piece of glassware designed by one of us (G.S.G.). It consists of a downflow condenser in which the condensate is returned to the flask by means of a siphon, as shown at right.

Any  $\text{Mo}(\text{CO})_6$  that condenses on the water-cooled condenser coils is automatically washed down and returned to the flask. A brace between the two vertical tubes makes the apparatus more robust, and the stopcock sidearm can be used to connect the apparatus by means of a hose to a source of  $\text{N}_2$ ; this sidearm is slanted slightly upward and is higher than the top of the siphon so that the condensed liquid does not enter the hose. The hot solvent vapors pass by the drip tube and travel up the left side of the apparatus, which is wrapped with insulation such as glass wool; the vapors are condensed on the right side and return to the flask. This apparatus is not commercially available, but can easily be made by a good glassblower. It can be used for many reactions that involve heating a solution containing a volatile solid component such as  $\text{I}_2$ , phenol, and so on.

<sup>†</sup>Trimethylamine *N*-oxide is added to help initiate the reaction by oxidizing the carbonyl ligands to  $\text{CO}_2$ .



sintered glass frit inside a fume hood. The crystals are washed with ethanol ( $3 \times 30$  mL) followed by ether ( $3 \times 30$  mL) and dried under high vacuum for several hours. The yield is typically greater than 9.0 g (80%).

### *Properties*

Tetra(acetato)dimolybdenum(II) is a bright yellow crystalline solid that is sparingly soluble in organic solvents. The compound decomposes slowly (days to weeks) in air and quite rapidly in solution. It is best stored in an inert atmosphere or under vacuum in the absence of light.  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  is a key starting material in dimolybdenum(II) chemistry and can be converted to many other quadruply bonded dimolybdenum(II) complexes, including  $[\text{Mo}_2\text{Cl}_8]^{4-}$ ,<sup>2</sup>  $\text{Mo}_2(\text{allyl})_4$ ,<sup>4</sup>  $[\text{Mo}_2(\text{CH}_3)_8]^{4-}$ ,<sup>4</sup>  $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$ ,<sup>5</sup> and  $[\text{Mo}(\mu\text{-}t\text{-Bu}_2\text{P})(t\text{-Bu}_2\text{P})]_2$ .<sup>6</sup>

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