Syntheses and Structures of Dinuclear Molybdenum Complexes Containing Reactive μ-Thiolate-Thioether Ligands

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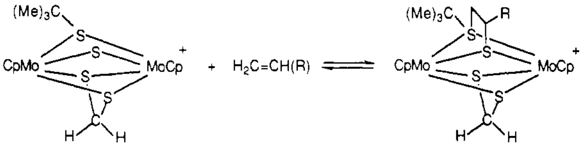
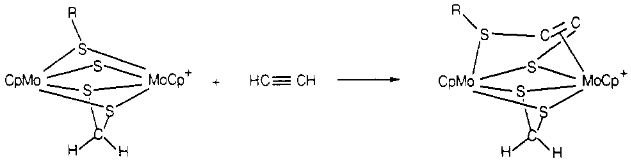
Received November 1, 1990

Certain thiolate-bridged cationic complexes of the formula $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]SO_3CF_3$ react reversibly with olefins:



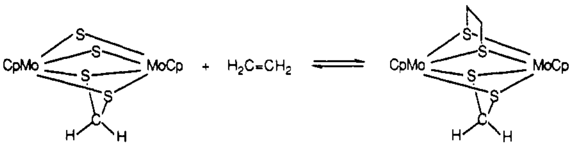
The resulting adduct contains a thiolate-thioether bridging ligand. The stability of the olefin adduct varies significantly as the R substituent on the thiolate ligand and the substituents on the olefin are varied. Equilibrium constants have been determined for the formation of selected olefin adducts. The reaction of allene with $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]SO_3CF_3$, where R = 2-propenyl, led to the formation of an isolable thiolate-thioether complex, $[(CpMo)_2(S_2CH_2)(SC({=}CH_2)CH_2SC(CH_3)({=}CH_2))]SO_3CF_3$ (**3**). Complex **3** crystallized in space group $P2_1/c$ with a = 15.498 (6) Å, b = 14.132 (6) Å, c = 24.130 (10) Å, β = 100.68 (3)°, V = 5193 (3) Å^3, and Z = 8. The structural study shows that the symmetrical $Cp_2Mo_2S_4$ core is retained; the coordination geometry about the bridging thioether sulfur atom is highly distorted tetrahedral. Complex **3** dissociates allene when heated. The reaction of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]SO_3CF_3$ (**2**; R = *tert*-butyl) with acetylene led to the isolation of a product of the formula $[(Cp\overline{Mo)(SCH}{=}CHSCMe_3)(S_2CH_2)\text{-}MoCp]SO_3CF_3$ (**4**). Complex **4** crystallized in space group $P2_1/c$ with a = 11.983 (7) Å, b = 13.839 (6) Å, c = 15.200 (6) Å, β = 109.71 (4)°, V = 2373 (2) Å^3, and Z = 4. The cation contains a thiolate-thioether ligand as a result of acetylene interaction with sulfur ligands. The double bond of the coordinated alkyne has inserted into the molybdenum-sulfur bond of the thioether ligand and undergoes a π interaction with one metal ion:



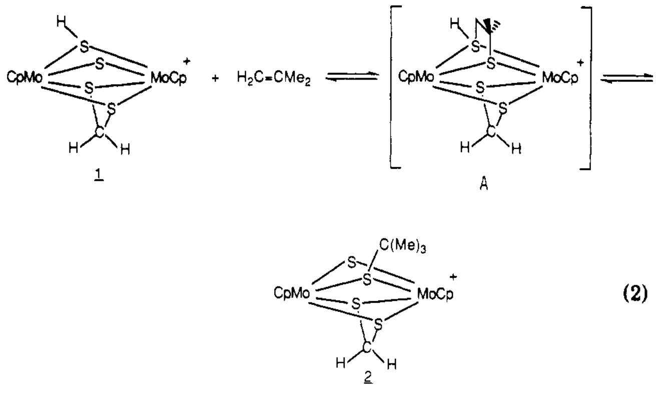
The complex represents the first structurally characterized $Cp_2Mo_2S_4$ derivative in which a Mo-S bond has been cleaved.

