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The Molybdenum–Molybdenum Triple Bond. 2.[1] Hexakis(alkoxy)dimolybdenum Compounds: Preparation, Properties, and Structural Characterization of $Mo_2(OCH_2CMe_3)_6$

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$Mo_2(NMe_2)_6$ reacts with alcohols and trialkylsilanols, ROH, to give alkoxides and trialkylsiloxides, respectively, of empirical formula $Mo(OR)_3$. Bulky RO groups, e.g., those with R = $PhMe_2C$, Me_3C, Me_2CH, Me_3CCH_2, Me_3Si, and Et_3Si, give dinuclear compounds $Mo_2(OR)_6$, which, on the basis of physicochemical studies, including vibrational spectroscopy, variable-temperature ^1H and ^{13}C NMR spectroscopy, and mass spectroscopy, are formulated as compounds containing molybdenum-to-molybdenum triple bonds unsupported by bridging alkoxy ligands. This claim is supported by a single-crystal x-ray diffraction study on the neopentoxide. For $Mo_2(OCH_2CMe_3)_6$ the space group is $P2_1/n$ with a = 18.160 (10) Å, b = 11.051 (7) Å, c = 9.956 (6) Å, β = 104.30 (4)°, V = 1936 (2) Å^3, and Z = 2. The central Mo_2O_6 skeleton has virtual D_{3d} symmetry, i.e., ethanelike geometry. The Mo–Mo distance is 2.222 (2) Å and the mean Mo–O distance is 1.88 (2) Å. The deviation from D_{3d} symmetry within the Mo_2O_6 core resides principally in the three crystallographically independent Mo–Mo–O angles: two are effectively identical (105.4 and 105.5°) while the third is smaller (98.3°). In hydrocarbon solvents $Mo_2(OCH_2CMe_3)_6$ is unstable and slowly and irreversibly oligomerizes to an insoluble form of the alkoxide, $[Mo(OCH_2CMe_3)_3]_n$. The less sterically demanding ethoxy and methoxy ligands also give rise to polymeric alkoxides. The ethoxide is diamagnetic and tetrameric, $Mo_4(OEt)_{12}$, in benzene solution. In the mass spectrometer polynuclear and mononuclear ions are observed; the most abundant ions are $Mo_4(OEt)_{12}^+$, $Mo_3(OEt)_9^+$, $Mo_2(OEt)_6^+$, and $Mo(OEt)_5^+$. The dinuclear alkoxides $Mo_2(OR)_6$, where R = $SiMe_3$ and CH_2CMe_3, react with amines to give adducts $Mo_2(OR)_6 \cdot 2L$. The chemistry of the dinuclear alkoxides of molybdenum is compared with that of the related M_2L_6 compounds, where M = Mo or W and L = R (alkyl) or NR_2, and with related organo derivatives of trivalent chromium.

Introduction

Metal alkoxides tend to undergo the minimum degree of oligomerization consistent with the attainment of the favored coordination number of the metal.[3] Thus for titanium tetraethoxide a tetrameric structure allows each titanium atom to achieve six-coordination by sharing of TiO_6 octahedra.[4] However, bulky alkoxy ligands may prevent the attainment of the favored coordination number of the metal: titanium tetra-*tert*-butoxide is monomeric. A similar situation is found in the chemistry of the alkoxides of trivalent chromium. $Cr(OR)_3$ compounds, where R = Me, Et, and *n*-Pr, are polymeric and, on the basis of magnetic susceptibility data and diffuse-reflectance spectra, are believed to have all chromium atoms in CrO_6 units.[3,5] Bulky *tert*-alkoxy ligands do not allow trivalent chromium to attain its favored six-coordination. For example, the polymeric compound $LiCr(O\text{-}t\text{-}Bu)_4$ provides a rare example of a trivalent chromium ion in a four-coordinated pseudotetrahedral environment.[6]

In this paper we describe a general preparation of alkoxides of trivalent molybdenum. For the first time in the chemistry of metal alkoxides, the existence of dinuclear compounds, $Mo_2(OR)_6$, containing metal-to-metal bonds unsupported by bridging ligands is demonstrated. Preliminary reports of this work have appeared.[7-9]

Results and Discussion

Synthesis. Alkane solutions of $Mo_2(NMe_2)_6$ react smoothly with alcohols or trialkylsilanols, ROH (≥6 equiv), to give $Mo(OR)_3$ compounds with the liberation of dimethylamine. This type of reaction is well documented for mononuclear transition metal dimethylamides, $M(NMe_2)_n$,[10] and has recently been studied in detail for $W(NMe_2)_6$.[11] In the present study alkoxy or trialkylsiloxy derivatives have been made for R = Me, Et, *i*-Pr, CH_2CMe_3, $SiMe_3$, $SiEt_3$, CMe_3, CMe_2Ph, and CEt_3 and for pinacol, $Me_2C(OH)C(OH)Me_2$. Qualitatively we observed that the rate of alcoholysis followed the order R = Me ≫ *t*-Bu. When R = Et_3C, successive substitution of $OCEt_3$ for NMe_2 groups slowed further alcoholysis to the extent that even under reflux in benzene the pure compound $Mo_2(OCEt_3)_6$ was not obtained. Mixed alkoxy-dimethylamido compounds, $Mo(NMe_2)_{6-x}(OCEt_3)_x$, were detected both by ^1H NMR spectroscopy and mass spectrometry (see Experimental Section).

Stripping the solvent in the above reactions gave crude samples of $[Mo(OR)_3]_x$ compounds or their amine adducts. Dinuclear compounds $Mo_2(OR)_6$, where R = *i*-Pr, CH_2CMe_3, *t*-Bu, $SiMe_3$, and $SiEt_3$, and $Mo_2(O_2C_2Me_4)_3$ were obtained by vacuum sublimation (100–160 °C (10^{-4} cmHg)) in an analytically pure form. Table I reports analytical data and other characterization data for these new compounds.

$Mo_2(OR)_6$ Compounds: Physical and Spectroscopic Properties. $Mo_2(OR)_6$ compounds, where R = *i*-Pr, CH_2CMe_3, *t*-Bu, CMe_2Ph, $SiMe_3$, and $SiEt_3$, and $Mo_2(O_2C_2Me_4)_3$ are crystalline, volatile substances. They show considerable thermal stability and are readily sublimed in the temperature range 70–170 °C at 10^{-4} cmHg. In this regard the isopropoxide is notably the most volatile (70 °C (10^{-4} cmHg)) and the pinacolate the least volatile (170 °C (10^{-4} cmHg)). Their colors, which vary from pale yellow to red depending on the nature of the R group, arise from a tailing of strong UV absorptions into the visible region of the electronic spectrum: they show no λ_{max} in the visible region of the spectrum. Although thermally quite stable, all compounds are oxygen and moisture sensitive and readily hydrolyzed. With the exceptions of R = CMe_2Ph and $C(CF_3)_3$ and of the pinacolate derivative, they are very soluble in hydrocarbon solvents. A cryoscopic molecular weight determination in benzene confirmed the dinuclear nature of the *tert*-butoxide, $Mo_2(O\text{-}t\text{-}Bu)_6$: calcd, 630; found, 618 ± 30. The similar physicochemical properties of the other alkoxides lead us to the assumption that they are also dinuclear. They are diamagnetic both in the solid state and in solution. In the mass spectrometer they show strong parent ions $Mo_2(OR)_6^+$ together with many other Mo_2-containing ions. Indeed the virtual absence of mononuclear ions is quite striking. A distinction between mono- (Mo) and dinuclear (Mo_2) ions is readily apparent due to the relative abundances of the naturally occurring isotopes of molybdenum. The observed vs. computed *m/e* distribution for the ion $Mo_2(OSiMe_3)_6^+$ is shown in Figure 1. Here the basic Mo_2 *m/e* pattern is further complicated by the presence of six silicon atoms.

