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Synthesis and Electronic Properties of Triply Bonded Hexakis(fluoroalkoxy)dimolybdenum Complexes. Structure of $Mo_2[OCMe(CF_3)_2]_6$ and Investigation of the Nature of the Frontier Orbitals in Triply Bonded M_2X_6 Compounds

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The compound "$MoCl_3(dme)$" (dme = 1,2-dimethoxyethane) was prepared in pure form and formulated as the dimeric $Mo_2Cl_6(dme)_2$ (**1**). This material proved an excellent starting material for the metathetical syntheses of metal–metal triply bonded Mo_2X_6 complexes, including the hexaalkyls $Mo_2(CH_2MMe_3)_6$ (M = C (**6**), Si (**7**)), the hexaalkoxides $Mo_2(OCMe_2CH_2R)$ (R = H (**2**), Me (**3**)), and the new hexakis(fluoroalkoxide) dimers $Mo_2[OCMe_{3-x}(CF_3)_x]_6$ (x = 1 (**4**), 2 (**5**)). The structure of **5** was determined by single-crystal X-ray diffraction: T = 253 K, $R\bar{3}$ (No. 148), a = 10.894 (8) Å, c = 29.255 (9) Å, V = 3006.8 Å^3, R = 0.071, R_w = 0.094, GOF = 0.50 for 747 observed reflections varying 113 parameters. The molecule exhibits disorder, some of which could be resolved, and typical Mo≡Mo (2.230 (3) Å) and Mo–O (1.88 (1) Å) bond lengths. The former observation is consistent with theoretical and experimental studies indicating that the triple bond is exclusively comprised of metal-based orbitals giving rise to a limiting $\sigma^2\pi^4$ description; the latter observation is somewhat at odds with previous suggestions that decreasing the π-donor ability of the alkoxide ligands in these systems increases the metal–oxygen distance. The electronic absorption spectra of the congeneric **2**, **4**, and **5** are essentially equivalent; this surprising result suggests that either the HOMO and LUMO are largely comprised of metal-based orbitals and contain little metal–ligand δ character or that these orbitals contain the same amount of ligand character and are equally affected by changes in the electronic properties of the ligands.

The application of main group and transition metal alkoxide complexes[2] to the preparation of ceramic materials[3] has motivated considerable effort toward the preparation of several subclasses of such compounds. Recent work has emphasized the preparation of complexes of low molecularity, with the attendant increases in solubility, volatility, ease of purification, and ease of characterization. One facet in this area has been an increased interest in fluoroalkoxide compounds,[4] since these are known to be generally more volatile than their alkoxide congeners, despite their increased molecular weight, and because the greater steric bulk of a fluorine atom as opposed to the hydrogen atom has sometimes allowed the preparation of a fluoroalkoxide of less molecularity than the corresponding alkoxide.

We are exploring the use of multiply bonded transition metal compounds,[5] including the d^3–d^3 triply bonded dimers $M_2(OR)_6$ (M = Mo, W), as precursors to "molecular wires" and potential photonic materials.[6] As part of this work, we reproduced the preparation of the hexakis(trifluoro-*tert*-butoxy) dimer $W_2(OCMe_2CF_3)_6$ reported by Schrock and co-workers[7] and noted as they did that this compound is considerably easier to purify and handle than the alkoxide analogue $W_2(OCMe_3)_6$ owing to its slightly decreased solubility. Additionally, we noted that the fluoroalkoxide dimer reacted differently with diynes than did the alkoxide dimer. This difference in reactivity was sufficiently striking to motivate us to investigate whether the same trends would obtain for molybdenum dimers. While $Mo_2(OCMe_3)_6$ has long been known,[8] we were surprised to learn that no hexakis(fluoroalkoxide) molybdenum dimers have been reported. This lack stems from the fact that alcoholysis of the dimethylamido dimer $Mo_2(NMe_2)_6$ (the most common method of preparing $Mo_2(OR)_6$ complexes) gives incomplete or complex reactions when the fluorinated alcohols such as $(CF_3)_3COH$ and C_6F_5OH are used.[9] This in turn probably arises from the low nucleophilicity of the fluoroalcohols and the poor π-bonding characteristics of fluoroalkoxide ligands.[4c,10]

We decided to develop a general route to the molybdenum hexakis(fluoroalkoxide) dimers, preferably one which avoided the complications of coordinated amine and/or incomplete alcoholysis. By analogy with the tungsten chemistry, we focused on the direct metathetical reactions of forms of "$MoCl_3$" with alkali metal alkoxides and report here the success of this methodology. Through the use of the new molybdenum(III) chloride starting material $Mo_2Cl_6(dme)_2$ (**1**) we have developed high-yield syntheses of the known hexaalkoxide $Mo_2(OCMe_3)_6$, (**2**), the new more soluble analogue $Mo_2(OCMe_2Et)_6$ (**3**), and the new hexakis(fluoroalkoxy) dimers $Mo_2(OCMe_2CF_3)_6$ (**4**) and $Mo_2[OCMe(CF_3)_2]_6$ (**5**). This material has also proved the best starting material available for the synthesis of the known hexaalkyl

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(1) Address correspondence regarding the crystallographic details to this author.

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dimers Mo$_2$R$_6$ (R = CH$_2$CMe$_3$ (**6**),[11] CH$_2$SiMe$_3$ (**7**)[12]). Finally, we describe the single-crystal X-ray diffraction study of the hexakis(hexafluoro-*tert*-butoxide) dimer **5** and the interpretation of these data and data from electronic absorption studies in light of theoretical work regarding the electronic structures of the d^3–d^3 alkoxide dimers.

Experimental Section

General Methods. Unless otherwise noted, all reactions and manipulations were performed under an inert atmosphere employing standard Schlenk or glovebox techniques. Evaporations of solvents were performed in vacuo. Ethylene glycol dimethyl ether (dme), diethyl ether, and pentane were distilled from purple potassium diphenyl ketyl. CH$_2$Cl$_2$ was distilled from CaH$_2$. (Me$_3$Si)$_2$O was distilled from potassium metal. Basic alumina (60–200 mesh) was activated by heating to 200 °C in a vacuum oven. Lithium alkoxides were prepared by dropwise addition of *n*-BuLi in hexanes (Aldrich) to a pentane solution of the appropriate alcohol at 0 °C. Sodium and potassium fluoroalkoxides were prepared by minor variations of a reported method.[13] MoCl$_4$(CH$_3$CN)$_2$ was prepared by a published method.[14]

NMR spectra were obtained on a Bruker WA-200 spectrometer at ambient temperature; chemical shifts are reported as ppm downfield of tetramethylsilane. Absorption spectra were obtained on a Cary 3 spectrometer (Varian) in spectroscopy grade solvents (Burdick and Jackson) purified as above. Elemental analyses were determined by Ms. Paulanne Rider, NIU Chemistry Analytical Services.

