from rhodium. There is no clear trend in the hydrogen atom displacements, which are probably dominated by intramolecular steric and crystal-packing forces. The rhodium atoms lie very nearly over the centers of the Cp rings: the angles between the Rh-ring center vectors and the normals to the ring planes are 1.3 and 2.3° for rings A and B, respectively. The angles defined by ring center–Rh–Rh or ring center–Rh–C are also very similar, with a mean value of 133 (1)°.

In reviewing the available structural results for μ-methylene complexes (**1**), Herrmann, Schweizer, Creswick, and Bernal[18] noted that the M–C–M angles (α) fall the range 75–87° and the R–C–R′ (β) angles in the range 92–115°. All known structures have the carbene ligand oriented approximately perpendicular to the M–M bond. Here we focus our attention on unsubstituted complexes, the geometries of which are summarized in Table IV. Application of the 18-electron rule to compounds I–VI predicts a formal M–M bond order of 1, which is consistent with results of a molecular orbital analysis of compound I.[19] Interestingly, the manganese dimers (II and III) have longer M–M distances than the rhodium dimer (I), and both II and III possess substantially the largest α angles in the group.[24a,b] In fact, in view of the differences in composition, the relative constancy of the α angles in the remaining six compounds is perhaps surprising. The H–C–H (β) angles from the present neutron diffraction study of I and that of VIII[13,14] are quite close to the tetrahedral value. By way of further comparison, in our recent neutron diffraction study of the terminal complex $(Cp)_2Ta(Me)CH_2$,[27] the methylene H–C–H angle is found to be 112.3 (2)°. The inadequacy of simple hybridization arguments in rationalizing these angles has been pointed out.[14] In the MO analysis of the bonding in I, Hofmann[19] has indicated that the H–C–H angle in such systems depends upon the details of a repulsive interaction between the low-lying filled π_{CH_2} orbital and the metal–metal bonding π_{xz} orbital extending normal to the M–C–M plane. Optimization of the H–C–H angle for compounds I and II has led to calculated[49] minimum energy angles of between 109 and 110° for I, in agreement with our experimental value, and about 100° for II compared to the value of 108.8 (1.5)° from the low-temperature X-ray study.[24a]

Acknowledgment. We are indebted to Åke Kvick for his careful reading of the manuscript and Joseph Henriques for technical assistance. We also wish to thank Thomas A. Albright and Michael B. Hursthouse for helpful discussions and Mark Beno, Raymond E. Davis, Peter Hofmann, Yvon Le Page, and Jack M. Williams for communicating results to us prior to publication.

Registry No. I, 65138-22-9.

Supplementary Material Available: A listing of observed and calculated squared structure factors (18 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Colorado,
Boulder, Colorado 80309

Syntheses, Structures, and Reactions of Molybdenum Complexes with Sulfido and Disulfido Ligands

M. RAKOWSKI DuBOIS,* D. L. DuBOIS, M. C. VANDERVEER, and R. C. HALTIWANGER

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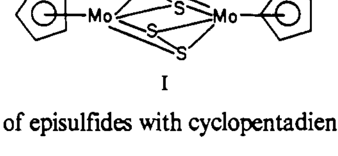
The reaction of elemental sulfur with $(CH_3)_5C_5Mo(CO)_3H$ produced $[(CH_3)_5C_5MoS_2]_2$ (II) and $[(CH_3)_5C_5MoS_5]_2$ (IV) in 65% and 10% yields, respectively. The remaining product was an insoluble, presumably polymeric, material. Complex II crystallizes in space group $P2_1/n$ with a = 10.069 (20) Å, b = 15.107 (4) Å, c = 7.889 (2) Å, and β = 104.81 (2)°. The molecule contains a planar $Mo_2(\mu\text{-}S)_2$ unit with terminal sulfido ligands in the anti configuration. In the presence of oxygen, complex II is converted to $[(CH_3)_5C_5MoO(S)]_2$, which crystallizes in space group $P4_2/n$ with $a = b$ = 16.342 (3) Å and c = 8.456 (1) Å. The molecule is similar to complex II with oxo ligands replacing the terminal sulfido ligands. Complex IV crystallizes in space group $Fdd2$ with a = 15.233 (3) Å, b = 45.205 (7) Å, and c = 8.051 (2) Å. The metal ions in this dimer are each coordinated to a single sulfur atom of a bridging disulfide ligand. The coordination sphere of each molybdenum ion also includes two η^2-S_2 ligands and the η^5-$(CH_3)_5C_5$ ligand. The reactions of $[CH_3C_5H_4Mo(CO)_3]_2$ and of $[C_5H_5Mo(CO)_3]_2$ with elemental sulfur resulted primarily in the formation of insoluble materials. The dimer $[CH_3C_5H_4MoS_2]_2$ (III) was isolated from the former reaction in very low yields. An X-ray diffraction study of this product confirms that it is also an anti isomer of a $[MoS(\mu\text{-}S)]_2$ dimer. The complex crystallizes in space group $P2_1/n$ with a = 7.023 (4) Å, b = 6.703 (2) Å, c = 16.227 (8) Å, and β = 95.86 (4)°. Complexes II–IV, as well as the insoluble products from these reactions, react with hydrogen under mild conditions to form in each case a complex with hydrosulfido ligands. In addition, III reacts with ethylene and acetylene at room temperature to form the known dimers with bridging ethane- and ethenedithiolate ligands, respectively. The insoluble materials $[(CH_3)_nC_5H_{5-n}MoS_x]_y$ (n = 1, 5) also react with these unsaturated hydrocarbons to form the same dithiolate-bridged dimers.

Introduction

A cyclopentadienylmolybdenum dimer with two bridging disulfide ligands (structure I) has been reported as a product of the reaction of episulfides with cyclopentadienylmolybdenum carbonyl hydrides.[1] Recently we reported that our efforts to reproduce this synthesis resulted in the formation of dimeric complexes with bridging alkanedithiolate ligands.[2] The bridging sulfur atoms in the latter complexes were found to undergo unusual reactions with unsaturated molecules, and



I

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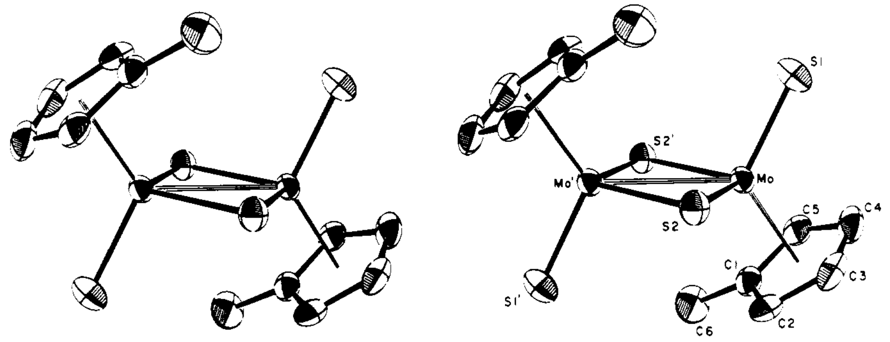