Introduction

Several years ago we found that the reactions of neutral bis(μ-sulfido)cyclopentadienylmolybdenum complexes with alkenes led to the reversible formation of μ-alkanedithiolate ligands (eq 1).[1] Equilibrium constants for the olefin adduct formation were very sensitive to the degree of substitution about the olefin and to the substituents on other ligands in the dinuclear molybdenum complex.[1] More recently we have proposed that the sulfur ligands in cationic thiolate-bridged derivatives interact with olefins in a similar way.[2] For example, an interaction of the protonated cation **1** with an olefin was proposed to precede the reversible insertion of the olefin into the S-H bond (eq 2). The high regioselectivity observed in these insertion reactions was attributed to a preferred orientation of the incoming olefin such that the more electron-rich carbon of the double bond interacted with the more electrophilic sulfur ligand in the cation. Although an intermediate of structure A was not observed in the insertion reactions, we now report the preparation and characterization of analogous structures that result from olefin interactions with alkanethiolate cations such as **2**. The cationic thiolate-thioether complexes provide a model for the insertion intermediate A and further demonstrate the extensive coordinating ability of bridging sulfur ligands in these dinuclear complexes.



(1)



(2)

An unusual feature of the thiolate-thioether ligands in these complexes is the weak nature of the C-S bonds,

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[1] McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* 1983, *105*, 5329.

[2] Birnbaum, J.; Laurie, J. C. V.; Rakowski DuBois, M. *Organometallics* 1990, *9*, 156.

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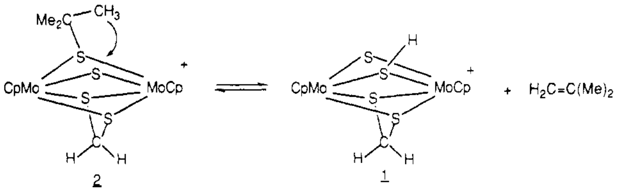
which leads to the facile reverse of the olefin addition. Many examples of metal complexes containing polydentate thiolate–thioether ligands have been reported.[3–6] The sulfur ligands in these systems are generally quite robust and lend stability to the complexes. Previous examples of relatively facile C–S bond cleavage have been reported for bidentate thiolate–thioether complexes.[7,8] These reactions involved R-group migration from thioether sulfur to either metal or alternate ligand sites.

Reactions of the alkanethiolate cations with alkynes have also been studied. Unlike the reversible olefin interactions, the alkyne interacts irreversibly with sulfur and metal sites to give a novel structure in which the double bond of an alkenedithiolate ligand has inserted into a Mo–S bond.

Results and Discussion

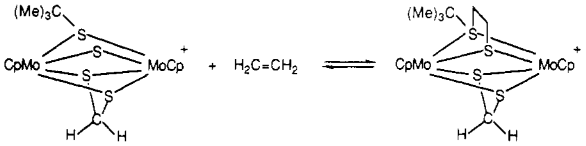
Reactions of the 2-Methyl-2-propanethiolate Cation with Alkenes. Previous studies have shown that $[(\mathrm{CpMo})_2(\mathrm{S}_2\mathrm{CH}_2)(\mu\text{-S})(\mu\text{-SCMe}_3)]^+$ (cation of **2**) is unstable in solution as a result of the equilibrium shown in eq 3.[2]



(3)

Thermodynamic information on this olefin deinsertion process has been obtained by the determination of equilibrium constants over a temperature range of 20–70 °C. The reversible thermal decomposition was carried out in CD_3CN[9] in a sealed NMR tube, and concentrations of each of the species in solution were determined by integrations of appropriate NMR resonances. At 20 °C the value of K_{eq} was found to be $(3.2 \pm 0.5) \times 10^{-4}$ M. The temperature variation of K_{eq} led to the approximate values of $\Delta H = 47$ kJ/mol and $\Delta S = 95$ J/(K mol) for the deinsertion reaction. These values are uncorrected for the competing reaction of **1**, which involves the irreversible anti-Markovnikov insertion of 2-methylpropene to form $[(\mathrm{CpMo})_2(\mathrm{S}_2\mathrm{CH}_2)(\mu\text{-S})(\mu\text{-SCH}_2\mathrm{CHMe}_2)]^+$.[2] This reaction was slow over the time period of the equilibrium studies (70 min) but approximately 5–10% of the molybdenum complex was consumed in this way.

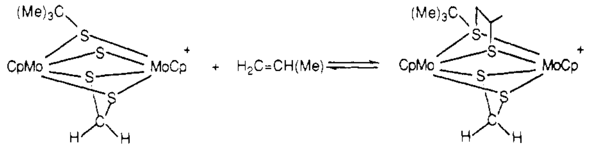
When excess ethene was added to a solution of **2** at 20 °C, the deinsertion shown in eq 3 was inhibited to some extent, and a new product was formed as shown in eq 4.



