atoms is again rather different from that in the present case, but the characteristics of the RCCR bridge are very similar. Thus, the torsion, C-C-C, and θ angles are 42, 125, and 55°, as compared to 43.8 (7), 125.3 (6), and 58.6 (3)°, respectively, in the present case. To explain the occurrence of the intermediate (i.e., neither perpendicular nor parallel) orientation of the bridging CH_3CCCH_3 molecule in the Chisholm compound, Calhorda and Hoffmann[14] examined model systems by employing extended Hückel calculations and came to the conclusion that the actual geometry could be attributed to second-order Jahn-Teller distortion from a truly perpendicular geometry.

To understand the deviation of the PhCCPh molecule from the perpendicular orientation to the Nb-Nb bond in our case, both SCF-Xα-Sw and Fenske-Hall molecular orbital calculations have been performed[15] on $Nb_2Cl_4O(PhCCPh)(THF)_4$. The results show that the deviation may also be explained in terms of second-order Jahn-Teller distortion. The detailed results and discussion for this and other compounds will be reported later.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for financial support (Grant No. A-494).

Supplementary Material Available: For **1**-**4**, tables of complete bond distances and angles and anisotropic displacements and figures showing stereoviews of unit cell contents and disorder of the THF solvent molecule (27 pages); tables of calculated and observed structure factors (76 pages). Ordering information is given on any current masthead page.

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Multiply Bonded Dimetal Fluoroalkoxides. 1. Pentafluorophenoxides of Dimolybdenum and Ditungsten

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A series of dimolybdenum and ditungsten pentafluorophenoxides has been prepared by alcoholysis of $M_2(NMe_2)_6$ (M = Mo, W) with pentafluorophenol. $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ has been isolated both from the reaction of $Mo_2(NMe_2)_6$ with 6 equiv of pentafluorophenol (**1a**) and as a disproportionation product with 2 equiv of pentafluorophenol (**1b**). The crystals are different but contain molecules with essentially identical structural features. Eight equivalents of pentafluorophenol react with $Mo_2(NMe_2)_6$ in benzene to yield $Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2 \cdot 2C_6H_6$ (**2**). From reactions with 10 or 12 equiv of pentafluorophenol, only low yields of $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**) and $[(NH_2Me_2)_2][Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4]$ (**4**) have been isolated, both of which are structurally characterized. $W_2(OC_6F_5)_6(NHMe_2)_2$ (**5**) has been prepared from the reaction of 10 equiv of pentafluorophenol with $W_2(NMe_2)_6$ and structurally characterized. Crystallographic parameters of these five alkoxides are as follows. $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (**1a**): space group $C2/c$, $a = 21.511$ (5) Å, $b = 9.057$ (2) Å, $c = 20.581$ (3) Å, $\beta = 103.88$ (1)°, $V = 3892$ (1) Å^3, $Z = 4$. **1b**: space group $Pbcn$, $a = 24.177$ (4) Å, $b = 10.927$ (3) Å, $c = 14.475$ (3) Å, $V = 3824$ (1) Å^3, $Z = 4$. $Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2 \cdot 2C_6H_6$ (**2**) space group $P\bar{1}$, $a = 11.785$ (3) Å, $b = 20.062$ (4) Å, $c = 11.686$ (2) Å, $\alpha = 93.14$ (2)°, $\beta = 91.39$ (2)°, $\gamma = 73.80$ (2)°, $V = 2649$ (1) Å^3, $Z = 2$. $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**): space group $C2/c$, $a = 19.799$ (8) Å, $b = 8.995$ (7) Å, $c = 22.248$ (6) Å, $\beta = 96.54$ (3)°, $V = 3937$ (1) Å^3, $Z = 4$. $[(NH_2Me_2)_2][Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4)]$ (**4**): space group $C2/c$, $a = 13.233$ (2) Å, $b = 11.276$ (3) Å, $c = 25.178$ (4) Å, $\beta = 102.82$ (1)°, $V = 3663$ (1) Å^3, $Z = 4$. $W_2(OC_6F_5)_6(NHMe_2)_2$ (**5**): space group $C2/c$, $a = 10.766$ (4) Å, $b = 22.020$ (7) Å, $c = 19.463$ (5) Å, $\beta = 96.78$ (2)°, $V = 4582$ (3) Å^3, $Z = 4$.

Introduction

Since the discovery of the first $X_3M{\equiv}MX_3$ type compounds (M = Mo, W; X = CH_2SiMe_3),[1,2] the preparation and characterization of additional group 6 dimers possessing an unbridged $\sigma^2\pi^4$ metal-metal bond has continued to be of much interest. $Mo_2(NMe_2)_6$[3] and $W_2(NMe_2)_6$[4] were the next dimers to be characterized in this series, with the hexakis(amides) soon becoming the starting materials used to produce a host of multiply bonded dimolybdenum and ditungsten alkoxides and mixed-ligand compounds.[5] Although $X_3Cr{\equiv}CrX_3$ compounds have been the subject of theoretical studies, no examples are known.[6]

Table I. Structural Features for Triply Bonded Dimolybdenum Compounds[a]

compd	bond dist, Å			ref
	Mo-Mo	Mo-N,O	Mo-Cl,C,S	
$Mo_2(NMe_2)_6$	2.214 [3]	1.98 [1]		3
$Mo_2(OCH_2Bu^t)_6$	2.222 (2)	1.88 [2]		7
$Mo_2(2,6\text{-}Me_2ArO)_4(OPr^i)_2$	2.245 (4)	1.885 [2] (OPr^i) 1.900 [2] (OAr)		9
$Mo_2(2,6\text{-}Me_2ArO)_4(NMe_2)_2$	2.227 (1)	1.94 [2] (OAr) 1.908 (4) (N)		10
$Mo_2(2\text{-}Bu^t\text{-}6\text{-}MeArO)_2(NMe_2)_4$	2.198 (14)	1.99 [2] (OAr) 1.944 [9] (N)		12
$Mo_2Cl_2(NMe_2)_4$	2.201 [1]	1.93 [1]	2.348 [5]	15
$Mo_2Me_2(NMe_2)_4$	2.201 [1]	1.954 [3]	2.175 [2]	17
$Mo_2(CH_2pyMe)_2(NMe_2)_4$	2.204 (1)	1.952 [8]	2.184 [7]	19
$Mo_2Me_2(OBu^t)_4(py)_2$	2.256 (1)	1.92 [6] (OR) 2.349 (6) (py)	2.167 [7]	20
$Mo_2(SBu^t)_2(NMe_2)_4$	2.2171 (1)	1.954 [5]	2.364 [1]	21

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Standard deviation given in square brackets is calculated as equal to $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$ in which Δ_i is the deviation of the *i*th of *n* values from the arithmetic mean of the set.

Alcoholysis of $Mo_2(NMe_2)_6$ results in compounds of the form $Mo_2(OR)_6$ or $Mo_2(OR)_6(NHMe_2)_2$, where R = Pr^i, Bu^t, Bu^tCH_2, Me_2PhC, Me_3Si, or Et_3Si.[7] $NHMe_2$ groups can be displaced by other σ-donors such as NHMeEt, $NHEt_2$, pyridine, or PR_3, and heating the non-siloxide compounds to 60 °C in vacuo removes two $NHMe_2$ groups, leaving $Mo_2(OR)_6$. $W_2(OSiMe_3)_6(NHMe_2)_2$, isolable by the analogous alcoholysis reaction with $W_2(NMe_2)_6$,[8] exhibits far less thermal stability; heating in vacuum

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Table II. Structural Features for Triply Bonded Ditungsten Compounds[a]

compd	bond dist, Å W–W	W–N,O	W–X,C	ref
$W_2(NMe_2)_6$	2.294 (1)	1.98 [1]		4
$W_2Cl_2(NMe_2)_4$	2.285 [2]	1.94 [1]	2.329 [3]	15
$W_2Cl_2(NEt_2)_4$	2.3012 (8)	1.936 [1]	2.332 [8]	14
$W_2Br_2(NEt_2)_4$	2.301 [2]	1.91 [1]	2.482 [6]	16
$W_2I_2(NEt_2)_4$	2.300 [4]	1.94 [2]	2.682 [1]	16
$W_2Me_2(NEt_2)_4$	2.291 (1)	1.967 [2]	2.17 (1)	18
$W_2(OPr^i)_6(py)_2$	2.332 (1)	1.95 [5] (OR) 2.26 [3] (py)		8
$W_2(OPr^i)_6$	2.315 (2)	1.87 [3]		24

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Standard deviation given in square brackets is calculated as equal to $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$ in which Δ_i is the deviation of the *i*th of *n* values from the arithmetic mean of the set.

fails to produce the hexakis(alkoxide) prior to decomposition. However, the $NHMe_2$ groups can be displaced by other σ-donors. Alcoholysis with Me_3COH gives $W_2(OCMe_3)_6$.