Figure 1. Stereoview of $[CH_3C_5H_4MoS(\mu\text{-}S)]_2$.

this reactivity has been studied extensively.[2-4] These studies renewed our interest in the synthesis and investigation of I. The reaction of elemental sulfur with cyclopentadienylmolybdenum carbonyl derivatives seemed like a reasonable alternate synthetic approach to this complex. Several transition-metal complexes with disulfide ligands have been synthesized by the reaction of sulfur with carbonyl derivatives or with coordinatively unsaturated complexes. These include monomeric complexes with η^2-S_2 ligands,[5-8] dinuclear complexes in which bridging S_2 ligands bond in a η^1 mode to each metal ion[9] or coordinate to M_1 and M_2 with η^1 and η^2 bonds, respectively,[10] and polynuclear derivatives in which the S_2 unit is involved in more complex bonding modes with three or more metal ions.[11,12]

The reaction which was of particular interest to us—that of bis(cyclopentadienylmolybdenum tricarbonyl) with sulfur—had been studied some time ago.[13] No soluble products were isolated in the earlier investigation. The insoluble, presumably polymeric, material resulting from the reaction was found to vary in sulfur content. We have carried out a more detailed investigation of this reaction system. By introducing methyl substituents on the cyclopentadienyl ligand, we were able to isolate soluble products with the formulations $[(CH_3)_5C_5MoS_2]_2$ (II), $[CH_3C_5H_4MoS_2]_2$ (III), and $[(CH_3)_5C_5MoS_5]_2$ (IV). Oxidation of II produced $[(CH_3)_5C_5Mo(O)S]_2$ (V). These products have been characterized by spectral methods and by X-ray diffraction studies, and their reaction chemistry has been investigated. The structure of IV is unprecedented. Compounds II, III, and V belong to a structural class which has been known for many years.[14-16] However, this is the first detailed study of these types of complexes which includes well-defined syntheses, complete spectral data, and characterization of their reactivity. In addition, we report that the insoluble polymeric products, $[Me_nCpMoS_x]_y$, formed in high yields in the reactions with sulfur also undergo interesting reactions with unsaturated molecules under mild conditions.

Results and Discussion

Syntheses. The reaction of $[C_5H_5Mo(CO)_3]_2$ with S_8 in a molar ratio of either 1:0.5 or 1:1 in refluxing benzene resulted in the formation of an insoluble material, as reported previously.[13] Chromatography of the deeply colored solution resulting from this reaction indicated that many species were present in low yields, and none of these have been characterized. The reaction of $[CH_3C_5H_4Mo(CO)_3]_2$ with sulfur proceeded in an analogous manner to form primarily an insoluble product. In addition, we were successul in isolating and characterizing one soluble product from this reaction by chromatography of the soluble material. Mass spectral data and the results of elemental analyses are consistent with the formulation of this product as $[CH_3C_5H_4MoS_2]_2$. Strong bands are observed in the infrared spectrum at 495 and 445 cm^{-1}. These absorptions occur at frequencies similar to those assigned to Mo–S_t stretches in molybdenum(V) dimers with two bridging and two terminal sulfido ligands.[17,18] Results of an X-ray diffraction study of a single crystal of $[CH_3C_5H_4MoS_2]_2$, which are discussed below, confirm that the complex has this configuration. A strong infrared band at 482 cm^{-1} reported for structure I[1] was not present in the spectrum of $[CH_3C_5H_4MoS_2]_2$, and no evidence for this isomer was observed.

The reaction of elemental sulfur with $(CH_3)_5C_5Mo(CO)_3H$ in a 1:1.5 molar ratio was carried out in refluxing THF. In addition to an insoluble product which we will refer to as $[(CH_3)_5C_5MoS_x]_y$, two soluble complexes were isolated in 65% and 10% yields, respectively. The infrared spectrum of the higher yield product is very similar to that of $[CH_3C_5H_4Mo(S)(\mu\text{-}S)]_2$ in the region 400–600 cm^{-1}; this complex was therefore formulated as $[(CH_3)_5C_5Mo(S)(\mu\text{-}S)]_2$. Because of inconsistencies in analytical data, which suggested a higher sulfur content, a crystal of this complex was also characterized by an X-ray diffraction study (vide infra) and found to agree with the original formulation. The second soluble product in the pentamethylcyclopentadienyl system was not readily characterized by spectral data. In the mass spectrum, the highest envelope was observed at *m*/*e* 622, consistent with $[(CH_3)_5C_5]_2Mo_2S_5$, but analytical data again indicated a higher sulfur content. The low-energy region of the infrared spectrum showed weak absorptions at 530 and 548 cm^{-1}. The results of the crystallographic study established

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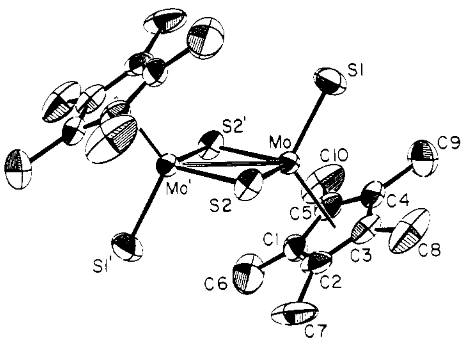

Figure 2. Perspective drawing of $[(CH_3)_5C_5MoS(\mu\text{-}S)]_2$.

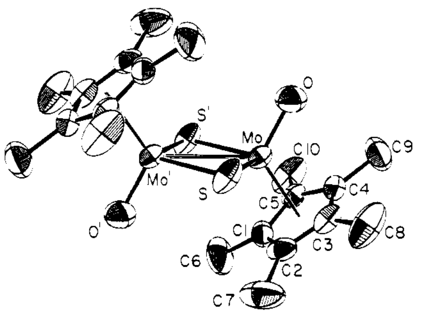

Figure 3. Perspective drawing of $[(CH_3)_5C_5MoO(\mu\text{-}S)]_2$.

that the complex is a dimer of formulation $[(CH_3)_5C_5MoS_5]_2$ with each metal ion coordinated by two η^2-S_2 ligands and one μ-η^1-S_2 unit. The structure is discussed in detail below. Attempts to maximize the yield of this complex by variation of Mo:S ratios and by variation of solvent polarity and boiling point were unsuccessful (see Experimental Section).

