bonyl bands were clearly seen in IR spectra at 1731 cm^{-1} (R = CO_2Me) and 1726 cm^{-1} (R = H), in addition to the usual dimer absorptions.[28] For ^{1}H NMR spectra, the vinyl proton assignments were unambiguous due to the use of $MeCO_2D$ in alternate syntheses, which gave the deuterioalkene derivative. Deuteriation gave the expected loss of SCCH alkene resonances for both products and resulted in a singlet for the SCH alkene resonance in the methyl propenoate derivative. The ^{1}H and ^{31}P NMR spectra also showed invertomers for both products in solution arising from inversion of the pyramidal sulfur bridge, a characteristic previously documented for other derivatives (**2**).[28]

For the dimethyl butenedioate product **3** (R = CO_2Me), invertomers were observed in a ratio of 2.5 with the major isomer as depicted by **3**, based on earlier conformational studies.[28] Coalescence in the ^{31}P NMR spectrum by 50 °C supports the assignments as invertomers and contraindicates the possibility that the two resonances are due to cis/trans isomers for this derivative. Indeed, no evidence for such stereoisomers was ever observed, and the actual stereochemistry of this product cannot be assigned on the basis of spectral data alone.

For the methyl propenoate product **3** (R = H), cis/trans isomers are indeed observed, each with its own pair of invertomers. The cis/trans mixed product is obtainable in high yields from the reaction and in ratios of approximately 4/1, but separation is difficult and has never been achieved in toto for either stereoisomer. Repeated recrystallization gives the cis isomer in high purity (~95%) but low overall yield. The trans derivative was never obtained in high purity and could at best be obtained as an enriched sample through EtOH digestion of mixed products. Attempts at column chromatography also failed to provide separation. Assignment of the major product as the cis isomer was based on $^3J_{HH} = 10$ Hz for the alkene protons, compared to $^3J_{HH} = 15$ Hz for those of the minor derivative (trans isomer). Such assignments are fully consistent with established vicinal couplings for alkenes[31] and parallel recent stereochemical conclusions regarding cyclopentadienylmolybdenum S,H-additions to ethyl 2-propynoate.[20,24] The major product therefore arises from trans addition across the alkyne triple bond and reflects the common stereochemistry of thiol addition to alkynes.[25] Invertomer ratios for the stereoisomers are 3.8 (cis) and 1.9 (trans), the major invertomer again being assigned the conformation at the pyramidal sulfur as given by **3**.

While dimethyl 2-butynedioate and methyl 2-propynoate readily gave addition products as per eq 1, no alkene products were observed for attempted reactions with acetylene, 1-hexyne, 4-octyne, diphenylacetylene, ethyl 3-phenyl-2-propynoate, or methyl 2-butynoate, suggesting that reaction was facile only with the most activated and sterically uninhibited alkynes. The reactions attempted with these alternate substrates gave only $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCH_2Cl)]$ (**2**, Z = CH_2Cl), which arises from nucleophilic substitution on solvent dichloromethane. This solvent reaction is notably slow and had posed no problem with earlier work on readily substituted substrates[28] but did interfere with the slower synthesis of $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SEt)]$ (**2**, Z = Et), which therefore required a different solvent.[29] The chloromethanethiolate-bridged dimer gives an invertomer ratio of 1.5 in $CDCl_3$. A peak at 728 cm^{-1} in the IR spectrum is tentatively attributed to a C–Cl stretch.

Acknowledgment. This work was supported by research awards from the Graduate School and from the College of Arts and Sciences of the University of Louisville and with funds from the National Science Foundation (Grant No. RII-8610671) and the Kentucky EPSCoR Program.

Registry No. **3** (R = CO_2Me), 112246-91-0; *cis*-**3** (R = H), 112295-33-7; *trans*-**3** (R = H), 112196-28-8; $[Mo(NAr)(S_2P(OEt)_2)S]_4$, 73037-71-5; $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCH_2Cl)]$, 112196-29-9; S, 7704-34-9; CH_2Cl_2, 75-09-2; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; methyl 2-propynoate, 922-67-8.