Dimolybdenum aryloxides of the types $Mo_2(OAr)_6$, $Mo_2(OAr)_4(NMe_2)_2$, $Mo_2(OAr)_4(O_2CNMe_2)_2$, and $Mo_2(OAr)_4(OPr^i)_2$ have also been reported recently.[9,10] The decreased π-donor capability of the phenoxide groups is manifested by Mo–O bonds that are approximately 0.10 Å longer than the aliphatic alkoxide Mo–O bonds, which typically have lengths of 1.80–1.96 Å. Other aryloxides of dimolybdenum and ditungsten include 3,5-dimethyl phenoxides,[11] 4-fluorophenoxides,[11] 2-*tert*-butyl-6-methylphenoxides,[12] and 2,6-diphenylphenoxides.[13]

Several additional $M_2X_2(NR_2)_4$ and $M_2X_2(OR)_4$ compounds have also been reported. The reaction of WCl_4 with four $LiNEt_2$ moieties yields $W_2Cl_2(NEt_2)_4$.[14] In a more general reaction, $Mo_2(NR_2)_6$ and $W_2(NR_2)_6$ can be converted to $M_2Cl_2(NR_2)_4$ by treatment with Me_3SiCl.[15] These $M_2Cl_2(NR_2)_4$ compounds, in turn, have proven to be useful starting materials for the syntheses of $M_2X_2(NR_2)_4$ X = Br, I,[16] $M_2R'_2(NR_2)_4$,[17-19] $M_2R_2(OR')_4$,[20] and $M_2(SR)_2(NR'_2)_4$[21] (see Tables I and II). In addition, alcoholysis of $M_2R_2(NMe_2)_4$ with a β-hydrogen-containing R group has recently produced the first quadruply bonded $Mo_2(OR)_4L_4$ dimers via β-hydrogen elimination.[22]

Two factors that are known to stabilize these triply bonded metal dimers[5] are ligand-to-metal π-donation and ligand steric bulk. Theoretical calculations support the assignment of one σ (d_{z^2}) and two π (d_{xz}, d_{yz}) bonds joining the two d^3 metals.[23] The empty d_{xy} orbitals remain available for L–M π-donation, which is extensive for alkoxides and amides, as shown by the fact that metal–ligand bond distances for these π-donors are significantly shorter than the single-bond radii of the atoms involved.

Table III. pK_a Values for Fluoro Alcohols in Comparison to Those for Conventional Alcohols[25]

alcohol	pK_a	fluoro alcohol	pK_a
CH_3CH_2OH	15.9	CF_3CH_2OH	12.8
$(CH_3)_2CHOH$	17.1	$(CF_3)_2CHOH$	9.30
$(CH_3)_3COH$	19.2	$(CF_3)_3COH$	5.4
C_6H_5OH	9.9	C_6F_5OH	5.52

The importance of steric factors is attributable to the fact that sterically demanding groups prevent oligomerization by inhibiting the formation of additional intermolecular M–M or M–L bonds. An illustration of the importance of steric bulk with regard to the nuclearity of the product is seen in the alkoxides of dimolybdenum and ditungsten. The $[M(OR)_3]_n$ compounds are dinuclear if R = Bu^t or Bu^tCH_2, but tetranuclear when R = Me or Et.[5] Interestingly, where R = Pr^i, the molybdenum alkoxide is dimeric, whereas an equilibrium between the dimeric and tetrameric isopropoxide is observed for the tungsten analogue in solution.[24]

The originally reported hexakis((trimethylsilyl)methyl)dimolybdenum and ditungsten compounds[1,2] remain the only known dimers of this type that do not possess ligands which are capable of π-donation and are thus solely dependent on steric bulk for stability. We became interested in synthesizing dinuclear alkoxides where the alkoxide ligands are poor π-donors with the expectation that these compounds should exhibit relatively long M–O bond distances and possibly other unusual chemical and structural characteristics.

We selected highly fluorinated alkoxides for this purpose. These anions are far less π-donating than conventional alkoxides or substituted aryloxides, and like carboxylate anions, they possess a C–O bond having multiple-bond character while remaining weakly basic (see Table III).[25] We now report our findings with regard to the alcoholysis of the $M_2(NMe_2)_6$ (M = Mo, W) compounds with pentafluorophenol.

Experimental Section

General Procedures. All manipulations were conducted by using standard Schlenk, vacuum-line, and drybox techniques. A blanket of predried argon was used over each reaction. All solvents were predried over molecular sieves, then refluxed over NaK (benzene, toluene, THF, and hexane) or P_2O_5 (CH_2Cl_2) for at least 24 h prior to use, and finally distilled under a blanket of dry nitrogen. All glassware and syringes were oven dried.

$MoCl_5$, WCl_6, and C_6F_5OH were purchased from Alfa, $Mo(CO)_6$ and $W(CO)_6$ were purchased from Pressure Chemical, *n*-butyllithium and $ClMgCH_2SiMe_3$ were purchased from Aldrich, and $NHMe_2$ was purchased from Matheson. Each was used as received. $LiNMe_2$ was synthesized by the condensation of $NHMe_2$ into a 1.6 M hexane solution of *n*-butyllithium at −78 °C. $MoCl_3$[26] and WCl_4[27] were prepared according to literature methods and used to synthesize $Mo_2(NMe_2)_6$[28] and $W_2(NMe_2)_6$.[4] $Mo_2(CH_2SiMe_3)_6$ was prepared by the reaction of $MoCl_3$ with 3 equiv of $ClMgCH_2SiMe_3$ in THF, followed by sublimation at 135 °C in vacuo.

^1H NMR spectra were recorded on a Varian XL-200 spectrometer, and infrared spectra were obtained by using a Perkin-Elmer 783 spectrophotometer. Microanalyses were provided by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (1a). C_6F_5OH (242 mg, 1.31 mmol) was dissolved in 25 mL of benzene and added to $Mo_2(NMe_2)_6$ (100 mg, 0.219 mmol). The solution immediately turned deep red, and a pale white precipitate was observed. After being stirred overnight, the red solution was filtered and dried in a vacuum and the resulting solid washed with hexane, producing a yellow-brown powder in

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62% yield. ^{1}H NMR (benzene-d_6): δ 6.42 (m, 1), 4.34 (s, 3), 2.52 (s, 3), 2.37 (d, 3), 2.18 (d, 3). Infrared (KBr/Nujol): 1507 (s), 1378 (s), 1019 (s), 995, 992, 900 (br) cm^{-1}.

Isolation of $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (1b). C_6F_5OH (81 mg, 0.44 mmol) was dissolved in 20 mL of toluene and added to $Mo_2(NMe_2)_6$ (100 mg, 0.219 mmol). The resulting red solution was stirred overnight, and the product was dried in vacuum. Heating to 120 °C in vacuum resulted in the sublimation of ca. 45 mg of $Mo_2(NMe_2)_6$.

The reaction was repeated using 10 mL of benzene and layering the reaction solution with 10 mL of hexane. After several days, a yellow-brown crystal of **1b** measuring ca. 2 × 2 × 1 mm of crystallographic quality had formed.

