

# Notes

## Synthesis and X-ray Crystal Structure of a Tetrahedral Bismuth–Molybdenum Carbonyl Complex Possessing Three Bridging Methoxy Ligands, $[\text{Et}_4\text{N}]_2[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]$

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The chemistry of transition metal clusters containing bismuth continues to be a rapid developing area. The work has illustrated diverse reactivity and interesting bonding modes caused by the introduction of a large bismuth atom into a transition metal cluster<sup>1</sup> and has prompted us to investigate the chemistry of mixed bismuth–molybdenum system.

The number of structurally characterized mixed bismuth–molybdenum carbonyl clusters remains small. Examples include  $[\text{BiX}\{\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)\}_2]$  ( $\text{X} = \text{Cl},^2 \text{Br},^3 \text{I}^3$ ),  $[\text{BiCl}\{\text{Mo}(\text{CO})_2(\text{CNBu}^t)(\eta\text{-C}_5\text{H}_5)\}_2]$ ,<sup>2</sup>  $[\text{PPN}][\text{BiCl}_2\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ ,<sup>4</sup> and  $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_4\text{Me})_2(\mu\text{-}\eta^2\text{-Bi}_2)]$ .<sup>5</sup> Aside from these complexes containing cyclopentadienyl ligands, no bismuth–molybdenum carbonyl clusters possessing bridging alkoxy groups have been reported. Here we describe the isolation and characterization of an unusual methoxy bismuth–molybdenum carbonyl anionic cluster,  $[\text{Et}_4\text{N}]_2[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]\cdot\text{CH}_2\text{Cl}_2$  (**1**), in which the methoxy ligands may act as five-electron or three-electron donors.

### Experimental Section

All reactions were performed under an atmosphere of pure nitrogen by using standard Schlenk line techniques. Solvents were purified, dried, and distilled under nitrogen prior to use. Infrared spectra were recorded on a Jasco 700 IR spectrometer using  $\text{CaF}_2$  liquid cells. <sup>1</sup>H NMR spectra were taken on a Jeol 400 (400 MHz) instrument. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Taiwan University, Taipei, Taiwan.

**Preparation of  $[\text{Et}_4\text{N}]_2[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]$ .** To a mixture of 0.50 g (1.78 mmol) of  $\text{NaBiO}_3$  and 1.87 g (7.11 mmol) of  $\text{Mo}(\text{CO})_6$  was added 35 mL of MeOH. The mixed solution was heated to reflux for 24 h, during which time it turned from yellow to brown. The solution was then filtered, and an aqueous solution of  $\text{Et}_4\text{NBr}$  was added to precipitate the dark brown product. The crude product was filtered out, washed with deionized  $\text{H}_2\text{O}$ , and dried under vacuum. Recrystallization from  $\text{CH}_2\text{Cl}_2$ /diethyl ether afforded 0.43 g (0.31 mmol) of the pure product (17.5% based on Bi). The product is soluble in  $\text{CH}_2\text{Cl}_2$ , THF,  $\text{CH}_3\text{CN}$ , and MeOH. Crystals suitable for diffraction were grown from a concentrated

Table I. Selected Crystallographic Data for  $[\text{Et}_4\text{N}]_2[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]\cdot\text{CH}_2\text{Cl}_2$  (**1**)

empirical formula	$\text{BiMo}_4\text{C}_{32}\text{H}_{51}\text{O}_{15}\text{N}_2\text{Cl}_2$	$V, \text{\AA}^3$	4808(3)
fw	1367.39	$Z$	4
cryst system	monoclinic	$D(\text{calc}), \text{Mg m}^{-3}$	1.889
space group	$P2_1/n$ (No. 14)	abs coeff, $\text{mm}^{-1}$	4.96
$a, \text{\AA}$	13.615(4)	radiation,	0.709 30
		$\lambda(\text{Mo K}\alpha), \text{\AA}$	
$b, \text{\AA}$	19.035(6)	temp, $^\circ\text{C}$	25
$c, \text{\AA}$	19.087(6)	$T_{\text{min}}/T_{\text{max}}$	0.74/1.00
$\beta, \text{deg}$	103.58(3)	resid: <sup>a</sup> $R_F, R_w$	0.049, 0.048

<sup>a</sup> The functions minimized during least-squares cycles were  $R_F = \sum(F_o - F_c)/\sum F_o$  and  $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$ .