(4)

The ^1H NMR spectrum of the product, which was invariant down to −50 °C, indicated that a plane of symmetry through the four sulfur atoms is maintained. Singlet resonances at 5.90 and 6.01 ppm were assigned to the Cp and methanedithiolate protons, respectively. The protons of the coordinated ethene were characterized by AA′XX′ patterns at 2.92 and 1.95 ppm, and a singlet at 1.27 ppm was assigned to the *tert*-butyl protons. Reaction 4 was readily reversed when the ethene was removed. The reaction mixture was kept at 20 °C in a sealed tube for a period of 3–5 h and monitored periodically by NMR spectroscopy. Relative intensities of resonances did not change after the first 1 h. An equilibrium constant for the reaction was determined to be 96 ± 5 M^{-1} at 20 °C by integration of appropriate resonances in the spectrum. After 90 min at 20 °C the NMR spectrum showed evidence for the presence of 5–10% of $[(\mathrm{CpMo})_2(\mathrm{S}_2\mathrm{CH}_2)(\mu\text{-S})(\mu\text{-SCH}_2\mathrm{CH}_3)]^+$,[2] and at higher temperatures this ethanethiolate cation was eventually formed quantitatively. This product resulted from insertion of ethene into the S–H bond of **1**, produced in the deinsertion equilibrium discussed above (eq 3).

The reaction of propene with the 2-methyl-2-propanethiolate cation **2** also resulted in the formation of a thiolate–thioether complex. The NMR spectrum was consistent with the formation of a single isomer, since only one methyl resonance was observed for the coordinated propene. The orientation of the propene with respect to the *tert*-butyl group is proposed to be that shown in eq 5 on the basis of steric considerations. The deinsertion of 2-methylpropene from **2** and the insertion of propene into the S–H bond of **1** to form the 2-propanethiolate cation was a competing reaction at room temperature, but this process was not observed at 0 °C.



(5)

Reaction 5 was equilibrated in a salted ice bath for 12 h, and the NMR spectrum was then monitored at 0 °C for 2 h to establish that relative intensities of resonances remained constant. The equilibrium constant for the propene adduct formation was determined to be 9.6 ± 0.3 M^{-1} at 0 °C and ≤ 4.1 M^{-1} at 20 °C. The value of K for the interaction of **2** with 1-butene at 0 °C was similar to that observed for propene (see Experimental Section). A decrease in K was observed as alkyl substituents on the olefin were increased; the trend is similar to that observed in the reactions of olefins with the neutral complex shown in eq 1.[1] As expected from this trend, interactions of **2** with internal butenes and with 2-methylpropene were not detected even at 0 °C. However, an adduct between the sulfur ligands of **2** and 2-methylpropene was tentatively identified by ^1H NMR spectroscopy when the reaction solution containing a large excess of olefin was maintained at −40 °C for several days. Oligomers of 2-methylpropene, ranging from C_8H_{16} to $C_{32}H_{64}$, were also produced when excess 2-methylpropene was reacted with **2**. Further studies of this carbon–carbon coupling reaction will be reported in a separate paper.

Reactions of Other Alkanethiolate Cations with Alkenes. The above studies demonstrated that the interaction of olefins with cationic alkanethiolate complexes was sensitive to the nature of the olefin, but the alkanethiolate substituent also had a strong influence on the equilibrium constant. Despite the relatively high equi-

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(3) Sellman, D.; Barth, I.; Moll, M. *Inorg. Chem.* **1990**, *29*, 176 and references within.

(4) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1358.

(5) Zubieta, J.; Nicholson, T. *Inorg. Chem.* **1987**, *26*, 2094.

(6) Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6951.

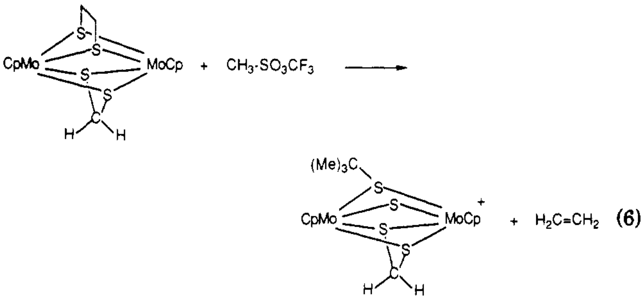
(7) Green, M.; Norman, N. C.; Orpen, A. G. *J. Organomet. Chem.* **1981**, *221*, C11.

(8) Schrauzer, G. N.; Zhang, C.; Schlemper, E. O. *Inorg. Chem.* **1990**, *29*, 3371.