Synthesis of $Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2{\cdot}2C_6H_6$ (2). C_6F_5OH (325 mg, 1.77 mmol) was dissolved in 10 mL of benzene and added to $Mo_2(NMe_2)_6$ (100 mg, 0.219 mmol). After the resulting deep red solution was stirred for 30 min, it was allowed to sit overnight, during which time a pale white precipitate formed. The solution was then filtered and allowed to crystallize at room temperature over the course of several days, with approximately 150 mg of product resulting. ^{1}H NMR (benzene-d_6): δ 5.40 (m, 2), 4.90 (s, 3), 2.75 (d, 6), 2.70 (s, 3), 2.18 (d, 6). Infrared (KBr/Nujol): 1515, 1510, 1315, 1170 (br), 1025 (br), 1005 (br), 985, 762, 690 cm^{-1}.

Isolation of $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (3). C_6F_5OH (410 mg, 2.23 mmol) was dissolved in 20 mL of toluene and added to $Mo_2(NMe_2)_6$ (100 mg, 0.219 mmol). The resulting deep red solution was stirred overnight, filtered to remove a pale white precipitate, and dried in vacuum. The red-brown solid was then washed with three 15-mL portions of hexane and redissolved in 10 mL of CH_2Cl_2, from which 50 mg of red crystals was obtained after several days at room temperature.

In a second reaction, C_6F_5OH (410 mg, 2.23 mmol) was dissolved in 10 mL of benzene containing pyridine (36 μL, 0.446 mmol) and added to $Mo_2(NMe_2)_6$ (100 mg, 0.219 mmol). The red solution was stirred overnight, filtered, and allowed to crystallize for several days at room temperature, during which the red crystals formed (yield ca. 75 mg).

Isolation of $[(NH_2Me_2)_2][Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4]$ (4). C_6F_5OH (500 mg, 2.72 mmol) was dissolved in 20 mL of benzene and added to $Mo_2(NMe_2)_6$ (100 mg, 0.219 mmol). The resulting red solution was stirred overnight, filtered, and allowed to crystallize at room temperature. Over the course of several days, many clusters of small red crystals formed, but none was of crystallographic quality. A small quantity of yellow crystals was also present, and one of these was selected and successfully characterized crystallographically.

Preparation of $W_2(OC_6F_5)_6(NHMe_2)_2$ (5). C_6F_5OH (590 mg, 3.21 mmol) was dissolved in 10 mL of benzene and added to $W_2(NMe_2)_6$ (200 mg, 0.32 mmol). Over the course of 10 min, the solution turned deep red with the formation of an insoluble pale white byproduct. The solution was stirred for 2 h and then allowed to settle overnight. The red solution was separated from the pale white precipitate by decanting to a separate Schlenk tube. Several days later, purple crystals were obtained in 60% yield. These crystals were found to be insoluble in all common organic solvents. Infrared (KBr/Nujol): 1652, 1500, 1489, 1310 (s), 1200, 1190, 1065, 1050 (br), 1020, 905 (br), 700 (s), 672 cm^{-1}.

Reaction of $Mo_2(CH_2SiMe_3)_6$ with C_6F_5OH. C_6F_5OH (0.32 g, 1.74 mmol) was dissolved in 50 mL of benzene and added to $Mo_2(CH_2SiMe_3)_6$ (200 mg, 0.28 mmol). The solution was stirred for 48 h during which time the solution color changed from yellow to red. The benzene was removed in vacuo, leaving behind a red-brown powder. After the powder was washed repeatedly with hexane and thoroughly dried, 235 mg of pure product was isolated. Infrared data (KBr/Nujol): 1515, 1505, 1312, 1170, 1025, 995, 900 (w), 685 (w), 675 (w) cm^{-1}.

Synthesis of $[NH_2Me_2][OC_6F_5]$ (6). An excess of $NHMe_2$ (ca. 20 mL) was condensed into a flask containing C_6F_5OH (500 mg, 2.72 mmol) at −78 °C. An insoluble white product formed quantitatively and was purified by removing all volatiles in vacuo for 3 h at room temperature. Anal. Calcd: C, 41.93; H, 3.52. Found: C, 41.71; H, 3.60. Infrared (KBr/Nujol): 1985, 1945, 1885, 1582, 1504, 1300, 1100, 905, 805, 722 cm^{-1}.

X-ray Crystallography. Because of the air and moisture sensitivity typical of these compounds, all crystals were isolated under a blanket of thoroughly dried and degassed mineral oil. Selected crystals were wedged into thin-walled Lindemann glass capillaries and sealed in a matrix of epoxy cement. Geometric and intensity data were gathered by automated four-circle diffractometers using routine procedures. Important crystal data and data-collection parameters are provided in Table IV. During data collection for each sample, monitor reflections were measured at regular intervals, in the usual check for sample and instrument stability. For each crystal, normal-beam axial photographs were used to verify the lattice dimensions and Laue group. In all cases except that of compound **2**, azimuthal scans of several reflections with Eulerian angle χ near 90° were used as the basis of empirical absorption corrections. We found it necessary to correct one set of measurements for decay: the monitor reflections from the sample of compound **1a** decreased in intensity by an average of 9.8% during 49 h of X-ray exposure.

The reduction of data and the structure solutions and refinements were conducted on the VAX 11/780 computer in the Department of Chemistry, Texas A&M University, and on the Laboratory for Molecular Structure and Bonding Local Area VAX Cluster. Space group ambiguities (i.e., *Cc* vs. *C*2/*c* and *P*1 vs. $P\bar{1}$) were resolved by successful refinement. For each structure, the position of the unique transition-metal atom(s) was determined either through Patterson synthesis (for **1a**) or from direct methods (for all of the others). The structures were developed and refined in sequences of difference Fourier maps and least-squares refinements. A summary of data relevant to the final least-squares refinements is given in Table IV.

Results

Synthesis and Physical Properties. $Mo_2(NMe_2)_6$ reacts immediately with C_6F_5OH. At room temperature, these reactions form deep red solutions, and if sufficient alcohol is present, $[NH_2Me_2][OC_6F_5]$ precipitates as a byproduct. This is the white or off-white precipitate that was initially formed in each case.

The room temperature addition of 6 equiv of pentafluorophenol to $Mo_2(NMe_2)_6$ in benzene yields $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (**1**) as shown in reaction 1.

$$Mo_2(NMe_2)_6 + 6C_6F_5OH \rightarrow Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2 + 2[NH_2Me_2][OC_6F_5] \quad (1)$$

The infrared spectrum of the white precipitate isolated from the reaction mixture and that of an authentic sample of $[NH_2Me_2][OC_6F_5]$ were identical, and the results of an elemental analysis were consistent with the composition $[NH_2Me_2][OC_6F_5]$. Dimethylammonium pentafluorophenoxide is completely insoluble in all common organic solvents, precluding any additional spectroscopic study.

$Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ exhibits a distinctive ^{1}H NMR spectrum, having diastereotopically split doublets from the dimethylamine donors (δ 2.37, 2.18), two widely separated singlets arising from the amide protons (δ 4.34, 2.52), and an amine proton broadened by quadrupolar coupling (δ 6.42). This separation due to the anisotropy of the Mo≡Mo bond at room temperature distinguishes **1** from $Mo_2(NMe_2)_6$, which exhibits a single amido methyl peak until the solution is cooled to −20 °C, where rotation about the Mo—N bond of $Mo_2(NMe_2)_6$ is slowed enough for the two methyl groups to become magnetically nonequivalent. The dimethylamine groups, unlike those observed among conventional alkoxides of dimolybdenum, show no sign of lability. $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ decomposes when heated above 100 °C in vacuo.

