

Note

# Microwave-assisted synthesis of dimolybdenum tetracarboxylates and a decanuclear osmium cluster

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## Abstract

An improved method for the synthesis of dimolybdenum tetracarboxylates has been developed. The standard procedure for the preparation of these compounds involves extended reflux (up to 20 h) of a mixture of  $\text{Mo}(\text{CO})_6$  and the appropriate carboxylic acid, along with its anhydride, under an inert atmosphere. Using a microwave reactor and a closed vessel,  $\text{Mo}_2(\text{acetate})_4$ ,  $\text{Mo}_2(\text{propionate})_4$  and  $\text{Mo}_2(\text{benzoate})_4$  have been prepared in superior yields in less than 1 h. Furthermore, this new method does not require the use of the acid anhydride or the use of an inert gas. An improved method for the preparation of  $[\text{N}(\text{PPh}_3)_2]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$  directly from  $\text{Os}_3(\text{CO})_{12}$  has also been developed. The published synthesis of this osmium cluster calls for the pyrolysis of  $\text{Os}_3(\text{CO})_{11}(\text{py})$  for 64 h. Microwave irradiation of a mixture of  $\text{Os}_3(\text{CO})_{12}$  and diglyme in a closed vessel yields the desired product in just over 1 h.

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## 1. Introduction

Tetra- $\mu$ -acetatodimolybdenum(II),  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ , is by far the most important synthon for preparing complexes with Mo–Mo quadruple bonds. It is the starting material of choice for many of the thousands of known quadruply bonded dimolybdenum compounds [1]. It has also found use as a chromophore in the determination of the absolute configuration of UV–Vis transparent amino acids, hydroxy acids, amino alcohols and 1,2- and 1,3-diols [2]. In such chiroptical studies,  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  is mixed with the chiral molecule in DMSO and the circular dichroism spectrum of the resulting solution is recorded and analyzed. Dimolybdenum tetracarboxylates are typically synthesized by refluxing the carboxylic acid (along with its anhydride when available) with hexacarbonylmolybdenum(0),  $\text{Mo}(\text{CO})_6$ , under an inert atmosphere [1]. This often takes many hours and results in a low yield even when measures are taken to

eliminate all traces of oxygen. For example, the standard procedure for the preparation of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  involves refluxing acetic acid, acetic anhydride and  $\text{Mo}(\text{CO})_6$  under  $\text{N}_2$  gas for 20 h to obtain a 37% yield [3]. The method is improved with the use of selected solvents with higher boiling points. As Cotton noted [1], “Superior yields (80%) are obtained only when a solvent such as diglyme or 1,2-dichlorobenzene is used.” However, a 20–24 h reflux period is still required. A significant hazard associated with this reaction is the ease with which  $\text{Mo}(\text{CO})_6$  sublims from the reaction mixture and deposits in the reflux condenser. The reaction setup has been known to explode as the condenser becomes completely blocked with small white crystals of  $\text{Mo}(\text{CO})_6$ .

We report herein the results of our attempts to improve upon the syntheses of dimolybdenum tetracarboxylates by using a microwave energy source and a closed reaction vessel. The use of microwave irradiation in chemical synthesis has grown increasingly more important and widespread [4]. Advantages include acceleration of reaction rates, improved yields and simplified procedures. Using

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an open vessel in a modified conventional microwave oven, Hogarth and coworkers have prepared  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  in 48% yield [5]. In the absence of an inert atmosphere, however, this experiment failed. We have found that a closed-vessel microwave method allows for the preparation of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  in yields as high as 89% without the use of a co-solvent or an inert gas and without concern for the buildup of  $\text{Mo}(\text{CO})_6$  deposits. Several other dimolybdenum tetracarboxylates can also be synthesized more efficiently via this method, and our success in preparing these  $\text{Mo}_2(\text{O}_2\text{CR})_4$  compounds in the microwave reactor led us to attempt the synthesis of a larger metal cluster complex. Our initial target was the decanuclear osmium cluster  $[\text{N}(\text{PPh}_3)_2]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ . The standard method for its synthesis involves pyrolysis for 64 h [6]. We have found that microwave irradiation can be used to make this cluster in just over 1 h.

