d orbital type (d_{xz}), whereas the a_2 orbital contains an in-phase combination of the d_{xz} orbitals and the e orbital an out-of-phase combination. These two orbitals will then essentially differ from one another only in respect to a single symmetry plane: one orbital will be symmetric with respect to this plane while the other will be antisymmetric. Since transitions between orbitals that differ from one another simply by behavior with respect to a symmetry plane are strongly allowed (e.g., atomic $s \leftrightarrow p$, $p \leftrightarrow d$, etc. transitions), it is expected that the $15e \rightarrow 5a_2$ should be strongly allowed. The same argument holds for the $14a_1 \rightarrow 17e$ transition since both orbitals have heavy contributions from the d_{z^2} orbitals.

The remaining two transitions are seen to be between molecular orbitals that are built up of different types of metal d orbitals: $15e(d_{xz}) \rightarrow 16e(d_{xy})$ and $15e(d_{xz}) \rightarrow 17e(d_{z^2}, d_{x^2-y^2})$. For this reason the two orbitals will differ from one another by more than behavior with respect to a single symmetry plane. These transitions should then be relatively weak as are most $d \rightarrow d$ transitions.

On the basis of the correlation of the predicted energies and intensities with the experimental data, the band assignments listed in Table IV are proposed. We are reasonably confident in the assignments of the two lower energy bands since no other allowed transitions are expected in this region. (The $15e \rightarrow 4a_2$ (2.11 V) and $14a_1 \rightarrow 16e$ (2.39 V) transitions are forbidden in D_{3h} symmetry though allowed in C_{3v}, and the $14a_1 \rightarrow 4a_2$ (2.99 V) transition is dipole forbidden in D_{3h} and C_{3v}.) The assignments of the two higher energy bands are much more speculative because the possibility of charge-transfer bands has not yet been considered. According to the calculation, the oxygen lone pairs of the terminal alkoxides ($3a_2$ etc.) occur at only slightly lower energies than the metal–metal bonding orbitals $14a_1$ and 15e. Therefore, oxygen ($p\pi$) to metal charge-transfer transitions are also expected to occur in the UV region (e.g., $3a_2 \rightarrow 16e$ at ~2.8 V). Clearly, polarization and/or resonance Raman studies on the absorption bands would be helpful in this regard. A photoelectron spectrum would also be useful in delineating the position of the oxygen lone pairs relative to the metal–metal bonds.

Since the singly reduced complex is stable in solution, it is interesting to consider what changes in the absorption spectra would be expected upon addition of an electron to the 16e orbital. First, two new low-energy transitions would be expected to appear: $16e \rightarrow 4a_2$ (0.60 V) and $16e \rightarrow 17e$ (2.07 V). Both of these are allowed in the idealized D_{3h} symmetry, the former being xy polarized and the latter z. Second, since the 16e orbital is now partially occupied, the $15e \rightarrow 16e$ transition might decrease in intensity.

A comparison of the spectra of the neutral and reduced species is shown in Figure 4. The reduced complex exhibits a new band at quite low energy ($\leq$0.6 V), which could be assigned to the anticipated $16e \rightarrow 4a_2$ transition. The $15e \rightarrow 16e$ transition of ~1.8 V is observed to lose intensity as expected and also appears to broaden somewhat. Whether the $16e \rightarrow 17e$ transition is responsible for this broadening or for the increased absorption at ~3 V is uncertain. Overall, however, the observed spectral changes are quite consistent with the added electron entering the 16e orbital.

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Contribution from the Department of Chemistry and Molecular Structure Center,
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The Molybdenum–Molybdenum Triple Bond. 14.[1] Preparation and Characterization of Mixed Alkoxy–Thiolate Compounds of Formula $Mo_2(OR)_2(SAr)_4$ (M≡M)