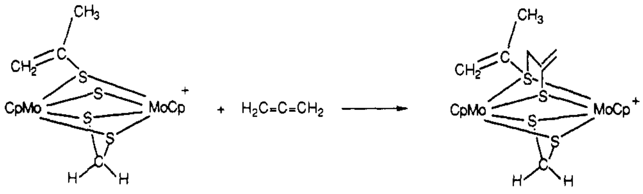
(9) Reactions of 1 with CD_3CN have been observed in the presence of hydrogen or excess protic acid.[10] In the absence of these reagents, a reaction of 1 with this solvent is not detected.

(10) Bernatis, P.; Laurie, J. C. V.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 1607.

librium constant observed for the reaction of the 2-methyl-2-propanethiolate cation with ethene at 20 °C, no interaction was detected between the 2-propanethiolate cation and ethene under similar conditions (~4 equiv of ethene in a sealed NMR tube, CD_2Cl_2 solvent). Similarly, no evidence was detected for an interaction of a large excess of ethene with the methanethiolate cation. The low affinity of this cation for ethene was further demonstrated when the neutral olefin adduct was reacted with methyl triflate. The quantitative release of ethene was observed in this case (eq 6). The trend observed in these studies suggests that electron-donating groups favor the formation of olefin adducts.



The 2-propenethiolate cation has been prepared by the reaction of the protonated cation with 1 equiv of allene. This cation did not undergo a detectable reaction with ethene at room temperature. However, it reacted readily with additional allene to form a stable cationic olefin adduct, 3, which was isolated in crystalline form (eq 7). The complex has been characterized by mass spectroscopy and by ^1H NMR data.



3

(7)

The NMR spectrum of a recrystallized sample showed the presence of two isomers in a 9:1 ratio. The isomers are presumably a result of different orientations of the propenedithiolate ligand with respect to the propenethiolate group. Chemical shift assignments, given in the Experimental Section, were made on the basis of homonuclear decoupling experiments.

Single crystals of 3 have been isolated from dichloromethane, and an X-ray diffraction study has been completed. The complex crystallized in space group $P2_1/c$ with two molecules per asymmetric unit. The two molecules were very similar structurally, and an Ortep plot of one of the cations is shown in Figure 1. Selected bond distances and angles are given in Table I, and atomic coordinates are listed in Table II. The structural features of the cation are very similar to those observed previously for molybdenum(III) cations of this general class.[11] The geometry about the four-coordinate sulfur atom, S(3), is distorted tetrahedral. The C(2)–S(3)–C(3) angle is 105°, but other angles deviate widely from the tetrahedral value. For example, the Mo(2)–S(3)–Mo(1) angle of 67.1 (2)° is similar to the other Mo–S–Mo angles in the molecule, while Mo–S(3)–C angles vary from 113 to 129°. The Mo–S(3) bonds are somewhat shorter than the other Mo–S bonds in the structure, as might be expected for a sulfur atom with a higher coordination number and a more negative formal oxidation state.

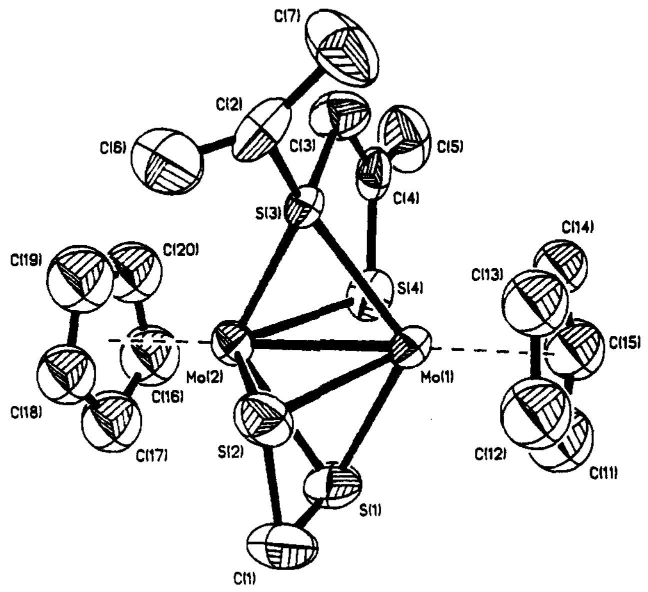


Figure 1. Perspective drawing and numbering scheme for the cation of $[(CpMo)_2(S_2CH_2)(SC({=}CH_2)(CH_2SC(CH_3)({=}CH_2)]SO_3CF_3$ (3). Thermal ellipsoids are drawn at the 50% probability level.

