



**HAL**  
open science

# Decarbonylation of molybdenum(II) carbonyl complexes: a new route to quadruply bonded molybdenum(II) dimers

F. Albert Cotton, Rinaldo Poli

► **To cite this version:**

F. Albert Cotton, Rinaldo Poli. Decarbonylation of molybdenum(II) carbonyl complexes: a new route to quadruply bonded molybdenum(II) dimers. *Journal of the American Chemical Society*, 1986, 108 (18), pp.5628-5629. <10.1021/ja00278a046>. <hal-03545270>

**HAL Id: hal-03545270**

**<https://hal.science/hal-03545270v1>**

Submitted on 27 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

**Decarbonylation of Molybdenum(II) Carbonyl  
Complexes: A New Route to Quadruply Bonded  
Molybdenum(II) Dimers**

F. Albert Cotton\* and Rinaldo Poli

*Department of Chemistry and Laboratory for  
Molecular Structure and Bonding, Texas A&M University  
College Station, Texas 77843*

*Received February 3, 1986*

Multiple metal-metal bonds are now well established and, among them, the quadruple bond between molybdenum(II) atoms has perhaps been the most intensively studied.<sup>1</sup> Despite this, most of the known Mo<sub>2</sub><sup>4+</sup> derivatives are still prepared via ligand-exchange reaction starting from the molybdenum(II) acetate, its preparation from Mo(CO)<sub>6</sub> being the most important route to the formation of the Mo<sub>2</sub><sup>4+</sup> core. Other synthetic routes to Mo<sub>2</sub><sup>4+</sup> species from mononuclear precursors generally involve reduction of higher oxidation state compounds, such as MoX<sub>3</sub> (X = Cl, Br),<sup>2</sup> MoCl<sub>4</sub>,<sup>3</sup> MoH<sub>4</sub>(PMePh<sub>2</sub>)<sub>4</sub>,<sup>4</sup> and MoO<sub>3</sub>.<sup>5</sup> Only one example seems

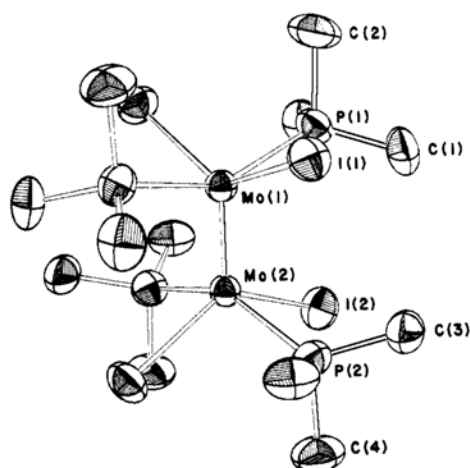
---

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.

(2) (a) Edwards, D. A.; Maguire, J. J. *Inorg. Chim. Acta* **1977**, *25*, L47.  
(b) Armstrong, J. E.; Edwards, D. A.; Maguire, J. J.; Walton, R. A. *Inorg. Chem.* **1979**, *18*, 1172.

(3) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.

(4) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1716.



**Figure 1.** ORTEP diagram of  $\text{Mo}_2\text{I}_4(\text{PMe}_3)_4$  in compound **5** with the atomic numbering scheme employed. Distances: Mo1–Mo2, 2.129 (1); Mo1–I1, 2.762 (1); Mo1–P1, 2.566 (2); Mo2–I2, 2.756 (1); Mo2–P2, 2.557 (2); P1–C1, 1.839 (5); P1–C2, 1.883 (8); P2–C3, 1.835 (5); P2–C4, 1.896 (8) Å. Angles: Mo2–Mo1–I1, 113.63 (2)°; Mo2–Mo1–P1, 104.39 (5)°; I1–Mo1–I1', 132.74 (3)°; I1–Mo1–P1, 84.28 (2)°; P1–Mo1–P1', 151.23 (9)°; Mo1–Mo2–I2, 113.83 (2)°; Mo1–Mo2–P2, 104.70 (4)°; I2–Mo2–I2', 132.35 (3)°; I2–Mo2–P2, 84.12 (2)°; P2–Mo2–P2', 150.60 (9)°.