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Hydrocarbon solutions of $Mo_2(NMe_2)_6$ react with mesitylenethiol (ArSH) to give $Mo_2(NMe_2)_2(SAr)_4$. Similarly, the alkoxides $Mo_2(OR)_6$ react with mesitylenethiol in hydrocarbon solvents to give $Mo_2(OR)_2(SAr)_4$ compounds, where R = *t*-Bu, *i*-Pr, and CH_2-*t*-Bu. These arenethiolato compounds are notably less air sensitive than their precursor amides and alkoxides. Solution ^1H NMR data are consistent with anti or rapidly interconverting anti and gauche rotamers of ethane-like dimers $(RO)(ArS)_2Mo{\equiv}Mo(SAr)_2(OR)$. In the solid state, $Mo_2(O\text{-}i\text{-}Pr)_2(SAr)_4$ adopts the anti conformation with crystallographically imposed C_i symmetry and the following important structural parameters: Mo–Mo = 2.230 (1) Å, Mo–S = 2.32 (1) Å (averaged), Mo–O = 1.878 (2) Å, Mo–Mo–S = 95.4 (1)° and 99.8 (1)° and Mo–Mo–O = 106.8 (1)°. Crystal data at −163 °C: a = 21.778 (2) Å, b = 8.600 (2) Å, c = 24.587 (2) Å, β = 108.90 (1)°, and Z = 4 in the space group $C2/c$.

Introduction

Homoleptic compounds of formula $X_3Mo{\equiv}MoX_3$ are known for X = bulky β-elimination-stabilized alkyls (CH_2CMe_3, CH_2SiMe_3), NMe_2, and OR (R = a bulky alkyl or trialkylsilyl group, e.g. *t*-Bu, *i*-Pr, CH_2-*t*-Bu, $SiMe_3$, $SiEt_3$, etc.).[2,3] We have wondered for some time whether this series could be extended to include thiolato (mercaptido), SR, ligands. Though there was no reason to believe that such compounds could not exist, our initial synthetic attempts were thwarted by problems arising from molybdenum's high affinity for sulfur, facile C–S bond cleavages, polymerization by μ-SR formation and oxidation of the Mo_2^{6+} center.[4] We were able, however, to attach two SR ligands to the $(Mo{\equiv}Mo)^{6+}$ unit

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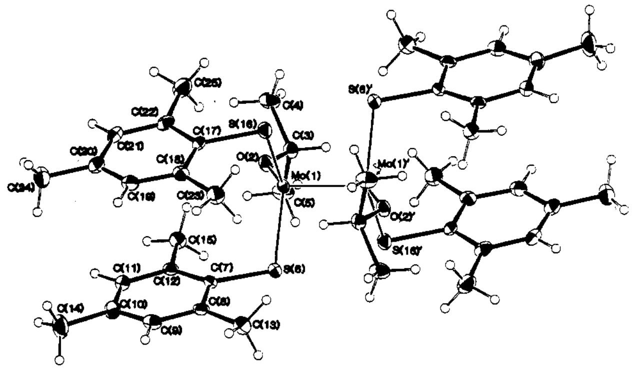

Figure 1. ORTEP view of the centrosymmetric $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ molecule giving the atom-number scheme used in the tables.

in the compound $1,2\text{-}Mo_2(S\text{-}t\text{-}Bu)_2(NMe_2)_4$.[5] We describe in this paper results obtained in our continuing quest for a $Mo_2(SR)_6$ compound.

Results and Discussion

Syntheses. Recognizing the problems associated with facile C–S bond cleavage and μ-SR formation, we chose to work with the bulky aromatic thiol 2,4,6-trimethylbenzenethiol (mesitylenethiol), hereafter referred to as ArSH. Koch and coworkers reported[6] the formation of $Mo_2(SPh)_9^{3-}$ salts from metathesis reactions involving molybdenum halides. On the basis of a preliminary X-ray study, they deduced that this diamagnetic anion has a confacial-bioctahedral geometry $[(SPh)_3Mo(\mu\text{-}SPh)_3Mo(SPh)_3]^{3-}$. We have found that benzenethiol and *p*-nitrobenzenethiol react with $Mo_2(NMe_2)_6$ and $Mo_2(OR)_6$ compounds to give hydrocarbon-insoluble, nonvolatile products for which elemental analytical data were ambiguous with regard to formulation. The requirement for at least one ortho methyl substituent to prevent μ-SR formation was implicated.