MoCl$_4$(dme). MoCl$_4$(CH$_3$CN)$_2$ (20.5 g, 64.1 mmol) was slurried in 200 mL of dme, and the slurry was stirred vigorously for 24 h, at which point most, but not all, of the red bisnitrile adduct had dissolved. The solution was filtered, and the solvent was evaporated from the mother liquor. The dark residue and the filtered bisnitrile were recombined and treated with 200 mL of fresh dme. The slurry was stirred for 24 h, during which all the solid dissolved. The solution was filtered, and the solvent was evaporated. The dark, somewhat crystalline residue was triturated with pentane (150 mL) and stirred for 30 min. The yellow-brown powder which resulted was filtered out, washed with pentane, and dried to give 19.9 g (60.7 mmol, 95%) of analytically pure material. Anal. Calcd for C$_4$H$_{10}$O$_2$MoCl$_4$: C, 14.65; H, 3.07. Found: C, 15.05; H, 3.04.

"MoCl$_3$(dme)" (1). MoCl$_4$(dme) (19.9 g, 60.8 mmol) was dissolved in dme (200 mL) in a 250-mL flask with vigorous stirring. The dark solution was treated with granular Sn (20 mesh, 1.80 g, 15.2 mmol). The slurry was stirred as vigorously as possible for 24 h, during which a brown-yellow solid precipitated and clung to the flask walls. The material was scraped from the walls, filtered out, washed with a small amount of dme followed by pentane, and dried, giving 16.8 g (28.7 mmol, 94%) of khaki-brown product. This material is insoluble in dme, dichloromethane, chloroform, ether, and hydrocarbons. It reacts slowly with acetonitrile to form MoCl$_3$(CH$_3$CN)$_3$. As noted under Results and Discussion, we believe this material is actually Mo$_2$Cl$_6$(dme)$_2$. Anal. Calcd for C$_8$H$_{20}$O$_4$Cl$_6$Mo$_2$: C, 16.43; H, 3.45. Found: C, 16.48; H, 3.56.

Mo$_2$(OCMe$_3$)$_6$ (2). A solution of LiOCMe$_3$ (2.40 g, 30.0 mmol) in dme (35 mL) was treated with solid Mo$_2$Cl$_6$(dme)$_2$ (2.92 g, 5.00 mmol) in small portions over 10 min. The khaki-brown powder dissolved rapidly as the solution darkened to red-brown and a white solid precipitated. The slurry was stirred for 18 h, whereupon the mixture was filtered through Celite. The filter cake was washed with pentane until the washings were colorless. The solvent was evaporated from the combined filtrates, giving a red-orange residue. This was extracted several times with small volumes of pentane, totaling ca. 20 mL. The extracts were filtered, giving a clear, deep red-black solution. This was treated with an equal volume of (Me$_3$Si)$_2$O and cooled to −30 °C for 24 h. The red blades which formed were filtered out and dried, giving a first crop of product. The mother liquor was then evaporated to approximately one-third volume and recooled. This gave a second crop of red blades. Reduction of the mother liquor to ca. 3 mL and recooling provided a third crop. The combined yield of product was 2.57 g (4.08 mmol, 81%). All crops of product were shown to be identical to each other and to the reported material[8] by ^{1}H NMR spectroscopy.

Mo$_2$(OCMe$_2$Et)$_6$ (3). A solution of LiOCMe$_2$Et (2.82 g, 30.0 mmol) in dme (50 mL) was added dropwise to a slurry of Mo$_2$Cl$_6$(dme)$_2$ (2.92 g, 5.00 mmol) in dme (100 mL) at 0 °C over 30 min. The reaction was allowed to warm slowly to room temperature and was then stirred overnight, during which it darkened from grayish-brown to red. The volatiles were evaporated in vacuo, and the resulting red-brown solid was pumped at 10^{-3} Torr for 1 h. Pentane (100 mL) was added, and the slurry was stirred 1 h. The insoluble material was removed by filtration through Celite, giving a clear, deep red-black solution. The filter cake was washed with 2 × 25 mL pentane, at which point the washings were essentially colorless. The solvent was then evaporated in vacuo to give a red-brown solid, which was shown to be pure by ^{1}H NMR spectroscopy. It was recrystallized from minimum (Me$_3$Si)$_2$O at −30 °C, giving dark red blades in three crops (3.02 g, 4.23 mmol, 84%). The material may be recrystallized from pentane with difficulty owing to its high solubility. ^{1}H NMR (C$_6$D$_6$): δ 1.81 (q, J_{HH} = 7.5 Hz, 2 H, CH_2CH$_3$), 1.48 (s, 6 H, Me), 1.09 (t, J_{HH} = 7.5 Hz, 3 H, CH$_2$CH_3). ^{13}C NMR (C$_6$D$_6$): δ 80.4 (s, OC), 37.5 (t, J_{CH} = 125 Hz, CH$_2$CH$_3$), 29.6 (q, J_{CH} = 125 Hz, Me), 8.8 (q, J_{CH} = 125 Hz, CH$_2$$CH_3$). Anal. Calcd for C$_{30}H_{66}O_6Mo_2$: C, 50.41; H, 9.31. Found: C, 50.06; H, 9.42.

Mo$_2$(OCMe$_2$CF$_3$)$_6$ (4). A vigorously stirring slurry of Mo$_2$Cl$_6$(dme)$_2$ (585 mg, 1.00 mmol) in CH$_2$Cl$_2$ (40 mL) was treated with solid NaOCMe$_2$CF$_3$ (901 mg, 6.00 mmol) in small portions over 15 min. The reaction was then stirred overnight, during which it darkened from khaki brown to red. The solution was filtered, and the filter cake was rinsed with CH$_2$Cl$_2$ until the rinsings were colorless. The volatiles were evaporated in vacuo, and the resulting orange-brown solid was pumped at 40 °C, 10^{-4} Torr overnight. The material was then extracted with several small volumes of boiling (Me$_3$Si)$_2$O (total volume ca. 50 mL). The extracts were filtered hot, giving a clear red-orange solution, and cooled to −30 °C overnight. The bright orange crystals which formed were filtered out, washed with cold (Me$_3$Si)$_2$O, and dried. A small second crop was obtained by evaporating the mother liquor to ca. 3 mL and recooling. The yield was 686 mg (0.719 mmol, 72%). ^{1}H NMR (C$_6$D$_6$): δ 1.37 (s). ^{1}H NMR (CDCl$_3$): δ 1.49 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 126.2 (q, J_{CF} = 285 Hz, CF$_3$), 81.9 (q, J_{CF} = 29 Hz, OC), 24.8 (s, Me). Anal. Calcd for C$_{24}$H$_{36}$F$_{18}$O$_6$Mo$_2$: C, 30.20; H, 3.80. Found: C, 29.88; H, 3.88.

