



20 min) gave a single hydroxy ester **14**, mp 78–79 °C (65% from **12**). Conversion of **14** to the tetracyclic dilactone **15** was accomplished by the sequence (1) mesylation (1.5 equiv of triethylamine, 3 equiv of mesyl chloride at –20 °C in CH<sub>2</sub>Cl<sub>2</sub> for 30 min, yield 94%) and (2) methyl ester hydrolysis (0.1 N lithium hydroxide in THF–water at 23 °C for 2 h) and acidification (84% yield). The short and simple synthesis of **15** illustrates the synthetic potential of the methodology described herein.

The widely different rates of the carbolactonization reaction with keto acids **2**, **7**, **9**, and **11** would seem to indicate that cyclization rather than  $\alpha$ -deprotonation may be rate limiting in these cases. If this is indeed so, it must also be true that the reactive intermediate in the C–C bond-forming step of the carbolactonization is not a conventional free radical but a Mn-stabilized "radicaloid" species, perhaps that derived by deprotonation of a bridged acetate in Mn<sub>3</sub>O(OCOCH<sub>3</sub>)<sub>7</sub>.

The extension of this methodology and its application to the synthesis of ginkgolides will be described in subsequent papers.<sup>13</sup>

**Registry No.** **2**, 91492-04-5; **2** methyl ester, 91492-15-8; **3**, 91492-05-6; **4**, 91492-06-7; **5**, 2138-99-0; **6**, 91492-07-8; **7**, 91492-08-9; **8**, 91492-09-0; **9**, 65180-53-2; **10**, 91492-10-3; **11**, 5650-68-0; **12**, 91492-11-4; **13**, 91492-12-5; **14**, 91492-13-6; **14** mesylate, 91492-16-9; **15**, 91492-14-7; Mn<sub>3</sub>O(OAc)<sub>7</sub>, 63338-46-5; CH<sub>3</sub>C(O)CH<sub>2</sub>C(O)OMe, 105-45-3; BrCH<sub>2</sub>C(O)OMe, 96-32-2; 3-bromocyclohexene, 1521-51-3.

**Supplementary Material Available:** Spectral data for compounds **3**, **4**, **6**, **8**, **10**, and **12–15** (1 page). Ordering information is given on any current masthead page.

(13) This research was assisted financially by a grant from the National Science Foundation.

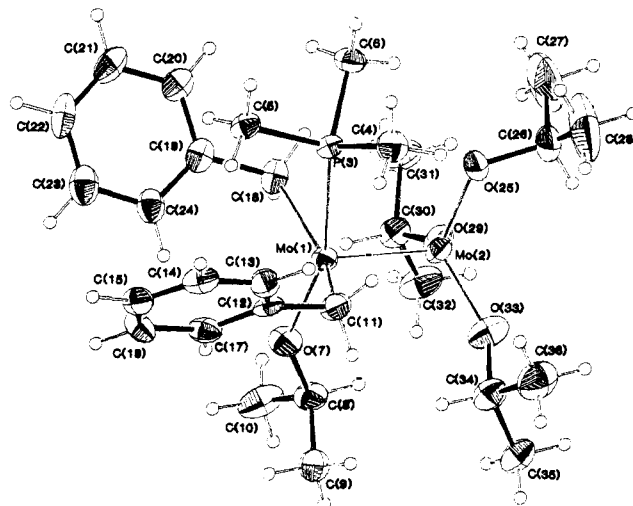
**(*i*-PrO)<sub>3</sub>Mo≡Mo(CH<sub>2</sub>Ph)<sub>2</sub>(O-*i*-Pr)(PMe<sub>3</sub>): The First Example of a Compound Containing a Triple Bond Uniting Three- and Four-Coordinate Molybdenum Atoms and the Observation of Phosphine-Promoted, Reversible Benzyl-Alkoxy Migrations at the (M≡M)<sup>6+</sup> Center**

Malcolm H. Chisholm,\* John C. Huffman, and Robert J. Tatz

Department of Chemistry and Molecular Structure Center  
Indiana University, Bloomington, Indiana 47405