to have appeared in the literature of a  $\text{Mo}_2^{4+}$  species having been prepared from a Mo(II) non-metal–metal-bonded starting material, i.e.,  $\text{Mo}_2\text{L}_2$  (L = porphyrin) from the corresponding mononuclear complex  $\text{MoL}(\text{PhC}\equiv\text{CPh})$ .<sup>6</sup> It is also to be noted that CO and other strong  $\pi$ -acidic ligands are generally found to destabilize M–M multiple bonds.<sup>1</sup> For these reasons, we consider it unusually interesting that dimolybdenum(II) species of the  $\text{Mo}_2\text{I}_4\text{L}_4$  and  $\text{Mo}_2\text{I}_4(\text{L-L})_2$  type [L =  $\text{PMe}_3$  (**1**); L–L = dppm (**2**)] can be prepared directly from Mo(II) carbonyl iodide starting materials;  $\text{Mo}_2\text{I}_4(\text{CO})_8$ ,<sup>7</sup> **3**, now easily available in large amounts,<sup>8</sup> was the system of our choice.

This synthetic method has other points of interest: it is a simple and direct route to dinuclear Mo(II) iodides, otherwise obtained by the longer procedure of halide exchange from the corresponding bromides,<sup>9</sup> by coordinative addition to  $\beta$ - $\text{MoI}_2$ ,<sup>10</sup> or by the recently developed<sup>11</sup> reaction of the acetate with  $\text{Me}_3\text{SiI}$  in the presence of the appropriate ligand. Furthermore, it represents the reverse process to the known<sup>12</sup> reaction of  $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$  complexes with carbon monoxide, in which there is disruption of the quadruple bond and formation of mononuclear carbonyl derivatives of Mo(II) and Mo(0). Finally, it is a new pattern of reactivity for complexes of the  $\text{M}_2\text{X}_4(\text{CO})_8$  type.

Treatment of **3** with 4 equiv of  $\text{PMe}_3$  in toluene as solvent at room temperature leads to CO evolution and formation of an orange solution. Reflux (5 h) results in a change of color to deep blue. From this solution compound **1** was isolated by evaporation to dryness and recrystallization from *n*-hexane, yield 41%. It was characterized by vibrational and electronic spectroscopy, <sup>1</sup>H and <sup>31</sup>P NMR, and elemental analysis.<sup>13</sup>

An analogous reaction was carried out from  $\text{MoI}_2(\text{CO})_3\text{THF}_2$  (**4**) and 4 equiv of the phosphine in refluxing THF, the carbonyl complex having been obtained in situ by dissolving **3** in THF.<sup>8</sup>

From the final blue-green solution a blue solid,  $\text{Mo}_2\text{I}_4(\text{PMe}_3)_4\cdot 2\text{THF}$  (**5**) crystallized upon cooling to room temperature. This had the same visible spectrum as **1**: the IR spectrum (Nujol mull), on the other hand, exhibited a strong band at  $1070\text{ cm}^{-1}$  which was not present in the corresponding spectrum of **1**. We assign this band to the C–O–C vibration of lattice THF. The presence of THF was confirmed by <sup>1</sup>H NMR (broad triplets at  $\delta$  1.48 and 3.62, 1:1 relative intensity) and by a crystal structure determination,<sup>14</sup> which established the nature of the compound as **5**. A view of the dimer in compound **5** is shown in Figure 1.

Compound **1** is air-sensitive, but it resists aerial oxidation for a few hours, even in  $\text{CH}_2\text{Cl}_2$  solution. Compound **5** loses its lattice THF when pumped or exposed to air, and the crystal for X-ray analysis had therefore to be mounted under solvent.

Reaction of **3** with 2 equiv of dppm in toluene at room temperature gave rise to an orange solution from which orange crystals soon began to form. Their analytical and spectroscopic data are in accord with their formulation as  $\text{MoI}_2(\text{CO})_3\text{dppm}$  (**6**).<sup>15</sup> Reflux of compound **6**, either isolated or obtained in situ as previously described, for 12 h in toluene as solvent afforded crystalline  $\text{Mo}_2\text{I}_4\text{dppm}_2\cdot 2\text{toluene}$  (**7**), identified by comparison of its vibrational and electronic spectra with those of an authentic sample<sup>11,16</sup> (yield 86%).