$Mo_2(NMe_2)_2(SAr)_4$. Hydrocarbon solutions of $Mo_2(NMe_2)_6$[7] reacted rapidly with mesitylenethiol to give $Mo_2(NMe_2)_2(SAr)_4$. If the reaction is carried out in hexane or pentane, the mixed dimethylamido–thiolato compound comes out of solution as an orange microcrystalline precipitate in near-quantitative yield. $Mo_2(NMe_2)_2(SAr)_4$ is more soluble in toluene, but even when the reaction is carried out in toluene, the same product is obtained.

The ^1H NMR spectrum for $Mo_2(NMe_2)_2(SAr)_4$ is not simple but can be rationalized in terms of a mixture of anti and gauche rotamers and hindered rotations about Mo–NMe_2 bonds. Furthermore, signals from an impurity, $Mo_2(NMe_2)_3(SAr)_3$, may be a complicating feature. The latter compound apparently crystallizes with the former.

In the mass spectrometer, there is a strong molecular negatively charged ion $Mo_2(NMe_2)_2(SAr)_4^-$ at $m/e = 888$ (^{98}Mo) and a weak ion at $m/e = 781$ (^{98}Mo) assignable to $Mo_2(NMe_2)_3(SAr)_3^-$.

$Mo_2(OR)_2(SAr)_4$ Compounds. Hydrocarbon solutions of $Mo_2(OR)_6$ compounds (R = *t*-Bu, *i*-Pr, and CH_2-*t*-Bu)[8] react with mesitylenethiol fairly slowly at room temperature to yield $Mo_2(OR)_2(SAr)_4$ compounds. When the reaction is carried out with use of concentrated hexane solutions of the $Mo_2(OR)_6$ compounds (R = CH_2-*t*-Bu and *i*-Pr), the mixed alkoxide–thiolates are obtained as yellow-orange microcrystalline precipitates, which can be recrystallized from toluene solutions. $Mo_2(O\text{-}t\text{-}Bu)_6$ and ArSH react slightly slower than the neopentoxy and isopropoxy compounds, and the resultant mixed alkoxy–thiolate is a scarlet solid and redder in solution than the other alkoxy derivatives. These compounds are notably less air sensitive than the $Mo_2(OR)_6$ compounds, presumably because the four aromatic groups provide a steric and hydrophobic shield against water molecules. The compounds must, however, be handled under inert atmospheres and in inert solvents.

The ^1H NMR spectra of the compounds in toluene-d_8 are quite simple and as expected for anti or rapidly interconverting anti and gauche $(RO)(ArS)_2Mo{\equiv}Mo(SAr)_2(OR)$ compounds.

