Supplementary Material Available: Crystal structure analysis reports (text and tables), tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, and bond lengths and angles in cations and solvent molecules of crystallization (Tables SI–SIX), and ORTEP plots of cations and solvent molecules of crystallization for $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18})][(n\text{-}C_4H_9)_4N]_3 \cdot H_2O$ (A), $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H)][(n\text{-}C_4H_9)_4N]_2 \cdot 0.5[C_6H_4(CH_3)_2]$ (B), and $[(\eta^5\text{-}C_5H_5)Ti(W_5O_{18}H_2)][(n\text{-}C_4H_9)_4N]_2Cl$ (C) (Figures S1–S3) (41 pages); tables of observed and calculated structure factors for A–C (80 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Indiana University,
Bloomington, Indiana 47405, and University of Durban-Westville, P/B 54001, Durban, South Africa

Synthesis and Substitution Reactions of Dinuclear Molybdenum Complexes Containing Mo–Mo Quadruple Bonds and Labile Solvent Ligands

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The kinetically labile acetonitrile ligands of $[Mo_2(O_2C\text{–}t\text{-Bu})_3(MeCN)_2]^+(BF_4^-)$ (**1**) have been selectively replaced by the anions derived from deprotonation of 6-hydroxy-2-methylpyridine (mhp) and 2,6-dimethylpyridine (dmp) to yield the triscarboxylate complexes $Mo_2(O_2C\text{–}t\text{-Bu})_3$ (mhp) (**3**) and $Mo_2(O_2C\text{–}t\text{-Bu})_3$ (dmp) (**4**), respectively. In contrast to complexes containing mixed tetracarboxylate ligand sets, the ligand sets of **3** and **4** were found to be inert with respect to scrambling reactions in solution. **4** crystallized in the centrosymmetric space group $C2/c$, $a = 19.732$ (3) Å, $b = 11.733$ (1) Å, $c = 24.648$ (3) Å, $\beta = 94.57$ (1)°, and $Z = 8$. Treatment of **1** with 1 equiv of 2-(diphenylphosphino)pyridine (dppy) promoted a ligand scrambling reaction to yield equimolar amounts of $[Mo_2(O_2C\text{–}t\text{-Bu})_2(dppy)_2]^{2+}(BF_4^-)_2$ (**5**) and $Mo_2(O_2C\text{–}t\text{-Bu})_4$. **5** was also prepared quantitatively by the reaction between $[Mo_2(O_2C\text{–}t\text{-Bu})_2(MeCN)_6]^{2+}(BF_4^-)_2$ (**2**) and 2 equiv of dppy. The MeCN ligands of **2** were also substituted with α,α'-bipyrimidine (bpym) to afford $[Mo_2(O_2C\text{–}t\text{-Bu})_2(bpym)_2]^{2+}(BF_4^-)_2$ (**6**). The crystal structure of **6** was solved in the monoclinic space group $P2_1/n$ at −177 °C, $a = 11.144$ (1) Å, $b = 10.054$ (1) Å, $c = 35.751$ (6) Å, $\beta = 91.32$ (1)°, and $Z = 4$. The two bpym ligands of **6** each formed five-membered chelate rings employing cis-equatorial positions on the Mo–Mo quadruple bond. Treatment of **6** with an equimolar amount of **2** did not result in a polymer supported by bpym bridges, rather ligand scrambling was again observed. The novel solvated complex $[Mo_2(mhp)_3(MeCN)_2]^+(BF_4^-)$ (**7**) was prepared by alkylation of $Mo_2(mhp)_4$ in acetonitrile. The cation in **7** crystallized as a dimer of Mo_2 units connected by two Mo–O axial interactions involving one mhp ligand on each dinuclear cation; at −172 °C, space group = $P2_1/n$, $a = 17.899$ (6) Å, $b = 14.515$ (4) Å, $c = 21.897$ (7) Å, $\beta = 97.04$ (2)°, and $Z = 4$.

Introduction

The wide variety of electrochemical, magnetic, and photochemical properties associated with complexes possessing metal–metal multiple bonds has prompted us to investigate the viability of preparing low-dimensional materials which incorporate such multiple bond subunits. Our initial efforts concentrated on the synthesis of polymers containing M–M quadruple bonds in a mixed carboxylate framework such as structure I.[1] Unfortunately the

$$\{[M_2(O_2CR)_2](O_2C\text{–}R'\text{–}CO_2)[M_2(O_2CR)_2](O_2C\text{–}R'\text{–}CO_2)\}_n$$

I

$$M = Mo, W$$

generality of polymers of this type turns out to be severely limited by facile carboxylate exchange reactions that often lead to unselective ligand scrambling on the M_2 cores.[1b] Such facile scrambling of carboxylate groups on dinuclear compounds was previously observed in a study of the self-exchange reactions of $Mo_2(O_2CCF_3)_4$ with NaO_2CCF_3 in acetonitrile by variable temperature ^{19}F NMR.[2] More recently, it was found that the rates of self-exchange reactions of $Mo_2(O_2C\text{–}t\text{-Bu})_4$ with $(n\text{-}Bu_4N)(O_2C\text{–}t\text{-Bu})$ as determined by variable temperature ^1H NMR are quite solvent dependent and in fact different mechanisms are operative in either coordinating or noncoordinating solvents.[3]

The preparation of polymers containing more kinetically persistent coordination spheres about the M–M quadruple bonds rested upon the development of suitable dinuclear starting materials and the selection of the ligand bridge. We found the solvated complexes $[Mo_2(O_2C\text{–}t\text{-Bu})_3(MeCN)_2]^+(BF_4^-)$ (**1**) and $[Mo_2(O_2C\text{–}t\text{-Bu})_2(MeCN)_6]^{2+}(BF_4^-)$ (**2**) to be extremely versatile reagents for the synthesis of tetranuclear complexes of the type shown in structure II[1b,4] and higher oligomers of formula

$$[Mo_2(O_2CR)_3](bridge)[Mo_2(O_2CR)_3]$$

II

$[Mo_2(O_2CR)_2(bridge)]_n$. During the course of this work, we expored a variety of substitution reactions involving the Mo_2-containing cations **1** and **2**, along with other related solvated dimolybdenum species, the results of which are presented here.

Results and Discussion

The replacement of carboxylate ligands in dimolybdenum tetracarboxylate complexes with labile solvent ligands has previously been studied under a variety of conditions.[5] The first such product to be structurally characterized was $[Mo_2(O_2CMe)_2(MeCN)_6]^{2+}(BF_4^-)_2$, obtained by the treatment of dimolybdenum tetraacetate with an excess of Meerwein's reagent in acetonitrile.[6] Following a similar reaction we isolated the *t*-Bu analogue, $[Mo_2(O_2C\text{–}t\text{-Bu})_2(MeCN)_6]^{2+}(BF_4^-)_2$ (**2**) as shown in eq 1.

[†] Indiana University.

[‡] University of Durban-Westville.

(1) (a) Cayton, R. H.; Chisholm, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 8921. (b) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. *J. Am. Chem. Soc.* **1991**, *113*, 8709.

(2) Teramoto, K.; Sasaki, Y.; Migita, K.; Iwaizumi, M.; Saito, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 446.

(3) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Folting, K. Manuscript in preparation.

(4) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 862.

(5) See, for example: (a) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287. (b) Bowen, A. R.; Taube, H. *Inorg. Chem.* **1974**, *13*, 2245. (c) Abbott, E. H.; Schownewolf, F., Jr.; Backstrom, T. *J. Coord. Chem.* **1974**, *3*, 255. (d) Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2774. (e) Telser, J.; Drago, R. S. *Inorg. Chem.* **1984**, *23*, 1798. (f) Cotton, F. A.; Wiesinger, K. J. *Inorg. Chem.* **1991**, *30*, 871.

(6) (a) Cotton, F. A.; Reid, A. H.; Schwotzer, W. *Inorg. Chem.* **1985**, *24*, 3695. (b) Pimblett, G.; Garner, C. G.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1986**, 1257.