Mo$_2$[OCMe(CF$_3$)$_2$]$_6$ (5). A vigorously stirring slurry of Mo$_2$Cl$_6$(dme)$_2$ (585 mg, 1.00 mmol) in CH$_2$Cl$_2$ (40 mL) was treated with solid NaOCMe(CF$_3$)$_2$ (1.22 g, 6.00 mmol) in small portions over 15 min. The reaction was then stirred overnight, during which it darkened from khaki brown to red, with a mixture of beige and orange precipitate. The solution was filtered, and the filter cake was rinsed with CH$_2$Cl$_2$ until the rinsings were colorless. The volatiles were then evaporated from the mother liquor. The red-purple residue which resulted was combined with the filter cake, and this solid was extracted with several 40-mL portions of boiling ether until the extracts were colorless (total volume ca. 200 mL). The extracts were filtered hot, giving a clear orange-red solution containing some bright orange precipitate. The solution was concentrated to ca. 75 mL, heated to boiling, and then cooled to −30 °C for several hours. The bright orange crystals which formed were filtered out, washed with cold ether, and dried. The yield was 375 mg (0.293 mmol, 29%). ^{1}H NMR (CDCl$_3$): δ 1.67 (s). The material is too insoluble in noncoordinating solvents to allow the ^{13}C{^{1}H} NMR spectrum to be obtained. Anal. Calcd for C$_{24}$H$_{18}$F$_{36}$O$_6$Mo$_2$: C, 22.55; H, 1.42. Found: C, 22.88; H, 1.30.

Mo$_2$(CH$_2$CMe$_3$)$_6$ (6). A 1:1 ether/pentane slurry (100 mL) of Mo$_2$Cl$_6$(dme)$_2$ (2.92 g, 5.00 mmol) at −78 °C was treated dropwise over 20 min with a solution of LiCH$_2$CMe$_3$ (2.34 g, 30.0 mmol) in pentane (100 mL). The resulting slurry was stirred and allowed to warm slowly to room temperature over 2 h. During this period the khaki-brown solid dissolved, providing a dark solution and a white precipitate. The reaction was stirred 18 h at room temperature, whereupon the solvent was evaporated. The residue was extracted with 4 × 100 and 1 × 50 mL volumes of pentane, and the extracts were filtered through 5 cm of activated basic alumina packed into a 60 M frit. The dark material was absorbed, and the bright yellow filtrate was collected. The solvent was evaporated to dryness. The bright yellow powder was then treated with 20 mL of (Me$_3$Si)$_2$O to loosen it from the flask walls, filtered, and dried, giving a first crop of material. The mother liquor was evaporated to ca. 10 mL and then heated to dissolution and cooled to −30 °C. After 1 day, the yellow-orange crystals were collected as a second crop. The total yield was 2.27 g (3.67 mmol, 73%), and the material was shown to be identical with the reported material[11] by ^{1}H NMR spectroscopy.

Mo$_2$(CH$_2$SiMe$_3$)$_6$ (7). A 1:1 ether/pentane slurry (80 mL) of Mo$_2$Cl$_6$(dme)$_2$ (2.92 g, 5.00 mmol) at −78 °C was treated dropwise over 30 min with a solution of LiCH$_2$SiMe$_3$ (2.82 g, 30.0 mmol) in pentane (100

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Table I. Crystal Data and Summary of Data Collection and Structure Refinement for 5

compd	$Mo_2[OCMe(CF_3)_2]_6$
fw	1278.23
space group	$R\bar{3}$ (No. 148)
T, °C	−20
cell constants[a]	
a, Å	10.894 (8)
c, Å	29.255 (9)
V, Å^3	3006.8
formula units/unit cell	3
D_{calc}, g cm^{-3}	2.12
μ_{calc}, cm^{-1}	8.41
radiation, graphite monochrom	Mo Kα (λ = 0.710 73 Å)
GOF[b]	0.50
R[c]	0.071
R_w[c]	0.094

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections with $\theta > 20°$. [b] $GOF = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2\}^{1/2}$.

Table II. Final Fractional Coordinates and *B*(eqv) Values (Å^2) for 5[a]

atom	*x/a*	*y/b*	*z/c*	*B*(eqv)[b]
Mo	0.3333	0.6667	0.20478 (5)	2.30
Mo′	0.242 (1)	0.572 (1)	0.1815 (3)	3.36
O	0.3455 (9)	0.502 (1)	0.2139 (4)	6.50
C1	0.355 (1)	0.413 (1)	0.2422 (4)	5.18
C2	0.218 (3)	0.274 (2)	0.2434 (8)	9.04
C3	0.505 (4)	0.425 (4)	0.243 (2)	19.54
C4	0.374 (5)	0.482 (3)	0.2989 (9)	16.10
F1	0.119 (2)	0.277 (2)	0.259 (1)	19.13
F2	0.223 (3)	0.200 (2)	0.2103 (8)	18.28
F3	0.224 (2)	0.188 (2)	0.2771 (8)	15.28
F4	0.498 (2)	0.345 (2)	0.2819 (6)	14.85
F5	0.476 (5)	0.370 (5)	0.199 (1)	25.42
F6	0.589 (2)	0.554 (2)	0.257 (1)	17.16

[a] Atoms with a prime (′) are in the secondary molecule. [b] $B(eqv) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

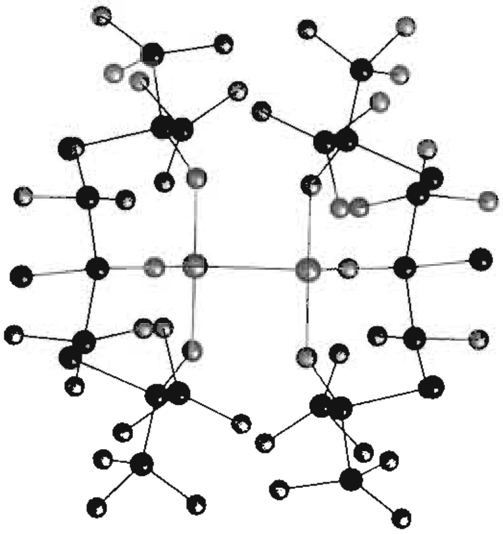


Figure 1. SYBYL (Silicon Graphics, Inc.) illustration of compound 5. Selected bond distances (Å) and angles (deg) for the predominant molecule: Mo–Mo = 2.230 (3), Mo–O = 1.88 (1), O–C1 = 1.32 (2); Mo–Mo–O = 98.2 (3), O–Mo–O = 118.0 (2), Mo–O–C = 149 (1).