X-ray Diffraction Studies of $[(CH_3)_nCH_{5-n}MoS(\mu\text{-}S)]_2$ (n = 1, 5) and $[(CH_3)_5C_5MoO(\mu\text{-}S)]_2$. Positional parameters and selected bond distances and angles for all of the structures are listed in Tables I and II, respectively. A stereoview of the molecular structure of $[CH_3C_5H_4MoS(\mu\text{-}S)]_2$ is shown in Figure 1. The structure is a centrosymmetric one with a planar $Mo_2(\mu\text{-}S)_2$ unit and terminal sulfido ligands oriented to give the anti isomer. The basic structural features are very similar to those reported for other cyclopentadienylmolybdenum dimers with bridging sulfido ligands and terminal oxo or imido ligands.[14,15]

The single-crystal characterizations of $[(CH_3)_5C_5MoS(\mu\text{-}S)]_2$ and $[(CH_3)_5C_5MoO(\mu\text{-}S)]_2$ establish that these also belong to the class of anti isomers. Perspective views of the molecules are shown in Figures 2 and 3, respectively. A comparison of the structural data shows little significant variation as the methyl substitution on the cyclopentadienyl ring is increased or as the nature of the terminal ligand is varied. The Mo—Mo and Mo═S distances in $[(CH_3)_5C_5MoS(\mu\text{-}S)]_2$ are significantly longer than those in $[CH_3C_5H_4MoS(\mu\text{-}S)]_2$, but it is unclear whether this is a characteristic feature resulting from the stronger electron donating ability of the $(CH_3)_5C_5$ ligand. A comparison of structural data for $[(CH_3)_5C_5MoO(\mu\text{-}S)]_2$ with that for the analogous unsubstituted cyclopentadienyl derivative[14] shows no differences in M–M or M–O distances, within experimental error.

Table I. Positional Parameters

atom	x^a	y	z
$[CH_3C_5H_4MoS(\mu\text{-}S)]_2$			
Mo	0.14518 (8)	0.14692 (8)	0.02353 (3)
S_1	0.24601 (28)	0.2960 (3)	−0.07987 (12)
S_2	0.18206 (24)	−0.18589 (26)	−0.00481 (11)
C_1	0.1030 (9)	0.2113 (11)	0.1702 (4)
C_2	0.2321 (10)	0.0491 (11)	0.1661 (4)
C_3	0.3952 (11)	0.1196 (12)	0.1286 (5)
C_4	0.3683 (11)	0.3242 (12)	0.1107 (5)
C_5	0.1830 (11)	0.3808 (11)	0.1330 (4)
C_6	−0.0851 (12)	0.2049 (16)	0.2081 (5)
$[(CH_3)_5C_5MoS(\mu\text{-}S)]_2$			
Mo	0.09713 (6)	−0.07296 (4)	0.02707 (8)
S_1	0.02582 (26)	−0.19142 (15)	0.1248 (4)
S_2	0.07235 (20)	0.03637 (14)	0.21900 (25)
C_1	0.3157 (7)	−0.0036 (6)	0.0394 (12)
C_2	0.2589 (8)	−0.0233 (6)	−0.1336 (11)
C_3	0.2430 (8)	−0.1162 (6)	−0.1481 (11)
C_4	0.2956 (8)	−0.1536 (5)	0.0192 (12)
C_5	0.3381 (7)	−0.0831 (6)	0.1372 (11)
C_6	0.3602 (10)	0.0890 (7)	0.1149 (17)
C_7	0.2254 (11)	0.0407 (8)	−0.2866 (15)
C_8	0.1948 (10)	−0.1690 (8)	−0.3188 (14)
C_9	0.3178 (10)	−0.2509 (6)	0.0577 (16)
C_{10}	0.4021 (10)	−0.0935 (9)	0.3308 (14)
$[(CH_3)_5C_5MoO(\mu\text{-}S)]_2$			
Mo	−0.037651 (24)	0.077200 (23)	0.04386 (4)
S	0.00870 (10)	0.03460 (7)	−0.20177 (14)
O	−0.14047 (23)	0.07833 (24)	0.0288 (5)
C_1	0.0719 (3)	0.14713 (29)	0.1886 (7)
C_2	0.0750 (3)	0.1755 (3)	0.0337 (7)
C_3	−0.0012 (4)	0.2145 (3)	−0.0026 (6)
C_4	−0.04907 (28)	0.21311 (27)	0.1370 (5)
C_5	−0.0062 (3)	0.16851 (26)	0.2520 (5)
C_6	0.1395 (4)	0.1063 (4)	0.2764 (10)
C_7	0.1465 (4)	0.1718 (5)	−0.0801 (11)
C_8	−0.0222 (5)	0.2591 (4)	−0.1534 (7)
C_9	−0.1307 (4)	0.2530 (4)	0.1592 (8)
C_{10}	−0.0320 (5)	0.1568 (4)	0.4196 (6)
$[(CH_3)_5C_5MoS_5]_2$			
Mo	0.02520 (5)	0.044641 (16)	0.414000
S_1	−0.02883 (16)	0.02036 (5)	0.6770 (4)
S_2	−0.11730 (18)	0.06815 (6)	0.4572 (5)
S_3	−0.07263 (22)	0.06859 (6)	0.2188 (4)
S_4	0.07887 (19)	0.02102 (6)	0.1665 (4)
S_5	0.09625 (16)	−0.00332 (5)	0.3753 (3)
C_1	0.1325 (8)	0.08231 (25)	0.3523 (17)
C_2	0.1789 (6)	0.05906 (21)	0.4403 (15)
C_3	0.1436 (7)	0.05678 (23)	0.6022 (15)
C_4	0.0762 (7)	0.07949 (25)	0.6169 (16)
C_5	0.0700 (8)	0.09549 (24)	0.4668 (18)
C_6	0.1566 (10)	0.0938 (3)	0.1829 (21)
C_7	0.2577 (7)	0.04329 (26)	0.3799 (18)
C_8	0.1819 (8)	0.03785 (27)	0.7353 (17)
C_9	0.0275 (8)	0.0887 (3)	0.7776 (18)
C_{10}	0.0185 (8)	0.12258 (22)	0.4367 (28)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

In the structures of each of the $[Me_nCpMoX(\mu\text{-}S)]_2$ (X = S, O) complexes reported here, an unsymmetrical coordination of the cyclopentadienyl ligands is observed. The C–C distances in the rings are consistent with a localized double bond at C_1–C_2 and delocalized unsaturation at C_3–C_4–C_5. In addition, the Mo–C_1 and Mo–C_2 distances are longer than the other three distances from metal to ligand, and the cyclopentadienyl ligands show some nonplanarity. Equations and deviations from planarity for these ligands are given in Table III. Similar distortions have been observed in other cyclopentadienyl complexes.[19,20] It has been suggested that such a distortion may result from electronic effects exerted by a ligand which is trans to C_1–C_2.[20,21] In the systems reported here, the effect is more clearly defined for the complex with terminal oxo ligands. This observation seems consistent with a stronger trans effect expected for this ligand.