0020-1669/92/1331-2928$03.00/0

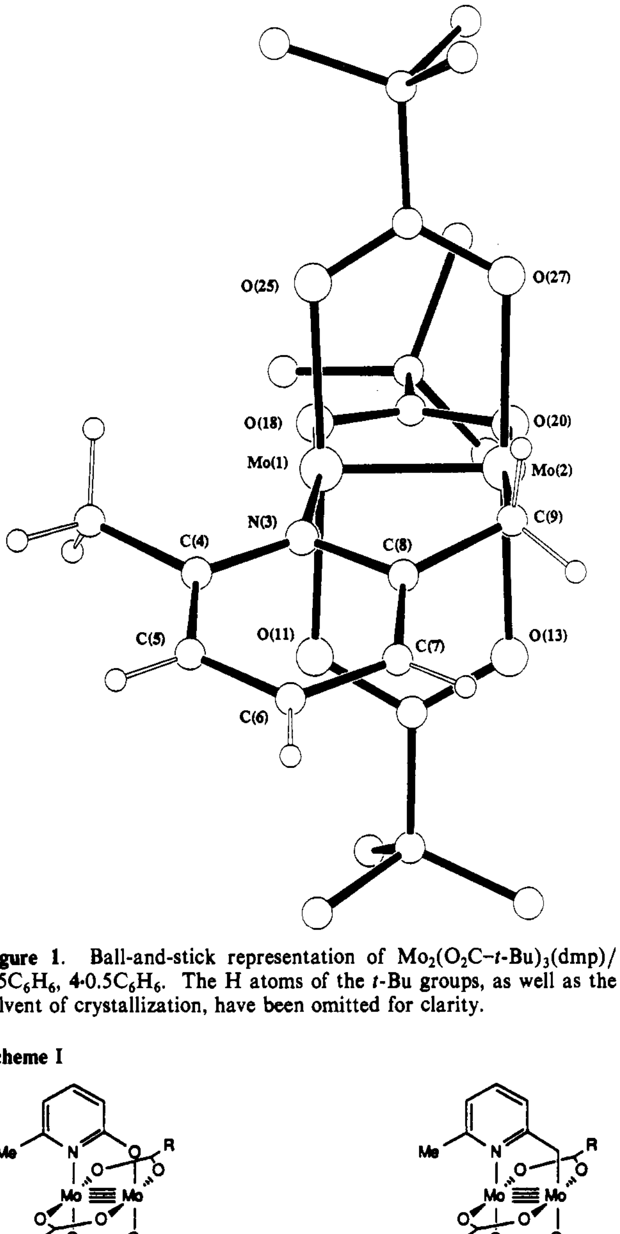
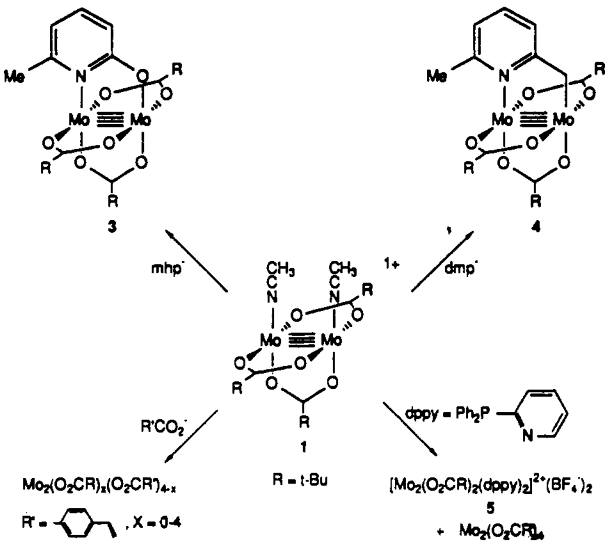


Figure 1. Ball-and-stick representation of $Mo_2(O_2C\text{-}t\text{-}Bu)_3(dmp)/0.5C_6H_6$, $4{\cdot}0.5C_6H_6$. The H atoms of the *t*-Bu groups, as well as the solvent of crystallization, have been omitted for clarity.

Scheme I



Furthermore, exploiting the inherent lability of carboxylate ligands on Mo–Mo quadruple bonds, we were able to prepare the triscarboxylate species $[Mo_2(O_2C\text{-}t\text{-}Bu)_3(MeCN)_2]^+(BF_4^-)$ (**1**) in ca. 90% purity from the reaction described in eq 2.[1b,7] The reactions of **1** with various bidentate ligands are summarized in Scheme I.

$$Mo_2(O_2C\text{-}t\text{-}Bu)_4 + \text{excess } Et_3OBF_4 \xrightarrow[CH_2Cl_2]{MeCN} \underset{\mathbf{2}}{[Mo_2(O_2\text{-}t\text{-}Bu)_2(NCMe)_6]^{2+}(BF_4^-)_2} \quad (1)$$

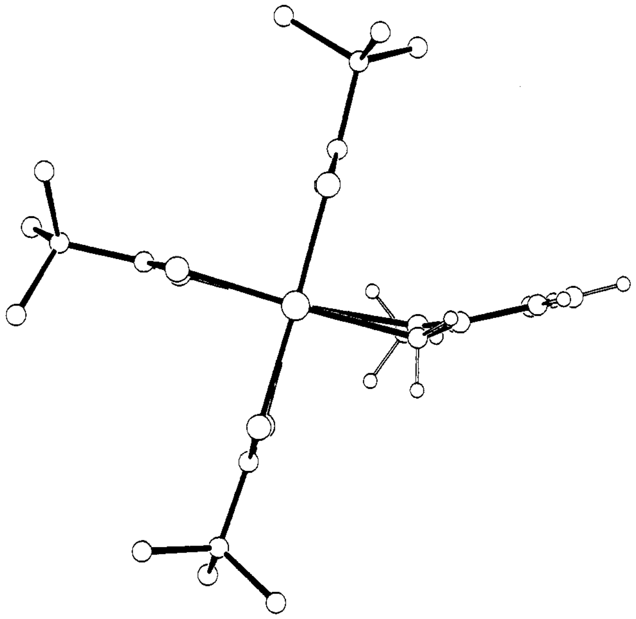


Figure 2. Ball-and-stick representation of **4** showing a view down the Mo–Mo bond. The tilting of the dmp ligand caused by the sp^3 hybridized CH_2 group is clearly evident.

Table I. Selected Interatomic Distances (Å) and Angles (deg) in $4{\cdot}0.5C_6H_6$

	Distances		
Mo(1)–Mo (2)	2.0828 (5)	O(20)–C(19)	1.284 (5)
Mo(1)–O(11)	2.1009 (26)	O(25)–C(26)	1.265 (4)
Mo(1)–O(18)	2.1189 (26)	O(27)–C(26)	1.279 (4)
Mo(1)–O(25)	2.0964 (25)	N(3)–C(4)	1.369 (5)
Mo(1)–N(3)	2.186 (3)	N(3)–C(8)	1.375 (5)
Mo(2)–O(13)	2.1113 (25)	C(4)–C(5)	1.375 (6)
Mo(2)–O(20)	2.1737 (26)	C(4)–C(10)	1.501 (6)
Mo(2)–O(27)	2.1393 (25)	C(5)–C(6)	1.377 (6)
Mo(2)–C(9)	2.215 (4)	C(6)–C(7)	1.383 (6)
O(11)–C(12)	1.276 (5)	C(7)–C(8)	1.389 (6)
O(13)–C(12)	1.275 (5)	C(8)–C(9)	1.474 (6)
O(18)–C(19)	1.272 (5)		
	Angles		
Mo(2)–Mo(1)–O(11)	92.5 (1)	Mo(1)–N(3)–C(4)	122.4 (3)
Mo(2)–Mo(1)–O(18)	91.9 (1)	Mo(1)–N(3)–C(8)	115.8 (3)
Mo(2)–Mo(1)–O(25)	92.4 (1)	C(4)–N(3)–C(8)	119.6 (3)
Mo(2)–Mo(1)–N(3)	96.0 (1)	N(3)–C(4)–C(5)	120.9 (4)
O(11)–Mo(1)–N(3)	84.1 (2)	N(3)–C(4)–C(10)	116.3 (4)
O(18)–Mo(1)–N(3)	170.0 (2)	C(5)–C(4)–C(10)	122.8 (4)
O(25)–Mo(1)–N(3)	96.6 (2)	C(4)–C(5)–C(6)	120.0 (4)
Mo(1)–Mo(2)–O(13)	91.4 (1)	C(5)–C(6)–C(7)	119.2 (4)
Mo(1)–Mo(2)–O(20)	92.0 (1)	C(6)–C(7)–C(8)	120.3 (4)
Mo(1)–Mo(2)–O(27)	91.2 (1)	N(3)–C(8)–C(7)	119.5 (4)
Mo(1)–Mo(2)–C(9)	92.4 (2)	N(3)–C(8)–C(9)	115.6 (3)
O(13)–Mo(2)–C(9)	88.5 (2)	C(7)–C(8)–C(9)	124.9 (4)
O(20)–Mo(2)–C(9)	174.9 (2)	Mo(2)–C(9)–C(8)	114.1 (3)
O(27)–Mo(2)–C(9)	93.4 (2)		