Table I. Selected Bond Distances (Å) and Angles (deg) for $[(CpMo)_2(S_2CH_2)(SC({=}CH_2)CH_2SC(CH_3)({=}CH_2))]SO_3CF_3$ (3)[a]

	Distances		
Mo(1)–Mo(2)	2.638 (3)	Mo(2)–S(1)	2.452 (8)
Mo(1)–S(1)	2.441 (8)	Mo(2)–S(2)	2.464 (8)
Mo(1)–S(2)	2.460 (8)	Mo(2)–S(3)	2.379 (7)
Mo(1)–S(3)	2.392 (7)	Mo(2)–S(4)	2.448 (8)
Mo(1)–S(4)	2.445 (8)	S(1)–C(1)	1.849 (34)
S(3)–C(2)	1.793 (33)	S(2)–C(1)	1.873 (30)
S(3)–C(3)	1.827 (28)	S(4)–C(4)	1.833 (26)
C(2)–C(6)	1.397 (46)	C(3)–C(4)	1.465 (39)
C(2)–C(7)	1.556 (46)	C(4)–C(5)	1.371 (47)
	Angles		
Mo(1)–S(1)–Mo(2)	65.3 (2)	Mo(1)–S(1)–C(1)	92.4 (10)
Mo(1)–S(2)–Mo(2)	64.8 (2)	Mo(1)–S(3)–C(3)	113.6 (9)
Mo(1)–S(3)–Mo(2)	67.1 (2)	Mo(2)–S(3)–C(3)	113.4 (9)
Mo(1)–S(4)–Mo(2)	65.2 (2)	S(1)–C(1)–S(2)	93.1 (13)
Mo(1)–S(3)–C(2)	125.3 (10)	S(3)–C(3)–C(4)	105.2 (18)
Mo(2)–S(3)–C(2)	128.9 (10)	S(4)–C(4)–C(3)	118.5 (20)
S(1)–C(1)–S(2)	93.1 (13)	S(4)–C(4)–C(5)	113.9 (22)
C(6)–C(2)–C(7)	126.6 (30)	C(3)–C(4)–C(5)	127.5 (25)

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

Complex 3 provided the first example of a stable thiolate–thioether-bridged complex in the cyclopentadienylmolybdenum systems. Its thermal stability was investigated briefly. The complex decomposed when a $CDCl_3$ solution was sealed under vacuum and placed in a 70 °C bath. The primary mode of decomposition followed those of the less stable thioether complexes discussed above; allene was released and the propenethiolate cation was produced. However, other processes were involved in the thermal decomposition that have not been completely characterized. A second unidentified molybdenum complex was produced (30–40% yield), and propene and 2-chloropropene were observed in the volatile products. Further studies of the reactions of thiolate–thioether complexes are in progress.

Because allene formed a more stable adduct than other olefins, we attempted to isolate the corresponding allene

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[11] Rakowski DuBois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

Table II. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for $[(\mathrm{CpMo})_2(\mathrm{S_2CH_2})(\mathrm{SC({=}CH_2)CH_2SC(CH_3)({=}CH_2)})]\mathrm{SO_3CF_3}\cdot 0.5\mathrm{CH_2Cl_2}$ (3)

