

as the isolation of a mixture of stereoisomers (i.e., **10** and **11**) when styrene is used as the trapping agent. Aryl-substituted alkenes are effective substrates, whereas simple or electron deficient olefins fail to react with the electronically excited triplet state. Finally, the triplet-induced photolysis of **1** in the presence of methyl phenylpropionate was also studied and was found to give cyclopentadiene **18** as the exclusive photoproduct. The formation of **18** is most readily accommodated by a (2 + 2) cycloaddition followed by an electrocyclic ring opening of the initially generated bicyclo[2.1.0]pentene intermediate (see Scheme II).

Further studies on the scope and mechanism of these cycloadditions are in progress and will be reported in due course.

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Registry No. **1**, 21603-24-7; **2**, 83831-84-9; **3**, 83831-85-0; **4**, 83831-86-1; **5**, 83831-87-2; **6**, 83831-88-3; **10**, 83831-89-4; **11**, 83861-14-7; **13**, 83831-90-7; **14**, 83861-15-8; **15**, 83831-91-8; **16**, 83861-16-9; **18**, 83831-92-9; PhCH=CH₂, 100-42-5; PhC≡CCO₂CH₃, 4891-38-7; (E)-PhCH=CHPh, 103-30-0; PhCH=CHCO₂CH₃, 103-26-4.

Supplementary Material Available: Structure and table of fractional coordinates for nonhydrogen atoms of 1,4-dicarboxymethoxy-2,2-dimethyl-3-phenyl-4-(1'-phenyl-2'-methylprop-1'-enyl)bicyclo[1.1.0]butane (**2**) (9 pages). Ordering information is given on any current masthead page.

Reaction of MoS₂²⁻ with Bis(carboxymethyl)acetylene. Crystal and Molecular Structure of (Ph₄P)₂Mo[S₂C₂(COOMe)₂]₃: A Trigonal Prismatic Complex with a New Dithiolenene Ligand

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The hydrodesulfurization of organosulfur compounds in petroleum distillates is catalyzed by alumina-supported "sulfided" molybdenum and cobalt salts.¹ The mechanism of the hydrodesulfurization reaction and the structure of the catalyst are not known; however, it has been proposed that the active sites are located on the molybdenum sulfide surfaces.² In the absence of primary information, essential for an understanding of the hydrodesulfurization reaction, we have initiated studies on the reactivity of specific binary Mo-S complexes toward organic molecules that may or may not contain sulfur. Thus far our studies have shown that the (MoS₉)²⁻,^{3,4} (Mo₂S₁₀)²⁻,^{4,5} and (Mo₂S₁₂)²⁻⁴ complexes react readily with CS₂, and two of the isolated, structurally characterized products, [(CS₄)₂MoS]²⁻ and [(CS₄)₂Mo₂S₄]²⁻, contain the S-S chelating perthiocarbonate ligand.⁶

In this communication we report on the reaction of dimethyl 2-butyndioate (DMA) with the [(S₄)₂MoS]²⁻ anion in CH₃CN and on the crystal and molecular structure of one of the products, (Ph₄P)₂[Mo(S₂C₂(COOCH₃)₂)₃]·DMF·C₆H₆ (**I**; DMF = dimethyl formamide).

The reaction of (Ph₄P)₂[(S₄)₂MoS]⁶ with excess DMA, under dinitrogen, in warm (50–60 °C) acetonitrile solution proceeds

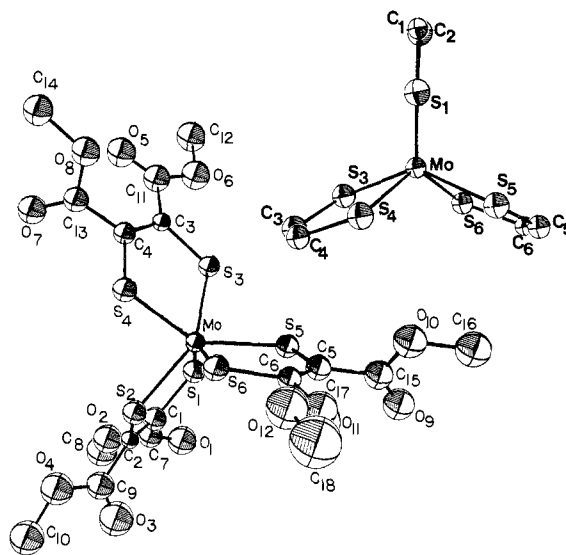


Figure 1. Structure of the Mo(S₂C₂(COOCH₃)₂)₃²⁻ anion, showing atom labeling scheme, and the MoS₆C₆ core illustrating the trigonal prismatic geometry. Thermal ellipsoids are drawn by ORTEP (Johnson, C. K., ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) and represent the 50% probability surfaces.