^1H and ^{13}C NMR data are recorded in Table II. In the temperature range +90 to −90 °C in toluene-d_8 only one type of OR ligand is observed. However, in the case of R = CH_2CMe_3 both proton and carbon-13 signals are lost into the baseline at low temperatures.

Infrared spectra were obtained in the region 4000–200 cm^{-1} and are recorded in the Experimental Section. Absorption bands in the region 50–650 cm^{-1} may be associated with

Table I. Analytical and Other Characterization Data for Molybdenum(III) Alkoxides

Compd	Color and form	Volatility (at 10^{-3} Torr)	Solubility[a]	% C		% H		% N	
				Calcd	Found	Calcd	Found	Calcd	Found
$Mo_2(OBu)_6$	Red-orange crystalline solid	Sublimes 100–120 °C	S; alkanes, benzene, toluene, THF	49.36	49.23	9.25	9.15		
$Mo_2(O\text{-}i\text{-}Pr)_6$	Yellow crystalline solid	Sublimes 70–90 °C	S; alkanes, benzene, toluene, THF	39.56	39.40	7.75	7.61	0.00	0.20
$Mo_2(OCH_2CMe_3)_6$	Yellow crystalline solid	Sublimes 110–130 °C	S; alkanes, benzene, toluene, THF	50.41	50.08	9.33	9.18	0.00	0.04
$Mo_2(OCMe_2Ph)_6$	Yellow-orange solid	Decomposes >90 °C	SS; alkanes, benzene, toluene, THF	64.67	64.56	6.59	6.50		
$Mo_2(OC(CH_3)_2C(CH_3)_2O)_3$	Yellow solid	Sublimes 170–190 °C	SS; alkanes, benzene, toluene, THF	40.01	39.96	6.73	6.61	0.00	0.12
$Mo_2(OSiMe_3)_6$	Red crystalline solid	Sublimes 100–120 °C	S; alkanes, benzene, toluene, THF	29.75	29.49	7.44	7.26		
$Mo_2(OSiEt_3)_6$	Red crystalline solid	Sublimes 150–170 °C	S; alkanes, benzene, toluene, THF	44.14	44.30	9.26	9.38	0.00	0.19
$Mo_2(OCH_2CMe_3)_6\cdot 2HNMe_2$	Red crystalline solid	Decomposes to $Mo_2(OCH_2CMe_3)_6$ and $HNMe_2$ above 60 °C	VS; alkanes, benzene, toluene, THF						
$Mo_2(OSiMe_3)_6\cdot 2HNMe_2$	Purple crystalline solid	Decomposes to $Mo_2(OSiMe_3)_6$ and $HNMe_2$ >50 °C	VS; alkanes, benzene, toluene, THF	32.35	32.11	8.33	8.22	3.43	3.20
$[Mo(OMe)_3]_x$	Brown solid		I; alkanes, benzene, toluene	19.06	18.89	4.80	5.45	0.00	1.01
$[Mo(OEt)_3]_x$	Black solid	Sublimes 110–130 °C (10^{-3} Torr)	VS; alkanes, benzene, toluene	31.18	31.08	6.54	6.54	0.00	0.22
$[Mo(OCH_2CMe_3)_3]_x$	Red solid		I; alkanes, benzene, toluene	50.41	50.31	9.33	9.14		

[a] VS = very soluble; S = soluble; SS = slightly soluble; I = insoluble.

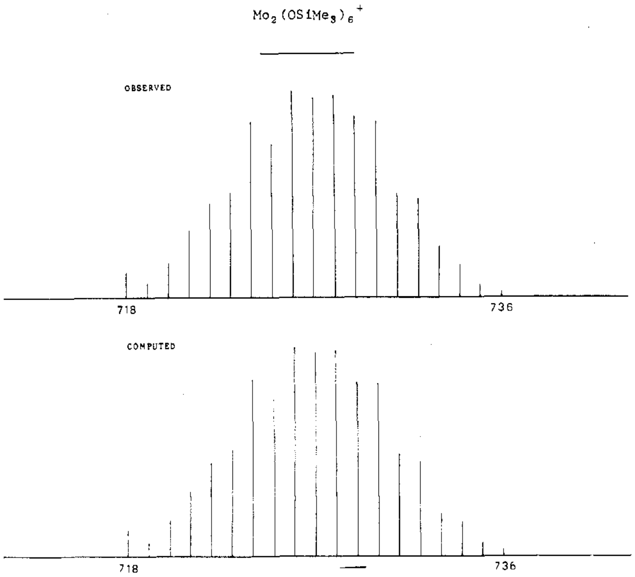


Figure 1. Observed (top) and computed (bottom) *m/e* distribution for the $Mo_2(OSiMe_3)_6^+$ ion.

ν_{str}(Mo–O). Raman spectra were also obtained for a limited number of these dinuclear compounds. (See Experimental Section for data.) An assignment of a Raman band to ν_{str}(Mo–Mo) is not immediately obvious. Indeed it appears that such a mode may be extensively coupled to other ligand vibrations thus precluding any simple assignment of the metal–metal stretch. This has been shown to be the case for the dimethylamides $M_2(NMe_2)_6$, where M = Mo and W.[12] In the present case deuterium-labeling studies were not undertaken.

All of the above data support the view that these dinuclear alkoxides are members of a structurally related series Mo_2L_6, where L = R (alkyl),[13,14] NR_2,[1] and OR, containing molybdenum-to-molybdenum triple bonds unsupported by bridging ligands. For L = CH_2SiMe_3[13] and NMe_2[1] this has been confirmed by single-crystal x-ray studies.

X-Ray Studies: Solid-State Structure of $Mo_2(OCH_2CMe_3)_6$. Originally crystals of Mo_2(O-*t*-Bu)$_6$ were examined but proved unsatisfactory for detailed x-ray work. Subsequently the neopentoxy derivative was examined because it existed in both a dinuclear form $Mo_2(OR)_6$ and a polymeric form $[Mo(OR)_3]n$ (see later).

The structure of $Mo_2(OCH_2CMe_3)_6$ is shown in Figure 2, together with the atomic numbering scheme. Tables III–V give atomic positional and thermal parameters, bond lengths, and bond angles, respectively.

This structural characterization confirms the expected $L_3M{\equiv}ML_3$ structure. The three crystallographically independent O–Mo–O angles are essentially equal, varying from 114.0 to 115.9°, with a mean value of 115.0 ± 0.7°. The essential trigonal symmetry on each end of the molecule combined with the crystallographically imposed inversion center leads to virtual D_{3d} symmetry for the Mo_2O_6 skeleton. The only significant deviation from D_{3d} symmetry within the Mo_2O_6 core arises from the inequality of the three crystallographically independent Mo′–Mo–O angles. Two of these are effectively identical (105.4 and 105.5°) while the third is much smaller (98.3°). It is our opinion that this results from packing forces in the crystal and that the molecule does not inherently tend to distort in this way.

The distance between the molybdenum atoms, 2.222 (2) Å, is very similar to that in $Mo_2(NMe_2)_6$, 2.214 (3) Å,[1] and that in $Mo_2(CH_2SiMe_3)_6$, 2.167 (3) Å.[13] The mean Mo–O distance, 1.88 (2) Å, is about 0.10 Å shorter than the Mo–N distance in $Mo_2(NMe_2)_6$ and 0.25 Å shorter than the mean Mo–C distance reported in $Mo_2(CH_2SiMe_3)_6$. This probably indicates that oxygen-to-molybdenum π bonding in $Mo_2(OCH_2CMe_3)_6$ is at least as important as nitrogen-to-molybdenum π bonding in $Mo_2(NMe_2)_6$.