$$Mo_2(O_2C\text{-}t\text{-}Bu)_4 + \mathbf{2} \xrightleftharpoons{MeCN} \underset{\mathbf{1}}{2[Mo_2(O_2C\text{-}t\text{-}Bu)_3(MeCN)_2]^+(BF_4^-)} \quad (2)$$

The treatment of **1** with 1 equiv of a carboxylate anion results in the formation of a mixture of products, $Mo_2(O_2C\text{-}t\text{-}Bu)_{4-x}(O_2CR)_x$, where $x = 0\text{–}4$. It has proven impossible to isolate the 3:1 mixed carboxylate intermediate since this species rapidly disproportionates in solution to yield the observed mixture of compounds. In contrast, the anions derived from deprotonation of 2-hydroxy-6-methylpyridine (mhp) and 2,6-dimethylpyridine (dmp) react with **1** to yield the triscarboxylate derivatives $Mo_2(O_2C\text{-}t\text{-}Bu)_3(mhp)$ (**3**) and $Mo_2(O_2C\text{-}t\text{-}Bu)_3(dmp)$ (**4**), respec-

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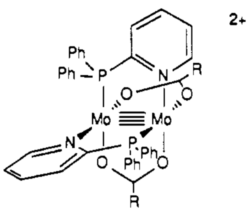
(7) Casas, J. M.; Cayton, R. H.; Chisholm, M. H. *Inorg. Chem.* **1990**, *30*, 358.

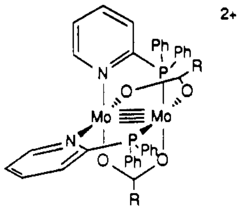
tively. The ^{1}H NMR spectra of **3** and **4** each show the expected 2:1 ratio of singlets due to the *cis*- and *trans*-*t*-BuCO$_2$ ligands, respectively, along with resonances associated with the corresponding pyridyl ligands. Most importantly, complexes **3** and **4** are kinetically persistent in solution and show no signs of ligand exchange. Because mixed ligand systems consisting of three carboxylate groups are somewhat rare for dimolybdenum complexes,[1b,8] we carried out a single-crystal X-ray structure determination of **4**. Ball-and-stick diagrams of **4** are shown in Figures 1 and 2 and pertinent bond lengths and angles provided in Table I.

The Mo–Mo bond [2.0828 (5) Å] of **4** is bridged by three carboxylate groups and the dmp ligand, resulting in the usual square pyramidal geometry about each metal center. The Mo–O bond lengths are not unusual [Mo–O = 2.11 (1) Å, av] with the exception of the Mo–O bond located trans to the Mo–C bond of the dmp ligand. This Mo–O bond is 0.06 Å longer than the average of the other Mo–O distances, presumably due to the stronger trans influence of the Mo–C bond. The dmp ligand in **4** appears to favor the resonance structure characterized by an anionic CH$_2$ group and a lone pair on the N atom. Evidence for this resonance form comes from the similar C–CH$_3$ and C–CH$_2$ bond lengths [1.501 (6) and 1.474 (6) Å, respectively], and the sp^3 hybridization of the CH$_2$ group. Figure 2 contains a view of **4** down the Mo–Mo bond. The sp^3 nature of the methylene group causes a folding of the five-membered dimetallacycle ring and a tilting of the dmp ligand to one side. In solution the dmp ligand is fluxional on the NMR time scale, resulting in a time-averaged structure of C_s symmetry.

Treatment of **1** with 1 equiv of the neutral bidentate ligand 2-(diphenylphosphino)pyridine (dppy) did not result in the expected replacement of the two equatorial MeCN ligands with a single dppy ligand. Rather ligand exchange was again observed (though here selectively) to yield the biscarboxylate compound $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(dppy)_2]^{2+}(BF_4^-)_2$ (**5**) along with half an equivalent of $Mo_2(O_2C\text{-}t\text{-}Bu)_4$ (Scheme I). It is also possible to prepare **5** quantitatively from the reaction of **2** with 2 equiv of dppy. Crystals of **5** were obtained from THF, but these diffracted too poorly for a structure determination to be made. However, the ^{1}H NMR spectrum of **5** in CD$_2$Cl$_2$ indicates only one type of *t*-BuCO$_2$ and dppy ligand. Assuming that the dppy ligands bridge the Mo–Mo bond and the carboxylate groups are bound in a cis geometry (as found for most of the structurally characterized biscarboxylate complexes of Mo$_2$)[9] there are two possible structures for **5**, depicted by III and IV. Structure III contains a C_2 axis perpendicular to the Mo–Mo bond, and structure IV contains a single mirror plane parallel with the Mo–Mo bond. On the basis of steric considerations alone, III would appear to be the more likely geometry.



III



IV

Table II. Selected Interatomic Distances (Å) and Angles (deg) in **6**·2MeCN

Distances			
Mo(1)–Mo(2)	2.1508 (9)	Mo(2)–N(14)	2.194 (7)
Mo(1)–O(27)	2.076 (6)	F(42)–B(41)	1.428 (13)
Mo(1)–O(36)	2.073 (6)	F(43)–B(41)	1.366 (14)
Mo(1)–N(15)	2.194 (7)	F(44)–B(41)	1.385 (14)
Mo(1)–N(26)	2.176 (7)	F(45)–B(41)	1.392 (14)
Mo(2)–O(29)	2.094 (6)	Mo(2)–N(51)	2.58 (2)
Mo(2)–O(34)	2.090 (6)	Mo(1)–F(42)	2.65 (2)
Mo(2)–N(3)	2.202 (7)		

Angles			
Mo(2)–Mo(1)–O(27)	91.2 (2)	Mo(1)–Mo(2)–O(29)	90.4 (2)
Mo(2)–Mo(1)–O(36)	90.5 (2)	Mo(1)–Mo(2)–O(34)	91.0 (2)
Mo(2)–Mo(1)–N(15)	102.1 (2)	Mo(1)–Mo(2)–N(3)	99.3 (2)
Mo(2)–Mo(1)–N(26)	105.1 (2)	Mo(1)–Mo(2)–N(14)	102.5 (2)
O(27)–Mo(1)–O(36)	91.9 (3)	O(29)–Mo(2)–O(34)	92.8 (3)
O(27)–Mo(1)–N(15)	163.6 (3)	O(29)–Mo(2)–N(3)	94.3 (3)
O(27)–Mo(1)–N(26)	92.9 (3)	O(29)–Mo(2)–N(14)	164.2 (3)
O(36)–Mo(1)–N(15)	97.5 (3)	O(34)–Mo(2)–N(3)	167.4 (3)
O(36)–Mo(1)–N(26)	163.6 (3)	O(34)–Mo(2)–N(14)	95.9 (3)
N(15)–Mo(1)–N(26)	74.5 (3)	N(3)–Mo(2)–N(14)	74.9 (3)