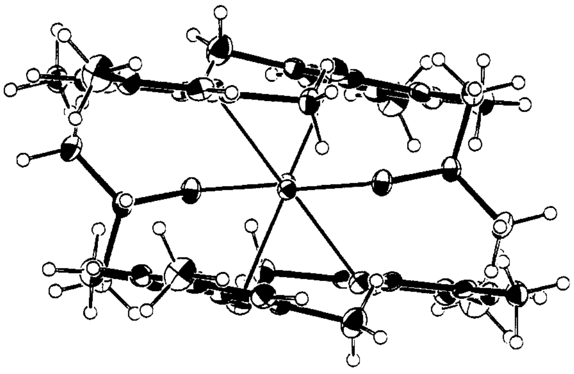

Figure 2. ORTEP view of the $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ molecule as one looks down the Mo–Mo bond.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	7436.5 (1)	2911.2 (3)	408.6 (1)	10
O(2)	8098 (1)	4364 (3)	731 (1)	15
C(3)	8605 (2)	5145 (4)	579 (2)	14
C(4)	9224 (2)	5018 (5)	1084 (2)	20
C(5)	8392 (2)	6793 (5)	418 (2)	20
S(6)	6387.5 (4)	3837 (1)	−16.9 (4)	13
C(7)	6038 (2)	4183 (4)	543 (1)	12
C(8)	5417 (2)	3523 (4)	458 (1)	14
C(9)	5110 (2)	3846 (4)	859 (2)	16
C(10)	5380 (2)	4787 (4)	1333 (1)	18
C(11)	5988 (2)	5406 (4)	1407 (2)	16
C(12)	6325 (2)	5137 (4)	1021 (1)	13
C(13)	5077 (2)	2528 (4)	−53 (2)	18
C(14)	5016 (2)	5144 (6)	1744 (2)	28
C(15)	6982 (2)	5881 (4)	1133 (2)	16
S(16)	7574.4 (4)	582 (1)	907.5 (4)	15
C(17)	7291 (2)	1286 (4)	1477 (1)	14
C(18)	6658 (2)	878 (4)	1460 (1)	15
C(19)	6444 (2)	1402 (4)	1902 (2)	16
C(20)	6819 (2)	2303 (4)	2353 (1)	19
C(21)	7444 (2)	2669 (4)	2359 (2)	17
C(22)	7698 (2)	2157 (4)	1939 (1)	16
C(23)	6215 (2)	−81 (5)	983 (2)	20
C(24)	6562 (2)	2873 (5)	2815 (2)	25
C(25)	8390 (2)	2551 (5)	1990 (2)	23

Table II. Selected Bond Distances (Å) for the $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ Molecule

A	B	dist	A	B	dist
Mo(1)	Mo(1)'	2.230 (1)	O(2)	C(3)	1.442 (4)
Mo(1)	S(6)	2.324 (1)	C(3)	C(4)	1.513 (5)
Mo(1)	S(16)	2.317 (1)	C(3)	C(5)	1.503 (5)
Mo(1)	O(2)	1.878 (2)	C	C	1.40 (1)[a]
S(6)	C(7)	1.800 (3)	C	C	1.50[b]
S(16)	C(17)	1.808 (3)			

[a] Ring, averaged. [b] Ring methyl.

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Table III. Selected Bond Angles (deg) for the $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ Molecule

A	B	C	angle
Mo(1)′	Mo(1)	S(6)	95.4 (0)
Mo(1)′	Mo(1)	S(16)	99.8 (0)
Mo(1)′	Mo(1)	O(2)	106.8 (1)
S(6)	Mo(1)	S(16)	118.3 (0)
S(6)	Mo(1)	O(2)	118.1 (1)
S(16)	Mo(1)	O(2)	113.7 (1)
Mo(1)	S(6)	C(7)	108.0 (1)
Mo(1)	S(16)	C(17)	95.9 (1)
Mo(1)	O(2)	C(3)	138.4 (2)

Solid-State and Molecular Structure of $Mo_2(O\text{-}i\text{-}Pr)_2(S\text{-}2,4,6\text{-}C_6H_2Me_3)_4$. In the space group $C2/c$, the $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ molecule has a crystallographically imposed center of inversion. An ORTEP view of the molecule showing the atom-number scheme used in the tables is shown in Figure 1, and a view of the molecule as one looks down the Mo–Mo bond is given in Figure 2. Fractional coordinates are given in Table I; selected bond distances and angles are given in Tables II and III, respectively.

The Mo–Mo distance, 2.230 (1) Å, is typical of those found in $(Mo{\equiv}Mo)^{6+}$-containing compounds and may be compared specifically with that found in $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$, 2.222 (2) Å.[8] The conformations of the mesityl and isopropyl groups are, with respect to the Mo≡Mo bond, distal and proximal, respectively. This no doubt reflects a minimization of steric repulsive interactions. The Mo–Mo–O and Mo–Mo–S angles are close to 100°, again typical of the angles seen in these so-called ethane-like d^3–d^3 dimers.

Evidence for Sulfur-to-Molybdenum π Bonding. The importance of Me_2N and RO to metal π bonding has been repeatedly noted in terms of both structural parameters and chemical reactivity in the chemistry of $(M{\equiv}M)^{6+}$-containing compounds. We see here unequivocal structural evidence for S-to-Mo π bonding.

The covalent radius of molybdenum in ethane-like $(M{\equiv}M)^{6+}$-containing compounds can be reasonably estimated from Mo–C distances. These can reliably be taken to be purely σ bonds involving sp^3 or sp^2 carbon atoms. Mo–C distances, found in a variety of ethane-like dimers, are summarized in Table IV, from which a r_{Mo} value of 1.40 Å is obtained with a maximum deviation of 0.04 Å. Small variations in Mo–C distances are to be expected as a result of the combined influences of electronic and steric factors associated with the other ligands at the $(M{\equiv}M)^{6+}$ center.