mL). The resulting slurry was then allowed to warm slowly to room temperature over 2 h. During this period the khaki brown solid dissolved, providing a dark solution and a white precipitate. The reaction was stirred 18 h at room temperature, whereupon the solvent was evaporated. The residue was extracted with several 50-mL portions of pentane, and the extracts were filtered through 5 cm of activated basic alumina packed into a 60 M frit. The dark material was absorbed, and the bright yellow filtrate was collected. The solvent was evaporated to a volume of 15 mL and then heated to dissolution and cooled to −30 °C. After 1 day, the yellow-orange crystals were collected. Evaporation of the mother liquor and recrystallization of the residue from $(Me_3Si)_2O$ at −30 °C provided another crop of product indistinguishable from the first. The total yield was 3.01 g (4.20 mmol, 84%) of material identical with that reported[12] as shown by ^1H NMR spectroscopy.

Single-Crystal X-ray Diffraction Study of 5. Dark orange, well-shaped single crystals of 5 were grown by slow cooling of a hot, saturated dme solution to room temperature. One of these was attached with silicone grease to the inner wall of a Pyrex capillary in the glovebox; the open end of the capillary was then plugged with Apiezon grease. The capillary was removed from the glovebox and immediately flame sealed. The crystal was inspected after 48 h at room temperature, whereupon it was determined to be acceptable for study. The capillary was attached to a goniometer head with putty, and the crystal was cooled to −20 °C. Data collection parameters were given in Table I.

The data provided by the direct methods program SHELXS86 indicated a likely position for the unique molybdenum atom. Refinement of this atom and inspection of both least-squares and difference Fourier data indicated that a more complex model was required. After considerable effort, we determined that refinement of the structure was only possible by considering the molybdenum positions disordered. Refinement proceeded acceptably using the following model. The major conformation has a molybdenum atom residing on a crystallographic 3-fold axis with an occupancy factor of 0.25, representing 75% of the dimeric molecules. A second molybdenum position just off the 3-fold was refined with an occupancy factor of 0.0833, representing 25% of the dimeric molecules. This position generates two other conformations of the Mo≡Mo moiety; therefore, there are four alternate positions for the dimer. The unique oxygen is within bonding distance of all four molybdenum positions. It is evident that some disorder of this position exists; however, the disordered sites are so close together they could not be resolved. All atoms of the alkoxide ligand exhibit large thermal parameters, most likely due to the presence of slightly different positions relative to the four different Mo≡Mo axes. In the case of the trifluoromethyl groups, it appears likely that the fluorine atoms are also rotationally disordered about the 3-fold methyl axis. Owing to these difficulties, the hydrogen atoms were not included in the refinement. The values of the positional parameters, with equivalent isotropic thermal parameters, are given in Table II. A SYBYL drawing of the predominant conformer of the molecule appears in Figure 1; an ORTEP drawing of the asymmetric unit (including the secondary molybdenum atom) showing the atomic anisotropic thermal ellipsoids appears in Figure 2; selected bond distances and angles are given in the caption to Figure 1.

We attempted to improve the quality of the data by cooling several crystals of 5 to temperatures below −20 °C. In every case, the peak widths increased as a function of temperature to the point where, at −80 °C, the peaks could not be centered by the diffractometer centering program. We attribute this behavior to a phase transition below ca. −40 °C, probably related to a "slowing down" of the trifluoromethyl/hexafluoro-*tert*-butoxide group rotations. We attempted to overcome this problem in several ways, including slow cooling of mounted crystals, growing crystals containing intercalated solvent molecules, and low-temperature crystallization, but we were unsuccessful.

Results and Discussion

As noted in the Introduction, this study developed from our interest in synthesizing a series of hexakis(fluoroalkoxy)dimolybdenum complexes, a previously unknown class of molecules. We initially attempted these syntheses by treating $Mo_2(OCMe_3)_6$ (**2**) with the fluoroalcohols $(CF_3)Me_2COH$ and $(CF_3)_2MeCOH$, expecting the greater acidities of the fluoroalcohols to drive the equilibrium to completion. These experiments provided red, crystalline products which exhibited very complex ^1H NMR spectra which were clearly inconsistent with those expected for the desired products. We suspect instead that these are mixed species of the type $Mo_2(OCMe_3)_x(OR_F)_{6-x}$ (OR_F = fluoroalcohol).

We then opted to explore metathetical routes. In order to conserve the somewhat expensive fluoroalcohols listed above, we began our studies by exploring several metathetical routes to the *tert*-butoxide dimer $Mo_2(OCMe_3)_6$ (**2**), since this molecule is known and since *tert*-butyl alcohol is inexpensive and alkali metal *tert*-butoxide reagents are easily prepared. Early synthetic

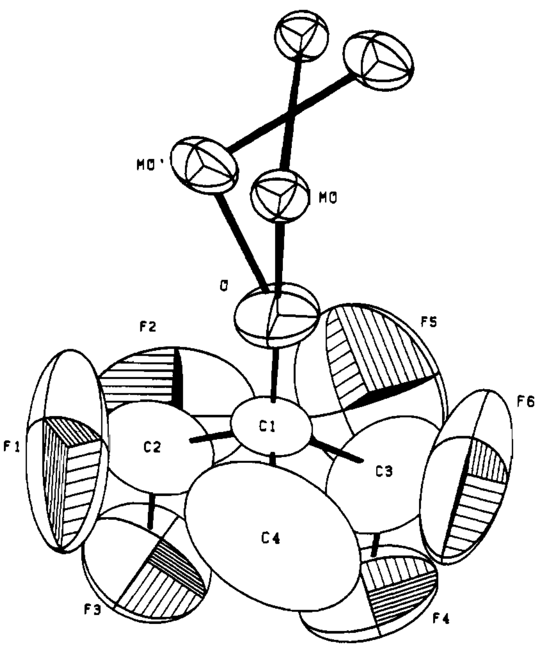


Figure 2. ORTEP illustration of the asymmetric unit of compound **5** with 50% probability ellipsoids for thermal motion.

attempts involved adding $MoCl_3$, prepared from $MoCl_5$ and $Mo(CO)_6$,[15] to sodium and lithium *tert*-butoxides in THF. These routes always provided some **2**, but the yields were poor and the impurities difficult to separate due to their similar solubilities, the instability of **2** to chromatography supports, and its substantial decomposition upon attempted sublimation on a multigram scale.