	x/a	y/b	z/c	U(eq)[b]		x/a	y/b	z/c	U(eq)[b]
Mo(1)	4376 (2)	1968 (2)	1613 (1)	35 (1)*	S(2′)	−2066 (5)	3369 (5)	2242 (3)	50 (3)*
Mo(2)	3691 (2)	546 (2)	971 (1)	42 (1)*	S(3′)	−2204 (4)	4386 (5)	1113 (3)	40 (3)*
S(1)	5021 (5)	387 (5)	1694 (3)	62 (3)*	S(4′)	−536 (5)	3658 (5)	1026 (3)	51 (3)*
S(2)	3426 (5)	776 (5)	1938 (3)	57 (3)*	S(5′)	887 (5)	3026 (6)	4216 (3)	81 (4)*
S(3)	3065 (4)	2088 (5)	916 (3)	41 (3)*	O(1′)	1583 (8)	3611 (12)	4482 (8)	117 (9)
S(4)	4743 (5)	1654 (5)	688 (3)	50 (3)*	O(2′)	686 (11)	3102 (13)	3625 (4)	111 (9)
S(5)	3637 (5)	6013 (5)	996 (3)	61 (3)*	O(3′)	921 (12)	2091 (8)	4427 (8)	145 (11)
O(1)	4461 (7)	6224 (12)	1327 (7)	111 (9)	F(1′)	−209 (13)	4395 (10)	4256 (10)	190 (12)
O(2)	3349 (10)	6664 (10)	554 (5)	84 (7)	F(2′)	−772 (8)	3013 (14)	4247 (10)	191 (12)
O(3)	3505 (10)	5054 (7)	836 (6)	74 (6)	F(3′)	41 (13)	3536 (18)	4997 (6)	207 (13)
F(1)	2078 (7)	5929 (13)	1240 (7)	149 (9)	C(1′)	−1163 (19)	2602 (20)	2642 (12)	58 (8)
F(2)	3120 (11)	5699 (11)	1942 (5)	137 (8)	C(2′)	−3273 (18)	4881 (19)	1114 (11)	48 (8)
F(3)	2853 (10)	7096 (8)	1613 (6)	103 (7)	C(3′)	−1880 (18)	4845 (19)	453 (11)	52 (8)
C(1)	4402 (20)	40 (21)	2248 (12)	65 (9)	C(4′)	−1091 (19)	4305 (20)	389 (12)	57 (8)
C(2)	2014 (20)	2452 (21)	1047 (13)	66 (9)	C(5′)	−723 (24)	4297 (25)	−53 (15)	93 (12)
C(3)	3212 (18)	2740 (19)	286 (11)	51 (8)	C(6′)	−3402 (21)	5420 (22)	1547 (13)	74 (10)
C(4)	4089 (17)	2480 (18)	194 (11)	45 (7)	C(7′)	−3955 (19)	4562 (19)	596 (12)	58 (8)
C(5)	4516 (23)	2811 (23)	−216 (14)	88 (11)	C(8′)	−71 (8)	3524 (11)	4443 (6)	186 (23)
C(6)	1433 (21)	1765 (23)	1176 (13)	76 (10)	C(11′)	−1462 (11)	1465 (16)	868 (10)	69 (10)
C(7)	1905 (23)	3544 (24)	1083 (15)	91 (12)	C(12′)	−1855	1178	1328	68 (9)
C(8)	2877 (8)	6195 (9)	1475 (5)	106 (13)	C(13′)	−2722	1545	1240	68 (9)
C(11)	5536 (12)	2504 (13)	2319 (9)	64 (9)	C(14′)	−2866	2059	726	68 (9)
C(12)	4734	2654	2510	70 (9)	C(15′)	−2088	2010	496	82 (11)
C(13)	4218	3292	2131	69 (9)	C(16′)	−132 (16)	4902 (15)	2664 (8)	74 (10)
C(14)	4701	3536	1706	54 (8)	C(17′)	−905	5463	2555	74 (10)
C(15)	5516	3050	1822	66 (9)	C(18′)	−913	5962	2043	85 (11)
C(16)	3908 (12)	−580 (17)	342 (10)	74 (10)	C(19′)	−144	5709	1836	91 (11)
C(17)	3687	−1068	811	73 (10)	C(20′)	338	5054	2220	77 (10)
C(18)	2809	−831	847	89 (11)	C(9)†	2695 (50)	3959 (21)	3167 (28)	146 (35)
C(19)	2487	−196	400	62 (9)	Cl(1)†	2150 (12)	3122 (20)	2678 (9)	168 (13)*
C(20)	3167	−41	88	70 (10)	Cl(2)†	3478 (18)	3405 (28)	3692 (11)	220 (20)*
Mo(1′)	−1710 (2)	2805 (2)	1342 (1)	40 (1)*	C(9′)†	2560 (52)	3833 (28)	3444 (15)	65 (26)
Mo(2′)	−971 (2)	4312 (2)	1864 (1)	44 (1)*	Cl(1′)†	2529 (21)	4429 (19)	2796 (11)	143 (17)*
S(1′)	−477 (5)	2710 (6)	2126 (3)	64 (3)*	Cl(2′)†	2966 (31)	2667 (25)	3424 (19)	191 (27)*

[a] Atoms have occupancies of 1.0 except as marked with †: C(9), 0.60; Cl(1), 0.60; Cl(2), 0.60; C(9′), 0.40; Cl(1′), 0.40; Cl(2′), 0.40. [b] For values marked with *, the equivalent isotropic U is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[(\mathrm{CpMo})(\mathrm{SCH{=}CHSCMe_3})(\mathrm{S_2CH_2})(\mathrm{MoCp})]\mathrm{SO_3CF_3}$ (4)