In the present compound, $1,2\text{-}Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$, we can obtain an estimate of the Mo–S single-bond distance by use of the simple equation $d_{Mo-S} = r_{Mo} + r_S$. A reasonable value of r_S may be determined from the S–C distances in the molecule: $d_{S-C} = r_S + r_{C(sp^2)}$. This gives $r_S = 1.07$ Å. Alternatively, $r_S = 1.03$ Å could be used, this being half the average S–S distance in S_8.[9] Using this approach, one obtains a predicted Mo–S single-bond distance to be within the range 2.43–2.47 Å. The observed Mo–S distance, 2.32 Å (averaged), is ca. 0.15 Å shorter than expected on the basis of these considerations. Some shortening of the Mo–S distance might be expected on the basis of the different electronegativities of the elements, though this can reasonably be taken to be a very small effect since, for the structurally related series of compounds $1,2\text{-}W_2X_2(NEt_2)_4$, where X = Cl, Br, I, and CH_2SiMe_3, which adopt the anti conformation, the value of $d_{W-X} - d_{X-X}$ varied by only 0.02 Å.[10] Thus, we believe it is reasonable to say that the Mo–S distances in $1,2\text{-}Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ are at least 0.1 Å shorter than would be expected on the basis of single-bond radii and that this is a result of supplemental S-to-Mo π bonding. It may also be noted that the Mo–O distance, 1.878 (2) Å, is essentially identical with the average Mo–O distance, 1.876 Å, in the compound $Mo_2(OCH_2\text{-}t\text{-}Bu)_6$.[8] This implies that the substitution of four alkoxy groups by four arenethiolate ligands has little overall effect on RO-to-Mo bonding in these compounds.

Table IV. Estimates of Single-Bond Radii for Molybdenum in Alkyl Dimolybdenum Dimers of the $X_3M{\equiv}MX_3$ Type[a]

compd	Mo–C, Å	r_{Mo}, Å	ref
$Mo_2(CH_2SiMe_3)_6$	2.13	1.36	*b*
$1,2\text{-}Mo_2(O\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_4$	2.13	1.36	*c*
$1,2\text{-}Mo_2Me_2(NMe_2)_4$	2.17	1.40	*d*
$1,2\text{-}Mo_2Et_2(NMe_2)_4$	2.17	1.40	*e*
$1,2\text{-}Mo_2(p\text{-}tolyl)_2(NMe_2)_4$	2.16	1.43	*f*
$1,2\text{-}Mo_2(o\text{-}tolyl)_2(NMe_2)_4$	2.17	1.44	*f*
$1,2\text{-}Mo_2(benzyl)_2(NMe_2)_4$	2.18	1.41	*f*

[a] Based on radii for $C(sp^3)$ and $C(sp^2)$ = 0.77 and 0.73 Å, respectively. [b] Huq, F.; Mowat, W.; Shortland, A.; Skapski, A. C.; Wilkinson, G. *J. Chem. Soc. D* **1971**, 1079. [c] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 252. [d] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 2388. [e] Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046. [f] Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C.; Janos, J. *Ibid.* 1983, *105*, 1163.

Concluding Remarks. It is not clear why reactions employing $Mo_2(NMe_2)_6$ or $Mo_2(OR)_6$ compounds with mesitylenethiol lead to only partial substitution. Steric or electronic factors, or both, could be responsible. In our quest for a $Mo_2(SR)_6$ compound, we are encouraged since it seems that relatively subtle changes in the steric properties of the thiol or changes in the leaving group should allow a successful synthesis of such a compound. The compounds $Mo_2(OR)_2(SAr)_4$ are in themselves of considerable interest since they afford interesting starting materials (that can be prepared in high yield) for comparative studies with reactions of $M_2(OR)_6$ compounds. The relative reactivities of the RO and SAr groups within the same molecule are also of interest.

Experimental Section

General Information. Standard procedures for the manipulation of air-sensitive materials were used throughout.