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Table II. Selected Bond Distances and Angles for Molybdenum Dimers

	$[CH_3C_5H_4MoS_2]_2$	$[(CH_3)_5C_5MoS_2]_2$		$[(CH_3)_5C_5MoO(S)]_2$	$[(CH_3)_5C_5MoS_5]_2$
		A. Distances, Å			
Mo-Mo	2.881 (1)	2.905 (1)		2.904 (1)	4.108 (1)
Mo-S_1	2.135 (2)	2.144 (2)	(Mo-O)	1.685 (4)	2.523 (3)
Mo-S_2	2.297 (2)	2.297 (2)	(Mo-S)	2.318 (1)	2.442 (3)
Mo-S_3					2.421 (3)
Mo-S_4					2.404 (3)
Mo-S_5					2.443 (2)
Mo-S_2'	2.302 (2)	2.301 (2)	(Mo-S′)	2.312 (1)	
Mo-S_5'					2.648 (2)
Mo-C_1	2.467 (6)	2.417 (7)		2.452 (5)	2.412 (11)
Mo-C_2	2.421 (7)	2.424 (8)		2.445 (5)	2.439 (9)
Mo-C_3	2.327 (7)	2.352 (7)		2.355 (5)	2.418 (10)
Mo-C_4	2.327 (7)	2.355 (7)		2.364 (4)	2.398 (11)
Mo-C_5	2.364 (6)	2.363 (7)		2.364 (4)	2.435 (11)
Mo-Cp	2.050	2.062		2.073	2.089
C_1-C_2	1.42 (1)	1.37 (1)		1.390 (7)	1.45 (2)
C_2-C_3	1.43 (1)	1.41 (1)		1.431 (8)	1.41 (2)
C_3-C_4	1.41 (1)	1.41 (1)		1.417 (7)	1.46 (2)
C_4-C_5	1.44 (1)	1.41 (1)		1.403 (6)	1.41 (2)
C_5-C_1	1.43 (1)	1.41 (1)		1.428 (7)	1.45 (2)
C-CH_3(av)	1.51 (1)	1.52 (2)		1.50 (1)	1.50 (3)
$S_2 \cdots S_2'$	3.585 (4)	3.563 (4)	(S· · ·S′)	3.606 (2)	
S_1-S_1'					2.040 (5)
S_2-S_3					2.037 (5)
S_4-S_5					2.026 (4)
		B. Angles, Deg			
Mo-S_2-Mo′	77.57 (6)	78.38 (6)	(Mo-S-Mo′)	77.68 (4)	
S_2-Mo-S_2'	102.43 (6)	101.61 (6)	(S-Mo-S′)	102.31 (4)	
Mo′-Mo-S_1	113.21 (6)	114.29 (7)	(Mo′-Mo-O)	114.4 (1)	
Mo′-Mo-S_2	51.29 (6)	50.86 (5)	(Mo′-Mo-S)	51.06 (3)	
Mo′-Mo-S_2'	51.14 (6)	50.75 (5)	(Mo′-Mo-S′)	51.25 (3)	
S_1-Mo-S_2	104.12 (7)	105.1 (1)	(O-Mo-S)	105.1 (1)	77.3 (1)
S_1-Mo-S_2'	104.47 (8)	105.1 (1)	(O-Mo-S′)	104.9 (1)	
S_1-Mo-S_5					82.28 (9)
S_2-Mo-S_3					49.5 (1)
S_2-Mo-S_4					127.9 (1)
S_2-Mo-S_5					142.96 (9)
S_3-Mo-S_4					82.5 (1)
S_3-Mo-S_5					125.9 (1)
S_4-Mo-S_5					49.4 (1)
Cp-Mo-S_5'					168.1
Mo-S_5-Mo′					107.5 (1)
C_5-C_1-C_2	107.9 (6)	109.1 (7)		107.7 (4)	108 (1)
C_1-C_2-C_3	108.0 (7)	107.8 (7)		108.7 (4)	109 (1)
C_2-C_3-C_4	108.2 (7)	108.3 (7)		107.1 (4)	107 (1)
C_3-C_4-C_5	108.1 (7)	107.1 (8)		108.1 (4)	110 (1)
C_4-C_5-C_1	107.6 (6)	107.7 (7)		108.2 (4)	107 (1)
C-C-C_{av}	108.0 (2)	108.0 (8)		108.0 (6)	108 (1)

Structural Characterization of $[(CH_3)_5C_5MoS_5]_2$. The complex crystallizes from dichloromethane in space group *Fdd*2 with molecular symmetry C_2. A stereoview of the molecule and numbering scheme are shown in Figure 4. Three types of S_2 ligands are found in the molecule. The two molybdenum ions are linked by a disulfide ligand which displays η^1 coordination to each metal ion. In addition, two η^2-S_2 ligands are coordinated to each molybdenum. Sulfur atoms 5 and 5′ of two of the ligands are 2.648 (2) Å from Mo′ and Mo, respectively, and this suggests additional bridging interactions in the molecule through these ligands. The metal–metal distance of 4.108 (.001) Å clearly precludes any direct interaction between molybdenum ions. When viewed down the S–S bond of the bridging ligand, the metal ions and sulfur lone pairs are in a staggered conformation with a torsion angle Mo′–S′–S–Mo = 59.7°.

Several examples of di- and polynuclear molybdenum anions containing disulfide and sulfide ligands have been reported recently.[22–27] A variety of ligand-bonding modes have been characterized in these systems. The cyclopentadienyl derivative reported here provides the first example in molybdenum chemistry of an S_2 ligand bridging two metal ions in an end-on fashion, and it is one of few complexes with this type of ligand to be characterized crystallographically.[28] We have reported previously that $[(CH_3)_5C_5MoS_5]_2$ undergoes an unusual reaction with hydrogen (1 atm) to form $[(CH_3)_5C_5Mo(S)SH]_2$ and H_2S.[29] In the complex $[Ru(NH_3)_5S]_2^{+4}$, the bridging S_2 ligand has been found to be subject to cleavage by nucleophiles.[28] The reactivity of the sulfur ligands in [(C-