The structure is notable for the very large amplitude of thermal motion for all of the atoms, especially the carbon atoms. This is manifest explicitly in the high thermal parameters listed in Table III and was foreshadowed by the unusually rapid decline in intensities with increasing 2θ angle. The vigorous thermal motion is consistent with the fact that the volume per (nonhydrogen) atom, 25.5 Å^3, is at the high end of the range, 15–25 Å^3, normally encountered in crystals containing first-row atoms.

Bonding in $Mo_2(OCH_2CMe_3)_6$. The bonding in $Mo_2(OCH_2CMe_3)_6$ and related $Mo_2(OR)_6$ compounds can be qualitatively described as follows. Each molybdenum atom forms four σ bonds, three to oxygen atoms and one to the other molybdenum atom, using approximately tetrahedral hybrid orbitals. These might be sp^3, sd^3, or any intermediate combination. Then, if we define the Mo–Mo axis as the *z* axis, two metal π bonds can be formed employing d_{xz}, d_{yz} and/or p_x, p_y orbitals on each atom. The Mo–Mo triple bond so formed parallels that in $Mo_2(CH_2SiMe_3)_6$ and readily accounts for the short Mo–Mo distance, which is ca. 1.0 Å less than that of a Mo–Mo single bond, the ethanelike geometry of the Mo_2O_6 core, and the diamagnetic nature of the compound. In addition the oxygen lone pairs may also enter into the bonding scheme. The rather short Mo–O distances, 1.88 Å, suggest that O-to-Mo π bonding should be considered. In this regard the bonding in $Mo_2(OCH_2CMe_3)_6$ may be viewed in a similar manner to that in $Mo_2(NMe_2)_6$.

For $Mo_2(NMe_2)_6$ the $Mo_2(NC_2)_6$ moiety has virtual D_{3d} symmetry; the $Mo–NC_2$ moieties are planar and the NC_2 planes deviate little from the Mo–Mo–N planes. Thus two pairs of molybdenum d_{xy} and $d_{x^2-y^2}$ atomic orbitals may ac-

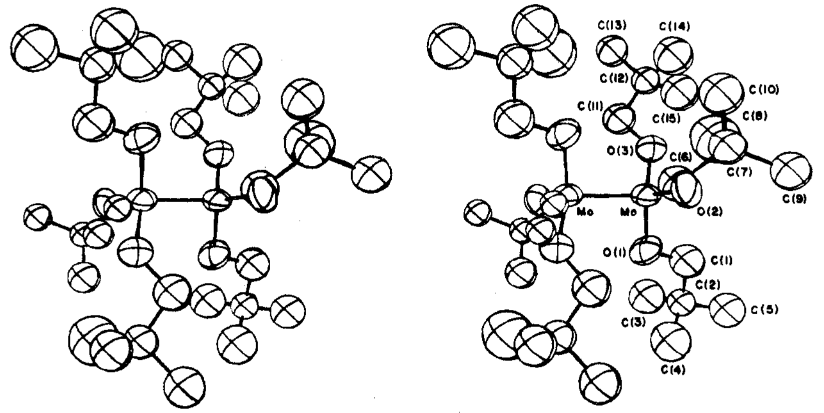


Figure 2. An ORTEP stereoscopic view of the $Mo_2(OCH_2CMe_3)_6$ molecule showing 50% probability ellipsoids and atomic numbering scheme.

Table II. ^1H and ^{13}C NMR Data for Molybdenum(III) Alkoxides[a]

Compd	Temp, °C	^1H (multiplicity, rel intens)		^{13}C (rel intens)	
$Mo_2(OCMe_3)_6$	+38	β	1.43 (s)	α	33.1 (1)
αβ				β	79.1 (3)
	−60	β	1.43 (s)	α	32.9 (1)
				β	79.2 (3)
$Mo_2(OCHMe_2)_6$	+38	β	1.37 (d, 6)	α	77.8 (1)
α β		α	5.48 (sept, 1)	β	26.6 (2)
	−60	β	1.37 (d, 6)	α	78.5 (1)
		α	5.45 (sept, 1)	β	26.6 (2)
$Mo_2(OCH_2CMe_3)_6$	+38	γ	0.97 (s, 9)	α	86.7 (1)
α βγ		α	4.82 (s, 2)	β	34.5 (1)
				γ	26.7 (3)
	−60	γ	0.95 (s, 9)	α	86.7 (1)
				β	34.6 (1)
		α	4.90 (s, 2)	γ	26.5 (3)
$Mo_2(OCMe_2Ph)_6$	+38	Me	1.62 (s, 6)		
		Ph	7.02 7.55 (m, 5)		
	−60	Me	1.62 (s, 6)		
		Ph	7.08 7.63 (m, 5)		
$Mo_2(OSiMe_3)_6$	+38	Me	0.25 (s)	Me	2.87
	−60	Me	0.32 (s)	Me	2.80
$Mo_2(OCH_2CMe_3)_6 \cdot 2HNMe_2$	+38	γ	1.05 (s, 9)	α	82.9 (3)
αβ γ		NMe_2	2.40 (d, 2)	NMe_2	40.3 (2)
		α	4.40 (s, 2)	β	34.3 (3)
				γ	27.3 (9)
$Mo_2(OSiMe_3)_6 \cdot 2HNMe_2$	+38	Me	0.22 (s, 9)	NMe_2	41.60 (2)
		NMe_2	2.28 (s, 2)	Me	4.19 (9)
	−60	Me	0.13 (s, 3)	NMe_2	41.03 (2)
			0.30 (s, 6)		4.38 (6)
		NMe_2	2.20 (d, 2)		3.35 (3)
$[Mo(OCH_2CH_3)_3]_x$	+38	Complex			72.87 (1)
α β					70.87 (2)
					70.76 (1)
				α	70.10 (2)
					67.73 (1)
					67.62 (2)
					66.82 (2)
					66.23 (1)
	+80	Complex			73.55 (1)
					72.04 (1)
					71.09 (2)
					70.46 (2)
				α	67.92 (1)
					67.60 (2)
					66.96 (1)
					66.41 (2)

[a] ^1H NMR spectra are reported in δ (ppm) relative to HMDS (hexamethyldisiloxane). ^{13}C NMR spectra are reported in δ (ppm) relative to TMS. The solvent is toluene-d_8. s = singlet; d = doublet; sept = septet; m = multiplet.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.04631 (6)	0.0641 (1)	0.0470 (1)	0.00347 (3)	0.01040 (8)	0.01317 (9)	0.0030 (1)	0.00454 (8)	−0.0022 (3)
O(1)	−0.0129 (5)	0.1802 (8)	0.1155 (9)	0.0060 (4)	0.0109 (8)	0.019 (1)	0.0014 (10)	0.0049 (11)	−0.009 (2)
O(2)	0.1151 (5)	−0.0250 (8)	0.1810 (9)	0.0034 (3)	0.0131 (10)	0.019 (1)	0.0029 (9)	−0.0013 (11)	−0.001 (2)
O(3)	0.0851 (5)	0.1168 (8)	−0.0986 (8)	0.0052 (3)	0.0161 (10)	0.015 (1)	−0.0023 (10)	0.0070 (9)	−0.004 (2)