## 2. Experimental

All reactions were carried out in a Discover-S microwave reactor (2455 MHz, CEM Corp., Matthews, NC) that allows for a maximum temperature of 300 °C and a maximum pressure of 300 psi. Thick-walled 35-mL reaction vessels with Teflon-lined caps were provided by CEM. Caution must be exercised due to the toxic nature of CO and  $\text{Mo}(\text{CO})_6$ . All manipulations must be carried out in a highly efficient fume hood. Extra care must be taken when the reactions are under pressure; the microwave reactor must be placed in the fume hood and the hood sash must be left down until a few minutes after the pressure has been released. Caution is also advised when using concentrated acids. A new cap should be used to seal the reaction vessel for each reaction described below. All chemicals were purchased from Aldrich and used as received. Infrared spectra were recorded on a Nicolet Avatar 320 FTIR spectrophotometer. The IR spectra of the dimolybdenum compounds were obtained using solid samples in attenuated total reflectance mode, hereafter denoted: solid, ATR. Elemental analyses were performed by QTI of Whitehouse, NJ.

### 2.1. Preparation of tetra- $\mu$ -acetatodimolybdenum(II), $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ , in an open vessel

$\text{Mo}(\text{CO})_6$  (1.15 g, 4.36 mmol) was added to 25 mL of acetic acid (437 mmol) and 10 mL of diglyme in a conventional 100-mL round-bottom glass flask equipped with a stir bar and connected to a large reflux condenser. The flask was placed in the microwave reactor cavity in open-vessel mode with the maximum temperature set to 135 °C. The mixture was irradiated at 150 W for 1 h, and then allowed to cool to room temperature. The bright yellow product was filtered off and washed with ethanol, hexane and diethyl ether. Yield: 0.603 g, 64.7%.

### 2.2. Preparation of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ in a closed vessel

$\text{Mo}(\text{CO})_6$  (0.397 g, 1.50 mmol) was added to acetic acid (7 mL, 122 mmol) in a 35-mL reaction vessel equipped with a stir bar. The vessel was capped, placed in the microwave reactor and irradiated at 300 W with the stirring rate set to high. After 7 min the power automatically dropped because the pressure was nearing the limit of 300 psi, but the power remained between 270 and 290 W for 3 more minutes. The maximum temperature reached was 185 °C and the maximum pressure reached was 287 psi. The reaction mixture was cooled to 54 °C and briefly vented before being irradiated for an additional 6 min at 300 W. The reaction mixture was cooled to room temperature, and then filtered through a glass frit. The yellow product was rinsed with ethanol, hexane, and ether, then placed in a vacuum desiccator for 12 h. Yield: 0.284 g, 88.5%. IR (solid, ATR): 1507 s, 1491 s, 1439 vs, 1407 s, 1352 m, 1045 m, 1033 m, 960 m, 937 m, 899 s, 854 m, 674 vs  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_8\text{H}_{12}\text{O}_8\text{Mo}_2$ : C, 22.45; H, 2.83. Found: C, 22.39; H, 2.76%.

### 2.3. Preparation of tetra- $\mu$ -propionatodimolybdenum(II), $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_4$

$\text{Mo}(\text{CO})_6$  (0.365 g, 1.38 mmol) was added to propionic acid (8 mL, 107 mmol) and hexane (2 mL) in a 35-mL reaction vessel equipped with a stir bar. The vessel was capped, placed in the microwave reactor and irradiated for 22 min at 300 W with the stirring rate set to high. The maximum temperature reached was 190 °C and the maximum pressure reached was 287 psi. The reaction mixture was cooled to 30 °C and briefly vented before being irradiated for an additional 10 min at 300 W. The mixture was cooled to 54 °C, removed from the microwave reactor, and placed in a freezer at -10 °C for 5 h. The yellow product was filtered off and washed with ethanol and diethyl ether. Yield: 0.238 g, 71.0%. IR (solid, ATR): 1506 vs, 1466 s, 1447 m, 1427 vs, 1382 m, 1296 s, 1082 m, 1074 m, 1005 m, 957 m, 888 vs, 859 s, 806 s, 735 m, 675 vs  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{12}\text{H}_{20}\text{O}_8\text{Mo}_2$ : C, 29.77; H, 4.16. Found: C, 30.08; H, 3.84%.