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The SMo_2SSR Unit. Cyanide Reactions and Crystal Structure

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Received July 22, 1987

Metal–sulfur complexes containing S–S bonds within the ligand framework have been the subject of much interest in recent years. Disulfide (S_2^{2-}), higher polysulfides (S_x^{2-}) and disubstituted organic disulfides (RSSR) have amply demonstrated ligative properties to metals and a large variety of structures and reactivities have been demonstrated.[1-5] Perthio chelates are also well-known in which a normal sulfur bidentate has one or more additional sulfurs in the chelate ring.[5-12]

Less developed are perthio derivatives of simple thiolates representable as RSS^-. Consideration of these ligands is a natural extension of the interest in M–S–S systems; furthermore, their roles as intermediates in thiolate–disulfide interconversions have been proposed for molybdenum systems[13,14] and have been more definitively established for reactions of $(C_5H_5)W(NO)R_2$ with sulfur.[15,16] A modest number of M–SSR complexes have been described.[5,15-25]

Compounds of the general formula $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR)]$ (**1**, R = Et, Bz, Ph, To;[26] dithiophosphate ligands are excluded from structure diagrams for clarity) have been previously reported and contain an imido(di-

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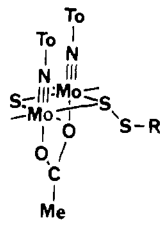
(26) Abbreviations used in this paper: Me, methyl; Et, ethyl; Bu, *n*-butyl; Ph, phenyl; To, *p*-tolyl; Bz, benzyl.

0020-1669/88/1327-0749$01.50/0



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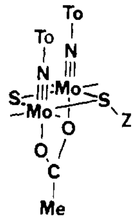

2

thiophosphato)molybdenum(V) dimer bridged by acetate, sulfide, and the RSS^- perthiolate bridging via its β-sulfur.[27] These are members of a more general class of S-derivatized dimers representable by **2**.[27] S–S photohomolysis within the RSS bridge has been shown for the $SMo_2{*}SSR$ ($Mo_2{*}$ = $[Mo_2(NTo)_2(S_2P(OEt)_2)_2(O_2CMe)]$) compounds.[28] As additional characterizations, cyanide reactions have been investigated and the crystal structure for **1**, R = Et has been determined; these are reported presently. Reactions of cyanide with molybdenum sulfide and disulfide complexes have been well characterized, as have also reactions with molybdenum oxidoreductase enzyme systems.[2,29-33] Cyanide reactivity toward M–SSR complexes in general, however, has received very limited study.[34]

Experimental Section

$SMo_2{*}SSR$ (**1**, R = Et and Bz) complexes were prepared as previously described.[27] $CDCl_3$ was dried, vacuum transferred, and subsequently stored under N_2. Other reagents were used as commercially available. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra were recorded on a Varian XL 300 spectrometer at 121, 75, and 300 MHz and are reported as downfield shifts from 85% H_3PO_4 (^{31}P) and Me_4Si (^{13}C, ^1H). IR spectra were obtained on a Perkin-Elmer 283 spectrophotometer by evaporating a $CDCl_3$ solution of the sample on a KBr plate in a glovebag under N_2; this evaporated smear was then sandwiched with a spacer and a second KBr plate in a demountable cell holder, and the spectrum was then promptly recorded.

Product identification was definitive by direct comparison to reference spectra (IR and NMR) of all components considered. Spectral data for $(Bu_4N^+)SCN^-$ were obtained by reacting $(Bu_4N^+)CN^-$ (0.01341 g, 0.050 mmol) with sulfur (0.00164 g, 0.051 mmol S) in $CDCl_3$ (1.0 mL) in a glovebag under N_2, and allowing the mixture to stand for 16 h. The ^{13}C NMR spectrum showed δ 130.9 for SCN^-; the IR spectrum gave $\nu(CN)$ = 2058 (s) cm^{-1} (lit. 2058 cm^{-1} for $(Ph_3PNPPh_3^+)SCN^-$ in acetonitrile[35]). Spectral data for the dimer anion, $SMo_2{*}S^-$,[36] were obtained by combining $[Mo(NTo)(S_2P(OEt)_2)S]_4$[36] (0.04184 g, 0.0250 mmol) and (Bu_4N^+) $MeCO_2^-$ (0.01512 g, 0.0501 mmol) in $CDCl_3$ (1.0 mL) in a glovebag under N_2. The ^{31}P NMR spectrum showed $SMo_2{*}S^-$ (δ 117.4) and a small equilibrium quantity of $[Mo(NTo)(S_2P(OEt)_2)S]_4$; minor, unknown peaks were also seen and corresponded to those also seen in CN^- reaction spectra. Furthermore, some slow decomposition was noted for this sample on long-term standing (2 days).