Addition of only 2 equiv of pentafluorophenol to $Mo_2(NMe_2)_6$ does not yield the disubstituted product $Mo_2(OC_6F_5)_2(NMe_2)_4(NHMe_2)_2$, but rather a mixture of the dimolybdenum starting material and **1**, as shown in reaction 2. $Mo_2(NMe_2)_6$ is isolable from the dried reaction mixture by sublimation, and $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (**1b**) readily crystallizes from the reaction solution.

$$Mo_2(NMe_2)_6 + 2C_6F_5OH \rightarrow \tfrac{1}{2}Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2 + \tfrac{1}{2}Mo_2(NMe_2)_6 + NHMe_2 \quad (2)$$

$Mo_2(NMe_2)_6$ reacted with 8 equiv of C_6F_5OH in benzene to yield $[(C_6F_5O)_4Mo{\equiv}Mo(OC_6F_5)(NMe_2)(NHMe_2)_2]{\cdot}2C_6H_6$ (**2**) as shown in reaction 3. The amide peaks are again observed as two singlets, separated by 2.20 ppm, with the dimethylamine methyl peaks showing the expected diastereotopic splitting. Of particular interest, for this mixed-valence dimer, is that it has a metal–metal bond length of 2.214 (1) Å, entirely consistent with a bond order of 3. We shall discuss this in more detail later.

$$Mo_2(NMe_2)_6 + 8C_6F_5OH \rightarrow Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2 + 3[NH_2Me_2][OC_6F_5] \quad (3)$$

$Mo_2(NMe_2)_6$ reacts with ten equivalents of pentafluorophenol to produce a variety of molybdenum-containing products. Two have been isolated, $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**) and

Table IV. Crystal Data for $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (**1a**,**b**), $Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2 \cdot 2C_6H_6$ (**2**), $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**), $[(NH_2Me_2)_2][Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4]$ (**4**), $W_2(OC_6F_5)_6(NHMe_2)_2$ (**5**)

	1a	**1b**	**2**	**3**	**4**	**5**
formula	$Mo_2O_4N_4C_{32}H_{26}F_{20}$	$Mo_2O_4N_4C_{32}H_{26}F_{20}$	$Mo_2O_5N_3C_{48}H_{32}F_{25}$	$Mo_2O_4N_4C_{32}H_{28}F_{20}$	$Mo_2O_8N_2C_{28}H_{16}F_{20}$	$W_2O_6N_2C_{40}H_{14}F_{30}$
fw	1102.44	1102.44	1397.64	1104.45	1080.30	1556.22
space group	*C2/c*	*Pbcn*	$P\bar{1}$	*C2/c*	*C2/c*	*C2/c*
syst abs	*hkl*; $h + k \neq 2n$ *h0l*; $h, l \neq 2n$ *0kl*; $k \neq 2n$	*0kl*; $k \neq 2n$ *h0l*; $l \neq 2n$ *hk0*; $h + k \neq 2n$		*hkl*; $h + k \neq 2n$ *h0l*; $h, l \neq 2n$ *0kl*; $k \neq 2n$	*hkl*; $h + k \neq 2n$ *h0l*; $h, l \neq 2n$ *0kl*; $k \neq 2n$	*hkl*; $h + k \neq 2n$ *h0l*; $l \neq 2n$ *0k0*; $k \neq 2n$
a, Å	21.511 (5)	24.177 (4)	11.785 (3)	19.799 (8)	13.233 (2)	10.766 (4)
b, Å	9.057 (2)	10.927 (3)	20.062 (4)	8.995 (7	11.276 (3)	22.020 (7)
c, Å	20.581 (3)	14.475 (3)	11.686 (2)	22.248 (6)	25.178 (4)	19.463 (5)
α, deg			93.14 (2)			
β, deg	103.88 (1)		91.39 (2)	96.54 (3)	102.82 (1)	96.78 (2)
γ, deg			73.80 (2)			
V, $Å^3$	3892 (1)	3824 (1)	2649 (1)	3937 (1)	3663 (1)	4582 (3)
Z	4	4	2	4	4	4
d_{calcd}, g/cm^3	1.881	1.915	1.752	1.863	1.959	2.256
cryst size, mm^3	0.50 × 0.50 × 0.20	0.50 × 0.50 × 0.50	0.50 × 0.30 × 0.30	0.15 × 0.20 × 0.20	0.25 × 0.25 × 0.25	0.40 × 0.30 × 0.15
μ(Mo Kα), cm^{-1}	7.632	7.769	5.937	7.547	8.149	54.98
data collcn instrum	Nicolet P3/F	Enraf-Nonius Cad-4S	Nicolet P3/F equivalent	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC5R
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)
orientation reflcns: no.; range (2θ), deg	25; $20.3 \leq 2\theta \leq 29.6$	25; $30.1 \leq 2\theta \leq 33.7$	20; $25.3 \leq 2\theta \leq 34.8$	25; $14.0 \leq 2\theta \leq 24.0$	25; $25.2 \leq 2\theta \leq 33.8$	24; $19.3 \leq 2\theta \leq 39.8$
temp, °C	20 ± 2	20 ± 2	20 ± 2	20 ± 2	20 ± 2	20 ± 2
scan method	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω	ω
data calcn range (2θ), deg	$4 \leq 2\theta \leq 45$	$4 \leq 2\theta \leq 54$	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 55$
no. of unique data	2941	4665	10136	3945	3667	5832
tot. no. of data with $F_o^2 > 3\sigma(F_o^2)$	1889	2458	4192	1219	1245	2691
no. of params refined	280	280	748	200	271	361
transm factors: max; min	0.9998; 0.8731	0.9996; 0.9275	0.9981; 0.9474	1.0000; 0.8595	1.0000; 0.8788	1.0000; 0.6921
R^a	0.04169	0.04276	0.05051	0.06746	0.04904	0.04717
R_w^b	0.05651	0.05579	0.06120	0.08487	0.06224	0.05753
quality-of-fit indicator^c	1.291	1.598	1.119	1.592	1.210	1.149
largest shift/esd, final cycle	0.00	0.04	0.27	0.34	0.05	0.05
largest peak, e/$Å^3$	0.412	0.878	0.539	0.552	0.174	0.872

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

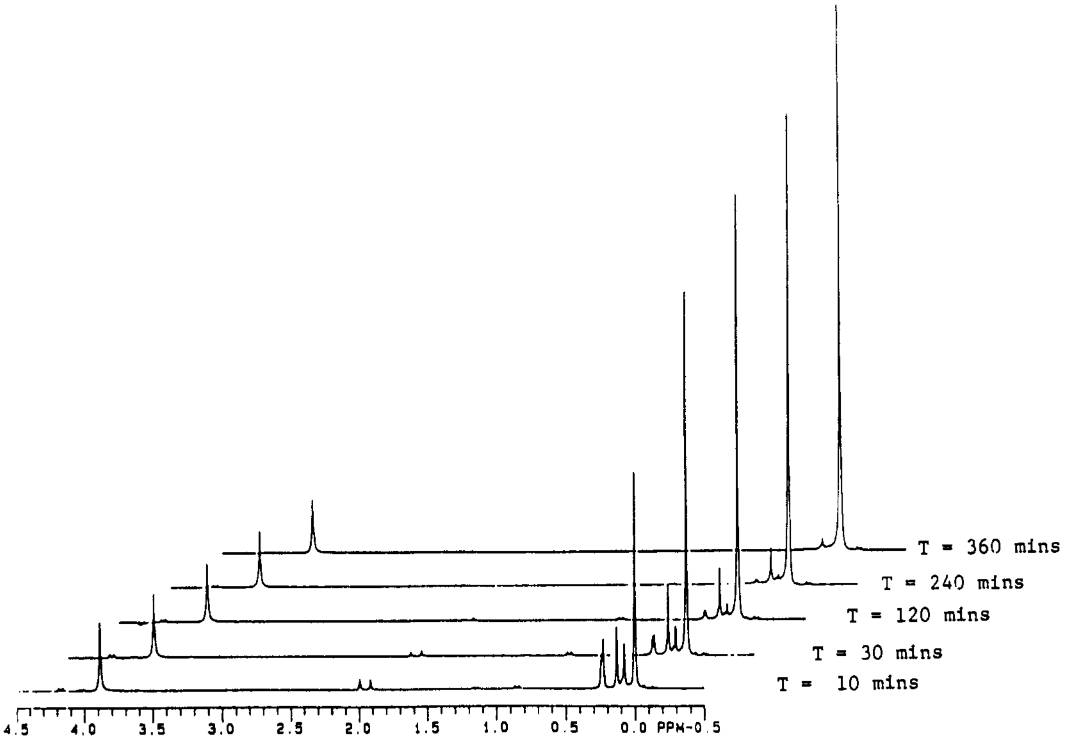

Figure 1. ^1H NMR spectra as a function of time for the reaction mixture of C_6F_5OH and $Mo_2(CH_2SiMe_3)_6$ in 8:1 mole ratio.