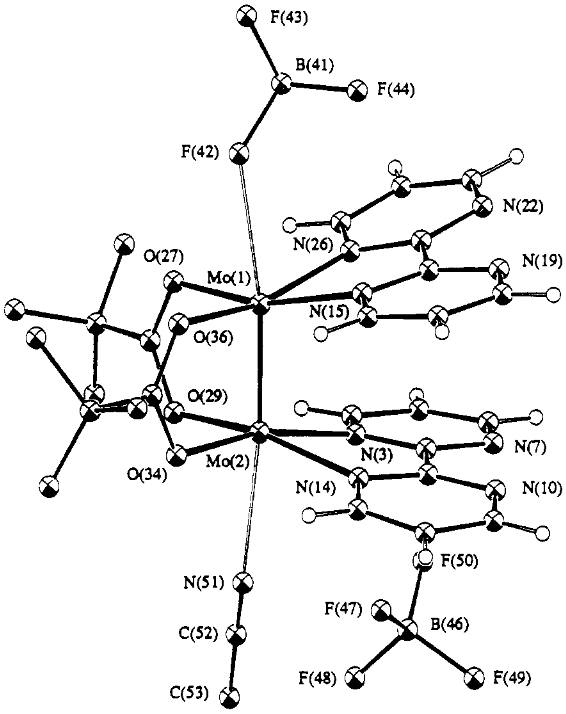
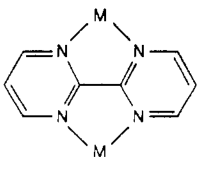


Figure 3. Ball-and-stick diagram of $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(bpym)_2]^{2+}(BF_4^-)_2 \cdot 2MeCN$, **6**·2MeCN. The H atoms of the *t*-Bu groups have been omitted for clarity. The axial sites on the Mo–Mo bond are occupied by one of the MeCN molecules and one of the BF$_4^-$ anions. The remaining MeCN molecule is not shown.



V

In an effort to assemble polymeric materials from the Mo$_2$-containing cations, we explored the ligating behavior of the α,α'-bipyrimidine (bpym) ligand. The bpym ligand is capable of forming and maintaining a conjugated π system between two chelated metal atoms (see structure V). These structural and electronic features are ideal for the conceptual construction of higher oligomers containing electronically coupled M–M quadruple bonds. Treatment of **2** with 2 equiv of bpym results in the replacement of the equatorial MeCN ligands affording $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(bpym)_2]^{2+}(BF_4^-)_2$ (**6**) in high yield (eq 3). The ^{1}H

$$\mathbf{2} + 2\text{bpym} \xrightarrow[\text{MeCN}]{\text{CH}_2\text{Cl}_2} \underset{\mathbf{6}}{[Mo_2(O_2C\text{-}t\text{-}Bu)_2(bpym)_2]^{2+}(BF_4^-)_2} \qquad (3)$$

NMR spectrum of **6** in CD$_3$CN indicates equivalent carboxylate and bpym ligands and that only one side of each bpym ligand is

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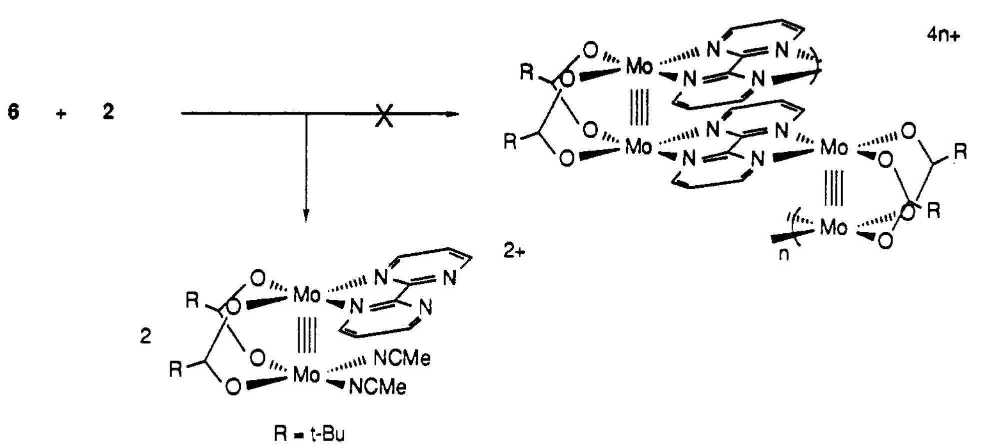
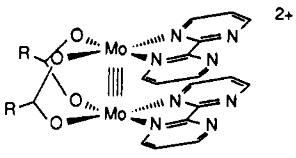
(8) (a) Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 2165. (b) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(9) One exception is the complex *trans*-$[Mo_2(MeCO_2)_2(dmpe)_2](BF_4)_2$, where dmpe = bis(dimethylphosphino)ethane: Farrugia, L. T.; McVilie, A.; Peacock; R. D. *Inorg. Chem.* **1988**, *27*, 1252.

Scheme II



bound to molybdenum. Under the assumption that the bpym ligands each chelate to a single Mo atom to form five-membered metallacyclic rings (rather than bridging the Mo–Mo bond to give six-membered dimetallacyclic rings), the resulting structure of **6** should resemble that shown in VI.



VI

X-ray quality crystals of **6** were obtained from MeCN/diethyl ether solutions and a ball-and-stick diagram is shown in Figure 3 along with pertinent bond lengths and angles in Table II. The overall structure is essentially that predicted from the spectroscopic data and depicted by VI. The metal–metal bond length [2.1508 (9) Å] is typical for a Mo–Mo quadruple bond, and the carboxylate ligands display no unusual bonding features. The bpym ligands each chelate to a single metal center and form essentially planar five-membered rings with Mo–N distances averaging 2.19 (2) Å. As is clearly evident from the view shown in Figure 3, the bpym ligands repel one another such that their planes are not parallel. The repulsion is likely electronic in origin and due to unfavorable interactions between the filled bpym π orbitals at distances of less than ca. 3.3 Å. A similar effect was observed in the solid-state structure of $[Mo_2(O_2CCF_3)_2(2,2'\text{-bipyridine})_2]^{2+}[O_2(CCF_3^-)_2]$ wherein the equatorially based bipyridine ligands exhibit a strong repulsion.[10] Not surprisingly, the axial positions of **6** contain weakly coordinated ligands. What is unusual in the structure of **6** is that although the compound crystallizes with two molecules of acetonitrile per Mo_2 unit, only one of these actually interacts with the Mo–Mo bond forming a weak axial Mo–N bond of 2.58 (2) Å. The other axial position is occupied by one of the BF_4^- counterions, resulting in a Mo–F distance of 2.65 (2) Å. Thus the dicationic portion of **6** chooses to bond the normally "noncoordinating" BF_4^- anion rather than the polar MeCN solvent (at least in the solid state).

The two open chelation sites on the bpym ligands of **6** make possible the formation of polynuclear systems. In an attempt to prepare a polymer containing Mo_2^{4+} units, we carried out the reaction of **6** with an equivalent of the $Mo_2(O_2C\text{-}t\text{-}Bu)_2^{2+}$ source (**2**), as outlined in Scheme II. Rather than forming the polymer, the reaction again results in ligand exchange to yield 2 equiv of $[Mo_2(O_2C\text{-}t\text{-}Bu)_2(bpym)(MeCN)_2]^{2+}(BF_4^-)_2$, as determined by ^1H NMR spectroscopy.