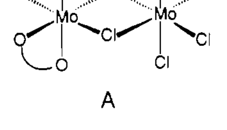
We surmised that the root of these difficulties lay in the insolubility of apparently polymeric $MoCl_3$ in THF and the resultant lowered rate and heterogeneity of the reaction, so we investigated similar metatheses using the monomeric compounds $MoCl_3(THF)_3$ and $MoCl_3(CH_3CN)_3$.[16] Generally, these reagents proved no better than $MoCl_3$, even when the reactions were run under homogeneous conditions in dichloromethane.

Qualitative observations suggested that the six-coordinate trichlorides reacted slowly or incompletely due to the low lability of the dative ligands. We were therefore struck by the report of $MoCl_3(dme)$,[17] which, as a five coordinate species, should be more reactive than the six-coordinate materials due to the "open" site. It also seemed plausible that the six-coordinate compounds react dissociatively, whereas the five-coordinate material could react associatively, and that this mechanistic difference could lead to a more efficient reaction. Finally, a body of work[18] indicated that putative five-coordinate complexes "$MoCl_3L_2$" should dimerize, and we were curious as to why the dme complex did not.

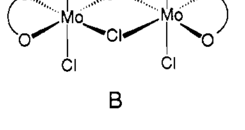
The original synthesis of $MoCl_3(dme)$ involved treatment of "$MoCl_3\cdot{}^5/_3THF$" with dme. The compound was described as a red powder and was characterized solely by molybdenum and chlorine analyses, for which the agreement between calculated and actual values was fair (although the poorest of any of the compounds reported in the paper). We attempted to reproduce this work by stirring $MoCl_3(THF)_3$ in dme and found that a pink powder precipitated. Elemental analysis of this material suggested a formulation of $MoCl_3(dme)_{1.5}$. As Wedd had shown that $MoCl_3(THF)_3$ decomposes in CH_2Cl_2/THF to give $Mo_2Cl_6(THF)_3$,[18b] we suspected that the pink powder was $Mo_2Cl_6(dme)_3$. However, further stirring of the pink powder in fresh dme caused the color of the material to change from pink to khaki-green. We analyzed this material qualitatively by treating it with CD_3CN, in which it slowly dissolves to give a yellow solution, presumably $MoCl_3(CD_3CN)_3$. Inspection of the ^1H NMR spectrum of the solution clearly indicated the presence of dme and THF, demonstrating that the THF ligands had not been completely displaced. Further stirring of the material over fresh dme continually lowered the amount of THF present in the isolated material, but we were never able to effect complete exchange. This held true when we attempted to exchange dme for the CH_3CN ligands of $MoCl_3(CH_3CN)_3$ as well. Even quite forcing conditions (vacuum evaporation of solvent at reflux temperature) did not result in complete removal of the monodentate ligands.

We then decided to attempt exchange of the CH_3CN ligands in the precursor $MoCl_4(CH_3CN)_2$, since the ligands should be more labile in d^2 pseudooctahedra than in d^3 systems. This proved out, and we were able to isolate $MoCl_4(dme)$ quite easily as a yellow-brown powder. The exchange equilibrium apparently lies on the side of the bis(acetonitrile) complex, and thus large-scale preparation of the dme complex requires filtration of unreacted starting material, evaporation of the solvent from the mother liquor, and recombination of the residue with the unreacted starting material in fresh dme for complete conversion. We then reduced the tetrachloride with tin and isolated a khaki-brown powder similar to that described above. This material was shown by elemental analysis to contain no nitrogen (thereby ruling out traces of CH_3CN being present) and to have a stoichiometry of $MoCl_3(dme)$. We are therefore confident of its purity. Since our trichloride is clearly different from that reported, we suggest that the previous "$MoCl_3(dme)$" contains both THF and dme ligands and could be the same as the pink material described above. This would account for the low molybdenum and chlorine analyses reported.

Unfortunately, the exact nature of our $MoCl_3(dme)$ (**1**) is unclear. It is completely insoluble in all noncoordinating solvents we have investigated, and thus we have been unable to characterize it by ^1H NMR and absorption spectroscopies or to determine its molecular weight by cryoscopy. The IR spectrum is uninformative. On the basis of previous work and on the fact that **1** is cleanly metathesized to Mo_2X_6 dimers, we tentatively suggest that the material is the dimer $Mo_2Cl_6(dme)_2$. Several plausible structures exist for such a species; on the basis of the work of Poli,[18a] we believe that the edge-shared bioctahedral forms A and B are the most likely.



A



B

The poor solubility of **1** removed the possibility of conducting the metathesis reaction homogeneously. We were forced to rely on the hope that preformation of a molybdenum dimer would provide hexaalkoxy dimers in good yield despite this difficulty. We thus treated **1** with lithium *tert*-butoxide and found that **2** formed smoothly, in good yield and with minimal purification necessary. Compound **1** proved equally able a starting material for the preparation of the *tert*-pentoxide dimer $Mo_2(OCMe_2Et)_6$ (**3**), which we prepared both to assess the generality of the reaction and because of related work in our group dealing with the properties of highly soluble complexes (we anticipated that **3** would prove more soluble than **2** due to the pendant ethyl group). Dimer **3** is indeed considerably more soluble in pentane and $(Me_3Si)_2O$ than is **2** and is thus somewhat difficult to isolate and

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crystallize. Save this, **2** and **3** exhibit similar spectroscopic and physical properties; for example, neither sublimes without extensive decomposition on a 1-g scale, and both give rise to straightforward NMR spectra.

As a sideline, we found that **1** is a superior starting material for the preparation of the hexaalkyl dimers $Mo_2(CH_2CMe_3)_6$ (**6**) and $Mo_2(CH_2SiMe_3)_6$ (**7**), first reported by Wilkinson and coworkers.[11,12] These were first prepared from $MoCl_5$ and 5 equiv of the alkyllithium, in less than 20% yield; modifications to these methods have resulted in minimal improvements.[19] The best yield reported is 74% of **7** from $Mo_2(O\text{-}iPr)_6$ and the alkyllithium;[20] however, the hexaisopropoxide must be prepared from the hexaamide $Mo_2(NMe_2)_6$, which in turn is prepared from $MoCl_3$ and $LiNMe_2$; therefore, the overall yield of this process based on commercially available $MoCl_5$ is about 25%, although it conserves alkyl groups well. We find that the hexaalkyls can be prepared from **1** and the alkyllithium in 70–90% yield, depending on the scale of the reaction, corresponding to an overall yield from $MoCl_5$ of ca. 50%, with excellent conservation of alkyl groups. As we can prepare these dimers in multigram quantities, we plan to investigate their reactivity toward a variety of protic reagents.