Cyanide Reactions. In a glovebag under N_2, $(Bu_4N^+)CN^-$ (0.050 mmol) was added to a solution of $SMo_2{*}SSR$ (R = Et or Bz; 0.0500 mmol) in $CDCl_3$ (1.0 mL). The solution was then periodically monitored by ^{31}P, ^1H, and ^{13}C NMR and IR spectroscopy. The ^{31}P NMR results provided the quantitative data.

Crystallography. A red irregular prism of **1** (R = Et) from THF/MeOH recrystallization was mounted on a glass fiber in a random orientation. Data were obtained on an Enraf-Nonius CAD4 diffractometer at room temperature with Mo Kα radiation, graphite monochromatized. Cell constants and the orientation matrix for data collection were based on 25 reflections; systematic absences ($h0l$, $l = 2n$; $0k0$, $k = 2n$) and subsequent refinement gave the space group unambiguously as $P2_1/c$. Relevant information is shown in Table I. Three representative reflections were measured every 120 min during data collection and proved to be constant within experimental error. Lorentz and polarization corrections were made; no absorption correction was utilized. Transmission factors ranged from 0.81 to 0.66. Intensities of equivalent reflections

Table I. Crystallographic Data for $Mo_2S_7P_2N_2O_6C_{26}H_{42}$

fw	956.9
cryst size, mm	0.2 × 0.3 × 0.4
space group	$P2_1/c$
a, Å	13.403 (6)
b, Å	24.817 (8)
c, Å	13.894 (6)
β, deg	116.27 (4)
V, Å^3	4144.0
Z	4
d_{calcd}, g cm^{-3}	1.53
λ, Å	0.71073 (Mo Kα)
μ, cm^{-1}	10.4
$F(000)$	1944
scan method	ω–2θ
scan width, deg	0.8 + 0.340 tan θ
max 2θ, deg	50.0
no. of measd reflcns	7798
no. of reflcns above 3σ	5243
extinction param	6.34 × 10^{-8}
R ($\sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$)	0.043
R_w ($[\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$	0.057

Table II. Positional Parameters for Non-Hydrogen Atoms and Equivalent Isotropic Temperature Factors