Table III. Selected Interatomic Distances (Å) and Angles (deg) in $(7)_2 \cdot 2MeCN$

Distances			
Mo(1)–Mo(2)	2.1026 (10)	Mo(3)–O(57)	2.110 (4)
Mo(1)–O(17)	2.045 (4)	Mo(3)–N(11)	2.194 (6)
Mo(1)–N(5)	2.182 (6)	Mo(3)–N(47)	2.178 (5)
Mo(1)–N(31)	2.178 (5)	Mo(4)–O(41)	2.035 (4)
Mo(1)–N(39)	2.168 (5)	Mo(4)–N(14)	2.180 (6)
Mo(2)–O(25)	2.053 (4)	Mo(4)–N(55)	2.169 (5)
Mo(2)–O(33)	2.116 (4)	Mo(4)–N(63)	2.176 (5)
Mo(2)–N(8)	2.185 (5)	Mo(2)–O(57)	2.69 (1)
Mo(2)–N(23)	2.165 (5)	Mo(3)–O(33)	2.70 (1)
Mo(3)–Mo(4)	2.1019 (9)		
Mo(3)–O(49)	2.071 (4)		

Angles			
Mo(2)–Mo(1)–O(17)	94.7 (2)	Mo(4)–Mo(3)–O(49)	95.1 (2)
Mo(2)–Mo(1)–N(5)	104.1 (2)	Mo(4)–Mo(3)–O(57)	92.7 (2)
Mo(2)–Mo(1)–N(31)	89.4 (2)	Mo(4)–Mo(3)–N(11)	98.7 (2)
Mo(2)–Mo(1)–N(39)	92.1 (2)	Mo(4)–Mo(3)–N(47)	89.9 (2)
O(17)–Mo(1)–N(5)	161.0 (2)	O(49)–Mo(3)–O(57)	172.1 (2)
O(17)–Mo(1)–N(31)	91.4 (2)	O(49)–Mo(3)–N(11)	87.2 (2)
O(17)–Mo(1)–N(39)	86.5 (2)	O(49)–Mo(3)–N(47)	89.8 (2)
N(5)–Mo(1)–N(31)	91.6 (2)	O(57)–Mo(3)–N(11)	90.2 (2)
N(5)–Mo(1)–N(39)	89.9 (2)	O(57)–Mo(3)–N(47)	91.7 (2)
N(31)–Mo(1)–N(39)	177.5 (2)	N(11)–Mo(3)–N(47)	171.1 (2)
Mo(1)–Mo(2)–O(25)	95.7 (2)	Mo(3)–Mo(4)–O(41)	95.1 (2)
Mo(1)–Mo(2)–O(33)	92.6 (2)	Mo(3)–Mo(4)–N(14)	103.8 (2)
Mo(1)–Mo(2)–N(8)	98.7 (2)	Mo(3)–Mo(4)–N(55)	89.9 (2)
Mo(1)–Mo(2)–N(23)	89.9 (2)	Mo(3)–Mo(4)–N(63)	92.4 (2)
O(25)–Mo(2)–O(33)	171.6 (2)	O(41)–Mo(4)–N(14)	161.1 (2)
O(25)–Mo(2)–N(8)	86.5 (2)	O(41)–Mo(4)–N(55)	90.8 (2)
O(25)–Mo(2)–N(23)	88.9 (2)	O(41)–Mo(4)–N(63)	89.8 (2)
O(33)–Mo(2)–N(8)	93.9 (2)	N(14)–Mo(4)–N(55)	89.3 (2)
O(33)–Mo(2)–N(23)	89.6 (2)	N(14)–Mo(4)–N(63)	89.4 (2)
N(8)–Mo(2)–N(23)	170.6 (2)	N(55)–Mo(4)–N(63)	177.6 (2)

The facile ligand exchange chemistry observed for the carboxylate-supported Mo–Mo quadruply bonded complexes led us to investigate the feasibility of using other, possibly less labile, ancillary ligands. The mhp ligand is *structurally* similar to the carboxylate anion in that it also forms a three-atom bridge across M–M bonds; however, it differs somewhat *electronically*.[11] Thus, "activated" dimetal complexes containing these mhp ligands (i.e., solvated complexes $M_2(mhp)_n^{(4-n)+}$ where $n = 2, 3$) might provide M_2 units more useful as polymer precursors by suppressing undesirable ligand exchange side reactions. Treatment of $Mo_2(mhp)_4$ with 1 equiv of Et_3OBF_4 in acetonitrile yields, after recrystallization, large red needles of $[Mo_2(mhp)_3(MeCN)_2]^+(BF_4^-)$ (**7**) (eq 4). The cationic portion of **7** actually crystallizes as a weakly

$$Mo_2(mhp)_4 + Et_3OBF_4 \xrightarrow[MeCN]{CH_2Cl_2} \underset{\mathbf{7}}{[Mo_2(mhp)_3(MeCN)_2]^+(BF_4^-)} \quad (4)$$

associated dimer of Mo_2^{1+} units as shown in the ball-and-stick diagram in Figure 4. Pertinent bond lengths and angles for **7** are given in Table III. The axial positions of each Mo–Mo bond

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Table IV. Summary of Crystal Data

	$4 \cdot 0.5C_6H_6$	6	$(7)_2 \cdot 2MeCN$
empirical formula	$C_{22}H_{35}Mo_2NO_6$	$Mo_2C_{30}H_{36}O_4N_{10}B_2F_8$	$Mo_4C_{48}H_{54}F_8O_6N_{12}B_2$
crystal dimensions (mm)	0.12 × 0.24 × 0.38	0.25 × 0.25 × 0.25	0.25 × 0.25 × 0.25
space group	$c2/c$	$P2_1/n$	$P2_1/n$
temperature (°C)	−170	−177	−172
cell dimensions			
a (Å)	19.732 (3)	11.144 (1)	17.899 (6)
b (Å)	11.733 (1)	10.054 (1)	14.515 (4)
c (Å)	24.648 (3)	35.751 (6)	21.897 (7)
β (deg)	94.57 (0)	91.32 (1)	97.04 (2)
Z (molecules/cell)	8	4	4
volume (Å^3)	5688.12	4004.65	5645.97
calculated density (g/cm^3)	1.496	1.603	1.709
wavelength (Å)	0.71069	0.71069	0.71069
molecular weight	640.46	966.17	1452.40
linear absorption coeff (cm^{-1})	8.955	6.928	9.290
total refluxions	5403	5962	8645
no. with $P > 2.33\sigma(F)$	3308	4277	5967
R(av)	0.019	0.101	0.040
octants collected	$h, k, \pm L$	$h, k, \pm L$	$h, k, \pm L$
$R(F)^a$	0.0290	0.0684	0.0458
$R_w(F)^a$	0.0331	0.0709	0.0476

$^a R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

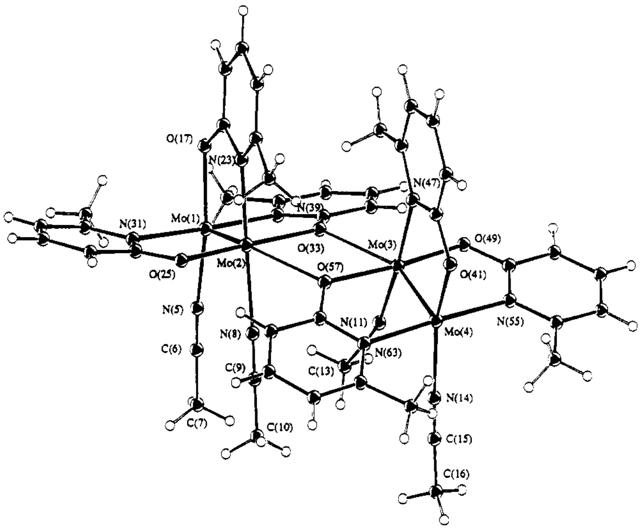

Figure 4. Ball-and-stick representation of the cationic portion of $(7)_2 \cdot 2MeCN$, $[Mo_2(mhp)_3(MeCN)_2{}^+]_2$. The weakly associated dimer of $Mo_2{}^{1+}$ units results from axial Mo–O interactions involving the mhp ligands.

are protected by two mhp methyl substituents on one end and only one methyl group on the other, allowing the dimerization to occur via relatively weak axial Mo–O interactions [2.70 (1) Å, av]. It is interesting to note that dimerization of the cations in **7** occurs despite crystallization from the coordinating acetonitrile solvent. This is in direct contrast to carboxylate-supported cations such as **2** that satisfy their axial sites with acetonitrile.[6] The structure of **7** is analogous to that of the triscarboxylate species **1**, and we may anticipate similar reaction chemistry. Preliminary results indicate that the tetranuclear complexes, $[Mo_2(mhp)_3]_2(\mu\text{-L})$, where L is oxalate or 2,3-dioxyquinoxaline, can be prepared and work is continuing toward the synthesis of higher polymers containing these ancillary ligands.