$[NH_2Me_2][Mo_2(OC_6F_5)_6(NHMe_2)_2]$.[29] The latter possesses a formal bond order of 3.5, but inadequate crystal quality has thus far prevented a complete structure refinement. Compound **3** has a bond order of 4. While no triply bonded dimolybdenum species has been isolated from this reaction to date, the analogous reaction with $W_2(NMe_2)_6$ results in a 60% yield of $W_2(OC_6F_5)_6(NHMe_2)_2$ (**5**), which will be further discussed later. Attempts to identify spectroscopically additional products in the molybdenum reaction have been frustrated by separation problems and the apparent presence of intractable amine-containing contaminants. Although the tungsten reaction gives good reason to suspect $Mo_2(OC_6F_5)_6(NHMe_2)_2$ may also be formed in this reaction, we have been unable to verify this.

The addition of ≥12 equiv of C_6F_5OH to $Mo_2(NMe_2)_6$ results in a characteristically deep red solution and precipitation of dimethylammonium pentafluorophenoxide. Traces of contaminants containing dimethylamine are consistently present in NMR spectra, regardless of the care taken to remove such impurities. All attempts to crystallize $Mo_2(OC_6F_5)_6$ have given an insoluble, red, polycrystalline material. One particular trial produced a high yield of this red compound together with a few yellow cubic crystals interspersed throughout the red product. One such crystal was isolated and crystallographically characterized as $[NH_2Me_2]_2[Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4]$, apparently the result of trace quantities of moisture in this very hygroscopic fluoroalcohol.

The alcoholysis of $Mo_2(CH_2SiMe_3)_6$ with $\geq 6C_6F_5OH$ was performed in an effort to eliminate problems with dimethylamine impurities (see reaction 4). Figure 1 shows a ^1H NMR stack

$$Mo_2(CH_2SiMe_3)_6 + 6C_6F_5OH \rightarrow Mo_2(OC_6F_5)_6 + 6SiMe_4 \quad (4)$$

plot of the reaction of $Mo_2(CH_2SiMe_3)_6$ (δ 2.04, 0.27) and an excess of C_6F_5OH (δ 3.89), resulting in "$Mo_2(OC_6F_5)_6$" and $SiMe_4$ (δ 0.0). The reaction is quantitative, with the isolated product exhibiting an infrared spectrum consistent with previously observed spectra from dimolybdenum and ditungsten pentafluorophenoxide compounds.

We believe this red compound is $Mo_2(OC_6F_5)_6$, since previous trends in reactivity suggest the dimer to be the most likely product. The steric nature of the pentafluorophenoxo groups and the known reluctance of fluoroalkoxide groups to act as bridging ligands[25] argue against oligomerization. A monomeric structure would also be unlikely since no alcoholysis reaction involving $Mo_2(NMe_2)_6$ has ever observed to cleave a Mo≡Mo bond. Efforts are continuing to obtain single crystals of this product.

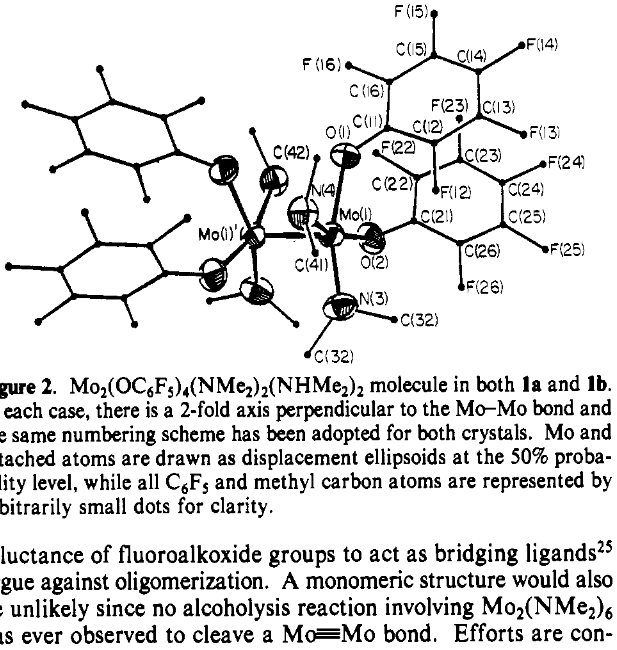

Figure 2. $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ molecule in both **1a** and **1b**. In each case, there is a 2-fold axis perpendicular to the Mo–Mo bond and the same numbering scheme has been adopted for both crystals. Mo and attached atoms are drawn as displacement ellipsoids at the 50% probability level, while all C_6F_5 and methyl carbon atoms are represented by arbitrarily small dots for clarity.

$W_2(NMe_2)_6$ reacts with 10 equiv of C_6F_5OH over the course of 10 min to produce a deep red solution and $[NH_2Me_2][OC_6F_5]$ (see reaction 5). Purple, air-stable crystals of $W_2(OC_6F_5)_6(NHMe_2)_2$ were isolated from the filtered reaction mixture in 60% yield, and a crystal structure has been successfully completed. After exposure to air for over 1 week, these crystals show no sign of decomposition, even after grinding.

$$W_2(NMe_2)_6 + 10C_6F_5OH \rightarrow W_2(OC_6F_5)_6(NHMe_2)_2 + 4[NH_2Me_2][OC_6F_5] \quad (5)$$

Molecular Structures

$Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (1a, 1b). Two crystal structures of this compound have been successfully completed, one in space group *C*2/*c* (**1a**) and one in space group *Pbcn* (**1b**). In each case the molecule resides on a crystallographic 2-fold axis. Figure 2 shows the molecule and defines an atom numbering scheme common to both structures. All bond distances and angles

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[29] Abbott, R. G. Ph.D. Thesis, Texas A&M University, 1988.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (**1a,b**)[a]

bonding param	**1a**	**1b**
Mo(1)-Mo(1)	2.218 (1)	2.222 (1)
Mo(1)-O(1)	2.073 (4)	2.048 (4)
Mo(1)-O(2)	2.060 (4)	2.072 (4)
Mo(1)-N(3)	1.922 (5)	1.931 (5)
Mo(1)-N(4)	2.267 (5)	2.268 (4)
Mo(1)-Mo(1)-O(1)	98.5 (1)	100.0 (1)
Mo(1)-Mo(1)-O(2)	100.7 (1)	99.0 (1)
Mo(1)-Mo(1)-N(3)	102.2 (2)	101.4 (1)
Mo(1)-Mo(1)-N(4)	92.4 (2)	92.8 (1)
O(1)-Mo(1)-O(2)	82.9 (2)	84.3 (2)
O(1)-Mo(1)-N(3)	158.8 (2)	157.4 (2)
O(1)-Mo(1)-N(4)	84.3 (2)	84.0 (2)
O(2)-Mo(1)-N(3)	97.4 (2)	99.2 (2)
O(2)-Mo(1)-N(4)	162.9 (2)	164.6 (2)
N(3)-Mo(1)-N(4)	90.5 (2)	88.0 (2)
O(1)-C(11)	1.314 (9)	1.324 (7)
O(2)-C(21)	1.314 (8)	1.346 (7)
N(3)-C(31)	1.492 (10)	1.491 (8)
N(3)-C(32)	1.502 (11)	1.479 (8)
N(4)-C(41)	1.467 (11)	1.505 (8)
N(4)-C(42)	1.462 (11)	1.496 (8)
Mo(1)-O(1)-C(11)	133.1 (4)	134.9 (4)
Mo(1)-O(2)-C(21)	134.6 (4)	126.0 (3)
Mo(1)-N(3)-C(31)	135.4 (5)	135.1 (4)
Mo(1)-N(3)-C(32)	113.9 (5)	114.7 (4)
C(31)-N(3)-C(32)	110.7 (6)	109.8 (5)
Mo(1)-N(4)-C(41)	115.9 (5)	117.7 (3)
Mo(1)-N(4)-C(42)	116.6 (5)	115.5 (4)
C(41)-N(4)-C(42)	108.4 (7)	108.6 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