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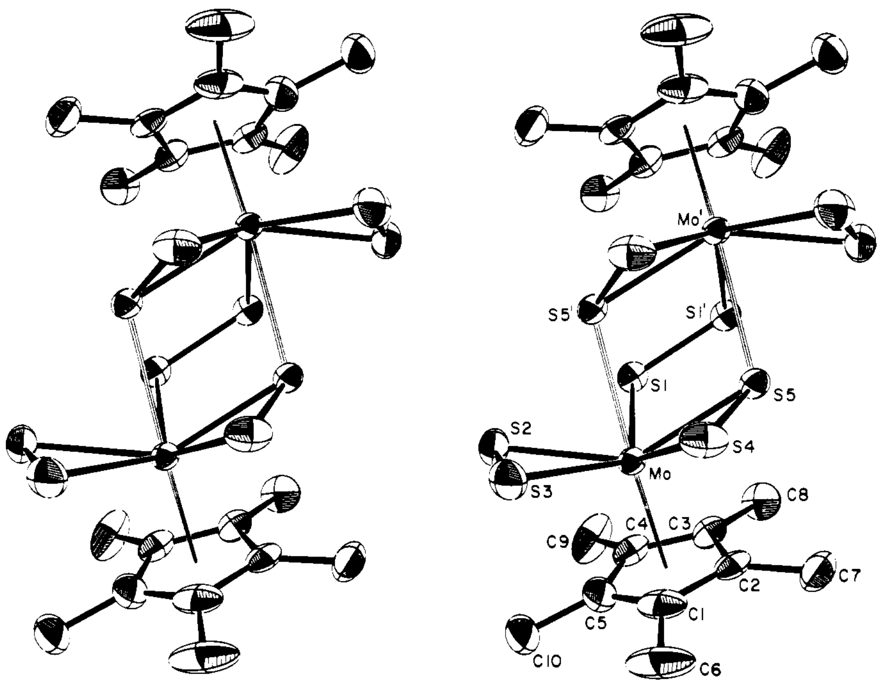


Figure 4. Stereoview of $[(CH_3)_5C_5MoS_5]_2$.

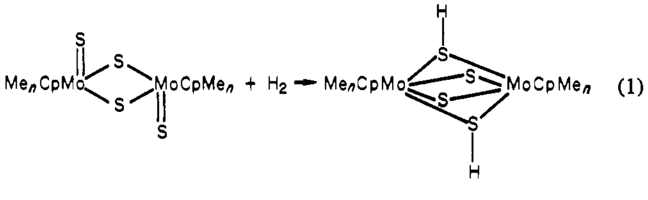
Table III. Coefficients[a] of Planes Calculated for the Cyclopentadienyl Ligands in the Molybdenum Dimers and Deviations (Å) of Selected Atoms from the Planes

	$[CH_3C_5H_4MoS_2]_2$	$[(CH_3)_5C_5MoS_2]_2$	$[(CH_3)_5C_5MoO(S)]_2$	$[(CH_3)_5C_5MoS_5]_2$
A	2.440	9.922	6.408	10.453
B	1.711	−0.995	14.099	29.496
C	13.989	−3.186	2.700	2.588
D	2.979	3.010	3.036	4.741
C_1	0.015 (6)	0.000 (7)	0.009 (5)	−0.017 (10)
C_2	−0.006 (6)	0.007 (7)	0.011 (5)	0.011 (9)
C_3	−0.011 (7)	−0.012 (7)	−0.026 (5)	−0.007 (10)
C_4	0.022 (7)	0.015 (7)	0.025 (4)	−0.003 (10)
C_5	−0.020 (6)	−0.010 (7)	−0.019 (4)	0.015 (11)
C_6	0.075	0.109	0.103	0.137
C_7		0.098	0.110	0.213
C_8		0.107	0.060	0.180
C_9		0.208	0.123	0.176
C_{10}		0.019	0.103	0.198

[a] The coefficients are given for an equation of the form $Ax + By + Cz - D = 0$, where *x*, *y*, and *z* are the fractional cell coordinates.

$H_3)_5C_5MoS_5]_2$ toward nucleophiles and electrophiles is currently being investigated.

Reactions of $[(CH_3)_nC_5H_{5-n}MoS(\mu\text{-}S)]_2$. Although complexes of this structural class have been known for many years,[14-16] no studies of their reactivity have been reported. The complexes may be regarded as electron deficient in the sense that the metal ions do not achieve an 18-electron configuration. It seems reasonable to expect that these dimers might react in some way with electron donors. We have reported previously that complexes of the above formula react with hydrogen under mild conditions to form a quadrupally bridged structure with two hydrosulfido ligands, $[(CH_3)_nC_5H_{5-n}Mo^{IV}(S)SH]_2$ (reaction 1).[29] The complex $[CH_3C_5H_4MoS(\mu\text{-}S)]_2$ also reacts with ethylene and acetylene at 25 °C to form the known dimers with ethane- and ethenedithiolate ligands, respectively (reactions 2 and 3). In the latter reactions the metal ions are reduced to the formal oxidation state of +3. The nature of the frontier molecular orbitals of $[C_5H_5MoS(\mu\text{-}S)]_2$ have been determined by extended Hückel calculations. The contribution from sulfur orbitals to the lowest unoccupied molecular orbital (b_u) suggests that an initial interaction of the alkene or alkyne π orbital could occur with bridging sulfido ligands or with one bridging and one terminal ligand (Figure 5). In addition we observe relatively high-energy occupied molecular orbitals which have appropriate symmetry for back-donation of electron density



(1)

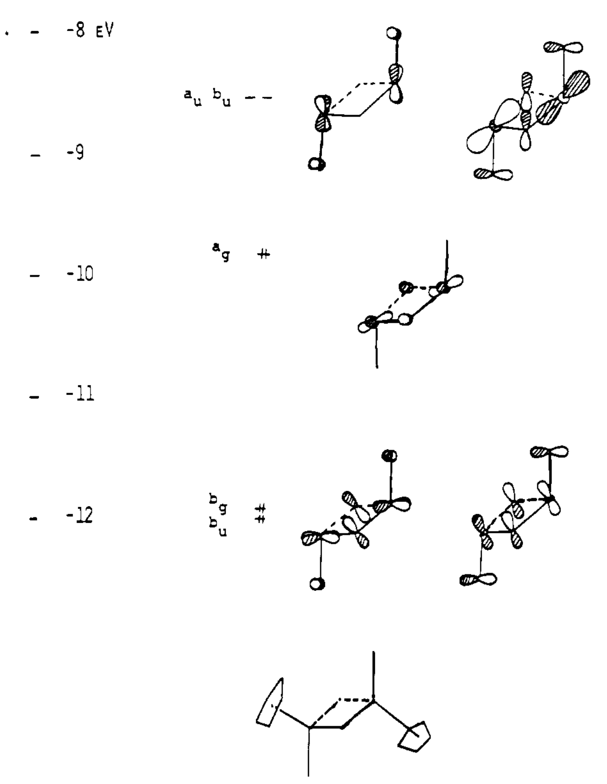
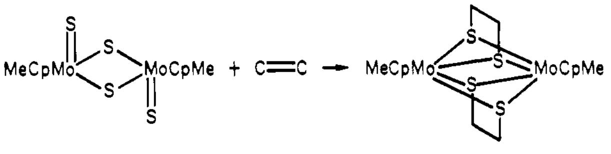
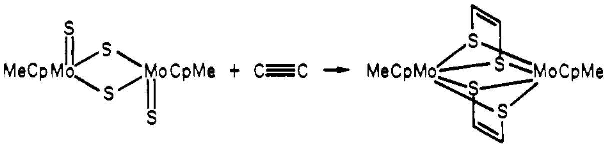


Figure 5. Frontier molecular orbitals of $[C_5H_5MoS(\mu\text{-}S)]_2$.