Table II. Selected Atomic Coordinates and Isotropic Displacement Coefficients for  $[\text{Et}_4\text{N}]_2[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]\cdot\text{CH}_2\text{Cl}_2$  (**1**)

	$x$	$y$	$z$	$B_{\text{iso}}, \text{\AA}^2$
Bi	0.48659(5)	0.12955(4)	0.03784(4)	4.73(3)
Mo(1)	0.62305(10)	0.12040(8)	-0.05153(7)	4.07(7)
Mo(2)	0.65968(10)	0.21496(8)	0.08322(7)	4.35(7)
Mo(3)	0.48836(10)	0.25032(8)	-0.04862(8)	4.60(7)
Mo(4)	0.73692(10)	0.28533(7)	-0.06731(7)	4.00(7)
C(1)	0.6919(13)	0.0710(10)	-0.1145(10)	7.1(11)
C(2)	0.5073(11)	0.0710(8)	-0.1092(7)	4.6(9)
C(3)	0.6681(11)	0.0410(9)	0.0097(8)	5.3(9)
C(4)	0.6975(11)	0.1365(9)	0.1453(8)	5.6(9)
C(5)	0.5787(12)	0.2464(9)	0.1493(8)	5.8(9)
C(6)	0.7716(13)	0.2596(10)	0.1557(9)	7.0(11)
C(7)	0.3712(12)	0.2016(10)	-0.1058(8)	6.1(11)
C(8)	0.4083(12)	0.2863(9)	0.0122(9)	6.5(11)
C(9)	0.4259(12)	0.3291(10)	-0.1073(9)	6.9(11)
C(10)	0.8514(10)	0.3356(8)	-0.0176(7)	3.8(8)
C(11)	0.7165(11)	0.3670(9)	-0.1234(9)	6.2(11)
C(12)	0.8176(11)	0.2573(8)	-0.1309(8)	5.3(9)
C(13)	0.8451(11)	0.1611(9)	0.0253(8)	5.4(9)
C(14)	0.6255(12)	0.3713(9)	0.0314(9)	6.0(11)
C(15)	0.5647(12)	0.2167(10)	-0.1873(8)	6.8(11)
O(1)	0.7255(11)	0.0349(7)	-0.1504(8)	10.2(1)
O(2)	0.4447(9)	0.0384(6)	-0.1471(6)	7.4(7)
O(3)	0.7044(9)	-0.0100(6)	0.0445(6)	7.3(7)
O(4)	0.7230(9)	0.0904(7)	0.1870(6)	7.5(7)
O(5)	0.5344(10)	0.2648(7)	0.1920(6)	9.1(9)
O(6)	0.8344(11)	0.2806(9)	0.1997(7)	11.7(1)
O(7)	0.2970(8)	0.1763(8)	-0.1402(7)	8.8(8)
O(8)	0.3583(10)	0.3121(7)	0.0503(7)	8.8(8)
O(9)	0.3846(10)	0.3764(8)	-0.1401(8)	11.4(1)
O(10)	0.9227(8)	0.3686(6)	0.0140(6)	7.0(7)
O(11)	0.7134(10)	0.4203(8)	-0.1571(8)	10.7(1)
O(12)	0.8656(9)	0.2420(7)	-0.1719(7)	8.2(8)
O(13)	0.7476(6)	0.1895(5)	0.0025(5)	4.3(5)
O(14)	0.6307(6)	0.3026(5)	0.0046(5)	3.9(5)
O(15)	0.5985(6)	0.2204(5)	-0.1109(5)	4.1(5)