atom	x	y	z	B, Å^2
Mo(1)	0.76673 (3)	0.34201 (2)	0.95290 (3)	3.304 (9)
Mo(2)	0.54442 (3)	0.34744 (2)	0.79074 (3)	3.582 (9)
S(1)	0.6571 (1)	0.27038 (5)	0.85168 (9)	4.16 (3)
S(2)	0.65555 (9)	0.42442 (5)	0.89131 (9)	3.89 (3)
S(3)	0.8952 (1)	0.26769 (6)	1.0618 (1)	4.91 (3)
S(4)	0.3923 (1)	0.27967 (6)	0.6994 (1)	5.51 (4)
S(5)	0.3704 (1)	0.40545 (6)	0.7347 (1)	5.21 (4)
S(6)	0.9037 (1)	0.39276 (6)	1.1185 (1)	4.73 (3)
S(7)	0.5902 (1)	0.45461 (6)	0.9901 (1)	5.60 (4)
P(1)	0.2823 (1)	0.33872 (7)	0.6740 (1)	5.52 (4)
P(2)	0.9776 (1)	0.32228 (6)	1.1736 (1)	4.40 (3)
O(1)	0.5089 (2)	0.3362 (1)	0.9285 (2)	4.23 (8)
O(2)	0.6842 (2)	0.3319 (1)	1.0555 (2)	4.04 (8)
O(3)	0.9872 (3)	0.3070 (2)	1.2861 (2)	5.3 (1)
O(4)	1.1058 (3)	0.3239 (2)	1.2077 (3)	5.9 (1)
O(5)	0.1953 (3)	0.3450 (2)	0.5546 (3)	7.3 (1)
O(6)	0.1954 (3)	0.3251 (2)	0.7184 (4)	7.5 (1)
N(1)	0.8310 (3)	0.3623 (2)	0.8746 (3)	3.76 (9)
N(2)	0.5670 (3)	0.3648 (2)	0.6820 (3)	4.09 (9)
C(1)	0.8754 (3)	0.3869 (2)	0.8133 (3)	3.8 (1)
C(2)	0.8746 (5)	0.3603 (2)	0.7252 (4)	5.4 (1)
C(3)	0.9192 (5)	0.3846 (3)	0.6656 (4)	7.0 (2)
C(4)	0.9657 (5)	0.4356 (3)	0.6897 (5)	6.9 (2)
C(5)	0.9626 (5)	0.4617 (3)	0.7729 (5)	7.6 (2)
C(6)	0.9193 (4)	0.4382 (2)	0.8374 (4)	6.0 (1)
C(7)	1.0201 (6)	0.4620 (4)	0.6226 (5)	11.1 (2)
C(8)	0.5815 (4)	0.3831 (2)	0.5957 (3)	4.2 (1)
C(9)	0.5757 (5)	0.3484 (2)	0.5173 (4)	6.1 (2)
C(10)	0.5879 (6)	0.3681 (3)	0.4285 (4)	8.0 (2)
C(11)	0.6052 (5)	0.4212 (3)	0.4174 (4)	7.4 (2)
C(12)	0.6100 (6)	0.4549 (3)	0.4952 (5)	8.3 (2)
C(13)	0.5986 (5)	0.4373 (2)	0.5860 (4)	6.6 (2)
C(14)	0.6194 (7)	0.4418 (3)	0.3202 (5)	11.3 (2)
C(15)	0.8901 (4)	0.2990 (3)	1.3051 (4)	5.8 (1)
C(16)	0.8821 (5)	0.3431 (3)	1.3726 (5)	8.1 (2)
C(17)	1.1475 (5)	0.3336 (4)	1.1289 (5)	8.7 (2)
C(18)	1.2575 (6)	0.3585 (4)	1.1819 (7)	12.1 (3)
C(19)	0.2342 (6)	0.3617 (4)	0.4754 (5)	8.6 (2)
C(20)	0.1834 (8)	0.4149 (4)	0.4303 (6)	10.9 (3)
C(21)	0.2368 (6)	0.3092 (6)	0.8337 (6)	14.1 (4)
C(22)	0.1623 (8)	0.3052 (5)	0.8653 (8)	14.6 (4)
C(23)	0.5800 (4)	0.3293 (2)	1.0249 (4)	4.1 (1)
C(24)	0.5384 (4)	0.3160 (3)	1.1069 (4)	6.0 (1)
C(25)	0.6940 (6)	0.5028 (3)	1.0679 (6)	10.8 (2)
C(26)	0.7123 (9)	0.5450 (4)	1.0103 (8)	15.4 (4)

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Table III. Selected Bond Distances (Å)

Mo(1)–Mo(2)	2.8336 (4)	S(2)–S(7)	2.068 (2)
Mo(1)–S(1)	2.338 (1)	S(3)–P(2)	1.987 (2)
Mo(1)–S(2)	2.451 (1)	S(4)–P(1)	1.996 (2)
Mo(1)–S(3)	2.520 (1)	S(5)–P(1)	1.992 (2)
Mo(1)–S(6)	2.553 (1)	S(6)–P(2)	1.988 (2)
Mo(1)–O(2)	2.171 (4)	S(7)–C(25)	1.789 (7)
Mo(1)–N(1)	1.734 (5)	O(1)–C(23)	1.266 (5)
Mo(2)–S(1)	2.350 (1)	O(2)–C(23)	1.269 (6)
Mo(2)–S(2)	2.446 (1)	N(1)–C(1)	1.380 (7)
Mo(2)–S(4)	2.511 (1)	N(2)–C(8)	1.375 (7)
Mo(2)–S(5)	2.552 (2)	C(23)–C(24)	1.510 (9)
Mo(2)–O(1)	2.185 (4)	C(25)–C(26)	1.41 (1)
Mo(2)–N(2)	1.721 (4)		

Table IV. Selected Bond Angles (deg)