(2)

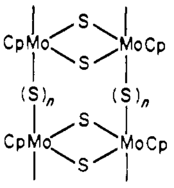


(3)

from these sulfido ligands to a π^* orbital of the unsaturated molecule (Figure 5, b_g or b_u). No mechanistic information is available on the rearrangement of the dimer to the quadrupally bridged structure. However, the tendency for the molybdenum(V) dimer to undergo such a rearrangement upon reduction has been considered in terms of the relative energies of the molecular orbitals involved.[4]

These molecular orbital studies also suggested a reason for our failure to isolate and identify structure I. The energies of the HOMO and LUMO for this structure were found to be nearly degenerate. This suggested that the complex may either exist as a paramagentic species or it may undergo a distortion to remove the near orbital degeneracy. The rearrangement of I to a $[C_5H_5MoS(\mu\text{-}S)]_2$ structure represents one such symmetry-allowed distortion which may occur under our reaction conditions.[4]

Reactions of $[(CH_3)_nC_5H_{5-n}MoS_x]_y$. The tendency of sulfido and disulfido ligands to undergo bridging interactions between two or more metal ions is well documented.[30] As a result insoluble polymeric species are often produced in reactions of elemental sulfur with transition-metal complexes.[13] The reactions of cyclopentadienylmolybdenum carbonyl derivatives with sulfur produced high yields of such derivatives. We have reported previously that this insoluble material reacts under an atmosphere of hydrogen to form the discrete dimer $[(CH_3)_nC_5H_{5-n}Mo(S)SH]_2$.[29] Excess sulfur in the material is converted to hydrogen sulfide. Unsaturated molecules, e.g., acetylene and ethylene, also cleave the polymeric structure at room temperature to form the dimers with bridging dithiolate ligands. The similarities of these reactions to those of $[CH_3C_5H_4MoS(\mu\text{-}S)]_2$ suggest that the insoluble material may be composed of dimeric units which are linked by sulfide or polysulfide bridges (structure II). The reactivity of the sulfido atoms in these systems may be relevant in understanding reactions known to be catalyzed by molybdenum sulfide surfaces, including hydrodesulfurizations,[31] hydrogenations,[32] and Fischer–Tropsch activity.[33] Investigations of the role of these simple molybdenum systems in these reaction types are in progress.



II

Experimental Section

Materials. $[C_5H_5Mo(CO)_3]_2$ and $[CH_3C_5H_4Mo(CO)_3]_2$ were purchased from Strem. Pentamethylcyclopentadiene was purchased from Aldrich, and $LiC_5(CH_3)_5$ was prepared by a published procedure.[34] $Mo(CO)_6$ was purchased from Alfa. Ethylene and acetylene were obtained from Matheson. Reagent grade sublimed sulfur was used.

Table IV. Crystal Data

formula	$C_{12}H_{14}$-Mo_2S_4	$C_{20}H_{30}$-Mo_2S_4	$C_{20}H_{30}$-$Mo_2O_2S_2$	$C_{20}H_{30}$-Mo_2S_{10}
M_r	478.38	590.60	558.47	782.98
space group	$P2_1/n$	$P2_1/n$	$P4_2/n$	$Fdd2$
a, Å	7.023 (4)	10.069 (2)	16.342 (2)	15.233 (3)
b, Å	6.703 (2)	15.107 (4)	16.342 (2)	45.205 (7)
c, Å	16.227 (8)	7.889 (2)	8.456 (1)	8.051 (2)
α, deg	90	90	90	90
β, deg	95.86 (4)	104.81 (2)	90	90
γ, deg	90	90	90	90
V, Å^3	759.8 (6)	1160.2 (5)	2258.3 (5)	5544 (2)
d_{calcd}, g cm^{-3}	2.09	1.69	1.64	1.88
d_{obsd}, g cm^{-3}	2.08	1.69	1.65	1.90
Z	2	2	4	8
$F(000)$	468	596	1128	3152
μ(Mo Kα), cm^{-1}	21.19	14.07	12.78	16.18

Physical Measurements. NMR spectra were recorded at 90 MHz on a Varian 390 spectrometer. Chemical shifts are referenced to tetramethylsilane. Infrared spectra were obtained on Nujol mulls with a Perkin-Elmer 337 spectrophotometer. Mass spectra were recorded with the use of a Varian MAT CH-5 instrument. Elemental analyses were provided by Spang Laboratory.

X-ray Crystallography. Data for all four structures (Table IV) were collected on a Syntex P$\bar{1}$ autodiffractometer equipped with a graphite monochromator. The procedures which were similar for all four structures are summarized in Table V. The cell parameters were refined by least-squares fit of the parameters as noted in Table V. The measured data were collected for Lorentz and polarization effects.[35] Data were corrected for absorption as noted in Table V.

Structure Solution and Refinement. Salient features of the solution and refinement of the four compounds are given in Table VI.

Syntheses. All reactions were carried out under a nitrogen atmosphere, but, unless noted, products were not protected from air during isolation procedures.

Reaction of $[C_5H_5Mo(CO)_3]_2$ with S_8. The molybdenum dimer (1.1 g, 2.2 mmol) and sulfur (0.57 g, 2.2 mmol) were dissolved in 150 mL of benzene. The solution was refluxed for ~4 days. The resulting black solid (~1.1 g) was filtered and washed with $CHCl_3$ until washings were colorless.

Reaction of $[CH_3C_5H_4Mo(CO)_3]_2$ with S_8. The molybdenum dimer (2.0 g, 3.86 mmol) and S_8 (0.53 g, 2.1 mmol) were refluxed in benzene for 2 days. The resulting black solid (~0.9 g) was isolated and washed as described above.

The filtrate from the reaction was evaporated to dryness, redissolved in $CHCl_3$, and eluted with $CHCl_3$ through an 8-in. column of neutral alumina. The initial red orange band was collected. Evaporation of solvent produced black crystals of $[CH_3C_5H_4MoS(\mu\text{-}S)]_2$: yield 0.040 g, 2.1%; IR (cm^{-1}): 495 s, 445 m; NMR ($CDCl_3$) δ 5.88 (2 m, intensity 8), 2.10 (s, 6); mass spectra m/e 478 (P), 463 (P − Me), 446 (P − S). Anal. Calcd: C, 30.13; H, 2.93; S, 26.78. Found: C, 30.08, H, 2.92; S, 26.84.

Reaction of the above reagents in a molar ratio of 1:1 did not produce any $[CH_3C_5H_4MoS(\mu\text{-}S)]_2$. The amount of insoluble material was approximately doubled.