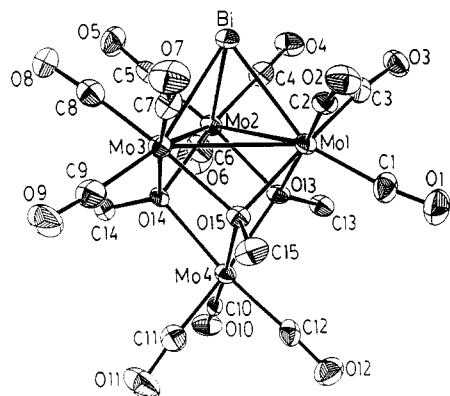
$\text{CH}_2\text{Cl}_2$  solution. IR ( $\nu(\text{CO}), \text{CH}_2\text{Cl}_2$ ): 1916 s, 1838 s, 1745  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, DMSO, 298 K):  $\delta$  3.68 (s) (chemical shift not given for  $[\text{Et}_4\text{N}]^+$ ). Anal. Calcd (found) for  $\text{BiMo}_4\text{C}_{32}\text{H}_{51}\text{O}_{15}\text{N}_2\text{Cl}_2$ : C, 28.11 (27.56); H, 3.75 (3.51); N, 2.04 (1.91).

**X-ray Structural Characterization.** A reddish brown crystal with dimensions  $0.25 \times 0.30 \times 0.45 \text{ mm}^3$  was selected for X-ray analysis. The crystal was mounted with epoxy on the tip of a glass fiber. The selected crystallographic data are given in Table I. Cell parameters were obtained from 25 reflections with  $2\theta$  angle in the range  $18.00\text{--}26.50^\circ$ . Systematic absences and intensity statistics indicated that the space group is  $P2_1/n$ . A total of 6258 unique reflections were collected, and the data were corrected for decay and absorption. A total of 3478 reflections with  $I > 2.0\sigma(I)$  were used in the refinement. The data reduction and structural refinement were performed using the NRCC-SDP-VAX packages. The structure was solved by the heavy-atom method and refined by least-squares cycles. All the non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix least-squares refinement led to convergence with  $R_F = 4.9\%$  and  $R_w = 4.8\%$ .

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**Figure 1.** ORTEP diagram showing the structure and atom labeling for the dianion of **1**.

**Table III.** Selected Bond Distances (Å) for  $[\text{Et}_4\text{N}]_2[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]\cdot\text{CH}_2\text{Cl}_2$  (**1**)

Metal-Metal Bond Lengths			
Bi-Mo(1)	2.807(2)	Bi-Mo(2)	2.826(2)
Bi-Mo(3)	2.833(2)	Mo(1)-Mo(2)	3.082(2)
Mo(1)-Mo(3)	3.087(2)	Mo(2)-Mo(3)	3.077(2)
Mo(1)-Mo(4)	3.545(2)	Mo(2)-Mo(4)	3.546(2)
Mo(3)-Mo(4)	3.548(2)		
Mo-C Bond Lengths			
Mo(1)-C(1)	1.934(16)	Mo(1)-C(2)	1.940(15)
Mo(1)-C(3)	1.922(16)	Mo(2)-C(4)	1.900(16)
Mo(2)-C(5)	1.953(16)	Mo(2)-C(6)	1.992(16)
Mo(3)-C(7)	1.944(17)	Mo(3)-C(8)	1.897(17)
Mo(3)-C(9)	1.944(18)	Mo(4)-C(10)	1.888(1)
Mo(4)-C(11)	1.871(17)	Mo(4)-C(12)	1.896(15)
Mo-O Bond Lengths			
Mo(1)-O(13)	2.202(9)	Mo(1)-O(15)	2.200(9)
Mo(2)-O(13)	2.216(9)	Mo(2)-O(14)	2.216(9)
Mo(3)-O(14)	2.204(8)	Mo(3)-O(15)	2.196(9)
Mo(4)-O(13)	2.243(9)	Mo(4)-O(14)	2.240(9)
Mo(4)-O(15)	2.245(9)		
Carbonyl Ranges			
C-O	1.138(20)-1.214(20)		

Selected atomic coordinates and isotropic displacement coefficients are given in Table II. Selected bond distances and angles are listed in Table III and IV, respectively. Additional crystallography data are available as supplementary material.