Materials. $Mo_2(NMe_2)_6$ and $Mo_2(OR)_6$ compounds were prepared as described previously.[7,8]

Mesitylenethiol was prepared from the reaction between mesityl Grignard reagent and elemental sulfur. To a solution of $C_6H_2Me_3MgBr$ (135 mL, 1 M) in THF, was added sulfur (0.135 mol) over a period of 20 min. The solution was stirred an additional 30 min. Water (15–20 mL) was added, followed by 6 N HCl (30–35 mL). The THF layer that separated was collected and dried overnight (10 h) over $MgSO_4$. The THF was removed in vacuo, leaving a clear yellow oil, which was distilled at ca. 10^{-4} torr, 50 °C: 2,4,6-trimethylbenzenethiol (16.74 g, 0.11 mol, 81% yield). This was dissolved in THF (15 mL) to give a 7.33 M solution.

$Mo_2(NMe_2)_2(SC_6H_2Me_3)_4$. $Mo_2(NMe_2)_6$ (0.68 g, 1.5 mmol) was dissolved in hexane (20 mL) and cooled to 0 °C. Mesitylenethiol (1.45 mL of a 7.33 M solution in THF, 10.5 mmol) was added via syringe. The solution was warmed to room temperature and stirred overnight (10 h). A yellow-orange precipitate formed, which was collected by filtration and recrystallized from toluene: $Mo_2(NMe_2)_2(SC_6H_2Me_3)_4$ (1.21 g, 1.37 mmol, 91% yield based on Mo). Anal. Calcd: C, 54.30; H, 6.33; N, 3.17; S, 14.48. Found: C, 53.95; H, 7.18; N, 3.92; S, 13.95.

In the mass spectrometer,[11] there was a M^- ion at m/e = 888 (^{98}Mo) and a weak M^- ion at m/e = 781 (^{98}Mo) arising from the impurity of $Mo_2(NMe_2)_3(SC_6H_2Me_3)_3$, which no doubt accounts for the de-

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(11) We thank Arlene Rothwell, Purdue University, for the courtesy of obtaining mass spectral results.

Table V. Summary of Crystallographic Data

formula	$C_{42}H_{58}Mo_2O_2S_4$
fw	915.04
space group	$C2/c$
a, Å	21.778 (6)
b, Å	8.600 (2)
c, Å	24.587 (7)
β, deg	108.90 (1)
Z	4
V, Å	4356.74
density (calcd), g/cm^3	1.395
cryst size, mm	0.27 × 0.22 × 0.20
cryst color	yellow-orange
radiation	Mo Kα (λ = 0.710 69 Å), graphite monochromator
linear abs coeff, cm^{-1}	7.78
temp, °C	−163
instrument	Picker 4-circle diffractometer locally modified and interfaced
detector aperture	3.0 mm wide × 4.0 mm high, 22.5 cm from cryst
sample to source distance, cm	23.5
takeoff angle, deg	2.0
scan speed, deg/min	8.0
scan width, deg	1.8 + 0.692 tan θ
bkgd counts, s	5 at each end of scan
2θ range, deg	6–45
data collected	4412 total
unique data	2874
unique data with $F_0 > 2.33\ \sigma(F_0)$	2516
$R(F)$	0.026
$R_w(F)$	0.029
goodness of fit	0.790
largest Δ/σ	0.05

viations in the observed analytical data (reported above) from that calculated for $Mo_2(NMe_2)_2(SC_6H_2Me_3)_4$. IR data (Nujol mull): 1595 m, 1260 m, 1240 m, 1170 m, 1140 m, 1050 m, 950 s, 930 s, 840 s, 720 w, 570 w, 400 w cm^{-1}. ^{1}H NMR data in toluene-d_8 at +45 °C: $\delta(NMe_2)$ = 3.3; δ(mesityl) = 2.12, 2.02, 6.60.

$Mo_2(OR)_2(SC_6H_2Me_3)_4$ Compounds (R = *t*-Bu, *i*-Pr, and CH_2-*t*-Bu). All compounds were prepared in a common manner and obtained in ca. 90% yield after recrystallization. The preparation of the isopropoxy compound is given.