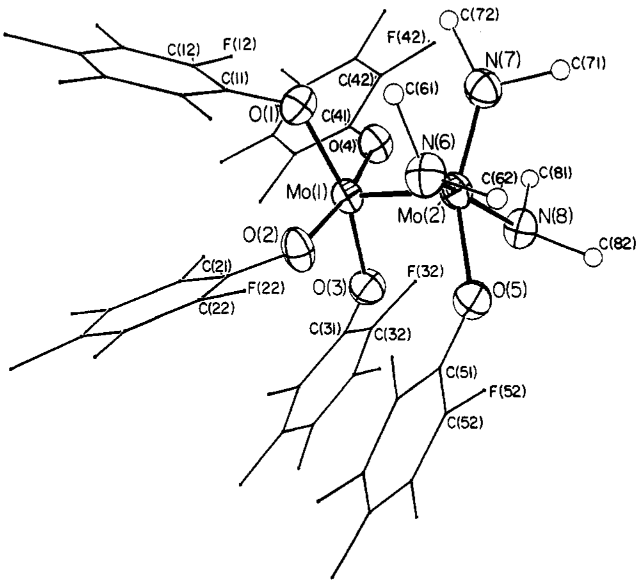

Figure 3. $Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2$ molecule (**2**), with inner atoms represented by displacement ellipsoids at the 30% probability level and the other atoms by points of arbitrarily small size for clarity.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2 \cdot 2C_6H_6$ (**2**)[a]

Mo(1)-Mo(2)	2.214 (1)	O(2)-C(21)	1.341 (10)
Mo(1)-O(1)	2.003 (7)	O(3)-C(31)	1.337 (12)
Mo(1)-O(2)	2.009 (5)	O(4)-C(41)	1.323 (11)
Mo(1)-O(3)	1.965 (7)	O(5)-C(51)	1.326 (12)
Mo(1)-O(4)	1.995 (6)	N(6)-C(61)	1.50 (2)
Mo(2)-O(5)	2.027 (7)	N(6)-C(62)	1.525 (14)
Mo(2)-N(6)	2.224 (7)	N(7)-C(71)	1.491 (13)
Mo(2)-N(7)	1.918 (9)	N(7)-C(72)	1.487 (15)
Mo(2)-N(8)	2.251 (7)	N(8)-C(81)	1.496 (13)
O(1)-C(11)	1.341 (12)	N(8)-C(82)	1.512 (13)
O(2)-Mo(1)-O(4)	170.0 (3)	Mo(1)-O(2)-C(21)	132.9 (6)
O(3)-Mo(1)-O(4)	90.8 (3)	Mo(1)-O(3)-C(31)	145.6 (6)
Mo(1)-Mo(2)-O(5)	102.2 (2)	Mo(1)-O(4)-C(41)	139.5 (6)
Mo(1)-Mo(2)-N(6)	100.6 (2)	Mo(2)-N(8)-C(82)	110.6 (5)
Mo(1)-O(1)-C(11)	127.8 (7)	C(81)-N(8)-C(82)	109.1 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

in the two molecules are essentially identical, as can be seen in Table V.

The Mo≡Mo bond lengths of **1a** and **1b** average to 2.220 [1] Å, which does not differ significantly from those of other triply bonded dimolybdenum compounds. However, the average Mo-O bond length is 2.063 [6] Å, which is 0.12 Å longer than is typical for Mo-OAr bonds and 0.16 Å longer than the average Mo-O bond for aliphatic alkoxides. Although no hydrogen atoms were located in the difference maps, two criteria clearly distinguish amido groups from amines. The Mo-N bond lengths for the neutral dimethylamine ligands are far greater than those of the anionic π-donating amides, and the angles about the nitrogen atoms (Mo-N-C, Mo-N-C′, and C-N-C′) reflect the hybridization at the atom. The sum of the sp^2 amide nitrogen angles is 360°, whereas the angular sum about the sp^3-hybridized amine nitrogen atoms is consistently about 340°.

As can be seen in Figure 2, the rotational conformation of the molecule is staggered. The two (equivalent) $NHMe_2$ groups are so oriented that the N-H bond is directed between the two oxygen atoms on the opposite metal atom. The Mo-Mo triple bond, of course, is essentially cylindrical and plays no part in determining the rotational conformation. The nonbonded repulsions strongly favor a staggered conformation. It is uncertain if this conformation is further stabilized by the formation of two bifurcated hydrogen bonds, since the N(4)-O(1)′ and N(4)-O(2)′ distances are 3.292 (6) and 2.940 (6) Å; only the latter is within the accepted range for hydrogen bonding.

$Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2 \cdot 2C_6H_6$ (2). This unsymmetrical molecule crystallizes in the triclinic space group $P\bar{1}$, with all atoms on general positions. One molybdenum atom, Mo(1), is bonded to four pentafluorophenoxide groups, while the other, Mo(2), is bonded to one pentafluorophenoxo, one amido and two amine groups, as shown in Figure 3. The principal bond lengths and angles are listed in Table VI. Both metal centers have a distorted-square-pyramidal geometry, with Mo-O distances reflecting the probable effective oxidation states of the molybdenum atoms. The Mo(2)-O bond distance of 2.027 (7) Å is greater than any of the Mo(1)-O distances, which are in the range 1.965 (7)-2.009 (5) Å. The Mo-NMe_2 bond length of 1.918 (9) Å is extremely short, particularly for an anionic ligand bonded to a formally *divalent* molybdenum atom. This bound amido group demonstrates the strong trans influence that both we and others[30] have observed for pentafluorophenoxide ligands. The Mo-Mo bond length of 2.214 (1) Å is consistent with previously reported triple bonds of homovalent dimolybdenum species. In accord with the presence of a triple bond between the metal atoms, the rotational conformation is staggered. The orientation of the $NHMe_2$ ligand about the Mo-N bond is such that no hydrogen bond is formed.

Although **2** is clearly an unexpected product, our isolation and characterization of the analogous hexafluoroisopropoxide dimer from the reaction of $Mo_2(NMe_2)_6$ with 8 equiv of hexafluoro-2-propanol shows that this reaction may be a general one for fluoroalcohols with $Mo_2(NMe_2)_6$.[31]

$Mo_2(OC_6F_5)_4(NHMe_2)_4$ (3). Low yields of the dimolybdenum(II) compound $Mo_2(OC_6F_5)_4(NHMe_2)_4$ were obtained through the alcoholysis of $Mo_2(NMe_2)_6$ with 10 equiv of C_6F_5OH. This compound crystallizes in space group *C*2/*c* with the molecule residing on a 2-fold axis. The molecule is shown in Figure 4, and Table VII lists the principal dimensions. The Mo-Mo bond length of 2.140 (2) Å falls within the expected range for a quadruply bonded dimolybdenum compound, and all ligands

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(30) Brinckman, F. E.; Johannesen, R. B.; Handy, L. B. *J. Fluorine Chem.* **1971/1972**, 493.

(31) Abbott, R. G.; Cotton, F. A.; Falvello, L. R. Unpublished work.