## Results

The reaction of  $\text{NaBiO}_3$  with  $\text{Mo}(\text{CO})_6$  proceeds in refluxing  $\text{MeOH}$  giving a methoxy bismuth-molybdenum carbonyl anion  $[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]^{2-}$ . The molecule  $[\text{Et}_4\text{N}]_2[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]\cdot\text{CH}_2\text{Cl}_2$  (**1**) has been characterized by IR,  $^1\text{H}$  NMR, and single-crystal X-ray diffraction methods. IR spectroscopy is not very informative but shows the absorptions characteristic of the terminal CO ligands in an anionic cluster. The  $^1\text{H}$  NMR spectrum of **1** exhibits a singlet at  $\delta$  3.68 indicative of one type of OMe ligand and the same as that seen for the ruthenium cluster.<sup>6</sup> Compound **1** crystallizes as an ionic complex, that consists of two  $[\text{Et}_4\text{N}]^+$  cations, a  $[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]^{2-}$  dianion, and a solvated  $\text{CH}_2\text{Cl}_2$  molecule in the asymmetric unit. The structure with labeling scheme for the dianion of **1** is shown in Figure 1. The metal core geometry of the anion of **1** can be best described as a  $\text{BiMo}_3$  tetrahedral framework with the external Mo(4) atom linked to the  $\text{Mo}_3$  triangle by three  $\mu_3\text{-OMe}$  groups. Alternatively, the  $\text{BiMo}_4$  cluster may be viewed as a trigonal-bipyramidal-type cluster in which three  $\text{Mo}_3$  triangles are capped with  $\mu_3\text{-OMe}$  groups. The dianion of **1** approximately has  $C_{3v}$

**Table IV.** Selected Bond Angles (deg) for  $[\text{Et}_4\text{N}]_2[\text{BiMo}_4(\text{CO})_{12}(\mu_3\text{-OMe})_3]\cdot\text{CH}_2\text{Cl}_2$  (**1**)