Experimental Section

^{1}H NMR spectra were recorded on a Varian XL300 spectrometer at 300 MHz in dry and oxygen-free solvents. All ^{1}H NMR chemical shifts are reported in parts per million relative to the protio impurity resonances in acetonitrile-d_3 (1.93 ppm), methylene chloride-d_2 (5.32 ppm), and benzene-d_6 (7.15 ppm). All reactions were carried out under an atmosphere of dry and oxygen-free nitrogen using standard Schlenk and glovebox techniques. All solvents were dried and degassed by standard methods and distilled prior to use. Triethyloxonium tetrafluoroborate and 2-hydroxy-6-methylpyridine (mhpH) were purchased from Aldrich, α,α'-bipyrimidine (bpym) was purchased from Lancaster Synthesis, and all chemicals were used as received. The compounds $Mo_2(mhp)_4$,[12] $Mo_2(O_2C\text{–}t\text{-}Bu)_3(MeCN)_2(BF_4)$,[1b] $Mo_2(O_2C\text{–}t\text{-}Bu)_2(MeCN)_6(BF_4)_2$,[1b] 2-(diphenylphosphino)pyridine (dppy),[13] and (6-methyl-2-pyridyl)methyllithium (Lidmp)[14] were prepared according to published procedures. Elemental analyses were performed by Oneida Research Services, Whitesboro, New York.

$Mo_2(O_2C\text{-}t\text{-}Bu)_3(mhp)$, 3. To a solution containing 0.030 g (0.27 mmol) of 2-hydroxy-6-methylpyridine (mhpH) in 10 mL of tetrahydrofuran was added 0.17 mL of a 1.6 M solution of *n*-butyllithium in hexane until a light yellow color persisted in solution. The Limhp solution was added to a solution containing 0.180 g (0.27 mmol) of $Mo_2(O_2C\text{-}t\text{-}Bu)_3(MeCN)_2(BF_4)$ in 25 mL of tetrahydrofuran. The solution turned from light orange to yellow upon mixing. After being stirred for 5 min at room temperature, the volatile components were removed under vacuum to yield a yellow-orange residue. The residue was extracted with 30 mL of toluene, filtered through a layer of celite, concentrated to 3 mL, and cooled to −20 °C. An initial crop containing 0.022 g of yellow crystals of $Mo_2(O_2C\text{-}t\text{-}Bu)_4$ formed overnight. The mother liquor was removed from these crystals via cannula, concentrated further and cooled to −20 °C to yield 0.060 g (37%) of yellow crystals of **3**. ^{1}H NMR (22 °C), benzene-d_6: δ 1.41 (s, 18 H), 1.45 (s, 3 H), 1.58 (s, 9 H), 5.84 (d, 1 H), 6.83 (dd, 1 H), 7.10 (d, 1 H). Anal. Calcd for $C_{21}H_{33}NO_7Mo_2$: C, 41.80; H, 5.51; N, 2.32. Found: C, 41.83; H, 5.32; N, 2.28.

$Mo_2(O_2C\text{-}t\text{-}Bu)_3(dmp)$, 4. To a suspension of 0.612 g (0.92 mmol) of $Mo_2(O_2C\text{-}t\text{-}Bu)_3(MeCN)_2(BF_4)$ in 25 mL of toluene was added 0.110 g (0.97 mmol) of (6-methyl-2-pyridyl)methyllithium (Lidmp) via a solids addition tube, and the resulting mixture was stirred for 12 h at room temperature. The resulting solution was dark red with some precipitate present. The volatile components were removed under vacuum, and the resulting residue was extracted with hexane. The hexane extract was filtered through celite and then concentrated to dryness under vacuum. The residue was dissolved in a minimum volume of benzene and then cooled to 10 °C to yield 0.250 g (42%) of red crystals of $4 \cdot 0.5C_6H_6$. ^{1}H NMR (22 °C), benzene-d_6: δ 1.45 (s, 18 H), 1.58 (s, 9 H), 2.43 (s, 3 H), 2.57 (s, 2 H), 5.99 (d, 1 H), 6.55 (d, 1 H), 6.67 (t, 1 H).

$[Mo_2(O_2C\text{-}t\text{-}Bu)_2(dppy)_2]^{2+}(BF_4^-)_2$, 5. To a 0 °C solution containing 0.232 g (0.28 mmol) of $Mo_2(O_2C\text{-}t\text{-}Bu)_2(MeCN)_6(BF_4)_2$ in 10 mL of methylene chloride was added a 0 °C solution containing 0.150 g (0.57 mmol) of dppy in 10 mL of methylene chloride via a narrow cannula. The color changed from red to purple upon mixing. The reaction was warmed to room temperature with stirring followed by removal of the volatiles under vacuum. The resulting residue was recrystallized from tetrahydrofuran at −20 °C to afford 0.190 g (62%) of large purple crystals. ^{1}H NMR (22 °C), methylene chloride-d_2: δ 1.68 (s, 18 H), aromatic resonances 7.62 (t), 7.77 (t), 8.09 (dd), 8.85 (m), 8.90 (d) 29

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Table V. Fractional Coordinates and Isotropic Thermal Parameters for Compound **4**·0.5C_6H_6

atom	10^4x	10^4y	10^4z	$10B_{iso}$
Mo(1)	3483.2 (2)	321.4 (3)	795.9 (1)	14
Mo(2)	2758.4 (2)	1563.1 (3)	576.2 (1)	14
N(3)	2819 (2)	−1138 (3)	601 (1)	18
C(4)	3007 (2)	−2232 (3)	734 (2)	21
C(5)	2527 (2)	−3065 (4)	788 (2)	23
C(6)	1847 (2)	−2808 (4)	700 (2)	26
C(7)	1655 (2)	−1715 (4)	543 (2)	23
C(8)	2145 (2)	−887 (4)	475 (2)	19
C(9)	2001 (2)	275 (4)	270 (2)	19
C(10)	3757 (2)	−2453 (4)	825 (2)	25
O(11)	3144 (1)	149 (2)	1578 (1)	19
C(12)	2637 (2)	758 (3)	1688 (2)	21
O(13)	2357 (1)	1457 (2)	1344 (1)	19
C(14)	2384 (3)	660 (4)	2251 (2)	35
C(15)	2951 (4)	1250 (6)	2652 (2)	51
C(16)	1734 (4)	1287 (6)	2288 (3)	60
C(17)	2361 (3)	−573 (5)	2416 (2)	40
O(18)	4195 (1)	1562 (2)	1102 (1)	18
C(19)	4021 (2)	2606 (3)	1085 (2)	20
O(20)	3427 (1)	2922 (2)	892 (1)	18
C(21)	4531 (2)	3512 (4)	1275 (2)	25
C(22)	4715 (3)	4187 (5)	768 (2)	39
C(23)	4214 (3)	4322 (5)	1661 (3)	44
C(24)	5183 (3)	2981 (5)	1549 (2)	38
O(25)	3899 (1)	413 (2)	40 (1)	17
C(26)	3663 (2)	1149 (3)	−299 (2)	16
O(27)	3155 (1)	1773 (2)	−201 (1)	16
C(28)	3998 (2)	1287 (3)	−829 (2)	16
C(29)	4611 (2)	490 (4)	−846 (2)	23
C(30)	4231 (2)	2531 (4)	−879 (2)	21
C(31)	3474 (2)	1002 (4)	−1303 (2)	21
C(32)	316 (2)	2770 (4)	2635 (2)	31
C(33)	637 (2)	3781 (5)	2771 (2)	31
C(34)	318 (3)	4779 (5)	2638 (2)	41

H in total. Anal. Calcd for $C_{44}H_{46}B_2F_8N_2O_4P_2Mo_2$·0.5$C_4H_8O$: C, 48.88; H, 4.46; N, 2.48. Found: C, 48.44; H, 4.74; N, 2.04.