Atom	x	y	z	B_{iso}, Å^2	Atom	x	y	z	B_{iso}, Å^2
C(1)	0.0278 (9)	0.275 (1)	0.185 (2)	8.3 (4)	C(9)	0.2544 (8)	−0.111 (1)	0.385 (1)	6.4 (3)
C(2)	−0.0285 (8)	0.367 (1)	0.232 (1)	6.0 (3)	C(10)	0.2374 (9)	−0.180 (2)	0.139 (2)	8.1 (4)
C(3)	−0.0884 (11)	0.418 (2)	0.110 (2)	10.9 (5)	C(11)	0.0678 (8)	0.090 (1)	−0.247 (1)	7.3 (4)
C(4)	−0.0683 (12)	0.312 (2)	0.331 (2)	11.4 (6)	C(12)	0.1385 (7)	0.113 (1)	−0.301 (1)	5.7 (3)
C(5)	0.0252 (10)	0.471 (2)	0.309 (2)	9.9 (5)	C(13)	0.1166 (9)	0.076 (1)	−0.456 (2)	8.0 (4)
C(6)	0.1201 (8)	−0.151 (1)	0.228 (1)	6.2 (3)	C(14)	0.2029 (10)	0.024 (2)	−0.220 (2)	9.9 (5)
C(7)	0.2062 (7)	−0.188 (1)	0.267 (1)	5.6 (3)	C(15)	0.1699 (11)	0.242 (2)	−0.277 (2)	11.4 (6)
C(8)	0.2052 (9)	−0.323 (2)	0.319 (2)	8.5 (4)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Here, and in other tables, numbers in parentheses are the estimated standard deviations in the least significant digits.

commodate eight electrons from the nitrogen lone pairs. This leads to 16 valence-shell electrons per molybdenum atom and leaves two nitrogen π-electron pairs in essentially nonbonding orbitals of A_{2g} and A_{1u} symmetry. If one considers that in $Mo_2(OCH_2CMe_3)_6$ the oxygen atoms are essentially sp^2 hybridized, or at least that each oxygen atom contributes only one pair of electrons toward forming a O-to-Mo π bond, then the same symmetry considerations are applicable. The

Table IV. Interatomic Distances (Å)[a]

Mo–Mo′	2.222 (2)	C(2)–C(5)	1.57 (1)
Mo–O(1)	1.905 (6)	C(6)–C(7)	1.57 (1)
Mo–O(2)	1.867 (6)	C(7)–C(8)	1.58 (1)
Mo–O(3)	1.855 (6)	C(7)–C(9)	1.54 (1)
C(1)–O(1)	1.36 (1)	C(7)–C(10)	1.52 (1)
C(6)–O(2)	1.47 (1)	C(11)–C(12)	1.53 (1)
C(11)–O(3)	1.46 (1)	C(12)–C(13)	1.55 (1)
C(1)–C(2)	1.60 (1)	C(12)–C(14)	1.58 (1)
C(2)–C(3)	1.52 (2)	C(12)–C(15)	1.54 (2)
C(2)–C(4)	1.49 (2)		

[a] Atoms are labeled as in Figure 2. Primed atoms are symmetry related to the corresponding unprimed atoms.

Table V. Bond Angles (deg)

Mo′–Mo–O(1)	98.3 (2)	C(3)–C(2)–C(4)	108.1 (10)
Mo′–Mo–O(2)	105.5 (2)	C(3)–C(2)–C(5)	111.0 (10)
Mo′–Mo–O(3)	105.4 (2)	C(4)–C(2)–C(5)	108.9 (10)
O(1)–Mo–O(2)	115.9 (3)	C(6)–C(7)–C(8)	103.5 (8)
O(1)–Mo–O(3)	115.2 (3)	C(6)–C(7)–C(9)	112.8 (8)
O(2)–Mo–O(3)	114.0 (3)	C(6)–C(7)–C(10)	109.6 (8)
Mo–O(1)–C(1)	114.5 (7)	C(8)–C(7)–C(9)	109.0 (8)
Mo–O(2)–C(6)	135.1 (6)	C(8)–C(7)–C(10)	111.4 (9)
Mo–O(3)–C(11)	134.2 (6)	C(9)–C(7)–C(10)	110.4 (9)
O(1)–C(1)–C(2)	109.5 (9)	C(11)–C(12)–C(13)	105.9 (9)
O(2)–C(6)–C(7)	107.7 (8)	C(11)–C(12)–C(14)	107.3 (9)
O(3)–C(11)–C(12)	109.3 (9)	C(11)–C(12)–C(15)	114.3 (10)
C(1)–C(2)–C(3)	112.5 (9)	C(13)–C(12)–C(14)	108.3 (9)
C(1)–C(2)–C(4)	112.2 (10)	C(13)–C(12)–C(15)	113.2 (10)
C(1)–C(2)–C(5)	104.0 (9)	C(14)–C(12)–C(15)	107.5 (9)

methylene carbons of the neopentoxy groups deviate little from the Mo–Mo–O planes: C(1), C(6), and C(11) deviate by 0.027, 0.036, and 0.018 Å, respectively, from their respective Mo–Mo–O planes. Four of the methylene carbons are distal and two are proximal with respect to the Mo–Mo triple bond. This structure is presumably favored by steric considerations.

The stereodynamic behavior of the molecule must parallel that of $Mo_2(NMeEt)_6$[1] and we believe that the slow interconversion of the isomers resulting from various arrangements of proximal and distal CH_2CMe_3 moieties is responsible for the observed loss of ^1H and ^{13}C NMR signals at low temperatures. If the configuration of the molecule found in the solid-state structure were frozen out on the NMR time scale, we would expect to observe a difference between proximal and distal alkyl resonances.[1]

In order to reach a more definitive understanding of the electronic structure in $Mo_2(OCH_2CMe_3)_6$ and related compounds we are undertaking UV photoelectron spectroscopic studies and SCF–Xα–SW molecular orbital calculations.

$Mo_2(OR)_6L_2$ Compounds. The reaction between $Mo_2(NMe_2)_6$ and ROH (≥6 equiv) leads to the initial formation of $Mo_2(OR)_6(HNMe_2)_2$ compounds when R = $SiMe_3$ and CH_2CMe_3. When heated in vacuo (>60 °C (10^{-4} cmHg)) these compounds give up the coordinated amine; only the dinuclear alkoxides sublime. Addition of $HNMe_2$ to a hydrocarbon solution of $Mo_2(OR)_6$, where R = $SiMe_3$ or CH_2CMe_3, rapidly regenerates the dimethylamine adducts. Thus it seems that there is an equilibrium, eq 1, which lies

$$Mo_2(OR)_6 + 2L \rightleftarrows Mo_2(OR)_6L_2 \qquad (1)$$

well to the right when R = $SiMe_3$ and CH_2CMe_3.

A cryoscopic molecular weight determination in benzene confirmed the dinuclear nature of $Mo_2(OSiMe_3)_6(HNMe_2)_2$. We have not yet extensively examined the requirements on L in eq 1, but such a reaction has been found for L = NH_3, H_2NMe, $HNMe_2$, NMe_3, and PMe_2Ph.