$(CH_3)_5C_5Mo(CO)_3H$. $Mo(CO)_6$ (3.4 g, 11.2 mmol) was added to a THF slurry of $(CH_3)_5C_5Li$ (11.5 mmol), and the solution was refluxed under nitrogen for 28 h. After the reaction mixture was cooled to 25 °C, glacial acetic acid (4 mL, 45 mmol) was added. The solution was stirred for ~12 h. Solvent was evaporated, and the remaining solid was sublimed at 90 °C to produce an air-sensitive orange crystalline product; yield 1.8 g, 44%; NMR ($CDCl_3$) δ 2.11 (s, 15),

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(30) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.

(31) (a) Shuit, J. *J. Catal.* **1969**, *15*, 179. (b) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 266.

(32) For example, Okuhara, T.; Tanaka, K.; Miyahara, K. *J. Catal.* **1977**, *48*, 229. (b) Wentrcek, P. R.; Wise, H. *Ibid.* **1976**, *45*, 349.

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(34) Feitler, D.; Whitesides, B. M. *Inorg. Chem.* **1976**, *15*, 446.

(35) The data reduction routine was written in this laboratory. All other programs used in the solution and refinement of these structures are contained or based on Dr. J. A. Ibers' Northwestern University Crystallographic Computing Package and Dr. P. Main's MULTAN 78 package. The scattering factors used were for neutral atoms as given in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table V. Experimental Conditions for Crystallographic Studies

	$C_{12}H_{14}Mo_2S_4$	$C_{20}H_{30}Mo_2S_4$	$C_{20}H_{30}Mo_2O_2S_2$	$C_{20}H_{30}Mo_2S_{10}$
crystal size, mm	0.07 × 0.10 × 0.30	0.04 × 0.10 × 0.45	0.07 × 0.14 × 0.45	0.02 × 0.54 × 0.55
crystal habit	thin plate	thin plate	thin plate	thin plate
recryst solvent	$CHCl_3$	THF/N_2	THF/air	CH_2Cl_2
T, K	298-300	298-300	298-300	298-300
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
cell parameter refinement, no. of reflections	15	25	25	15
scan mode	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
min 2θ, deg	3.0	3.0	3.0	3.0
max 2θ, deg	45.0	50.0	50.0	50.0
scan speed, deg min^{-1}	4.0	2.0-24.0	2.0-24.0	4.0-24.0
scan range	from 1.0° below 2θ for $K\alpha_1$ to 1.0° above 2θ for $K\alpha_2$			
bkgd mode	stationary crystal-stationary counter			
bkgd time/scan time	0.25	0.5	0.5	0.5
no. of data points $F_o^2 \geq 3\sigma(F_o^2)$				
measd	1308	2338	3454	1859
obsd	866	1379	1450	1345
abs cor	no	yes	yes	yes
transmission coeff				
min		0.783	0.518	0.478
max		0.950	0.639	0.923

Table VI. Crystallographic Data. Solution and Refinement Details

	$C_{12}H_{14}Mo_2S_4$	$C_{20}H_{30}Mo_2S_4$	$C_{20}H_{30}Mo_2O_2S_2$	$C_{20}H_{30}Mo_2S_{10}$
phase determination	multiple solution tangent formula			
least-squares refinement	full-matrix anisotropic			
hydrogen contribution	not included	fixed idealized isotropic	fixed idealized isotropic	not included
weighting scheme	based on counting statistics			
final residuals				
R	0.0297	0.0436	0.0327	0.0401
R_w	0.0434	0.0495	0.0415	0.0491
no. of variables	82	118	118	144
observations/ parameters	10.6	11.7	12.3	9.3
esd of observation of unit weight	1.648	1.382	1.385	1.370
max shift over error	0.000	0.002	0.004	0.009
final difference maps	featureless			

-5.41 (s, 1); IR (cyclohexane) 2030, 2010, 1960, 1930 (s) (1895 (w));[36] mass spectra m/e = 316 (P), 287 (P - CO, H), 259 (P - 2CO, H), 231 (P - 3CO, H). Anal. Calcd: C, 49.38; H, 5.10. Found: C, 49.20; H, 5.00.

Reaction of $(CH_3)_5C_5Mo(CO)_3H$ with S_8. A freshly sublimed sample of the molybdenum complex (1.94 g, 6.1 mmol) and S_8 (1.0 g, 3.9 mmol) were refluxed in 100 mL of THF for 12 h. The resulting black solid was filtered and washed with THF until washings were colorless. The solid was then washed with approximately ten 50-mL portions of CS_2. The remaining solid (~1.0 g) was insoluble in common solvents and presumed to be polymeric.

The THF washings were evaporated to ~15 mL, and the resulting brown black product, $[(CH_3)_5C_5MoS(\mu\text{-}S)]_2$, was filtered and recrystallized from THF: yield 1.17 g, 65%; IR (cm^{-1}): 488 s, 444 m; NMR ($CDCl_3$) δ 2.05 (s); mass spectra m/e 590 (P), 558 (P - S), 526 (P - 2S).

The CS_2 washings were evaporated to 10 mL to crystallize $[(CH_3)_5C_5MoS_5]_2$ as black crystals: yield 0.25 g, 10%; IR (cm^{-1}): 548, 530 m; NMR (CS_2) δ 1.69 (s); mass spectra m/e 622 (P - 5S), 590 (base, $[Me_5C_5MoS_2]_2$).

Other Attempted Syntheses of $[(CH_3)_5C_5MoS_5]_2$. (A) $(CH_3)_5C_5Mo(CO)_3H$ (0.98 g, 3.11 mmol) and S_8 (0.21 g, 0.82 mmol) were combined in 25 mL of CS_2 and refluxed for 18 h under a nitrogen atmosphere until no more gas evolution was evident. The nearly clear solution was filtered, and the solvent was removed at reduced pressure, yielding 0.86 g of dark red material that still contained CO (IR). The product was not characterized. (B) $(CH_3)_5Mo(CO)_3H$ (0.97 g, 3.08 mmol) and S_8 (0.51 g, 2.00 mmol) were combined in 100 mL of benzene and refluxed for 20 h under a nitrogen atmosphere. The solvent was removed from the clear, dark red solution at reduced pressure, yeilding 1.30 g. An NMR spectrum in $CDCl_3$ indicated that no $[(CH_3)_5C_5MoS_5]_2$ was produced. The product decomposed during recrystallization and was not characterized. (C) $(CH_3)_5C_5Mo(CO)_3H$ (0.50 g, 1.58 mmol) and S_8 (0.51 g, 1.98 mmol) were combined in 50 mL of THF and refluxed under a nitrogen atmosphere for 22 h. The mixture was filtered, and the insoluble product was washed with THF (2 × 20 mL) until the wash was colorless. Washing with CS_2 yielded no $[(CH_3)_5C_5MoS_5]_2$. The soluble product decomposed into an insoluble material upon standing in air and was not characterized.