S(1)–Mo(1)–S(2)	107.53 (4)	Mo(2)–S(2)–S(7)	109.42 (7)
S(1)–Mo(1)–S(3)	83.41 (4)	Mo(1)–S(3)–P(2)	88.04 (7)
S(2)–Mo(1)–S(6)	89.24 (5)	Mo(2)–S(4)–P(1)	88.21 (7)
S(3)–Mo(1)–S(6)	78.00 (4)	Mo(2)–S(5)–P(1)	87.19 (7)
O(2)–Mo(1)–N(1)	169.7 (2)	Mo(1)–S(6)–P(2)	87.12 (6)
Mo(2)–Mo(1)–O(2)	82.26 (6)	S(2)–S(7)–C(25)	101.5 (3)
Mo(2)–Mo(1)–N(1)	97.3 (1)	S(4)–P(1)–S(5)	106.40 (9)
S(1)–Mo(2)–S(2)	107.35 (4)	S(3)–P(2)–S(6)	106.82 (7)
S(1)–Mo(2)–S(4)	83.43 (5)	Mo(2)–O(1)–C(23)	126.3 (3)
S(2)–Mo(2)–S(5)	88.67 (4)	Mo(1)–O(2)–C(23)	126.3 (3)
S(4)–Mo(2)–S(5)	78.21 (5)	Mo(1)–N(1)–C(1)	170.4 (4)
O(1)–Mo(2)–N(2)	172.6 (2)	Mo(2)–N(2)–C(8)	174.9 (4)
Mo(1)–Mo(2)–O(1)	81.81 (8)	O(1)–C(23)–O(2)	123.3 (5)
Mo(1)–Mo(2)–N(2)	100.3 (2)	O(1)–C(23)–C(24)	118.1 (4)
Mo(1)–S(1)–Mo(2)	74.37 (5)	O(2)–C(23)–C(24)	118.6 (4)
Mo(1)–S(2)–Mo(2)	70.73 (4)	S(7)–C(25)–C(26)	116.1 (6)
Mo(1)–S(2)–S(7)	116.19 (7)		

were averaged; the agreement factor for the averaging was 2.0%. The structure was solved by direct methods. Mo, S, and P atoms were located from an *E* map; the remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions except for those bound to C(7), C(14), and C(24), where the methyl rotation angle could not be determined from the difference Fourier. Non-hydrogen atoms were refined with anisotropic temperature factors by full-matrix least-squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma_F{}^2$. Scattering and anomalous dispersion factors were taken from the literature.[37] A small extinction correction was included in the final refinement cycles. All calculations were performed with the Enraf-Nonius SDP package.

Positional parameters and equivalent isotropic temperature factors for non-hydrogen atoms are given in Table II. Several peripheral portions of the molecule show large thermal motions. This is particularly acute for C(21) and C(22), which may in fact be disordered: the derived bond length is 1.27 (2) Å, which is clearly too small and which differs distinctly from the other dithiophosphate ethoxy C–C bonds of 1.46 (2)–1.49 (1) Å. Such disorder and thermal motion are not unusual for the alkoxy groups of dithiophosphate ligands.[36,38,39] Despite the peripheral motions, the majority of the structure was clearly defined.

Selected bond distances and angles are given in Tables III and IV. Figure 1 shows the molecular structure.

Results

Reaction of $SMo_2{}^*SSBz$ with 1 equiv of CN^- rapidly gave the dimer anion $SMo_2{}^*S^-$ as the major product at 15 min. Small quantities of the thiolate-bridged dimer $SMo_2{}^*SBz$ (**2**, Z = Bz)[27] and of unreacted $SMo_2{}^*SSBz$ were also evident. These were not individually integrable by the ^{31}P NMR spectra due to overlap; the $SMo_2{}^*SSBz$ did appear to remain constant throughout the course of study (4 days) and was estimated at less than 10%. Traces of unidentified components were also observable in the ^{31}P NMR spectrum but were not considered significant to the main reaction. The ^1H (at 30 min) and ^{13}C (at 135 min) NMR results verified the Mo products and clearly showed BzSCN as a major component; the ^{13}C spectrum furthermore indicated free SCN^-. The infrared spectra verified the NMR results.

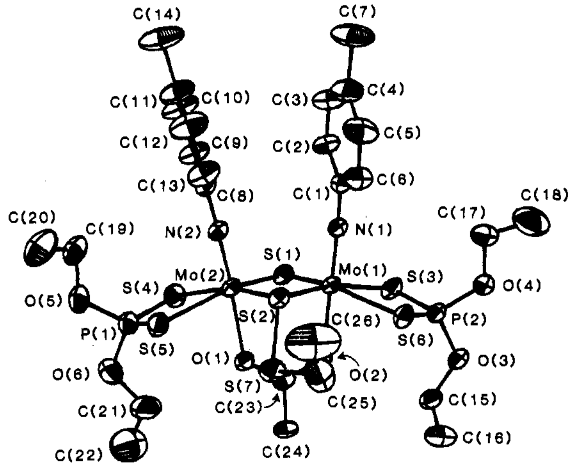
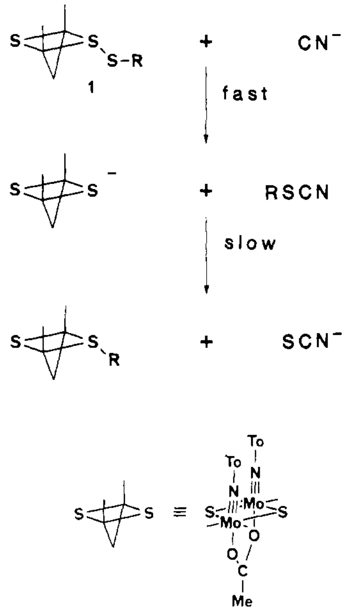