### 2.4. Preparation of tetra- $\mu$ -benzoatodimolybdenum(II), $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$

$\text{Mo}(\text{CO})_6$  (0.317 g, 1.20 mmol) and benzoic acid (1.710 g, 13.99 mmol) were added to diglyme (2 mL) and hexane (2 mL) in a 35-mL reaction vessel equipped with a stir bar. The vessel was capped, placed in the microwave reactor and irradiated for 10 min at 300 W with the stirring rate set to high. The maximum temperature reached was 200 °C and the maximum pressure reached was 232 psi. The reaction mixture was cooled to 54 °C and briefly vented before being irradiated for an additional 5 min at 300 W. The mixture was cooled to 54 °C, removed from the microwave reactor, and allowed to cool to room tem-

perature. The orange-yellow product was filtered off and washed with diethyl ether. Yield: 0.366 g, 90.0%. IR (solid, ATR): 1490 s, 1478 m, 1438 m, 1400 vs, 1070 m, 1027 m, 959 m, 929 m, 896 m, 854 m, 842 s, 721 vs, 709 vs, 681 vs  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{28}\text{H}_{20}\text{O}_8\text{Mo}_2$ : C, 49.72; H, 2.98. Found: C, 49.69; H, 2.81%.

### 2.5. Preparation of $[\text{N}(\text{PPh}_3)_2]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$

$\text{Os}_3(\text{CO})_{12}$  (0.250 g, 0.276 mmol) was added to 8 mL of diglyme in a 35-mL reaction vessel equipped with a stir bar. The vessel was capped, placed in the microwave reactor and irradiated at 300 W with the stirring rate set to high. After 38.5 min, the temperature had reached 231 °C and the pressure had reached 287 psi, so the reactor automatically reduced the power to 100 W over the next 30 s. The power remained between 90 and 110 W for 9 additional minutes of irradiation. The reaction vessel was cooled to 50 °C and briefly vented before being irradiated at 300 W for 4 more min. At that time, the power began to drop steadily over the next 1 min until it reached 140 W. The vessel was then cooled to 54 °C and briefly vented again before being irradiated at 300 W for an additional 4 min. The mixture was cooled to 54 °C, poured into a watch glass over a steam bath, and evaporated to a volume of less than 0.5 mL. The residue was washed with warm hexane, dissolved in a mixture of 12 mL of acetone and 3 mL of methanol, and then filtered through a glass frit. A solution of 0.105 g (0.164 mmol) of  $[\text{N}(\text{PPh}_3)_2]_2\text{Cl}$  in 3 mL methanol was added to the filtrate. Slow evaporation of the resulting solution led to the formation of small crystals of dark red-brown  $[\text{N}(\text{PPh}_3)_2]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ , which was then recrystallized from an acetone/methanol solution. Finally, the product was filtered off and washed with cold 1-propanol. Yield: 0.174 g, 57.4%. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$ : 2034 s, 1986 s  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{97}\text{H}_{60}\text{N}_2\text{O}_{24}\text{P}_4\text{Os}_{10}$ : C, 31.80; H, 1.65; N, 0.76. Found: C, 31.92; H, 1.54; N, 0.81%.

## 3. Results and discussion

### 3.1. Preparation of $\text{Mo}_2(\text{carboxylate})_4$

The synthesis of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  has been known since 1964 [7] and its structure since 1965 [8]. As is the case in the other dimolybdenum tetracarboxylates prepared herein, the pair of quadruply bonded Mo atoms is bridged by the four carboxylate ligands in an eclipsed conformation so that the oxygen atoms for each ligand are directly opposite one another. In 2004, Hogarth and coworkers reported obtaining a 48% yield by heating a mixture of acetic acid, diglyme and  $\text{Mo}(\text{CO})_6$  under argon in an open vessel for 45 min in a modified conventional microwave oven [5]. We decided to perform a similar experiment with the computer-controlled microwave reactor. Irradiation at 150 W of a mixture of acetic acid, diglyme and  $\text{Mo}(\text{CO})_6$  under

nitrogen in an open vessel for 1 h produced a 65% yield. Although these open-vessel methods drastically reduce the reaction time, they still require a large amount of solvent and an inert atmosphere.