Table VII. Selected Bond Distances (Å) and Angles (deg) for $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**)[a]

Mo(1)–Mo(1)	2.140 (2)	O(4)–C(41)	1.31 (2)
Mo(1)–O(2)	2.081 (11)	N(1)–C(11)	1.48 (2)
Mo(1)–O(4)	2.060 (12)	N(1)–C(12)	1.49 (3)
Mo(1)–N(1)	2.244 (13)	N(3)–C(31)	1.51 (3)
Mo(1)–N(3)	2.243 (13)	N(3)–C(32)	1.52 (3)
O(2)–C(21)	1.32 (2)		
Mo(1)–Mo(1)–O(2)	98.2 (3)	N(1)–Mo(1)–N(3)	164.3 (5)
Mo(1)–Mo(1)–O(4)	98.2 (3)	Mo(1)–O(2)–C(21)	141 (1)
Mo(1)–Mo(1)–N(1)	98.3 (3)	Mo(1)–O(4)–C(41)	140 (1)
Mo(1)–Mo(1)–N(3)	97.4 (3)	Mo(1)–N(1)–C(11)	118 (1)
O(2)–Mo(1)–O(4)	163.6 (4)	Mo(1)–N(1)–C(12)	117 (1)
O(2)–Mo(1)–N(1)	87.1 (5)	C(11)–N(1)–C(12)	108 (1)
O(2)–Mo(1)–N(3)	91.0 (5)	Mo(1)–N(3)–C(31)	115 (1)
O(4)–Mo(1)–N(1)	90.7 (5)	Mo(1)–N(3)–C(32)	116 (1)
O(4)–Mo(1)–N(3)	86.7 (5)	C(31)–N(3)–C(32)	107 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

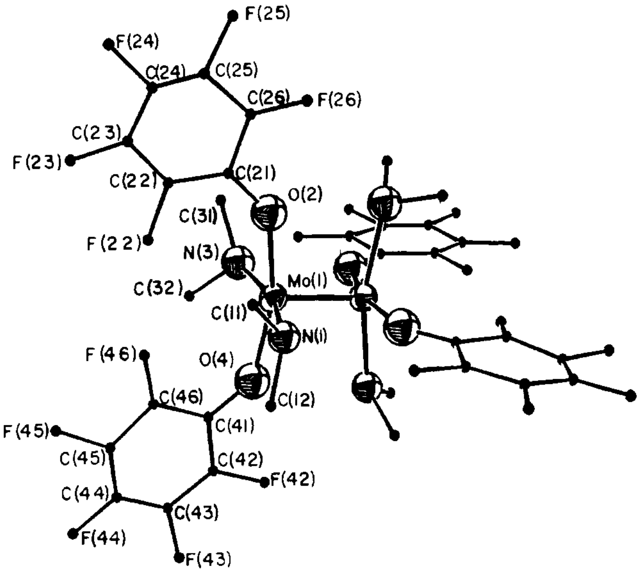

Figure 4. $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**) molecule with inner atoms represented by displacement ellipsoids at the 50% probability level and others by points of arbitrarily small size for clarity.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $[(NH_2Me_2)_2][Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4]$ (**4**)[a]

Mo(1)–Mo(1)	2.556 (1)	Mo(1)–O(4)	1.681 (9)
Mo(1)–O(1)	1.903 (6)	O(2)–C(21)	1.31 (1)
Mo(1)–O(1)	1.920 (7)	O(3)–C(31)	1.32 (1)
Mo(1)–O(2)	2.035 (8)	N(1)–C(1)	1.43 (2)
Mo(1)–O(3)	2.012 (8)	N(1)–C(2)	1.43 (2)
Mo(1)–Mo(1)–O(1)	48.3 (2)	O(1)–Mo(1)–O(3)	83.2 (3)
Mo(1)–Mo(1)–O(1)	47.8 (2)	O(1)–Mo(1)–O(4)	107.1 (4)
Mo(1)–Mo(1)–O(2)	131.1 (2)	O(2)–Mo(1)–O(3)	77.2 (3)
Mo(1)–Mo(1)–O(3)	127.0 (2)	O(2)–Mo(1)–O(4)	105.0 (4)
Mo(1)–Mo(1)–O(4)	103.6 (3)	O(3)–Mo(1)–O(4)	110.1 (4)
O(1)–Mo(1)–O(1)	91.6 (3)	Mo(1)–O(1)–Mo(1)	83.9 (2)
O(1)–Mo(1)–O(2)	83.8 (3)	Mo(1)–O(2)–C(21)	124.0 (7)
O(1)–Mo(1)–O(3)	135.2 (3)	Mo(1)–O(3)–C(31)	123.8 (8)
O(1)–Mo(1)–O(4)	113.9 (3)	C(1)–N(1)–C(2)	116 (2)
O(1)–Mo(1)–O(2)	146.6 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

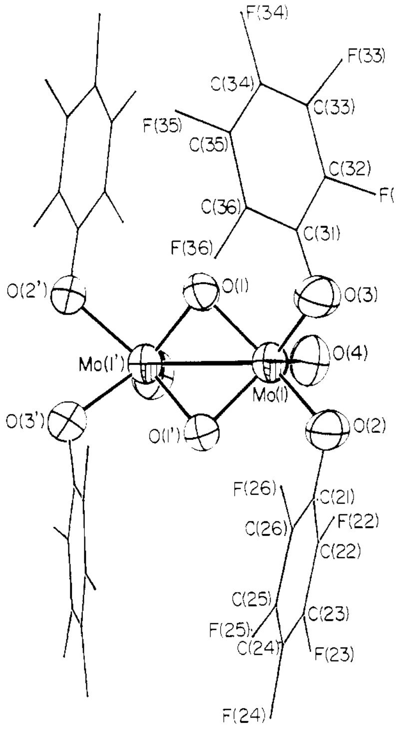

Figure 5. The anion, $[Mo_2O_4(OC_6F_5)_4]^{2-}$, in compound **4**.

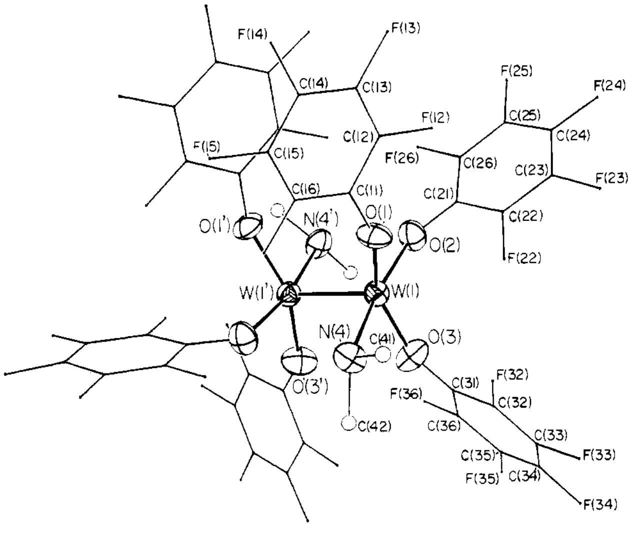

Figure 6. $W_2(OC_6F_5)_6(NHMe_2)_2$ molecule (**5**).

are in an eclipsed configuration.

Each molybdenum atom is bonded to two alkoxides (Mo–O = 2.07 [1] Å) and two dimethylamine molecules (Mo–N = 2.24 [1] Å). The close N···O distances of 2.75 [2] Å, the orientations of the methyl groups, and the relatively small Mo′–Mo–L bond angles provide evidence for hydrogen bonding between syn amine and alkoxide groups. Similar distances have been observed for other dimeric compounds with syn ligand hydrogen bonding.[32]

$[NH_2Me_2]_2[Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4]$ (4). The anion is shown in Figure 5, and the principal dimensions are listed in Table VIII. This is a rather common type of dinuclear Mo^V compound. The cis arrangement of the Mo═O moieties in **4** is the most commonly observed configuration for $[Mo_2O_2(\mu\text{-}O)_2X_4]^{2-}$ compounds; few trans dimers are known.[33]

$W_2(OC_6F_5)_6(NHMe_2)_2$ (5). A crystallographically imposed 2-fold axis perpendicular to the W–W bond relates the equivalent halves of the molecule, which is shown in Figure 6. Principal dimensions are given in Table IX. The rotational conformation is nearly but not fully eclipsed, with an average torsion angle of 10.6°. (See Figure 7.)