The ready formation of the adducts $Mo_2(OR)_6\cdot 2L$, when R = $SiMe_3$ and CH_2CMe_3, indicates that these compounds are coordinatively unsaturated. The failure of other $Mo_2(OR)_6$ compounds to form stable adducts presumably is a result of steric factors: $Et_3Si > Me_3Si$ and $Me_3C > Me_3CCH_2$. It is interesting to note that the related dialkylamides[2] and alkyls[14] Mo_2L_6 (L = R, NR_2) do not show this affinity for Lewis base molecules such as amines. It could be that $Mo_2(NMe_2)_6$ is too sterically crowded to allow coordination of an additional ligand. (We have found[12] that $W_2(NMe_2)_6$ does not undergo exchange with $HN(CD_3)_2$.) However, the steric requirements of the alkyl and alkoxide ligands, CH_2SiMe_3 and $OSiMe_3$, must be very similar. This raises the question: Why do the alkoxides, but not the alkyls, form adducts with Lewis bases? A rationale may lie in the preferential ability of the alkoxy ligand to form M–L–M bridges. It could then be that the adducts $Mo_2(OR)_6\cdot 2L$ adopt a $L(RO)_2Mo(\mu\text{-}OR)_2Mo(OR)_2L$ structure. Consistent with, but by no means conclusive evidence for this proposal, is our observation that at low temperatures both ^1H and ^{13}C NMR spectra indicate two types of OR ligands in $Mo_2(OSiMe_3)_6L_2$ compounds. The structure and dynamical solution behavior of these $Mo_2(OR)_6\cdot 2L$ compounds will be the subject of further investigation.

Polymeric Molybdenum(III) Alkoxides. In hydrocarbon solvents $Mo_2(OCH_2CMe_3)_6$ undergoes a slow and irreversible reaction leading to the formation of a brick red precipitate. Elemental analyses and infrared data are entirely consistent with the view that this is a polymeric form of the alkoxide: $[Mo(OCH_2CMe_3)_3]_n$.

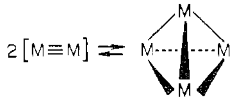
The reaction between $Mo_2(NMe_2)_6$ and MeOH (≥6 equiv) leads to a nonvolatile, hydrocarbon-insoluble, brown solid which, on the basis of elemental analyses and infrared data, we formulate as a polymeric alkoxide $[Mo(OMe)_3]_n$. Rather interestingly the analogous reaction involving ethanol leads to a black compound which is very soluble in hydrocarbon solvents. Elemental analyses support the empirical formula $Mo(OEt)_3$. A cryoscopic molecular weight determination suggests a tetrameric species might be present in solution: calcd for $Mo_4(OEt)_{12}$, 924; found, 1027 ± 90. In the mass spectrometer the ion of highest mass corresponded to $Mo_4(OEt)_{12}^+$. Other polynuclear ions were observed and the ions $Mo_3(OEt)_9^+$ and $Mo_2(OEt)_6^+$ were very prominent. Mononuclear species such as $Mo(OEt)_5^+$ and $Mo(OEt)_4^+$ were also observed. The ethoxide $[Mo(OEt)_3]_n$ is diamagnetic and gives a very complex ^1H NMR spectrum due to the overlapping of several ethyl resonances. In the $^{13}C[^1H]$ spectrum obtained at 40 °C in benzene-d_6 eight methylene carbon signals were observed in the intensity ratio 1:1:1:1:2:2:2:2. This remarkable observation is consistent with the view that the ethoxide is tetrameric, $Mo_4(OEt)_{12}$. While a number of structures may be ruled out by this observation, e.g., structures[15] akin to $Ir_4(CO)_{12}$ or $Rh_4(CO)_4$, we are not able to postulate any that are consistent with it. Whatever the structure, molybdenum-to-molybdenum bonding must presumably be present in order to account for the observed diamagnetic nature of the compound.

Our observation that the neopentoxide exists in both a dimeric form, $Mo_2(OCH_2CMe_3)_6$, and a polymeric form, $[Mo(OCH_2CMe_3)_3]_n$, has precedent in the chemistry of metal alkoxides and a comparison with aluminum alkoxides $Al(OR)_3$ is particularly pertinent. Aluminum isopropoxide is dimeric in the vapor state and is dimeric when freshly distilled or sublimed.[16] With time an "aging effect" occurs and the observed degree of polymerization increases.[16] According to Bradley's[17] original "structural theory for metal alkoxide polymers" these aging effects arise from structural rearrangements as aluminum realizes its maximum coordination number. An octamer is predicted if each aluminum atom is to attain six-coordination; however, discrete tetrameric and hexameric species may exist involving both four- and six-coordinated aluminum atoms. Bradley's theory[17] is, however, inapplicable to molybdenum(III) alkoxides since metal-to-metal bonding is important and may determine the preferred structure. This is clearly seen for the dinuclear compounds $Mo_2(OR)_6$ which contain molybdenum-to-molybdenum triple bonds unsupported by bridging alkoxy ligands.

A distinction between bridging and terminal alkoxy ligands has been proposed from infrared spectroscopic studies. Assignments of M–O and C–O stretching frequencies for both bridging and terminal OR ligands have been made for a large number of alkoxides, including ^{18}O-labeled derivatives.[18] If these assignments are valid and can be extended to $[Mo(OR)_3]_n$ compounds, we would predict that $[Mo(OEt)_3]_n$ contains only terminal alkoxy ligands: the spectrum of $[Mo(OEt)_3]_n$, both in solution and as a Nujol mull, is similar to that reported for $U(OEt)_6$.[18] On the other hand the insoluble methoxide, $[Mo(OMe)_3]_n$, appears to have predominantly bridging OMe ligands. IR data are given in the Experimental Section.

Conclusions

We have now established that there exists a structurally related series of compounds of general formula Mo_2L_6, where L = R (alkyl), NR_2, and OR. A similar series exists for tungsten, although as yet an alkoxide, $W_2(OR)_6$, has not been structurally characterized by x-ray studies. In all of these compounds there exist metal-to-metal triple bonds unsupported by bridging ligands. In the chemistry of molybdenum(III) alkoxides a transition from dinuclear to polynuclear chemistry is seen. It is possible that this transition involves a reorganization of metal-to-metal bonding of the type



This, however, remains to be proven and will be subject for future investigations.

Experimental Section

Materials. $Mo_2(NMe_2)_6$ was prepared as previously described.[1] The alcohols were commercially available. *tert*-Butyl alcohol (Mallinckrodt) was distilled from benzene as an azeotrope and the azeotrope was stored under nitrogen over molecular sieves prior to use. Neopentyl alcohol (Aldrich) and pinacol (Matheson Coleman and Bell) were dissolved in benzene and stored over molecular sieves. Methanol (Mallinckrodt), ethanol (Mallinckrodt), and 2-propanol (Mallinckrodt) were distilled over sodium under a nitrogen atmosphere and stored over molecular sieves. Triethylcarbinol (3-ethyl-3-pentanol, Aldrich), perfluoro-*tert*-butyl alcohol (PCR, Inc.), and α,α-dimethylbenzyl alcohol (Eastman) were stored over molecular sieves. Trimethylsilanol and triethylsilanol were prepared according to the method of Sommer et al.[19]

Physical and Analytical Methods. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, using drybox sampling techniques. Molecular weight determinations were made under a purified nitrogen atmosphere in an all-glass cryoscopic apparatus incorporating a thermistor bridge.

Infrared spectra were obtained from Nujol mulls or from solutions in hexane between CsI plates/windows using a Beckman IR-12 or Perkin-Elmer IR 283 spectrophotometer.

Raman spectra were obtained on a spectrophotometer equipped with a coherent Radiation Model CR5 Ar^+ laser, a Spex Model 1401 double monochromator, and a cooled ITT 5W-130 Startracker photomultiplier tube, using the 5145-Å exciting line. Solution spectra were obtained from THF solutions sealed in capillary tubes.