Figure 1. ORTEP view of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSEt)]$.

Scheme I



Time monitoring via all above spectroscopies over 4 days clearly showed nearly complete disappearance of $SMo_2{}^*S^-$ and BzSCN while $SMo_2{}^*SBz$ increased. The ^{31}P NMR results gave 46% $SMo_2{}^*S^-$ at 2 h, 12% at 8 h, 3% at 24 h, and 5% at 98 h, with $SMo_2{}^*SBz$ as the only species increasing throughout. SCN^- was clearly observed throughout in all ^{13}C NMR spectra, as was BzSCN, which only appeared in quite small quantity after 99 h. ^1H NMR data supported these results. IR spectra remained essentially unchanged in the $\nu(CN)$ region through 101 h.

Reaction of $SMo_2{}^*SSEt$ with 1 equiv of CN^- also rapidly gave the dimer anion as the major component (84%) at 15 min; 8% unreacted $SMo_2{}^*SSEt$ was seen, as were also minor, unidentified components. The ethanethiolate-bridged dimer $SMo_2{}^*SEt$ (**2**, Z = Et),[28] however, was absent. The ^1H (at 20 min) and ^{13}C (at 75 min) NMR spectra clearly also showed EtSCN, but no evidence for SCN^- was seen in the latter or in the IR spectrum at 60 min.

Time monitoring over 4 days showed very slow, further reaction. $SMo_2{}^*SEt$ was indeed observed by ^{31}P NMR at 8 h (1%) and reached 11% at 96 h, but $SMo_2{}^*S^-$ decomposition (see Experimental Section) was competitive, such that this component decreased to 62% at 96 h. IR and ^1H NMR spectra supported these results.

Discussion

The path of reaction of cyanide with $SMo_2{}^*SSR$ (R = Bz, Et) is summarized in Scheme I. Initial nucleophilic attack by CN^-

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on the bridge perthiolate α-sulfur gives the dimer anion and alkyl thiocyanate in a very rapid step. The dimer anion, analogous to previously established nucleophilic reactions with alkyl or sulfur halides,[27] then attacks the alkyl thiocyanate to generate the alkanethiolate-bridged dimer and thiocyanate ion. This second reaction was slow for R = Bz and extremely slow for R = Et and may in fact have been an equilibrium step for either.

The first reaction follows standard RSSR/$\mathrm{CN^-}$ chemistry,[40,41] while the desulfurization overall parallels production of organic sulfides from RSSR/$\mathrm{CN^-}$.[42] Desulfurization is also characteristic of cyanide reactions with molybdenum sulfide and disulfide complexes, as well as some molybdenum enzymes, and thiocyanate is a common product.[2,30–33] The methaneperthiolate system $\mathrm{[Ir(SSMe)(Ph_2PC_2H_4PPh_2)_2]^{2+}}$ has also been reported to react with cyanide.[34] In that complex, the $\mathrm{MeSS^-}$ unit is η^2-bound, and cyanide attacks at the β-sulfur. S–S cleavage is obtained, but thiocyanate is retained as a ligand.

Crystal Structure of $\mathrm{SMo_2}$*SSEt. The $\mathrm{SMo_2}$*S core of the current $\mathrm{SMo_2}$*SSEt is similar to the previously analyzed cores of $\mathrm{SMo_2}$*SH[36] and $\mathrm{SMo_2}$*SMe.[38] These contained bridging hydrosulfide and methanethiolate groups, and both also contained bridging trifluoroacetate as opposed to acetate in $\mathrm{SMo_2}$*SSEt. Only some aspects of the core in $\mathrm{SMo_2}$*SSEt are therefore currently addressed.