Angles within the $\text{BiMo}_4$ Cluster			
Mo(1)-Bi-Mo(2)	66.34(5)	Mo(1)-Bi-Mo(3)	66.36(4)
Mo(2)-Bi-Mo(3)	65.87(5)	Bi-Mo(1)-Mo(2)	57.13(4)
Bi-Mo(1)-Mo(3)	57.23(4)	Mo(2)-Mo(1)-Mo(3)	59.84(5)
Mo(2)-Mo(1)-Mo(4)	64.25(5)	Mo(3)-Mo(1)-Mo(4)	64.25(5)
Bi-Mo(2)-Mo(1)	56.53(4)	Bi-Mo(2)-Mo(3)	57.17(4)
Mo(1)-Mo(2)-Mo(4)	64.23(5)	Mo(3)-Mo(2)-Mo(4)	64.33(5)
Mo(1)-Mo(2)-Mo(3)	60.15(5)	Bi-Mo(3)-Mo(1)	56.41(4)
Bi-Mo(3)-Mo(2)	56.95(4)	Mo(1)-Mo(3)-Mo(2)	60.00(5)
Mo(1)-Mo(3)-Mo(4)	64.15(4)	Mo(2)-Mo(3)-Mo(4)	64.26(5)
Mo(1)-Mo(4)-Mo(2)	51.53(4)	Mo(1)-Mo(4)-Mo(3)	51.59(4)
Mo(2)-Mo(4)-Mo(3)	51.41(4)		
Bi-Mo-CO Angles			
Bi-Mo(1)-C(1)	153.5(5)	Bi-Mo(1)-C(2)	79.0(4)
Bi-Mo(1)-C(3)	80.9(4)	Bi-Mo(2)-C(4)	79.8(5)
Bi-Mo(2)-C(5)	79.5(5)	Bi-Mo(2)-C(6)	154.8(5)
Bi-Mo(3)-C(7)	79.8(5)	Bi-Mo(3)-C(8)	81.5(5)
Bi-Mo(3)-C(9)	154.0(5)		
Mo-Mo-CO Angles			
Mo(2)-Mo(1)-C(1)	142.7(5)	Mo(2)-Mo(1)-C(2)	135.0(4)
Mo(2)-Mo(1)-C(3)	89.2(4)	Mo(2)-Mo(3)-C(7)	136.0(5)
Mo(2)-Mo(3)-C(8)	90.7(5)	Mo(2)-Mo(3)-C(9)	141.7(5)
Mo(3)-Mo(1)-C(1)	141.1(6)	Mo(3)-Mo(1)-C(2)	89.5(5)
Mo(3)-Mo(1)-C(3)	136.5(4)	Mo(3)-Mo(2)-C(4)	136.4(5)
Mo(3)-Mo(2)-C(5)	91.5(5)	Mo(3)-Mo(2)-C(6)	141.6(5)
Mo(1)-Mo(2)-C(4)	91.7(5)	Mo(1)-Mo(2)-C(5)	135.4(5)
Mo(1)-Mo(2)-C(6)	140.9(5)	Mo(1)-Mo(3)-C(7)	91.2(5)
Mo(1)-Mo(3)-C(8)	136.8(5)	Mo(1)-Mo(3)-C(9)	142.1(5)
Mo-O-Mo Angles			
Mo(1)-O(13)-Mo(2)	88.5(3)	Mo(1)-O(13)-Mo(4)	105.8(4)
Mo(2)-O(13)-Mo(4)	105.4(4)	Mo(2)-O(14)-Mo(3)	88.3(3)
Mo(2)-O(14)-Mo(4)	105.5(4)	Mo(3)-O(14)-Mo(4)	106.0(4)
Mo(1)-O(15)-Mo(3)	89.2(3)	Mo(1)-O(15)-Mo(4)	105.8(4)
Mo(3)-O(15)-Mo(4)	106.1(4)		
M-M-O Angles			
Bi-Mo(1)-O(13)	103.0(2)	Bi-Mo(1)-O(15)	102.6(2)
Mo(2)-Mo(1)-O(13)	45.9(2)	Mo(2)-Mo(1)-O(15)	84.3(2)
Mo(3)-Mo(1)-O(13)	84.8(3)	Mo(3)-Mo(1)-O(15)	45.4(2)
Bi-Mo(2)-O(13)	102.1(2)	Bi-Mo(2)-O(14)	102.9(2)
Mo(1)-Mo(2)-O(13)	45.6(2)	Mo(1)-Mo(2)-O(14)	84.6(2)
Mo(3)-Mo(2)-O(13)	84.8(2)	Mo(3)-Mo(2)-O(14)	45.7(2)
Bi-Mo(3)-O(14)	103.0(2)	Bi-Mo(3)-O(15)	101.8(3)
Mo(1)-Mo(3)-O(14)	84.7(2)	Mo(1)-Mo(3)-O(15)	45.5(2)
Mo(2)-Mo(3)-O(14)	46.0(2)	Mo(2)-Mo(3)-O(15)	84.5(2)
Mo-C-O Angle Ranges			
Mo-C-O	171.6(2)-177.5(2)		

symmetry. The acute angles at bismuth and Mo(4) average  $66.19(5)$  and  $51.51(4)^\circ$ , respectively, and deviate a bit from a perfect tetrahedral angle ( $60^\circ$ ). The average bond distances for Bi-Mo and Mo-Mo are  $2.822(2)$  and  $3.084(2)$  Å, respectively. As shown in Figure 1, the Mo(4)-Mo(1), -Mo(2), and -Mo(3) distances,  $3.547(2)$  Å (average), preclude significant interaction.<sup>7</sup>

## Discussion

Compound **1** can be isolated from the reaction of  $\text{NaBiO}_3$  with  $\text{Mo}(\text{CO})_6$  in refluxing  $\text{MeOH}$  solution overnight, which indicates the reaction involves solvent participation. Although the direct reaction of alcohol with electronically saturated carbonyl complexes is rare, the formation of alkoxy cluster complexes does occur under appropriate conditions,<sup>8</sup> as exemplified by the formation of  $\text{Ru}_3(\mu\text{-OC}_6\text{H}_4\text{OMe})_2(\text{CO})_8$  from the reaction of  $(\text{MeO})_2\text{C}_6\text{H}_4\text{OH}$  with  $\text{Ru}_3(\text{CO})_{12}$  in the presence of  $\text{Me}_3\text{NO}$ .<sup>6</sup>

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The mechanism for the formation of compound **1** is not clear now, but it is likely that  $\text{Mo}(\text{CO})_6$  and  $\text{MeOH}$  are both oxidized by  $\text{NaBiO}_3$  along with the production of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . For an anionic cluster complex, compound **1** is quite air stable. A preliminary test shows that **1** retains its metal skeleton according to IR spectroscopy when treated with mild oxidants such as  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$  and  $\text{CH}_3\text{I}$ . This suggests that **1** could be an attractive candidate to be used as a catalyst model.<sup>9</sup> The examination of the catalytic reactivity of **1** is under investigation.