^1H and ^{13}C NMR measurements were made on Varian Associates A-60 and XL-100 spectrometers, respectively. Both instruments were equipped with a variable-temperature probe. Toluene-d_8 was used as the solvent and chemical shifts are reported as ppm downfield from hexamethyldisiloxane (HMDS) (for ^1H NMR data) or as ppm downfield from TMS (^{13}C NMR data).

General Procedures. All preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere or in vacuo, using standard Schlenk-type techniques.[20] Solvents were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, phenyl ether, and sodium. When not needed for immediate use, solvents were stored over calcium hydride under nitrogen. Samples were stored and handled in a Vacuum Atmospheres Dri Lab system.

Preparation of $Mo_2(O\text{-}t\text{-}Bu)_6$. *t*-BuOH (20.8 mmol) in benzene was added to $Mo_2(NMe_2)_6$ (3.47 mmol) dissolved in hexane (40 mL). After 24 h of stirring, the solvent was removed in vacuo and the residue dried under vacuum for 2 h. The residue was purified by sublimation (100–120 °C (10^{-3} Torr)), followed by recrystallization in pentane to yield red-orange $Mo_2(O\text{-}t\text{-}Bu)_6$ (747 mg). For shorter reaction times, a larger excess of *tert*-butyl alcohol can be used and purification can proceed directly through recrystallization. Analytical data are given in Table I. A valency determination[26] yielded 3.1 for Mo; calcd valency for Mo, 3.0. A cryoscopic molecular weight determination in benzene gave 618 ± 30; calcd mol wt for $Mo_2(O\text{-}t\text{-}Bu)_6$, 630. NMR data ($^1H$ and ^{13}C) are reported in Table II.

Infrared data (Nujol mull between CsI plates): 260 (w, br), 298 (m), 312 (w), 362 (m), 382 (m), 396 (m), 470 (m), 560 (m), 605 (m), 775 (s), 790 (s), 900 (s), 930 (s, br), 970 (vs), 1028 (m), 1170 (vs), 1235 (s), 1262 (m) cm^{-1}.

A parent ion at *m/e* 630 in the mass spectrum corresponds to $Mo_2(O\text{-}t\text{-}Bu)_6^+$ (based on ^{96}Mo).

Preparation of $Mo_2(OCMe_2Ph)_6$. α,α-Dimethylbenzyl alcohol (14.5 mmol) was added to $Mo_2(NMe_2)_6$ (2.4 mmol) dissolved in pentane (25 mL). The reaction flask was cooled in an ice bath during the addition. The solution was stirred for 12 h during which time a yellow-orange solid precipitated. The solution was cooled for several hours in an ethanol/CO_2 ice bath to promote further precipitation, and the yellow-orange solid was filtered off and collected on a frit. The solid was washed with cold pentane to obtain ca. 0.5 g of yellow-orange $Mo_2(OCMe_2Ph)_6$. Analytical data are given in Table I. ^1H NMR data are reported in Table II.

Infrared data (Nujol mull between CsI plates): 355 (w), 411 (w), 540 (sh), 552 (m), 564 (sh), 607 (sh, br), 626 (m), 640 (m), 696 (s), 705 (s), 733 (s), 763 (s), 868 (vs), 908 (m), 941 (vs), 990 (s), 1006 (m), 1026 (w), 1072 (s), 1097 (m), 1135 (s), 1142 (s), 1175 (m), 1251 (m, br), 1261 (sh) cm^{-1}.

Preparation of $Mo_2(O\text{-}i\text{-}Pr)_6$. Isopropyl alcohol (9.3 mmol) was added to $Mo_2(NMe_2)_6$ (1.5 mmol) dissolved in pentane (30 mL). The reaction flask was cooled in an ice bath. Upon addition of the alcohol, the solution immediately turned red-brown. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was then removed in vacuo. Some yellow crystals came out of solution as the solvent was removed. The residue, obtained upon complete evaporation to dryness, consisted of a yellow powder which was sublimed (70–90 °C (10^{-3} Torr)) to yield yellow crystalline $Mo_2(O\text{-}i\text{-}Pr)_6$ (590 mg). Analytical data are given in Table I. NMR data (^1H and ^{13}C) are reported in Table II.

Infrared data (Nujol mull between CsI plates): 1326 (s), 1261 (w), 1241 (vw), 1167 (s), 1129 (s), 1110 (vs), 978 (vs), 944 (s), 852 (s), 831 (s), 653 (m), 624 (s), 451 (m), 323 (w), 302 (m) cm^{-1}. Raman data (THF solution in capillary tube, 120–900-cm^{-1} scan): 176 (m), 216 (w), 258 (m), 267 (sh), 287 (s), 389 (s), 432 (m), 623 (s), 854 (m) cm^{-1}. All bands are polarized.

Preparation of $Mo_2(OCH_2CMe_3)_6 \cdot 2HNMe_2$, $Mo_2(OCH_2CMe_3)_6$, and $[Mo(OCH_2CMe_3)_3]_x$. Neopentyl alcohol (13.3 mmol) dissolved in benzene (5 mL) was added to $Mo_2(NMe_2)_6$ (2.22 mmol) dissolved in 20 mL of hexane. The reaction flask was cooled in an ice bath. Upon addition of the alcohol, the solution immediately turned red. The red solution was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed in vacuo to yield a red solid, $Mo_2(OCH_2CMe_3)_6 \cdot 2HNMe_2$ (1.2 g). NMR data (^1H and ^{13}C) are reported in Table II.

Infrared data (Nujol mull between CsI plates): 265 (w), 312 (m), 332 (w), 400 (m), 410 (sh), 456 (s), 547 (w), 656 (vs), 754 (s), 804 (m), 907 (s), 932 (s), 1020 (vs), 1048 (vs), 1073 (vs), 1216 (s), 1260 (s), 1291 (m), 3225 (m) cm^{-1}.

Upon heating in vacuo at 60 °C, $Mo_2(OCH_2CMe_3)_6 \cdot 2HNMe_2$ (ca. 1.5 g) decomposed to yield $HNMe_2$ (2 equiv) and a yellow solid. The yellow solid sublimed (110–130 °C (10^{-3} Torr)) to yield the yellow crystalline compound $Mo_2(OCH_2CMe_3)_6$ (ca. 1.0 g). Analytical data are given in Table I. NMR data (^1H and ^{13}C) are reported in Table II.

Infrared data (Nujol mull between CsI plates): 260 (w, br), 328 (m), 403 (s), 465 (s), 687 (vs), 756 (s), 901 (s), 932 (s), 987 (vs), 1020 (vs), 1050 (vs, br), 1216 (s), 1258 (s), 1293 (s) cm^{-1}. Raman data (THF solution in capillary tube, 120–900-cm^{-1} scan): 192 (w, br), 288 (m, br), 305 (m), 382 (m), 454 (m), 462 (m), 755 (s) cm^{-1}. All bands are polarized.

A parent ion at *m/e* 714 in the mass spectrum corresponds to $Mo_2(OCH_2CMe_3)_6^+$ (based on ^{96}Mo).

Yellow $Mo_2(OCH_2CMe_3)_6$ can be recrystallized from cold pentane over short periods of time (~6 h); however, over prolonged periods (ca. several days) at ca. 0 °C, precipitation of a red solid occurs. The red solid, $[Mo(OCH_2CMe_3)_3]_x$, was collected by filtration and washed with cold pentane to remove any residual $Mo_2(OCH_2CMe_3)_6$. Analytical data are given in Table I. $[Mo(OCH_2CMe_3)_3]_x$ is completely insoluble in hydrocarbon solvents such as hexane, benzene, and toluene.