The efficacy of **1** in preparing hexaalkoxide dimers encouraged us to attempt the preparation of hexakis(fluoroalkoxide) dimers. Interestingly, treatment of **1** with lithium fluoroalkoxides resulted in intractable black or purple materials. However, when sodium or potassium fluoroalkoxides were employed, we isolated the new hexakis(fluoroalkoxy) dimers $Mo_2(OCMe_2CF_3)_6$ (**4**) and $Mo_2[OCMe(CF_3)_2]_6$ (**5**) in fair to good yields with minimal workup. These new materials resemble the *tert*-butoxide dimer **1** in that they are orange-red and crystalline, but they are less soluble in hydrocarbon solvents. Interestingly, the hexakis(trifluoro-*tert*-butoxide) dimer **4** is only slightly less soluble than **1**, being sparingly soluble in pentane and extremely soluble in benzene and toluene, but the hexakis(hexafluoro-*tert*-butoxide) dimer **5** is essentially insoluble in all hydrocarbon solvents and indeed is not particularly soluble in any solvent we have tested. Like **1**, **4** shows no tendency to coordinate ligands such as acetonitrile, while addition of acetonitrile to solid **5** causes the instantaneous change of the orange color to dark purple. This presumably signals the formation of the complex $1,2\text{-}Mo_2[OCMe(CF_3)_2]_6(CH_3CN)_2$, for which many analogues are known,[21] but since this material is as insoluble as **5**, we have not yet investigated it in detail.

The NMR spectra of the dimers **4** and **5** are unexceptional at room temperature. Qualitatively, these dimers decompose significantly less than does **2** upon sublimation at 100 °C; presumably this reflects the statistically lessened potential for hydride abstraction from the methyl groups by the metal.

Structure of 5. Very few homoleptic triply bonded molybdenum–molybdenum compounds have been structurally characterized by X-ray diffraction; structural characterization of mixed species of the type $Mo_2X_2Y_4$ is considerably more common.[9b] All such compounds examined to date exhibit an ethane-like D_{3d} geometry, with metal–metal bond lengths in the remarkably small range 2.167–2.24 Å [$Mo_2(OCH_2CMe_3)_6$, 2.222 (2) Å;[8] $Mo_2(NMe_2)_6$, 2.214 (2) Å;[22] $Mo_2(CH_2SiMe_3)_6$, 2.167 Å[23]]. This evidence gives credence to the idea that the metal–metal bonding orbitals are nearly purely metal-based, with little contribution from ligand σ or π orbitals (see below).

We felt that comparison of structural data of **2**, **4**, and **5** could prove fruitful, since these are all based on a $M_2(O\text{-}tBu)_6$ template and represent a continuum of decreasing alkoxide π-donating ability. Of particular interest here would be the relationship, if any, between the ligand donor ability and the metal–metal and metal–oxygen bond distances.

Unfortunately, the crystal structure of **2** is unknown; crystals of this dimer were described as "unsatisfactory for detailed X-ray work".[8] However, the structure of the neopentoxy analogue $Mo_2(OCH_2CMe_3)_6$ was successfully determined and provides benchmark data regarding the molybdenum–molybdenum triple bond length and the molybdenum–oxygen bond length in such compounds. We therefore attempted to determine the structures of **4** and **5**. Crystals of **4** appear to suffer from the same difficulty as **2**; we have collected a data set which indicates that the molybdenum atoms occupy three orientations within the pseudooctahedral oxygen framework to a nearly equal extent. This difficulty is well-known in metal–metal triply and quadruply bonded species;[5] a recent example is the quadruply bonded $Re_2I_8^{2-}$ ion,[24] for which the Re–Re orientations are occupied to equivalent extents. Cayton and Chisholm examined this phenomenon theoretically[25] and showed that, for triply bonded M_2X_6 complexes, no orbital symmetry constraints exist to prohibit "internal flip" mechanisms which equilibrate the metal positions within the oxygen octahedron. While no barriers to this process could be calculated, it appears that no particular metal orientations are theoretically favored, as long as they maintain each metal atom within bonding distance of three oxygens. The difficulties we observed with complex **4** corroborate this view. All we are able to say at this time is that the apparent $Mo\equiv Mo$ bond distance (2.21 Å) lies in the expected range.

We were more fortunate with the hexafluoro-*tert*-butoxide dimer **5**, although disorder problems still exist. In this case, there is one significantly preferred orientation (75% occupancy) and three minor ones generated by the orientation of one metal–metal pair rotated about the crystallographic 3-fold axis (25% occupancy total). The asymmetric unit is shown in Figure 2. As is evident, significant disorder/thermal motion also appears in the hexafluoro-*tert*-butoxy ligands, particularly in the trifluoromethyl groups, lowering the quality of the refinement. The data are sufficient to define the molecule as the expected D_{3d} ethane-like complex (Figure 1) and to give reasonable distances and angles involving the molybdenum and oxygen atoms, but the other parts of the molecule remain poorly defined. The discussion below involves only the predominant molecule (except as noted), since the bond lengths and angles are acceptably well-defined only for this molecule.[26]

The $Mo\equiv Mo$ distance is 2.230 (3) Å, within the anticipated range (Figure 1). The fact that this distance occurs despite the considerably lessened π-donating ability of the hexafluoro-*tert*-butoxide ligand provides further evidence that the metal–metal bonding orbitals are essentially pure metal–metal σ and π, giving rise to a limiting description of the triple bond as $\sigma^2\pi^4$. The geometry around each molybdenum atom is that of a considerably flattened tetrahedron, with a Mo–Mo–O angle of 98.2 (3)° and an O–Mo–O angle of 118.0 (2)°. These values are quite similar to those observed for the hexaneopentoxide dimer, for which the average angles are 103.1 and 115.0°, respectively. As expected,

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(19) The best yield resulting from the metathesis of a readily available molybdenum chloride starting material is 25%: Andersen, R. A.; Chisholm, M. H.; Gibson, J. F.; Reichert, W. W.; Rothwell, I. P.; Wilkinson, G. *Inorg. Chem.* **1981**, *20*, 3934–3936.