Received May 23, 1984

Of all the compounds containing multiple bonds between metal atoms,<sup>1</sup> the d<sup>3</sup>-d<sup>3</sup> dimers of molybdenum and tungsten show the most varied and fascinating coordination chemistry. There are compounds with M–M triple bonds of configuration  $\sigma^2\pi^4$  in which the metal atoms are each coordinated to three, four, five, and even six ligand atoms.<sup>2,3</sup> Though *ligand* atoms may span the two metal atoms, there are no bridging *atoms* in this group of d<sup>3</sup>-d<sup>3</sup> dimers. However, compounds with bridging atoms are known as in W<sub>2</sub>Cl<sub>6</sub>(py)<sub>4</sub><sup>4</sup> and the salts containing M<sub>2</sub>X<sub>9</sub><sup>3-</sup> ions (X = Cl, Br)<sup>5</sup> which adopt structures based on edge- and face-shared octahedra, respectively. Within the former group of compounds of formula X<sub>n</sub>M≡MX<sub>n</sub> or X<sub>n</sub>Y<sub>m</sub>M≡MX<sub>n</sub>Y<sub>m</sub>, where X and Y = a ligand atom and *n* or (*n* + *m*) = 3 → 6, there has been no example of a compound where the coordination number at each metal atom has been different, e.g., in Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>, Mo<sub>2</sub>(O-*i*-Pr)<sub>6</sub>(py)<sub>2</sub>, W<sub>2</sub>Me<sub>2</sub>(O<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>, and W<sub>2</sub>(O<sub>2</sub>CNMe<sub>2</sub>)<sub>6</sub> *n* or (*n* + *m*) = 3, 4, 5, and 6, respectively. The apparent desire of the metal atoms to maintain this equality in coordination number is exemplified



**Figure 1.** ORTEP view of the (*i*-PrO)<sub>3</sub>Mo≡Mo(CH<sub>2</sub>Ph)<sub>2</sub>(O-*i*-Pr)(PMe<sub>3</sub>) molecule. Some pertinent bond distances (Å) and angles (°) (averaged where appropriate): Mo–Mo = 2.235 (1) Mo–C = 2.22 (1), Mo(1)–O(7) = 1.920 (4), Mo(2)–O = 1.89 (2), Mo–P = 2.581 (2); Mo–Mo–C = 101.3 (6), Mo(2)–Mo(1)–O(7) = 106.5 (1), Mo–Mo–P = 94.65 (4), Mo(1)–Mo(2)–O = 107.2 (20), Mo–C–C = 114.4 (11).

by the pair-wise insertion of CO<sub>2</sub> into OR<sup>6</sup> and NMe<sub>2</sub><sup>7</sup> ligands and the cooperative binding of Lewis bases to M<sub>2</sub>(OR)<sub>6</sub> compounds:<sup>8</sup> M<sub>2</sub>(OR)<sub>6</sub> + 2L → M<sub>2</sub>(OR)<sub>6</sub>L<sub>2</sub>. We report here the first example of a compound having a central (M≡M)<sup>6+</sup> unit in which the metal atoms have different coordination numbers, namely, 3 and 4.

Hexane solutions of 1,2-Mo<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub><sup>9</sup> react with *i*-PrOH (4 equiv) to yield 1,2-Mo<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub>(O-*i*-Pr)<sub>4</sub>.<sup>10</sup> The <sup>1</sup>H NMR spectra<sup>11</sup> confirm the 1,2-dibenzyl substitution pattern and are consistent with a rapidly interconverting (NMR time scale) mixture of anti and gauche rotamers, through the presence of only the anti rotamer cannot be excluded: the benzyl methylene protons appear as a singlet, and there is only one type of O-*i*-Pr ligand which contains diastereotopic methyl groups.