While eclipsed or nearly eclipsed ligands often suggest a δ component of the M–M bond, no δ bonding exists in this case. Rather, hydrogen bonding between the amine proton of N(4) and syn alkoxide O(2)′ (and also between N(4)′ and O(2)) cause this

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(32) Cotton, F. A.; Falvello, L. R.; Fredrich, M. F.; DeMarco, D.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 3088.

(33) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley & Sons: New York, 1988; p 828.

Table IX. Selected Bond Distances (Å) and Angles (deg) for $W_2(OC_6F_5)_6(NHMe_2)_2$ (**5**)[a]

W(1)-W(1)	2.316 (1)	O(1)-C(11)	1.340 (15)
W(1)-O(1)	1.917 (8)	O(2)-C(21)	1.319 (15)
W(1)-O(2)	1.992 (9)	O(3)-C(31)	1.28 (2)
W(1)-O(3)	1.949 (10)	N(4)-C(41)	1.51 (2)
W(1)-N(4)	2.210 (10)	N(4)-C(42)	1.51 (2)
W(1)-W(1)-O(1)	107.8 (3)	O(2)-W(1)-N(4)	168.0 (4)
W(1)-W(1)-O(2)	97.4 (2)	O(3)-W(1)-N(4)	90.0 (4)
W(1)-W(1)-O(3)	99.2 (3)	W(1)-O(1)-C(11)	156.6 (8)
W(1)-W(1)-N(4)	93.9 (3)	W(1)-O(2)-C(21)	134.1 (7)
O(1)-W(1)-O(2)	89.0 (4)	W(1)-O(3)-C(31)	149.5 (8)
O(1)-W(1)-O(3)	152.7 (4)	W(1)-N(4)-C(41)	116.5 (8)
O(1)-W(1)-N(4)	83.9 (4)	W(1)-N(4)-C(42)	116.8 (8)
O(2)-W(1)-O(3)	92.0 (4)	C(41)-N(4)-C(42)	107 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

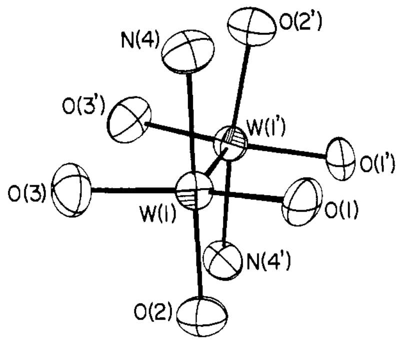

Figure 7. Core of molecule **5** viewed along the W–W bond, showing the nearly eclipsed conformation.

dimer to adopt a *sterically* less favored configuration to accommodate two hydrogen bonds. Of the three W–O bonds, two are relatively short, averaging 1.93 (1) Å, while the third, W(1)–O(2), is 1.992 (9) Å. In addition, W–O–C angles are approximately 150° or more for alkoxide groups that are not involved with hydrogen bonding, whereas W–O(2)–C(21) measures 134°. A N···O distance of 2.75 (1) Å and unusually low W′–W–N(4) and W′–W–O(2) angles provide further evidence of an O(2)···H···N(4)′ interaction.

Discussion

In general, the relatively acidic C_6F_5OH reacts with $Mo_2(NMe_2)_6$ avidly, but the course of the reaction and the products isolated are strongly dependent on the mole ratio used. In all cases some of the Me_2NH that is generated turns up coordinated to the dimolybdenum unit in the product. We failed to find conditions that allow the isolation of $Mo_2(OC_6F_5)_2(NMe_2)_4(NHMe_2)_2$, but because of time limitations not all possibilities were examined.

In Table X, the various types of bond length found in the four Mo–Mo multiply-bonded compounds are tabulated for comparison. It is clear by comparison of these results, which are very consistent among themselves, with those in Table I that while the Mo–Mo triple bonds have the lengths normally found, the Mo–O bonds are markedly longer (by 0.12–0.16 Å) and the Mo–N bonds somewhat shorter (by ca. 0.03 Å) than those in the compounds without fluoroalkoxide groups. On the other hand, the W–O bond length in $W_2(OC_6F_5)_6(NHMe_2)_2$, 1.95 [2] Å, is the same length as that in $W_2(OPr^i)_6(py)_2$, 1.95 [5] Å.[8] The reason for this is not clear, and speculation based on a comparison of only one compound of each type would be inadvisable.

It has also been found that the separate NMR signals from the distal and proximal methyl groups of the remaining NMe_2 groups of **1** and **2** persist at room temperature, whereas in $Mo_2(NMe_2)_6$ and $W_2(NMe_2)_6$ they were averaged at room temperature and observable separately only at about −20 °C and below. To the extent that averaging is inhibited by increased M–N π-bonding, this result is in accord with the structural results, where shorter Mo–N bonds are found.

Table X. Structural Parameters for $Mo_2(OC_6F_5)_n(NMe_2)_m(NHMe_2)_l$[a]

	bond dist, Å			
compd	Mo–Mo	Mo–O	Mo–NMe₂	Mo–NHMe₂
$Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (**1a**)	2.218 (1)	2.067 [7]	1.922 (5)	2.267 (5)
$Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (**1b**)	2.222 (1)	2.06 [1]	1.931 (5)	2.268 (4)
$Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2 \cdot 2C_6H_6$ (**2**)	2.214 (1)	2.027 (7) 1.99 [1]	1.918 (9)	2.24 [1]
$Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**)	2.140 (2)	2.07 [1]		2.24 [1]

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Standard deviation given in square brackets is calculated as equal to $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$ in which Δ_i is the deviation of the *i*th of *n* values from the arithmetic mean of the set.

Each of the compounds, **1**, **2**, and **5**, provides an example of the triply bonded dimetal unit with four ligands on each metal atom. In two cases, **1** and **5**, these are of the usual type in which there are two equivalent metal atoms in oxidation state III. In compound **2** we have an example of the rare situation in which the metal atoms are in different environments, with the difference such as to suggest that different formal oxidation states be assigned to them, namely, II and IV. Earlier examples of this situation were provided by $Cl_4ReRe(MeSCH_2CH_2SMe)_2Cl$,[34] $(RO)_2X_2ReReX_2(PPh_3)_2$,[35] and $[(CH_3)_2CHO]_4MoMo(Me_2PCH_2CH_2PMe_2)_2$,[36] where formal oxidation state assignments of (III,II), (IV,II), and (IV,0), respectively, have been proposed.

If, in compound **2**, we formally assign oxidation states IV and II to the $Mo(OC_6F_5)_4$ and $Mo(OC_6F_5)(NMe_2)(NHMe_2)_2$ halves, we then have d^2 and d^4 metal atoms uniting to form a triple bond. Therefore, this bond has about one-third dative character. Nevertheless, the bond length, 2.214 (1) Å, is the same as those in symmetrical, triply bonded Mo_2^{6+} species. Undoubtedly, the assignments of formal oxidation states in such compounds greatly exaggerate the true state of affairs, but they probably suggest correctly the direction of a more moderate degree of charge separation.

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Registry No. 1a, 124461-91-2; **2**, 124461-93-4; **3**, 124461-94-5; **4**, 124481-47-6; **5**, 124481-48-7; **6**, 4127-67-7; $Mo_2(NMe_2)_6$, 51956-20-8; $W_2(NMe_2)_6$, 54935-70-5; $Mo_2(CH_2SiMe_3)_6$, 34439-17-3; $NHMe_2$, 124-40-3; $Mo_2(OC_6F_5)_6$, 124461-95-6; C_6F_5OH, 771-61-9; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Full listings of anisotropic displacement parameters, positional parameters, bond lengths, and bond angles for the crystal structures **1a**, **1b**, **2**, **3**, **4**, and **5** and torsional angles for compounds **3** and **5** (58 pages); tables of observed and calculated structure factors (73 pages). Ordering information is given on any current masthead page.

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