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(26) A reviewer commented that the disorder present in **5** should negate any comparisons of the distance and angle data with other published work. We agree that the reader should bear in mind the difficulties we encountered during the structure determination but feel that the molybdenum and oxygen atoms of the predominant molecule are sufficiently well-determined to allow such comparisons within the limits of precision set by the esd's. We note that useful structural data have been obtained from similarly disordered compounds; see, for example, refs 5, 9a, and 24.

the tertiary hexafluoroalkoxide ligand exerts a more pronounced steric effect in these molecules than does the primary neopentoxide ligand; the Mo–O–C angles in **5** are crystallographically equivalent at 149 (1)° (this value may be less well-determined than is apparent from the esd because of the error associated with the carbon atom location), while, in the hexaneopentoxide compound, two angles are near this value but definitely smaller [134.2 (6) and 135.1 (6)°] and the third is considerably more acute [114.5 (7)°]. (It may be this angle variation that accounts for the lower symmetry space group ($P2_1/n$) in which the hexaneopentoxide crystallizes.) Owing to the disorder/thermal motion affecting our structure, we cannot further quantify the steric demand of the hexafluoro-*tert*-butoxide ligand in these compounds.

A relatively narrow range of values has been previously observed for the molybdenum–oxygen bond lengths in alkoxide-substituted dimers (1.86–1.95 Å).[9b] Comparison of these bond lengths with the metal–carbon bond length in $Mo_2(CH_2SiMe_3)_6$ provides good evidence for the importance of π-bonding in the alkoxides: the bond length is some 0.25–0.30 Å shorter for the alkoxide than the alkyl. Recent structural studies of aryloxide complexes $Mo_2(OAr)_xX_{6-x}$ have demonstrated that these compounds exhibit slightly longer metal–oxygen bonds (1.90–1.98 Å),[9b] although the ranges overlap; this is attributed to the decreased π-donor ability of aryloxide ligands. If this is true, the molybdenum–oxygen bond distances in $Mo_2(OCH_2CMe_3)_6$, **4**, and **5** should exhibit a regular increase coinciding with the regular decrease in alkoxide π-donor ability as the number of fluorine atoms increases. The data (Figure 1) suggest that this does not hold. The molybdenum–oxygen distance for **5** is 1.88 (1) Å, which is the same as the average of the three unique Mo–O bonds in $Mo_2(OCH_2CMe_3)_6$. It is possible that this value is less correct than indicated by the esd due to the mediocre resolution of the structure, but the following factors argue against the actual bond length being significantly longer: (1) The thermal parameters of the molybdenum and oxygen are acceptable, although admittedly the parameter for the oxygen is somewhat large. (2) The molybdenum–oxygen distances in the disordered secondary molecules average 1.91 Å, very near the value for the predominant molecule and, at worst, on the short end of the aryloxide range. (3) The oxygen–carbon bond length is anomalously short and would become shorter if the metal–oxygen bond lengthened (all other issues being equal). We therefore believe the length to be essentially correct. It appears, therefore, that steric factors may be as important as electronic ones in determining the molybdenum–oxygen bond length; possibly the breadth of the phenyl ring in aryloxide compounds contributes to lengthening the Mo–O bond. An interesting check on this issue would be the structural determination of $Mo_2(OC_6F_5)_6$, reported by Cotton,[9b] but to our knowledge this has not been performed.

Electronic Spectra of 2, 4, and 5. The electronic structures of ethane-like d^3–d^3 dimers present an interesting challenge. Considerable theoretical effort and an increasing amount of experimental work has been devoted to determining which metal and ligand orbitals are involved in bonding and to what extent. The 3-fold D_{3d} symmetry of the system makes such distinctions difficult, because the π and δ interactions are of the same symmetry and, therefore, potentially mixed. This is particularly brought out in the Raman spectra of $Mo_2(NMe_2)_6$ and $Mo_2[N(CD_3)_2]_6$: no metal–metal stretch could be assigned in this labeling experiment because all the bands in the spectrum move on deuteration.[22]

Because the oxygen orbitals are of considerably lower energy than the metal orbitals, the bonding in alkoxide dimers $M_2(OR)_6$ as determined by theoretical studies is the most straightforward. All the calculations[27–29] agree that the HOMO is a nearly pure metal–metal π set, the SHOMO is a nearly pure metal–metal σ set and that these are well-separated from any metal–ligand bonding orbitals (δ). The triple bond is thus described most accurately as $\sigma^2\pi^4$. This interpretation is borne out by photoelectron spectra,[27,28] which display π and σ ionizations separated by ca. 0.6 eV from each other and by at least 0.5 eV from the oxygen lone pair ionizations. Further corroboration is provided by the similarity of the metal–metal bond lengths of these compounds; the fact that the range spans only ca. 0.07 Å despite the wide variation in electronic properties of the ligands suggests that the ligand contribution to the metal–metal bonding orbitals is minimal.

Table III. Absorption Bands (nm) and Molar Absorptivity Coefficients (M^{-1} cm^{-1}) for $Mo_2(OR)_6$ Complexes

$OCMe_3$		$OCMe_2CF_3$		$OCMe(CF_3)_2$
2-methylpentane	CH_2Cl_2	2-methylpentane	CH_2Cl_2	CH_2Cl_2
445 sh (460)	443 sh (700)	436 sh (810)	438 sh (800)	451 sh (700)
406 (820)	406 (1200)	397 (1500)	399 (1500)	413 (1200)
300 sh (630)	293 sh (1100)	291 sh (1200)	292 sh (1300)	299 sh (1200)
269 (1200)	261 sh (2400)	262 (2000)	259 sh (2100)	273 sh (2000)
222 (8800)				
202 (28 000)				

Surprisingly, the evidence from the photoelectron studies and crystallography has been little extended by other spectroscopic or electrochemical[30] techniques. In particular, absorption spectra of triply bonded complexes are rare. The spectrum of $Mo_2(O\text{-}iPr)_6$ in hexane solution was described in a review in 1983;[21] it consists of a band at 360 nm (ε 1400) tailing into the visible, a shoulder at ca. 255 nm (ε ca. 3000), a shoulder at ca. 222 nm (ε ca. 14 000), and a band at 210.5 nm (ε 22 400). The lowest energy band was assigned as the M–M π → M–L π* (M–M π → M–M δ) transition, and the highest energy band, as the M–M π → M–M π* transition. The shoulders were not assigned. The spectrum of **2** in THF was fully reported in 1987;[31] it consists of a band at 392 nm (ε 1400) tailing into the visible and a shoulder at 285 nm (ε 6400). The former was assigned as a π → π* transition, possibly suggesting that the authors had reassessed their assignment of the lowest energy band of $Mo_2(O\text{-}iPr)_6$; the shoulder was not assigned. We are not aware of any further studies of this type. Because **2**, **4**, and **5** represent a congeneric and presumably isostructural trio of triply bonded compounds containing alkoxide ligands with regularly decreasing π-donating ability, we anticipated that their absorption spectra would provide an interesting study of the relationship between π-donor ability and band position, which might provide further clues regarding the nature of the HOMO and LUMO in these compounds.