Reactions of $[CH_3C_5H_4MoS(\mu\text{-}S)]_2$ with Unsaturated Molecules. The molybdenum complex (0.10 g, 0.2 mmol) was dissolved in $CHCl_3$. The solution was degassed, and 1 atm of C≡C was added. After 1 day of stirring at 25 °C, the solution was evaporated to ~2 mL and filtered to isolate the yellow green product. The complex $[CH_3C_5H_4MoSC_2H_2S]_2$ was recrystallized from CHCl and characterized by comparison of spectral data with that of the known complex.[29]

The reaction with C=C was carried out in an analogous procedure but with a reaction time of 2 weeks.

Reactions of $[(CH_3)_nC_5H_{5-n}MoS_x]_y$ with Unsaturated Molecules. The molybdenum complex (0.2 g) was slurried in 25 mL of $CHCl_3$. The solution was degassed and 1 atm of C=C or C≡C was added. After 10-14 days of stirring at 25 °C, the solution was filtered. The filtrate was evaporated to ~5 mL, and the crystalline product was filtered; typical yields 60%.

$[(CH_3)_5C_5MoO(\mu\text{-}S)]_2$. Slow crystallization of $[(CH_3)_5C_5MoS(\mu\text{-}S)]_2$ from CH_2Cl_2 in air produced bright red crystals which proved

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(36) A small amount (~7%) of $[(CH_3)_5C_5Mo(CO)_3]_2$ was also present in the product and identified by NMR (δ 1.99) and by IR (1933, 1895 cm^{-1}).[37]

(37) (a) King, R. B.; Iqbal, M. Z., King, A. D., Jr. *J. Organomet. Chem.* **1979**, *171*, 53. (b) Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 3533.

to be $[(CH_3)_5C_5MoO(\mu\text{-}S)]_2$. A chloroform solution of $[(CH_3)_5C_5MoS(\mu\text{-}S)]_2$ (0.1 g) was stirred under an atmosphere of O_2 for 3 days at 70 °C. The solvent was evaporated, and the remaining solid was characterized spectrally. No starting complex remained. Spectral data suggest a mixture of isomers may be present. IR: 907, 900 cm^{-1} ($\nu_{Mo{=}O}$). NMR ($CDCl_3$): δ 1.97, 1.99. A reaction of $[(CH_3)_5C_5MoS(\mu\text{-}S)]_2$ with water in the absence of O_2 under similar conditions did not produce the desired complex.

Acknowledgment. Support for this work from the National Science Foundation (Grant No. CHE-7922250) and from the University of Colorado Computing Center is gratefully acknowledged.

Registry No. II, 78085-81-1; III, 78018-24-3; IV, 78003-90-4; V, 78003-91-5; $(CH_3)_5C_5Mo(CO)_3H$, 78003-92-6; $[C_5H_5Mo(CO)_3]_2$, 12091-64-4; $[CH_3C_5H_4Mo(CO)_3]_2$, 33056-03-0; S_8, 10544-50-0; $Mo(CO)_6$, 13939-06-5; acetylene, 74-86-2; ethylene, 74-85-1.

Supplementary Material Available: Tables of thermal parameters and of observed and calculated structure amplitudes (20 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

Crystal Structures of a Tetraoxy Spirocyclic Selenurane and Tellurane. Lone Pair Effects[1]

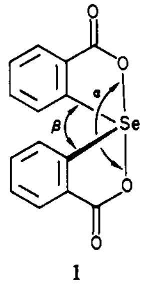
ROBERTA O. DAY and ROBERT R. HOLMES*

Received December 15, 1980

The crystal structures of the tetraoxy spirocyclic selenurane $(C_6H_{12}O_2)_2Se$ (3) and corresponding tellurane $(C_6H_{12}O_2)_2Te$ (4) have been determined by single-crystal X-ray diffraction analysis. Both compounds crystallize in the monoclinic space group $C2/c$ with $Z = 4$ and with the central atom on a crystallographic twofold axis. For 3, $a = 10.442$ (6) Å, $b = 10.545$ (5) Å, $c = 13.910$ (3) Å, and $\beta = 110.27$ (3)°. For 4, $a = 19.108$ (7) Å, $b = 10.469$ (4) Å, $c = 7.705$ (2) Å, and $\beta = 97.83°$. Data for both compounds were collected on an Enraf-Nonius CAD4 diffractometer out to a maximum $2\theta_{Mo\,K\bar{\alpha}}$ of 50°. Full-matrix least-squares refinement led to $R = 0.042$ and $R_w = 0.055$ for 3 and $R = 0.034$ and $R_w = 0.042$ for 4. Both exist in a trigonal-bipyramidal structure distorted in compliance with the presence of an equatorially positioned lone electron pair. In the Te compound intermolecular Te–O contacts indicate a degree of polymerization making the Te atoms pseudo six-coordinated. No such contact is observed in the Se moiety.

Introduction

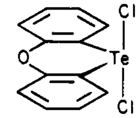
Although the molecular structures of spirocyclic phosphoranes have been extensively studied[2] and those of spirocyclic sulfuranes[3] studied to a lesser extent, spirocyclic selenuranes[4] have received little attention and related telluranes apparently none at all. The structure of 3,3′-spirobi(3-selenaphthalide) (1) is known[4] (for this and other structures to follow, the axial angle α and equatorial angle β refer to the angles as designated in 1). Like most cyclic sulfuranes,[3] the structure of the selenurane 1 shows the axial angle O–Se–O and equatorial angle C–Se–C bent away from the fifth coordination site, an equatorial site presumed to be occupied by a lone electron pair. This contrasts with the structures of cyclic phosphoranes which show the axial and equatorial angles bent in mutually opposing directions (i.e., along the Berry coordinate[5]) and yield a range of structures between the idealized trigonal bipyramid and square (or rectangular) pyramid.[2,6]



1

$O_{ax}\text{-}Se\text{-}O_{ax} = 172.4\ (3)°$
$C_{eq}\text{-}Se\text{-}C_{eq} = 101.0\ (3)°$

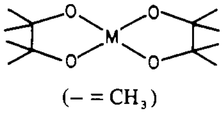
A number of monocyclic tellurane structures has been reported[7] which have axial and equatorial angles bent in the same direction as that for the selenurane 1. Tellurane 2[8] is representative of this class.



2

$Cl_{ax}\text{-}Te\text{-}Cl_{ax} = 176.8\ (1)°$
$C_{eq}\text{-}Te\text{-}C_{eq} = 90.7\ (3)°$

In order to strengthen the structural basis for determining pentacoordinate principles[2] applicable to group 6 derivatives, we carried out a single-crystal X-ray study of the similarly formulated spirocyclic selenurane 3 and the spirocyclic tellurane 4. Temperature-dependent ^{13}C and ^{1}H NMR data support trigonal-bipyramidal ground-state structures for both



(– = CH_3)
3, M = Se
4, M = Te

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(1) Presented in part at the 178th National Meeting of the American Chemical Society, Washington, D.C., Sept 9–14, 1979; INOR 281.

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