Infrared data (Nujol mull between CsI plates): 287 (m), 321 (w), 352 (w), 380 (w), 396 (m), 425 (w), 450 (m), 468 (m), 509 (vs), 568 (s), 647 (vs), 662 (s), 672 (s), 751 (m), 753 (sh), 804 (m), 897 (w), 912 (w), 934 (s), 1002 (vs), 1021 (vs), 1052 (vs), 1212 (m), 1260 (m), 1290 (w), 1301 (w), 1310 (w) cm^{-1}.

Preparation of $Mo_2[OC(CH_3)_2C(CH_3)_2O]_3$. Pinacol (3.96 mmol) dissolved in benzene (4 mL) was added to $Mo_2(NMe_2)_6$ (1.32 mmol) dissolved in hexane (30 mL). The reaction flask was cooled in an ice bath. Upon addition of the pinacol, the solution was allowed to warm to room temperature, and, after 5 min, a yellow solid precipitated. A yellow crystalline solid, $Mo_2[OC(CH_3)_2C(CH_3)_2O]_3$ (ca. 0.5 g), was obtained by filtration. Analytical data are given in Table I. This compound is only very sparingly soluble in CH_2Cl_2, benzene, and toluene. The ^1H NMR data (Table II) are inconclusive with regard to structure. $Mo_2[OC(CH_3)_2C(CH_3)_2O]_3$ sublimes at 170–180 °C (10^{-3} Torr).

Infrared data (Nujol mull between CsI plates): 300 (vw), 334 (s), 382 (m), 413 (w), 474 (m), 488 (s), 556 (s), 571 (m), 583 (s), 624 (s), 732 (vs), 861 (s), 902 (vs), 936 (s), 952 (vs), 1008 (m), 1014 (m), 1125 (vs), 1153 (m), 1161 (s), 1185 (m), 1261 (w) cm^{-1}.

A parent ion at *m/e* 540 in the mass spectrum corresponds to $Mo_2(OC(CH_3)_2C(CH_3)_2O)_3^+$ (based on ^{96}Mo).

Preparation of $Mo_2(OSiMe_3)_6 \cdot 2HNMe_2$ and $Mo_2(OSiMe_3)_6$. Trimethylsilanol[19] (12.0 mmol) was added to $Mo_2(NMe_2)_6$ (2.0 mmol) dissolved in hexane (30 mL). The reaction flask was cooled in an ice bath. Upon addition of the silanol, the solution immediately turned purple. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed in vacuo to yield a purple solid. The purple solid was recrystallized from pentane to yield a purple crystalline solid, $Mo_2(OSiMe_3)_6 \cdot 2HNMe_2$ (0.82 g). Analytical data are given in Table I. A cryoscopic molecular weight determination in benzene gave mol wt 790 ± 20; calcd mol wt for $Mo_2(OSiMe_3) \cdot 2HNMe_2$, 816. NMR data ($^1H$ and ^{13}C) are reported in Table II.

Infrared data (Nujol mull between CsI plates): 234 (w), 292 (m), 310 (m), 331 (m), 345 (m), 441 (s), 486 (s), 627 (m), 675 (s), 746 (s), 836 (s), 920 (vs, br), 952 (vs), 995 (s, br), 1022 (s), 1122 (m), 1208 (w), 1248 (s), 1260 (sh), 1306 (m), 3302 (m), 3309 (m) cm^{-1}.

Upon heating in vacuo at 50–60 °C, $Mo_2(OSiMe_3)_6 \cdot 2HNMe_2$ (0.6 g) decomposed to yield $HNMe_2$ (2 equiv) and a red solid. The red solid sublimed (100–120 °C (10^{-3} Torr)) to yield the red crystalline $Mo_2(OSiMe_3)_6$ (0.4 g). Analytical data are given in Table I. NMR data (^1H and ^{13}C) are reported in Table II.

Infrared data (Nujol mull between CsI plates): 295 (m), 310 (m), 460 (m), 502 (m), 630 (m), 686 (s), 749 (s), 844 (vs), 887 (vs, vbr), 920 (vs, br), 1251 (vs) cm^{-1}.

A parent ion at *m/e* 726 in the mass spectrum corresponds to $Mo_2(OSiMe_3)_6^+$ (based on ^{96}Mo).

Preparation of $Mo_2(OSiEt_3)_6$. Triethylsilanol[19] (14.1 mmol, 2.3 mL) was added to $Mo_2(NMe_2)_6$ (2.35 mmol) dissolved in hexane (25 mL). The reaction flask was cooled in an ice bath. The solution turned reddish brown and was allowed to warm to room temperature. After 4 h of stirring, the solvent was removed in vacuo leaving a gummy red solid. The red solid sublimed (150–170 °C (10^{-3} Torr)) to give the red crystalline solid $Mo_2(OSiEt_3)_6$. Analytical data are given in Table I. The ^1H NMR spectrum is complex, exhibiting an expected A_3B_2 pattern.

Infrared data (Nujol mull between CsI plates): 319 (m), 389 (m), 490 (m), 730 (vs, br), 910 (vs, br), 1020 (s), 1162 (w), 1171 (w), 1241 (s) cm^{-1}.

A parent ion at *m/e* 978 in the mass spectrum corresponds to $Mo_2(OSiEt_3)_6^+$ (based on ^{96}Mo).

Preparation of $[Mo(OMe)_3]_x$. Methanol (5.6 mmol) was added to $Mo_2(NMe_2)_6$ (0.93 mmol) dissolved in pentane (25 mL). The solution turned red-brown immediately and then dark brown. After a few minutes, a brown solid precipitated. The solution was concentrated and filtered. The brown solid was washed with cold pentane and dried in vacuo yielding the brown polymeric compound, $[Mo(OMe)_3]_x$ (ca. 0.25 g), which was completely insoluble in hydrocarbon solvents. Analytical data are given in Table I.

Infrared data (Nujol mull between CsI plates): 390 (m), 465 (s, br), 510 (s, br), 802 (m), 900 (w), 934 (m), 1050 (vs, br), 1156 (m), 1261 (m), 1305 (w) cm^{-1}.

Preparation of $[Mo(OEt)_3]_x$. Ethanol (6.9 mmol) was added to $Mo_2(NMe_2)_6$ (1.15 mmol) dissolved in pentane (30 mL). The solution turned reddish brown immediately. After 1 h of stirring, the solvent was removed in vacuo leaving a black solid which sublimed (100–120 °C (10^{-3} Torr)) to give a black solid of empirical formula $Mo(OEt)_3$. Analytical data are given in Table I. A cryoscopic molecular weight determination in benzene gave mol wt 1027 ± 90. The molecular weight appeared to increase with increasing concentration of $[Mo(OEt)_3]_x$ in solution, but the significance of this observation is unknown.

Infrared data (Nujol mull between CsI plates): 350 (w), 452 (w), 587 (s, br), 718 (m), 804 (m), 909 (vs), 1058 (vs, br), 1099 (vs), 1143 (sh), 1261 (m) cm^{-1}. Infrared data (hexane solution in a KBr cell, 500–600 cm^{-1}): 590 (s, br), 536 (sh), 508 (sh) cm^{-1}.

A parent ion at *m/e* 924 in the mass spectrum corresponds to $[Mo(OEt)_3]_4^+$ (based on ^{96}Mo). Peaks at *m/e* 693 ($[Mo(OEt)_3]_3^+$) and 462 ($[Mo(OEt)_3]_2^+$) were also observed.