Addition of PMe<sub>3</sub> (2 equiv) to a hexane solution of 1,2-Mo<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> yields (*i*-PrO)<sub>3</sub>Mo≡Mo(CH<sub>2</sub>Ph)<sub>2</sub>(O-*i*-Pr)(PMe<sub>3</sub>) as red crystals upon cooling. The molecular structure, deduced from an X-ray study,<sup>12</sup> is shown in Figure 1. The Mo–Mo distance, 2.235 (1) Å, is comparable to those in Mo<sub>2</sub>(OCH<sub>2</sub>-*t*-Bu)<sub>6</sub><sup>13</sup> 2.222 (2) Å, and Mo<sub>2</sub>Me<sub>2</sub>(O-*t*-Bu)<sub>4</sub>(py)<sub>2</sub><sup>14</sup> 2.256

(6) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 1727.

(7) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 603.

(8) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

(9) Chetouti, M. J.; Chisholm, M. H.; Foltling, K.; Haitko, D. A.; Huffman, J. C.; Janos, J. *J. Am. Chem. Soc.* **1983**, *105*, 1163.

(10) Dry and oxygen free solvents and atmospheres (N<sub>2</sub>) were used throughout.

(11) <sup>1</sup>H NMR data obtained from toluene-*d*<sub>6</sub> at 360 MHz for 1,2-Mo<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub>(O-*i*-Pr)<sub>4</sub> (+20 °C): δ (CH<sub>2</sub>Ph) 4.13 (s); (CH<sub>2</sub>Ph) *o* 7.05 (d, *J* = 7.6 Hz), *m* 6.99 (dd, *J* = 7.6 Hz), *p* 6.79 (t, *J* = 7.6 Hz); (CHMe<sub>2</sub>) 5.39 (sept, *J* = 5.8 Hz); (CHMe<sub>2</sub>) 1.32 (d, *J* = 5.8 Hz), 1.26 (d, *J* = 5.8 Hz). (*i*-PrO)<sub>3</sub>Mo≡Mo(CH<sub>2</sub>Ph)<sub>2</sub>(O-*i*-Pr)(PMe<sub>3</sub>) (–20 °C): δ (CH<sub>2</sub>Ph) 4.63 (2 H, dd, <sup>2</sup>*J*<sub>H–H</sub> = 11.8 Hz; <sup>3</sup>*J*<sub>H–P</sub> = 15.5 Hz), 4.46 (2 H, dd, <sup>2</sup>*J*<sub>H–H</sub> = 11.8 Hz, <sup>3</sup>*J*<sub>H–P</sub> = 11.8 Hz); (CH<sub>2</sub>Ph) *o* 7.07 (4 H, d, *J* = 7.6 Hz), *m* 6.96 (4 H, d, *J* = 7.6 Hz), *p* 6.71 (2 H, d, *J* = 7.6 Hz); (OCHMe<sub>2</sub>) 6.08 (1 H, sept, *J* = 5.8 Hz); (OCHMe<sub>2</sub>) 1.83 (6 H, d, *J* = 5.8 Hz); (OCHMe<sub>2</sub>)' 4.68 (3 H, sept, *J* = 5.8 Hz); (OCHMe<sub>2</sub>)' 1.30 (18 H, d, *J* = 5.8 Hz).

(12) Crystal data at –159 °C: *a* = 16.779 (3) Å, *b* = 10.104 (1) Å, *c* = 19.555 (4) Å, β = 90.59 (1)°, *Z* = 4 and space group P2<sub>1</sub>/c. Of the 4823 reflections collected using Mo Kα, 6° < 2θ < 45°, the 3665 having *F* > 3σ(*F*) were used in the full-matrix least-squares refinement. All the H atoms were located and refined. Final residuals are *R*(*F*) = 0.037 and *R*<sub>w</sub>(*F*) = 0.041. For general operating procedures and listings of programs employed at the IUMSC, see: Chisholm, M. H.; Foltling, K.; Huffman, J. C.; Kirkpatrick, C. C., *Inorg. Chem.* **1984**, *23*, 1021.

(13) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

(14) Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2075.

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

(2) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 356.

(3) Chisholm, M. H. *Symp. Farad. Soc.* **1980**, No. 14, 194.

(4) Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760.

(5) See: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 864–866 and references cited therein.