The $\mathrm{Mo_2S_2}$ unit is planar; all atoms are within 0.01 Å of the least-squares plane. Disparity in Mo–S bonding within the dimer is obvious both at the bridge sulfur sites ($\mathrm{S_b}$) and at dithiophosphate sulfur sites. Mo–$\mathrm{S_b}$ bonds are clearly longer to the tricoordinate sulfur S(2) than to S(1), the differences being 0.113 (1) Å and 0.096 (1) Å for Mo(1)–$\mathrm{S_b}$ and Mo(2)–$\mathrm{S_b}$, respectively.

The acetate is symmetrically bridging within experimental error. Mo–O bonds are approximately 0.09 Å shorter for $\mathrm{SMo_2}$*SSEt than corresponding lengths in $\mathrm{SMo_2}$*SH and $\mathrm{SMo_2}$*SMe which instead possessed trifluoroacetate.

The most important structural feature for $\mathrm{SMo_2}$*SSEt is the clear definition of the ethaneperthiolate group. The orientation of this group shows some skew in the S(2)–S(7) bond vector away from a symmetric position relative to the $\mathrm{Mo_2S_2}$ core. The displacement can be seen in Mo···S(7) distances which are 3.841 (2) Å for Mo(1) and 3.690 (2) Å for Mo(2) although Mo–S(2) distances are comparable. These distances are too long for significant, direct Mo···S(7) interaction, confirming the earlier assignment of the $\mathrm{EtSS^-}$ ligand as bridging only by its β-sulfur.[27] Earlier structural studies on M-SSR complexes have revealed both η^1- and η^2-bonding modes for the two sulfurs of the $\mathrm{RSS^-}$ ligand.[16,18,22–25] The β-sulfur bridge structure has also been reported for $\mathrm{[(C_5H_5)_2Cr_2(NO)_2(SCMe_3)(SSCMe_3)]}$.[21]

The C(25)–S(7)–S(2) linkage is quite normal[40,41] with no serious perturbation due to the β-sulfur bridging arrangement. One notable feature is the manifestation of the well-established dihedral angle for –S–S– compounds. For disubstituted organic disulfides, C–S–S–C dihedral angles tend to be 90° unless sterically precluded.[40,41,43] Present angles are 94.5 (3)° for Mo(1) and 172.0 (3)° for Mo(2) for the Mo–S(2)–S(7)–C(25) dihedral set. C(25) is thus normally posed relative to Mo(1) but trans to Mo(2). While this may indeed represent a preferred molecular geometry, fortuitous crystal packing may also be responsible.

A notable short intermolecular contact exists between S(7) atoms on one molecule and the molecule related to it by inversion but in the adjacent unit cell. The S(7)···S(7)′ distance is only 3.40 Å while the sum of van der Waals radii is 3.7 Å.[44] Interestingly, the previously addressed skew in Mo–S(2)–S(7) angles is in the direction of shortening that contact.

Acknowledgment. This work was supported by research awards from the Graduate School and from the College of Arts and Sciences of the University of Louisville and with funds from the National Science Foundation (Grant No. RII-8610671) and the Kentucky EPSCoR Program.

Registry No. **1** (R = Et), 103368-81-6; **1** (R = Bz), 103368-82-7; **2** (R = Bz), 103383-36-4; $\mathrm{SMo_2}$*$\mathrm{S^-}$, 112482-65-2; BzSCN, 3012-37-1; EtSCN, 542-90-5; BzSSH, 3492-66-8; EtSSH, 74004-30-1; $\mathrm{CN^-}$, 57-12-5.

Supplementary Material Available: Calculated hydrogen positions (Table V), displacement parameters (Table VI), bond lengths (Table VII) and angles (Table VIII) excluded from main text, Mo(1)–Mo(2)–S(1)–S(2) least-squares plane (Table IX), and unit cell diagram (Figure 2) (9 pages); a table of calculated and observed structure factors (53 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of Niobium(V) and Tantalum(V) Organoimido Compounds Containing 2,6-Diphenylphenoxide Ligation

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Received July 16, 1987

There is currently considerable research interest in the inorganic and organometallic chemistry associated with 2,6-dialkylphenoxide[2,3] and thiophenoxide[4,5] ligation. Our group has been particularly interested in the use of the sterically bulky 2,6-di-*tert*-butylphenoxide group as an ancillary ligand attached to early transition-metal centers.[6] However, the ligand itself has been found, under somtimes mild conditions, to undergo cyclometalation reactions to form six-membered metallacycle rings derived by activation of one of the carbon–hydrogen bonds of a *tert*-butyl

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