[$Mo_2(O_2C$-*t*-Bu$)_2$(bpym)$_2$]$^{2+}$(BF_4^-)$_2$, 6. To a flask containing 0.042 g (0.27 mmol) of α,α'-bipyrimidine (bpym) dissolved in 20 mL of methylene chloride was added a solution containing 0.100 g (0.12 mmol) of $Mo_2(O_2C$–*t*-Bu$)_2(MeCN)_6(BF_4)_2$ in 5 mL of acetonitrile. The solution turned red-gray upon mixing, and after 1 h of stirring at room temperature a precipitate had formed. The volatile components were removed under vacuum, and the resulting solid was dissolved in 5 mL of acetonitrile and then transferred to a 10-mm i.d. Schlenk tube. Diethyl ether was carefully layered on top of the acetonitrile solution, and after slow diffusion of the solvents large dark red crystals formed. The crystals were isolated by cannula removal of the solvents and dried under an N_2 stream to yield 0.094 g (76%) of **6**·2MeCN. ^1H NMR (22 °C), acetonitrile-d_3: δ 1.82 (s, 18 H), 1.95 (s, 3 H), 7.89 (t, 4 H), 9.00 (dd, 4 H), 9.22 (dd, 4 H). Anal. Calcd for $C_{28}H_{33}B_2F_8N_9O_4Mo_2$: C, 36.35; H, 3.60; N, 13.63. Found: C, 36.00; H, 3.69; N, 13.83.

[Mo_2(mhp)$_3$(MeCN)$_2$]$^+$(BF_4^-), 7. To a 100 mL flask containing 0.600 g (1.00 mmol) of $Mo_2(mhp)_4$ (mhp = anion derived from deprotonation of 6-hydroxy-2-methylpyridine) and 0.142 g (1.00 mmol) of trimethyloxonium tetrafluoroborate was added 40 mL of acetonitrile. The reaction was warmed to 70 °C, and within 30 min all of the orange solid had dissolved and the solution was violet in color. The reaction was kept at 70 °C for 1 h and then slowly cooled to room temperature. The red-violet solution was concentrated to 10 mL and cooled to −20 °C for 24 h to yield a few orange crystals of $Mo_2(mhp)_4$. The mother liquor was separated from the crystals by cannula and concentrated to 5 mL. Toluene (10 mL) was added to the solution to yield a red precipitate. The red solid was collected by filtration, washed with toluene, and dried under vacuum. The solid was recrystallized from a concentrated acetonitrile solution to yield 0.635 g (87%) of red-violet needles of (**7**)$_2$·2MeCN. ^1H NMR (22 °C), acetonitrile-d_3: δ 1.57 (s, 3 H), 1.73 (s, 6 H), 1.95 (s, 9 H), 6.45 (d, 1 H), 6.68 (d, 1 H), 6.71 (d, 1 H), 7.24 (d, 2 H), 7.39 (dd, 1 H), 7.64 (dd, 2 H). The sample selected for elemental analysis was crystallized from CD_3CN. Anal. Calcd for $C_{22}H_{18}D_6BF_4N_5O_3Mo_2$·$CD_3CN$: C, 39.21; H, 3.70; N, 11.43. Found: C, 38.85; H, 3.71; N, 11.05.

Crystallographic Studies. General operating procedures and listings of programs have been described.[15] A summary of crystal data is given

Table VI. Fractional Coordinates and Isotropic Thermal Parameters for **6**

atom	10^4x	10^4y	10^4z	$10B_{iso}$
Mo(1)	9977.6 (3)	4616.1 (4)	2901.4 (3)	10
Mo(2)	10382.4 (3)	5964.3 (4)	3066.6 (3)	9
Mo(3)	9521.8 (3)	8366.5 (4)	2446.4 (3)	10
Mo(4)	10061.2 (3)	9553.2 (4)	2167.1 (3)	10
N(5)	10330 (3)	4259 (4)	2012 (3)	15
C(6)	10480 (4)	4129 (5)	1532 (3)	22
C(7)	10688 (5)	4003 (7)	912 (4)	33
N(8)	10932 (3)	6147 (4)	2237 (2)	10
C(9)	11323 (4)	6338 (5)	1888 (3)	18
C(10)	11838 (5)	6617 (7)	1464 (4)	42
N(11)	9544 (3)	7537 (4)	1612 (2)	14
C(12)	9477 (4)	6974 (5)	1246 (3)	16
C(13)	9398 (5)	6212 (6)	804 (4)	31
N(14)	10287 (3)	9226 (4)	1235 (3)	14
C(15)	10420 (4)	9092 (5)	748 (3)	17
C(16)	10564 (4)	8922 (6)	110 (3)	27
O(17)	9459 (2)	4551 (3)	3682 (2)	14
C(18)	9519 (4)	5229 (5)	4070 (3)	11
C(19)	9130 (4)	5214 (5)	4593 (3)	17
C(20)	9250 (4)	5906 (5)	5010 (3)	16
C(21)	9749 (4)	6621 (5)	4915 (3)	16
C(22)	10111 (4)	6629 (5)	4396 (3)	14
N(23)	9965 (3)	5953 (4)	3954 (2)	9
C(24)	10673 (4)	7343 (5)	4292 (3)	17
O(25)	11421 (2)	5581 (3)	3495 (2)	12
C(26)	11548 (4)	4710 (5)	3625 (3)	14
C(27)	12200 (4)	4432 (5)	4005 (3)	14
C(28)	12290 (4)	3512 (5)	4161 (3)	16
C(29)	11743 (4)	2877 (5)	3920 (3)	17
C(30)	11133 (4)	3167 (5)	3539 (3)	13
N(31)	11022 (3)	4083 (4)	3389 (2)	11
C(32)	10526 (4)	2526 (5)	3256 (3)	20
O(33)	9356 (2)	6558 (3)	2671 (2)	12
C(34)	8794 (4)	6046 (5)	2431 (3)	13
C(35)	8110 (4)	6417 (5)	2158 (3)	17
C(36)	7550 (4)	5837 (5)	1909 (3)	20
C(37)	7675 (4)	4888 (5)	1924 (3)	19
C(38)	8341 (4)	4536 (5)	2197 (3)	15
N(39)	8912 (3)	5111 (4)	2441 (2)	13
C(40)	8497 (4)	3528 (5)	2262 (3)	19
O(41)	10019 (2)	10250 (3)	2969 (2)	12
C(42)	9692 (4)	9882 (5)	3411 (3)	16
C(43)	9659 (4)	10365 (5)	3970 (3)	18
C(44)	9283 (4)	9979 (5)	4414 (3)	21
C(45)	8933 (4)	9126 (5)	4306 (3)	18
C(46)	8978 (4)	8666 (5)	3759 (3)	15
N(47)	9371 (3)	9035 (4)	3313 (2)	12
C(48)	8583 (4)	7776 (5)	3626 (3)	18
O(49)	8450 (2)	8778 (3)	2085 (2)	13
C(50)	8357 (4)	9591 (5)	1815 (3)	16
C(51)	7647 (4)	9891 (5)	1563 (3)	17
C(52)	7575 (4)	10737 (5)	1294 (3)	17
C(53)	8209 (4)	11287 (5)	1272 (3)	18
C(54)	8900 (4)	10974 (5)	1522 (3)	14
N(55)	8979 (3)	10116 (4)	1792 (2)	12
C(56)	9602 (4)	11534 (5)	1537 (3)	18
O(57)	10546 (2)	7767 (3)	2831 (2)	11
C(58)	11189 (4)	8181 (5)	2799 (3)	12
C(59)	11882 (4)	7774 (5)	3030 (3)	15
C(60)	12533 (4)	8228 (5)	2950 (3)	15
C(61)	12511 (4)	9093 (5)	2667 (3)	17
C(62)	11830 (4)	9474 (5)	2467 (3)	13
N(63)	11170 (3)	9029 (4)	2519 (2)	11
C(64)	11755 (4)	10422 (5)	2182 (3)	19
B(65)	1468 (6)	11696 (7)	573 (5)	33
F(66)	1199 (3)	11996 (4)	1152 (3)	51
F(67)	2207 (3)	11859 (4)	672 (2)	45
F(68)	1111 (3)	12238 (3)	102 (2)	36
F(69)	1266 (4)	10817 (4)	511 (3)	69
B(70)	8632 (5)	3752 (6)	242 (4)	23
F(71)	8940 (3)	3765 (4)	845 (2)	49
F(72)	8617 (5)	4576 (4)	1 (3)	91
F(73)	9125 (5)	3265 (7)	−82 (3)	102
F(74)	7984 (5)	3333 (7)	130 (3)	103
N(75)	1646 (4)	10361 (5)	3919 (4)	41
C(76)	1887 (4)	9795 (6)	4237 (4)	26
C(77)	2215 (5)	9075 (6)	4643 (4)	37
N(78)	8763 (5)	2450 (4)	3963 (3)	40
C(79)	8193 (5)	2647 (6)	4097 (4)	27
C(80)	7464 (5)	2877 (7)	4258 (4)	39