Compound **5** appears to be the first Mo(II) iodide of the  $\text{Mo}_2\text{I}_4\text{L}_4$  type and one of the few iodide-containing compounds of the  $\text{Mo}_2^{4+}$  core to be crystallographically characterized. The dinuclear molecule has imposed  $C_{2v}$  symmetry, the Mo–Mo vector lying along the twofold axis and the two planes passing through Mo(1), Mo(2), I(1), I(1'), P(2), and P(2') and through Mo(1), Mo(2), I(2), I(2'), P(1), and P(1'). Although it is not isostructural with  $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ ,<sup>17</sup> the two molecules have essentially the same geometry, typical of  $\text{Mo}_2\text{X}_4\text{L}_4$  compounds. The Mo–Mo distances in compound **5** and its chlorine analogue are exactly the same, and this confirms the rule<sup>18</sup> that halogen exchange has little, if any, effect on the metal–metal bond length. The Mo–I distance [average 2.759 (1) Å] is a little shorter than those found for trans iodides in the  $[\text{Mo}_2\text{I}_6(\text{H}_2\text{O})_2]^{2-}$  anions<sup>19</sup> [average 2.790 (1) Å for both the pyridinium<sup>19a</sup> and 2-picolinium<sup>19b</sup> salts]. This may be due to the negative charge of the latter species, since the Mo–Cl and Mo–I distances in the  $\text{Mo}_2\text{X}_4(\text{PMe}_3)_4$  molecules differ by 0.345 Å, which is the accepted difference in the covalent radii of Cl and I. The Mo–P distances in **5** are virtually the same as the corresponding ones found in  $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$  [2.556 (2) vs. 2.545 (1) Å].<sup>17</sup> Further work is under way to explore the generality of this new synthetic method for molybdenum as well as tungsten dimers, with the attention also focused on the characterization of intermediate species.

**Acknowledgment.** We thank the National Science Foundation for support.

**Supplementary Material Available:** Tables of fractional atomic coordinates and temperature parameters, anisotropic temperature parameters, and bond distances and angles for **5** (3 pages); tables of observed and calculated structure factors for **5** (8 pages). Ordering information is given on any current masthead page.

(14) Crystallographic data: Orthorhombic,  $Cmcm$ ,  $a = 19.412$  (5) Å,  $b = 9.789$  (5) Å,  $c = 20.165$  (8) Å,  $Z = 4$ ,  $R = 0.033$ ,  $R_w = 0.058$ . 64 parameters were refined using 1487 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The THF molecule was found to be disordered, the two independent configurations having about half-occupancy each, and the parameters of the corresponding atoms were fixed during the last cycles of refinement.

(15) Compound **6**: Anal. Calcd for  $\text{C}_{28}\text{H}_{22}\text{I}_2\text{MoO}_3\text{P}_2$ : C, 41.1; H, 2.7. Found: C, 41.7; H, 2.9. IR (toluene) 2043 m, 1973 s, 1921 m  $\text{cm}^{-1}$ ; (Nujol mull), 3020 w, 2040 m, 1940 vs br, 1910 m, 1590 w, 1575 w, 1485 m, 1435 m, 1310 w, 1190 w, 1160 vw, 1095 s, 770 w, 740 s, 690 s, 675 w, 575 s, 525 s, 500 m, 490 m, 470 m s, 455 m, 350 m  $\text{cm}^{-1}$ .

(16) Walton, R. A.; personal communication.  
(17) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

(18) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 4384.

(19) (a) Brencic, J. V.; Segedin, P. *Inorg. Chim. Acta* **1978**, *29*, L281. Brencic, J. V.; Golic, L. *J. Cryst. Mol. Struct.* **1977**, *7*, 183.

(5) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1980**, *102*, 4277.

(6) Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684.

(7) Colton, R.; Rix, C. *J. Aust. J. Chem.* **1969**, *22*, 305.

(8) Calderazzo, F.; Poli, R.; Zanazzi, P. F., unpublished results.

(9) Brencic, J. V.; Dobcnik, D.; Segedin, P. *Monatsh. Chem.* **1976**, *107*, 395.

(10) Glicksman, H. D.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 200.

(11) Dunbar, K. R., unpublished work in this laboratory.

(12) Cotton, F. A.; Darendsbourg, D. J.; Kolthammer, B. W. S. *J. Organomet. Chem.* **1981**, *217*, C14.

(13) Compound **1**: Anal. Calcd for  $\text{C}_{12}\text{H}_{36}\text{I}_4\text{Mo}_2\text{P}_4$ : C, 14.4; H, 3.6%. Found: C, 14.5; H, 3.8%. IR (Nujol mull) 1420 m, 1415 sh, 1295 m, 1280 m, 1165 w, 900 s, 850 w, 730 m, 670 w, 345 w, 335 w  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  1.76 s; <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ , ppm from external  $\text{H}_3\text{PO}_4$ )  $\delta$  -14.98; vis ( $\text{CH}_2\text{Cl}_2$ , 25 °C) 631 ( $\epsilon$   $4.33 \times 10^3$ ), 394 ( $\epsilon$   $8.55 \times 10^3$ ) nm.