We obtained the spectra of **2** and **4** in the noninteracting solvent 2-methylpentane but were unable to obtain spectra of **5** in this solvent owing to its extremely low solubility. We then acquired spectra of all three complexes in dichloromethane. Table III gives the band data in both solvents, and plots of the three spectra taken in dichloromethane appear in Figure 3. Two conclusions can be drawn: (1) the similarity of the spectra of **2** and **4** in 2-methylpentane and dichloromethane suggests that the more polar solvent does not coordinate or otherwise perturb the molecules and that solvent–molecule charge-transfer bands, if they exist at all, are insignificant or lie at high energies and (2) decreasing the π-donating ability of the alkoxides by replacing hydrogens with fluorines does not greatly affect the transition

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(29) Chisholm, M. H.; Clark, D. N.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 574–586.

(30) The electrochemistry of a related hexakis(arenethiolato)dimolybdenum compound has been described, but no conclusions were drawn from the data. See: Blower, P. J.; Dilworth, J. R.; Zubieta, J. *Inorg. Chem.* **1985**, *24*, 2866–2868.

(31) Chisholm, M. H.; Clark, D. L.; Kober, E. M.; Van der Sluys, W. G. *Polyhedron* **1987**, *6*, 723–727.

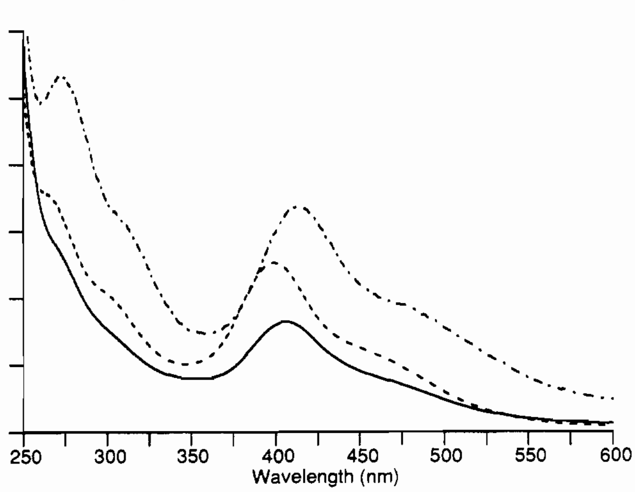

Figure 3. Absorption spectra of **2** (—), **4**, (- - -), and **5** (- · · -) in CH_2Cl_2 solution. The abscissa is in arbitrary units; the spectra are uncorrected for solvent absorption.

energies of any of the four observable bands. The spectra are nearly identical in terms of band position and molar absorptivity coefficient; the range spanned by the reasonably well-resolved band near 400 nm in each spectrum is only 850 cm^{-1}. While the other bands appear as shoulders, and therefore have less well-defined positions, they appear unlikely to lie more than 1500 cm^{-1} apart from spectrum to spectrum.

This result was entirely unexpected. We had anticipated that decreasing the π-donor ability of the alkoxides would lead to decreased mixing of ligand character into the LUMO, raising the energy of this orbital and therefore the transition energy. While we have not attempted to assign the bands,[32] their similarity of shape and molar absorptivity coefficient suggests that they arise from transitions between the same states. It thus appears that all of the discernible bands may arise from the nominal HOMO–LUMO transition; at the very least, the lowest energy bands should correspond to this transition. The equivalent energies of the bands suggest the following possibilities: (1) neither the HOMO or LUMO contains any ligand contribution, so that changing the alkoxide ligand has no effect on the transition energy or (2) the HOMO and LUMO are composed of approximately the same significant ligand contribution such that they are affected equally by a change in alkoxide ligand and the energy gap between them is therefore constant. Evidence exists for and against each of these interpretations. As noted above, theoretical, crystallographic, and photoelectron spectroscopic data indicate that the HOMO is metal–metal π and contains at most a very small ligand contribution; this argues for the first possibility. Conversely, recent calculations[29] on the congeneric model $W_2(OH)_6$ by Chisholm and co-workers employing the Fenske–Hall method indicate that the LUMO, nominally characterized as metal–metal π^*,[27] is composed of a greater amount of metal δ than metal π. Since the metal–ligand interactions are also of δ symmetry, it seems likely that the metal–metal δ and metal–ligand δ would mix, resulting in a LUMO containing significant ligand character. In addition, the Raman experiments mentioned above suggest that the symmetric vibration of the metal–metal bond is affected by the nature of the ligands; to the extent that this correlates with the orbital nature of the bonding, these results argue for the second possibility.

We are not currently in a position to select between these possibilities. We tentatively lean toward the idea that both orbitals are equally ligand-mixed, even though this necessitates we accept that the metal–metal bond length must vary little with the orbital overlap character and that the previous calculations do not represent the system accurately. We recognize, however, that the evidence is by no means unarguable and therefore plan to investigate further. Photoelectron spectroscopy should indicate whether the energy of the HOMO ionization shifts regularly as the π-donor ability of the alkoxide changes. Assuming that we can separate inductive effects from orbital overlap effects, if the band position is constant, this provides evidence for the first possibility; if the band position shifts, the second possibility is more likely. We also hope to undertake electron transmission spectroscopy experiments to probe the nature of the LUMO more directly.

Conclusion

While metathetical methods have proved useful for the synthesis of many transition metal alkoxide complexes, this study describes their first general application to the preparation of homoleptic d^3–d^3 triply bonded dimolybdenum compounds. We hope that this methodology stimulates the synthesis of many new analogues, including thiolates, phosphides, and silyls; we plan to explore some of these ourselves.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We appreciate comments and suggestions from Professor Michael Hopkins (University of Pittsburgh) and Professor Joseph Heppert (University of Kansas).

Supplementary Material Available: Complete tables of crystal data and experimental methods, bond distances and angles, and anisotropic thermal parameters and a packing diagram for **5** (5 pages). Ordering information is given on any current masthead page.

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(32) The ground state in these D_{3d} compounds is $^1A_{1g}$. Assuming that the HOMO is the metal–metal π orbital, of E_u symmetry, and that the LUMO is π^*, of E_g symmetry, then excited states generated by the HOMO–LUMO (nominal $\pi \rightarrow \pi^*$) excitation are A_{2u}, E_u, and A_{1u}. The transitions $A_{1g} \rightarrow A_{2u}$ and $A_{1g} \rightarrow E_u$ are LaPorte allowed in D_{3d} symmetry. Including vibronic and spin–orbit coupling, both of which might be substantial effects in **2**, **4**, and **5**, would increase the number of possible transitions.