Table VII. Fractional Coordinates and Isotropic Thermal Parameters for 7

atom	10^4x	10^4y	10^4z	$10B_{iso}$
Mo(1)	371 (1)	522 (1)	3534.7 (2)	16
Mo(2)	1173 (1)	1745 (1)	3965.9 (2)	16
N(3)	2604 (6)	2682 (8)	3643 (2)	18
C(4)	3681 (9)	2159 (10)	3572 (3)	24
C(5)	4445 (8)	2784 (10)	3323 (3)	22
C(6)	4052 (9)	3928 (11)	3156 (3)	25
N(7)	2983 (7)	4484 (8)	3231 (2)	23
C(8)	2318 (8)	3843 (10)	3475 (3)	19
C(9)	1140 (8)	4437 (9)	3578 (3)	17
N(10)	825 (7)	5577 (8)	3427 (2)	23
C(11)	−194 (8)	6146 (10)	3555 (3)	21
C(12)	−852 (8)	5542 (10)	3826 (3)	22
C(13)	−517 (8)	4311 (10)	3951 (3)	23
N(14)	490 (7)	3732 (7)	3823 (2)	16
N(15)	−613 (6)	1989 (8)	3192 (2)	16
C(16)	−1674 (8)	2582 (10)	3274 (3)	21
C(17)	−2117 (8)	3606 (10)	3059 (3)	22
C(18)	−1469 (9)	4039 (10)	2768 (3)	25
N(19)	−428 (6)	3459 (8)	2674 (2)	18
C(20)	−72 (8)	2470 (9)	2889 (3)	18
C(21)	1067 (8)	1761 (9)	2793 (3)	18
N(22)	1575 (6)	2049 (8)	2472 (2)	17
C(23)	2594 (9)	1366 (10)	2397 (3)	24
C(24)	3058 (8)	405 (10)	2634 (3)	23
C(25)	2448 (8)	159 (10)	2957 (3)	19
N(26)	1460 (6)	846 (7)	3045 (2)	17
O(27)	1382 (5)	−1107 (6)	3710 (2)	35
C(28)	2167 (8)	−953 (10)	3973 (3)	20
O(29)	2246 (5)	148 (6)	4146 (2)	36
C(30)	3047 (9)	−2059 (11)	4066 (3)	30
C(31)	2338 (11)	−3107 (12)	4286 (3)	37
C(32)	4100 (10)	−1549 (12)	4298 (3)	36
C(33)	3458 (9)	−2676 (11)	3698 (3)	29
O(34)	−197 (6)	1260 (7)	4331 (2)	38
C(35)	−1035 (9)	477 (11)	4214 (3)	23
O(36)	−1015 (5)	21 (6)	3885 (2)	35
C(37)	−2030 (9)	91 (11)	4479 (3)	29
C(38)	−2395 (13)	−1346 (14)	4402 (4)	55
C(39)	−3144 (12)	948 (16)	4345 (5)	67
C(40)	−1712 (14)	320 (22)	4863 (4)	81
B(41)	−690 (10)	−1391 (13)	2722 (3)	27
F(42)	−927 (5)	−1103 (6)	3105 (2)	14
F(43)	−1379 (5)	−2445 (5)	2607 (2)	14
F(44)	−926 (5)	−257 (5)	2513 (1)	10
F(45)	527 (5)	−1691 (6)	2702 (2)	24
B(46)	6142 (11)	4670 (13)	4092 (4)	32
F(47)	4924 (6)	4407 (7)	4131 (2)	31
F(48)	6288 (6)	6037 (7)	4044 (2)	37
F(49)	6782 (7)	4348 (9)	4410 (2)	44
F(50)	6569 (6)	3999 (9)	3797 (2)	43
N(51)	2212 (9)	2957 (10)	4520 (3)	39
C(52)	3034 (13)	3242 (12)	4706 (3)	44
C(53)	4095 (14)	3582 (20)	4922 (4)	81
N(54)	−3724 (9)	7441 (11)	3181 (3)	52
C(55)	−3957 (10)	8875 (14)	3271 (3)	37
C(56)	−4156 (12)	9934 (12)	3331 (4)	41

in Table IV, and listings of atomic coordinates for compounds **4**, **6**, and **7** are given in Tables V, VI and VII, respectively.

$Mo_2(O_2C$–*t*-Bu$)_3$(dmp), 4. A suitable single crystal was selected for the bulk sample in a dry nitrogen glove bag. The crystal was affixed to a glass rod with silicone grease and was transferred to the goniostat where it was cooled to −170 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic (2/*m*) lattice symmetry. The systematic extinction of *hkl* reflections for $h + k = 2n + l$, and of *h0l* for $l = 2n + l$ limited the choice of space groups to *Cc* (no. 9) or *C*2/*c* (no. 15). The choice of the centrosymmetric space group *C*2/*c* was confirmed by the subsequent solution and refinement of the structure. Unit cell dimensions were determined by a least-squares fit of the setting angles of 54 reflections having $22.0° < 2\theta < 34.0°$. No correction for absorption was performed. A plot of the four standard reflections (0 0 8, −10 0 0, 3 3 3, and 0 6 0) measured every 400 reflections did not show any significant variations.

The structure was solved by the usual combination of direct methods (MULTAN) and difference Fourier iterations. The two Mo atoms were located in the initial E-map, and the remaining non-hydrogen atoms were located without difficulty. Following the initial refinement almost all of the hydrogen atoms were located in a difference map. The full matrix least-squares refinement was completed using anisotropic thermal parameters on all non-hydrogen atoms, and the hydrogen atoms were refined using isotropic thermal parameters. In addition to the molecule of interest the asymmetric unit was found to contain one-half molecule of benzene solvent situated at a center of symmetry [*C*(32)–*C*(34)]. All reflections were used for the solution and refinement of the structure; however, reflections having $F < 2.33\sigma(F)$ were given zero weight in the least-squares refinement. The final *R*(*F*) was 0.029; *Rw*(*F*) was 0.033.

The final difference map was essentially featureless, the maximum peak being 0.53 e/Å^3 in the vicinity of Mo(1); the minimum was −0.40. Psi scans indicated that no absorption correction was necessary.

$[Mo_2(O_2C$–*t*-Bu$)_2$(bpym$)_2]^{2+}(BF_4^-)_2$, 6. A suitable crystal was located and transferred to the goniostat using standard inert atmosphere handling techniques and cooled to −172 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected in the usual manner using a continuous $\theta - 2\theta$ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated sigmas in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using idealized geometries and *d*(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement.

A final difference Fourier was featureless, with the largest peak being 0.45 e/Å^3. No absorption correction was performed.

$[Mo_2$(mhp$)_3$(MeCN$)_2]^+(BF_4^-)$, 7. A suitable crystal was located and transferred to the goniostat using standard inert atmosphere handling techniques and cooled to −177 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/n$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected in the usual manner using a continuous $\theta - 2\theta$ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated sigmas in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using idealized geometries and *d*(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement.

A final difference Fourier was featureless, with the largest peaks being 0.45 e/Å^3. No absorption correction was performed.

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Registry No. **1**, 134078-49-2; **2**, 134078-47-0; **3**, 141197-81-1; **4**·$0.5C_6H_6$, 141197-83-3; **5**, 141197-85-5; **6**·2MeCN, 141197-88-8; **7**·2MeCN, 141220-83-9; $Mo_2(mhp)_4$, 67634-80-4; Mo, 7439-98-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, complete listings of bond distances and angles, and VERSORT stereodrawings (35 pages); listings of F_o and F_c values (37 pages). Ordering information is given on any current masthead page.

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