Distances			
Mo(1)–Mo(2)	2.742 (2)	Mo(2)–S(1)	2.428 (3)
Mo(1)–S(1)	2.449 (3)	Mo(2)–S(2)	2.443 (3)
Mo(1)–S(2)	2.438 (3)	Mo(2)–S(3)	2.433 (4)
Mo(1)–S(3)	2.414 (3)	Mo(2)–S(4)	2.512 (3)
Mo(1)–C(2)	2.206 (10)	Mo(1)–C(3)	2.267 (10)
S(3)–C(2)	1.758 (12)	S(4)–C(3)	1.727 (12)
S(1)–C(1)	1.833 (12)	S(4)–C(4)	1.897 (10)
C(2)–C(3)	1.449 (18)		
Angles			
Mo(1)–S(1)–Mo(2)	68.4 (1)	S(3)–C(2)–C(3)	116.2 (9)
Mo(1)–S(2)–Mo(2)	68.4 (1)	C(3)–S(4)–C(4)	106.5 (6)
Mo(1)–S(3)–Mo(2)	68.9 (1)	Mo(1)–C(3)–S(4)	110.0 (6)
Mo(2)–S(4)–C(3)	90.5 (4)	C(2)–C(3)–S(4)	122.0 (9)
Mo(2)–S(3)–C(2)	61.5 (3)	Mo(1)–C(2)–S(3)	74.1 (4)
S(1)–C(1)–S(2)	96.7 (6)		

adducts of other alkanethiolate cations. The reaction of the methanethiolate cation with excess (~4 equiv) allene did lead to an isolable adduct. Several days were required for the reaction to reach completion at room temperature. Characterization data are included in the Experimental Section. Under similar reaction conditions with allene at room temperature, the 2-methyl-2-propanethiolate cation underwent preferential elimination of 2-methylpropene (eq 3). The protonated cation formed in this process reacted with allene to produce 3.

Reactions of Alkanethiolate Cations with Alkynes. The interactions of alkynes with the bridging sulfide ligands in $(\mathrm{CpMo}(\mu\text{-S}))_2\mathrm{S_2CH_2}$ (see eq 1) were irreversible and led to stable alkenedithiolate complexes.[1] We, therefore, attempted to prepare stable thiolate–thioether derivatives by the reactions of thiolate cations with acetylene. The 2-methyl-2-propanethiolate cation reacted with acetylene (4 equiv) at room temperature, but the reaction was considerably slower than the one observed between the same cation and ethene. For example, after 100 min, the reaction was only 55% complete. An orange cationic product, 4, was isolated after 12 h and its characterization is discussed below. In addition to this major product, products resulting from alkyne insertion into the S–H bond of 1[12] were also tentatively identified in the NMR spectrum of the product solution, and a small amount of 2-methylpropene was detected.

The ^{1}H NMR spectrum of 4 confirmed that 1 equiv of acetylene had reacted with the dimer; inequivalent vinyl protons were observed at 5.39 and 3.84 ppm. The inequivalent Cp and methanedithiolate protons in the spectrum showed that the plane of symmetry though the sulfur ligands had been removed and indicated that the acetylene adduct was not structurally analogous to the alkene adducts. An interaction of the alkenedithiolate olefin with one of the metal ions would account for the low symmetry. A similar interaction has been postulated previously for related cationic derivatives.[13]

Single crystals of the acetylene addition product, grown from a dichloromethane solution, crystallized in space group $P2_1/c$. A perspective drawing of the cation of 4 and

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(12) Birnbaum, J. Ph.D. Dissertation, University of Colorado, Boulder, CO, 1990.

(13) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234.

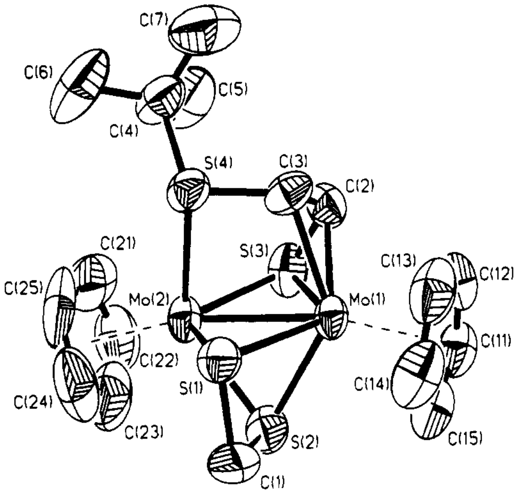


Figure 2. Perspective drawing and numbering scheme for the cation of [(CpMo)(SCH=CHSCMe$_3$)(S$_2$CH$_2$)(MoCp)]SO$_3$CF$_3$ (4). Thermal ellipsoids are drawn at the 50% probability level.