Reaction of $Mo_2(NMe_2)_6$ and Et_3COH. Triethylcarbinol (7.35 mmol, 1 mL, 10% excess) was added to $Mo_2(NMe_2)_6$ (1.11 mmol) dissolved in hexane (25 mL). After 6 h, the solution turned from yellow to orange. The solution was refluxed for 2 days. The solvent was removed in vacuo to yield an orange-yellow oil which sublimed (130–150 °C (10^{-3} Torr)) to a red-orange waxy solid. ^1H NMR, IR, and mass spectra indicated a mixture of compounds with both $-OCEt_3$ and $-NMe_2$ ligands, possibly of formula $Mo(OCEt_3)_{6-x}(NMe_2)_x$, $x = 2–4$. A parent ion at *m/e* 740 in the mass spectrum corresponded to $Mo_2(OCEt_3)_4(NMe_2)_2^+$ (based on ^{96}Mo). There were also peaks at *m/e* 669 and 598 corresponding to $Mo_2(OCEt_3)_3(NMe_2)_3^+$ and $Mo_2(OCEt_3)_2(NMe_2)_4^+$, respectively (based on ^{96}Mo).

Reaction of $Mo_2(NMe_2)_6$ and $(CF_3)_3COH$. Perfluoro-*tert*-butyl alcohol (14.8 mmol) in benzene (4 mL) was added to $Mo_2(NMe_2)_6$ (1.23 mmol) in hexane (20 mL). The solution turned red-orange immediately. The solution was stirred for 45 min and the solvent was removed in vacuo to give a yellow-orange powder. The yellow-orange solid was recrystallized from toluene to give a mixture of orange and white crystals. The white crystals, $H_2NMe_2(OC(CF_3)_3)$, sublimed (50–60 °C (10^{-3} Torr)). Anal. Calcd for $H_2NMe_2(OC(CF_3)_3)$: C, 25.63; H, 2.87; N, 4.98; F, 60.82. Found: C, 25.72; H, 2.99; N, 5.05; F, 60.58. The remaining orange crystals were recrystallized from toluene. NMR data (^1H and ^{19}F), IR data, and analysis indicated a mixture of compounds containing both $-OC(CF_3)_3$ and $-NMe_2$ ligands. A parent ion at *m/e* 1220 in the mass spectrum corresponds at $Mo_2(OC(CF_3)_3)_4(NMe_2)_2^+$ (based on ^{96}Mo).

Crystal X-Ray Data Collection and Structure Determination. A yellow crystal of $Mo_2(OCH_2CMe_3)_6$, obtained by recrystallization from hexane, measuring about 0.27 × 0.37 × 0.45 mm, was sealed in a glass capillary under argon and examined on a Syntex $P\bar{1}$ four-circle automatic diffractometer. In both ω and θ–2θ scans some peaks were slightly unsymmetrical or showed small satellites, but rotation photographs suggested that the crystal was of tolerable quality for data collection. Despite its imperfections, this crystal was by far the best one among many that were screened.

For calculation of lattice parameters, 15 of the strongest reflections in the range $18 < 2\theta < 25°$ were selected to give a variety of crystal orientations. On the basis of angular settings for these reflections, the refined lattice parameters obtained from the Syntex software package are (Mo Kα, λ 0.71073 Å) $a = 18.160$ (10) Å, $b = 11.051$ (7) Å, $c = 9.956$ (6) Å, $\beta = 104.30$ (4)°, and $V = 1936$ (2) Å^3. For the monoclinic space group $P2_1/n$ with $Z = 2$ and mol wt 757.08, the calculated density is 1.299 g cm^{-3}.

Intensity data were collected at 24 ± 1 °C using graphite-monochromatized Mo Kα radiation and a θ–2θ scan rate varying from 4 to 24°/min, depending on the intensity of the reflection. Background measurements were made at both limits of each scan. Of the 2739 integrated intensities collected in the range $0 < 2\theta(\text{Mo K}\alpha) < 47°$, only those 1588 unique observations with $I > 3\sigma(I)$ were retained as observed data and corrected for Lorentz and polarization effects. Three standard reflections remeasured every 50 data points showed significant but essentially linear decreases in intensity. The experimental structure factors were corrected accordingly. The linear absorption coefficient of this compound is 6.7 cm^{-1} and therefore no absorption correction was applied.

A three-dimensional Patterson map gave the position of the molybdenum atom (the other molybdenum atom is symmetry related by an inversion center). A difference Fourier synthesis based on the refined molybdenum position revealed the rest of the nonhydrogen atoms. All atoms were assigned isotropic thermal parameters and least-squares refinement then gave the discrepancy indices

$$R_1 = \Sigma ||F_o| - F_c|| / \Sigma |F_o| = 0.095$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.116$$

Since the thermal motion of the crystal seemed high, refinement was continued with anisotropic thermal parameters for the molybdenum and oxygen atoms and isotropic thermal parameters for the carbon atoms. Convergence occurred at $R_1 = 0.071$ and $R_2 = 0.088$, and the error in an observation of unit weight was 1.9. The high thermal motion indicated by the vibration amplitudes is consistent with the rather rapid manner in which the intensities of the reflections fell at high 2θ values. No attempt was made to locate the hydrogen atoms. The function minimized in refinement was $\sum w(|F_o| - |F_c|)^2$ where $p = 0.06$ in the previously defined expression for the weights[21,22] and the scattering factors were from ref 23. Corrections for anomalous scattering by the molybdenum atom were taken from Cromer and Liberman.[24]

A final difference map was judged to be free of significant features. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ showed that the original choice for the p parameter used in the calculation of the standard deviation of the intensity (cf. the data reduction program[25]) was satisfactory. No unusual trends were observed in an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of the reflection number, $\lambda^{-1} \sin \theta$, or various classes of indices. A list of observed and calculated structure factors is available.[27]

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Registry No. $Mo_2(O\text{-}t\text{-}Bu)_6$ (coordination), 60764-63-8; $Mo_2(O\text{-}t\text{-}Bu)_6$ (salt), 62509-80-2; $Mo_2(OCMe_2Ph)_6$ (coordination), 62521-19-1; $Mo_2(OCMe_2Ph)_6$ (salt), 62509-79-9; $Mo_2(O\text{-}i\text{-}Pr)_6$ (coordination), 62521-20-4; $Mo_2(O\text{-}i\text{-}Pr)_6$ (salt), 62509-78-8; $Mo_2(OCH_2CMe_3)_6 \cdot 2HNMe_2$, 62521-25-9; $Mo_2(OCH_2CMe_3)_6$ (coordination), 62521-24-8; $Mo_2(OCH_2CMe_3)_6$ (salt), 62506-11-0; $[Mo(OCH_2CMe_3)_3]_x$, 62506-12-1; $Mo_2[OC(CH_3)_2C(CH_3)_2O]_3$, 62586-30-5; $Mo_2(OSiMe_3)_6 \cdot 2HNMe_2$, 62521-21-5; $Mo_2(OSiMe_3)_6$ (coordination), 62521-22-6; $Mo_2(OSiMe_3)_6$ (salt), 62509-77-7; $Mo_2(OSiEt_3)_6$ (coordination), 62521-23-7; $Mo_2(OSiEt_3)_6$ (salt), 62509-76-6; $[Mo(OMe)_3]_x$, 62506-16-5; $[Mo(OEt)_3]_x$, 62506-14-3; $H_2NMe_2(OC(CF_3)_3)$, 62506-17-6; $Mo_2(NMe_2)_6$ (coordination), 51956-20-8; $Mo_2(NMe_2)_6$ (salt), 33851-48-8; Et_3COH, 597-49-9; ^{13}C, 14762-74-4.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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