Table I. Selected Distances and Angles in [Mo(S₂C₂(COOMe)₂)₃]²⁻

	<i>n</i> ^a	mean value ^b	range
Bond Lengths (Å)			
Mo-S	6	2.393 (5)	2.385 (6)–2.399 (5)
C-S	6	1.74 (2)	1.72 (2)–1.76 (2)
C=C	3	1.34 (5)	1.28 (2)–1.38 (2)
C-O	6	1.32 (2)	
O-CH ₃	6	1.46 (2)	
C=O	6	1.19 (2)	
C-C	6	1.50 (3)	
S-S _{intra} ^c	3	3.09 (2)	
S-S _{inter} ^d	6	3.18 (6)	
Angles (deg)			
S-Mo-S _{intra} ^c	3	80.5 (5)	80.1 (2)–81.1 (2)
S-Mo-S _{inter} ^d (cis)	6	83 (2)	81.4 (2)–85.9 (2)
S-Mo-S _{inter} ^d (trans)	6	135 (8)	125.0 (3)–143.9 (3)
Mo-S-C	6	109 (1.5)	107.1 (6)–110.9 (6)

^a Number of independent measurements. ^b The standard deviations of the averages were taken as the larger of the individual standard deviations or the standard deviation from the mean $\sigma = [\sum_i^n (\chi_i^2 - n\bar{\chi}^2)/(n-1)]^{1/2}$. ^c Intraligand. ^d Interligand.

readily. Addition of diethyl ether to the green solution results in the deposition of a green solid which can be recrystallized from dimethyl formamide–benzene mixtures. The green crystals retain a molecule of both benzene and DMF of solvation. Anal. Calcd for (Ph₄P)₂Mo[S₂C₂(COOMe)₂]₃·DMF·C₆H₆ (**I**; C₇₅H₇₁S₆P₂O₁₃NMo): C, 58.71; H, 4.63; S, 12.52; Mo, 6.26. Found: C, 58.50; H, 4.53; S, 12.15; Mo, 6.36. The electronic spectrum of **I** in CH₂Cl₂ is characterized by absorptions at 650 nm (ϵ 5800), 450 (sh), and 356 (ϵ 11500). In the infrared spectrum, two overlapping bands at 1710 and 1730 cm⁻¹ are assigned tentatively to the C=O stretching vibrations of the ligand and the DMF molecule of solvation respectively.

Single-crystal X-ray diffraction and intensity data on **I** were collected on a Nicolet P3 automatic diffractometer by using an ω scan technique. The data corrected for Lorentz, polarization, and absorption effects were used for the solution of the structures by direct methods. Refinement by full-matrix least-squares

(7) Crystal and refinement data for (Ph₄P)₂[Mo(S₂C₂(COOMe)₂)₃]·DMF·C₆H₆: *a* = 22.907 (14) Å, *b* = 14.619 (9) Å, *c* = 43.746 (21) Å, β = 95.34(5)°; space group C_{2/c}, *z* = 8; $2\theta_{\max}$ 35° (Mo radiation); $F^2 \geq 3\sigma(F^2)$, 2637 reflections used; 389 parameters.

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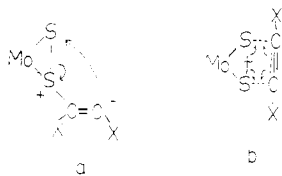


Figure 2. Proposed schemes for the addition of an acetylene to the Mo-S-S unit.