On the other hand, the closed-vessel microwave method offers multiple advantages over the previously published procedures. No longer is nitrogen or argon gas required nor is anhydride or an extra solvent needed. There is no need to monitor the buildup of sublimed  $\text{Mo}(\text{CO})_6$  in a condenser. The reaction time is short, yet the desired product is formed in 89% yield. This new method requires less energy and uses fewer chemicals. The acetic acid-to- $\text{Mo}(\text{CO})_6$  mole ratio in the standard method is 230:1 while this ratio is 81:1 in our closed-vessel microwave approach. Venting the reaction vessel after the initial irradiation period is necessary in order to release some of the CO gas generated by the reaction. If the second period of irradiation is not performed, then a small amount of unreacted  $\text{Mo}(\text{CO})_6$  remains deposited near the top of the reaction vessel. Alternatively, we have found that the reaction may be carried out in a single step if it is done on a smaller scale and for a longer period of time (less than 0.3 g of  $\text{Mo}(\text{CO})_6$  and over 30 min of irradiation).

We were unable to find any mention in the scientific literature of a yield associated with the preparation of  $\text{Mo}_2(\text{propionate})_4$ , although it was also first reported in 1964 [7]. Unlike the acetate, which is insoluble in acetic acid and readily precipitates, the propionate is somewhat soluble in propionic acid. When microwave reactions were performed with  $\text{Mo}(\text{CO})_6$  in propionic acid alone, the highest yield obtained was 61%. We chose to include a small amount of hexane to accelerate the dissolution of  $\text{Mo}(\text{CO})_6$  and to expedite the precipitation of the desired product. The addition of hexane allowed us to achieve a 71% yield.

The standard synthesis of  $\text{Mo}_2(\text{benzoate})_4$  is fairly similar to that of  $\text{Mo}_2(\text{acetate})_4$  and  $\text{Mo}_2(\text{propionate})_4$  with the exception of the use of diglyme as a solvent and a much shorter reflux period of 4 h. The published procedure stresses that the diglyme must be dried and that there must be no presence of oxygen whatsoever [3]. Yields up to 65% may be obtained by this method, but the closed-vessel microwave technique offers several advantages. In our experiments no measures were taken to exclude all moisture from the diglyme nor was nitrogen or argon used to exclude  $\text{O}_2$ , yet we obtained a better yield of the same orange-yellow solid in only 20 min. This new method also reduces the amount of diglyme used per gram of  $\text{Mo}(\text{CO})_6$  by 83%, although it does require the addition of a small amount of hexane.

### 3.2. Preparation of $[\text{N}(\text{PPh}_3)_2]_2[\text{Os}_{10}\text{C}(\text{CO})_{24}]$

The  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$  anion of this compound has virtual  $T_d$  symmetry and consists of a carbide atom surrounded by a tetracapped octahedral osmium framework

with two terminal carbonyl ligands per osmium in the central Os<sub>6</sub> octahedron and three terminal CO ligands per capping osmium atom. The published procedure for the synthesis of this decanuclear osmium cluster involves converting Os<sub>3</sub>(CO)<sub>12</sub> to Os<sub>3</sub>(CO)<sub>11</sub>(C<sub>5</sub>H<sub>5</sub>N), sealing it under vacuum in a Carius tube and heating it at 250 °C for 64 h to obtain a 65% yield [6]. This represents a 58% yield based on Os<sub>3</sub>(CO)<sub>12</sub> since Os<sub>3</sub>(CO)<sub>11</sub>(py) is prepared from Os<sub>3</sub>(CO)<sub>12</sub> in 90% yield [6]. Previous attempts to prepare the Os<sub>10</sub> cluster by the pyrolysis of Os<sub>3</sub>(CO)<sub>12</sub> resulted in only a 5% yield, while the pyrolysis of Os<sub>3</sub>(CO)<sub>11</sub>(py) for 15 h instead of 64 h gave a 15% yield [6]. The microwave-assisted technique proved superior once again since a 57% yield was obtained directly from Os<sub>3</sub>(CO)<sub>12</sub> in just over 1 h.

#### 4. Conclusion

Closed-vessel microwave-assisted synthesis of metal cluster complexes offers a number of advantages over conventional methods of preparation. These include greatly enhanced reaction rates, improved yields, and the use of fewer reagents. The increased temperature and pressure associated with a closed vessel allow for a more efficient reaction compared to an open-vessel approach, although venting the vessel is often necessary to release gaseous byproducts. All of the dimolybdenum tetracarboxylates were prepared in better yields than ever reported before and in a fraction of the time required by conventional techniques. Similarly, the Os<sub>10</sub> cluster was produced very quickly and in very high yield for a single step process. We believe that a broad range of both new and existing transition-metal clusters may be more conveniently prepared by this method.

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