$Mo_2(O\text{-}i\text{-}Pr)_6$ (0.22 g, 0.403 mmol) was dissolved in hexane (5 mL). One milliliter of a 7.33 M solution of mesitylenethiol in THF (7.33 mmol) was added by syringe at room temperature. The solution changed from yellow to yellow-orange. The solution was stirred for 10 h, and the yellow-orange precipitate was collected by filtration and recrystallized from toluene (note that, even if the reaction is carried out in toluene solution, no further replacement of the alkoxy groups is observed): $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ (0.34 g, 0.374 mmol, 92% yield). Anal. Calcd: C, 55.14; H, 6.35; S, 14.00. Found: C, 55.08; H, 6.48; S, 13.93.

The compound showed a molecular ion, M$^-$, at m/e = 918 (^{98}Mo).[11] ^{1}H NMR data in benzene-d_6 at 34 °C and 220 MHz: O-*i*-Pr, δ(methyne) = 5.9, δ(methyl) = 1.7, J = 7 Hz; δ(mesityl) = 2.1 (*o*-Me), 1.85 (*p*-Me), 6.3 (*m*-H). IR data (Nujol mull): 1595 m, 1320 s, 1290 s, 1155 m, 1100 s, 1040 ms, 965 s, 840 s, 705 m, 610 ms, 570 wm, 550 wm, 450 m, 420 ms, 400 m, 370 m, 320 m cm^{-1}.

$Mo_2(O\text{-}t\text{-}Bu)_2(SC_6H_2Me_3)_4$. Anal. Calcd: C, 56.05; H, 6.58; S, 13.59. Found: C, 55.96; H, 6.61; S, 13.51. ^{1}H NMR data in benzene-d_6 at 34 °C and 220 MHz: δ(O-*t*-Bu) = 1.84; δ(mesityl) = 2.20 (*o*-Me), 2.00 (*p*-Me), and 6.50 (*m*-H). IR data (Nujol mull): 1595 m, 1315 ms, 1290 m, 1160 m, 1100 s, 1040 ms, 970 s, 870 wm, 840 s, 705 m, 610 s, 570 wm, 550 m, 445 wm, 420 ms, 370 m, 320 m cm^{-1}.

$Mo_2(OCH_2\text{-}t\text{-}Bu)_2(SC_6H_2Me_3)_4$. Anal. Calcd: C, 56.91; H, 6.80; S, 13.20. Found: C, 56.82; H, 6.92; S, 13.12. ^{1}H NMR data in benzene-d_6 at 34 °C and 220 MHz: δ(neopentoxide) = 5.83 (CH_2), δ(methyl) 1.20; δ(mesityl) = 2.20 (*o*-Me), 2.00 (*p*-Me), 6.45 (*m*-H). IR data (Nujol mull): 1595 m, 1315 ms, 1295 m, 1155 m, 1100 s, 1040 ms, 970 ms, 870 wm, 840 s, 705 m, 610 s, 570 wm, 550 m, 450 wm, 420 ms, 370 m, 320 m cm^{-1}.

X-ray Structure Determination. General operating facilities, procedures, and programs have been described previously.[12,13]

Crystal data are summarized for $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ in Table V.

A well-defined multifaceted crystal was selected. All handling operations were performed under a nitrogen atmosphere. The crystal was characterized with use of a reciprocal lattice search technique at −167 °C, and data were consistent with a monoclinic lattice of space group $C2/c$. Subsequent solution and refinement confirmed this choice.

The molybdenum and two sulfur atoms in the asymmetric unit were located by direct methods (MULTAN 78), and all other atoms (including hydrogen atoms) were located in subsequent Fouriers. Hydrogen atoms were assigned isotropic thermal parameters and all other atoms anisotropic parameters for the full-matrix least squares. A final difference Fourier was featureless, the largest peak being 0.3 e/Å^3. No absorption correction was necessary.

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Supplementary Material Available: Complete listings of atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and structure factor amplitudes and stereoviews for the $Mo_2(O\text{-}i\text{-}Pr)_2(SC_6H_2Me_3)_4$ molecule (23 pages). Ordering information is given on any current masthead page. The complete structure report, MSC No. 83037, is available from the Indiana University Library in microfiche form only, at $2.50 per report.

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