techniques has progressed to a conventional R value of 0.069.⁸

The structure of the dianion in I (Figure 1, Table I) shows three bidentate dithiolene (1,2-dicarbomethoxy-1,2-dithiolate) ligands coordinated to Mo(IV). The S_6 coordination polyhedron shows only small deviations from a trigonal prismatic geometry (D_{3h} symmetry). The three rectangular faces of the prism, S(1)S(2)S(3)S(4), S(3)S(4)S(5)S(6), and S(1)S(2)S(5)S(6), are nearly planar and are located 0.90, 0.91 and 0.92 Å from the Mo atom. The dihedral angles (δ) made by the S_6 polyhedron trigonal faces as described by Muetterties and Guggenberger⁹ are 11.67, 15.36, and 19.70° at b_1 and 120.33, 119.84, and 119.88° at b_2 and range from 87.0 to 93.0° at the remaining edges of the polyhedron.¹⁰ The mean value of the S-Mo-S interligand trans angles at 135° is quite close to the average value of $136 \pm 1^\circ$ found for the same angles in other trigonal prismatic complexes such as $\text{Re}[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]_3$,¹¹ $\text{V}[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]_3$,¹² $\text{Mo}(\text{S}_2\text{C}_2\text{H}_2)_3$,¹³ $\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3$,¹⁴ and $[\text{Nb}(\text{S}_2\text{C}_6\text{H}_4)_3]^-$.¹⁴ In the structure of the $[\text{Mo}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^{2-}$ complex¹⁵ (the only other structurally characterized tris(dithiolene) Mo(IV) complex) the MoS_6 polyhedron (average Mo-S = 2.373 Å) is close to being midway between the octahedron and the trigonal prism. The apparent structural differences between the MoS_6 polyhedra in I and $[\text{Mo}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^{2-}$ very likely reflect differences in covalency in the Mo-L bond that stem from differences in the relative energies of the Mo(IV) d orbitals and the appropriate ligand orbitals.¹⁴ On the basis of σ bonding, the trigonal prismatic coordination is favored over the octahedral one for highly covalent 4d and 5d transition-metal complexes containing metal ions in the d^0 , d^1 , and d^2 electronic configurations.¹⁶ Not unlike other dithiolene complexes,¹⁷ I undergoes two reversible one-electron oxidations¹⁸ in CH_2Cl_2 at +0.02 and +0.48 V vs. SCE. The low oxidation potentials and the apparent stability of the monoanionic and neutral derivatives of I.

The synthesis of I and in particular the generation of the dithiolene ligands¹⁹ present an interesting problem from a mecha-

nistic point of view. The formation of the 1,2-ethylene dithiolate ligand in I parallels the formation of the same ligand and its selenium analogue in reaction 1 ($\text{R} = \text{H}, \text{CH}_3; \text{E} = \text{S}, \text{Se}$). A $(\text{C}_5\text{H}_4\text{R})_2\text{TiE}_5 + \text{DMA} \rightarrow (\text{C}_5\text{H}_4\text{R})_2\text{TiE}_2\text{C}_2(\text{CO}_2\text{CH}_3)_2$ (1)

kinetic study of this reaction shows a second-order process with activation parameters of $-19 \text{ cal}/(\text{mol K})$ for ΔS^\ddagger and 19 kcal/mol for ΔH^\ddagger . An associative mechanism involving electrophilic attack on the E_5 ligand and a dipolar intermediate have been suggested for this reaction.²⁰ The large negative value for ΔS^\ddagger , however, also is indicative of a highly ordered transition state and may be consistent with a cycloaddition reaction. The isolation of $(\text{Ph}_4\text{P})_2[(\text{S}_4)\text{Mo}_2\text{S}_4(\text{S}_2)]$ from solutions of $(\text{Et}_4\text{N})_2[(\text{S}_4)_2\text{MoS}]$ following the addition of Ph_4PCl suggests the presence of equilibria such as $[(\text{S}_4)_2\text{MoS}]^{2-} \rightleftharpoons [(\text{S}_4)\text{MoS}(\text{S}_2)]^{2-} + \text{S}_2^0$. In solutions of $[(\text{S}_4)_2\text{MoS}]^{2-}$ therefore, either MoS_2 or $\text{Mo}(\text{S}_4)$ units are possible reactive species toward DMA. By analogy to the $(\text{C}_5\text{H}_4\text{R})_2\text{TiE}_5/\text{DMA}$ system,²⁰ formation of the ethylene dithiolate ligand in I may proceed either by an associative mechanism involving a dipolar intermediate (Figure 2a) or by a Diels-Alder type (4 + 2) cycloaddition mechanism (Figure 2b). The interactions of other activated acetylenes and olefins with binary Mo-S complexes are currently under study in our laboratories.

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Supplementary Material Available: Structure factor tables for $(\text{Ph}_4\text{P})_2[\text{Mo}(\text{S}_2\text{C}_2(\text{COOCH}_3)_2)_3] \cdot \text{DMF} \cdot \text{C}_6\text{H}_6$ (28 pages) and positional and thermal parameters for the Ph_4P^+ cations and the DMF and benzene molecules of solvation. Ordering information is given on any current masthead page.

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Synthesis and Reactivity of a "Semi" Triply Bridging Methylidyne Complex. Crystal Structure of $\text{HOs}_3(\text{CO})_{10}(\text{CH})$

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The methylidyne (CH) ligand—the simplest hydrocarbon ligand and a potential intermediate in the hydrogenolysis of carbon monoxide—is an object of current attention. Examples of methylidyne groups bound to one,¹ two,² three,³ and four⁴ transition-metal atoms have been reported recently. In this communication we report a new complex with a triply bridging methylidyne ligand, which in contrast with previous examples^{3,5} is found

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