Since the methoxy groups are face-capping ligands, each oxygen atom can be considered to donate five of its valence electrons for bonding. In terms of electron counting, four  $\text{Mo}(\text{CO})_3$  groups have 12 electrons each and the apical Bi atom contributes its three electrons in bonding, which gives a total of 68 electrons or 7 skeletal electron pairs for the dianion of **1**. Accordingly, the dianion of **1** does not obey Wade's rules<sup>10</sup> for a trigonal bipyramidal or a tetrahedral skeleton and would have two more electrons than for a conventional structure. In order to conform to the EAN rule, it is, therefore, more likely that one of the three methoxy groups may act as a 3-electron donor. The consideration of the face-capping alkoxy groups as 3-electron donors is also seen for  $[\text{Ru}_4(\text{CO})_{10}\text{Cl}_2(\mu_3\text{-OEt})_2]$ .<sup>11</sup>

Although quite a few *closo*-structures have been known for bismuth-containing transition metal clusters,<sup>1</sup> compound **1** provides the first example of a tetrahedral geometry for mixed bismuth–molybdenum clusters. For comparison, the average Bi–Mo distance of 2.822(2) Å in **1** is consistent with single bonding but significantly shorter than that found for the above-mentioned

molybdenum–bismuth complexes such as 2.954(4) Å in  $[\text{BiBr}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ ,<sup>3</sup> 2.945(2) Å in  $[\text{BiI}\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ ,<sup>3</sup> 2.917(2) Å in  $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_4\text{Me})_2(\mu\text{-}\eta^2\text{-Bi}_2)]$ ,<sup>5</sup> 2.988(3) Å in  $[\text{PPN}][\text{BiCl}_2\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ ,<sup>4</sup> and 2.954(2) Å in  $[\text{BiCl}\{\text{Mo}(\text{CO})_2(\text{CNBu}^t)(\eta\text{-C}_5\text{H}_5)\}_2]$ .<sup>2</sup> The Mo–Mo distances have an average value of 3.082(2) Å and compare well to the distances in  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2\{\text{C}(\text{C}_6\text{H}_4\text{CH}_3)_2\}\{\text{N}_2\text{C}(\text{C}_6\text{H}_4\text{CH}_3)_2\}(\text{CO})_3]$  (3.052(2) Å),<sup>12</sup>  $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_4\text{Me})_2(\mu\text{-}\eta^2\text{-Bi}_2)]$  (3.167(2) Å),<sup>5</sup> and  $[\text{Mo}_2(\text{CO})_{10}]^{2-}$  (3.123(7) Å)<sup>13</sup> but are a bit shorter than those in  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_4\text{CHPh}_2)_2(\text{CO})_6]$  (3.227(1) Å)<sup>14</sup> and  $[\text{Mo}_2(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_2(\text{CO})_6]$  (3.213(8) Å).<sup>15</sup> The shorter Bi–Mo and Mo–Mo bond lengths may be in part the cause of the good stability of the molecule in solution and the solid state. The average Mo– $\mu_3$ -O distance is 2.218(9) Å, close to 2.15(1) Å found for  $\text{Mo}_4\text{Br}_4(\text{O-}i\text{-Pr})_8$ .<sup>16</sup> Interestingly, the Mo(4) atom is pseudo-octahedrally coordinated, and the Mo(1), Mo(2), and Mo(3) atoms are in an irregular 8-fold coordination that is intermediate between a square-antiprism and a dodecahedron.

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**Supplementary Material Available:** Listings of complete crystallographic data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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