its numbering scheme are given in Figure 2. Selected bond distances and angles are summarized in Table III, and atomic coordinates are given in Table IV. The structure shows that acetylene has reacted with the cation by adding to two sulfurs and by inserting into the molybdenum–sulfur bond of the alkanethiolate ligand. The resulting alkenethiolate–thioether ligand, *t*-Bu—S—CH=CHS$^-$, interacts with Mo(2) through the two sulfur donors and with Mo(1) through the thiolate sulfur and the π system of the double bond. The average of the Mo–C bond lengths of the coordinated olefin (2.206 (10) and 2.267 (10) Å) is slightly shorter than the average of those in the Mo(0) complex (PMe$_3$)$_4$Mo(C$_2$H$_4$)$_2$ (2.270 (5) Å)[14] and slightly longer than average Mo–C distances for the μ_2-acetylene in Cp$_2$(CO)$_4$Mo$_2$(μ-C$_2$H$_2$) (2.172 Å).[15] The C–C distance of the alkenethiolate ligand is lengthened relative to that of a normal double bond to a distance of ~1.45 Å.

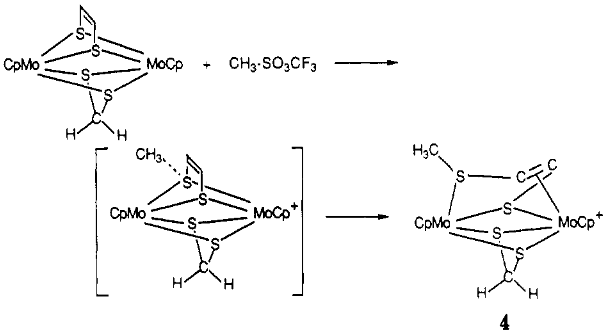
Alkene insertion into the Mo–S(4) bond significantly distorts the molybdenum–sulfur core of the dimer. The S(1), S(2), and S(3) atoms are retained in a plane[16] that is perpendicular to and bisects the metal–metal vector, but S(4) is displaced from this plane by 0.83 Å. The M–M distance is lengthened to 2.842 (1) Å compared to the distance 2.599 (1) Å for a symmetrically bridged cation with a similar formal oxidation state.[11] Complex 4 provides the first structurally characterized example of a Cp$_2$Mo$_2$S$_4$ derivative in which a molybdenum–sulfur bond has been cleaved, and the symmetry of the four sulfide bridges has been disrupted. The mild conditions required for this distortion are notable. Previous work has shown that temperatures of 90–100 °C are necessary to exchange bridging thiolate ligands with free thiols in [CpMo(μ-S)(μ-SR)]$_2$ derivatives,[17] and Mo–S bond cleavage has not been achieved in reactions of (CpMo(μ-S))$_2$S$_2$CH$_2$ with phosphines as sulfur abstraction reagents even at similar high temperatures.[18]

Table IV. Atomic Coordinates[a] (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [(CpMo)(S$_2$CH$_2$)(SCH=CHSCMe$_3$)(MoCp)]SO$_3$CF$_3$ (4)

	x/a	*y/b*	*z/c*	*U*(eq)[b]
Mo(1)	1524 (1)	534 (1)	3709 (1)	47 (1)*
Mo(2)	2099 (1)	2068 (1)	4921 (1)	55 (1)*
S(1)	175 (2)	1282 (2)	4414 (2)	56 (1)*
S(2)	1086 (3)	2214 (2)	3237 (2)	71 (1)*
S(3)	3489 (3)	1212 (2)	4347 (2)	71 (1)*
S(4)	2399 (2)	656 (2)	6014 (2)	61 (1)*
C(1)	−320 (12)	2113 (9)	3418 (8)	80 (5)*
C(2)	3264 (10)	14 (8)	4634 (8)	67 (4)*
C(3)	2442 (9)	−122 (9)	5137 (7)	62 (4)*
C(4)	3807 (11)	435 (11)	7040 (8)	83 (5)*
C(5)	4920 (12)	603 (14)	6855 (11)	121 (8)*
C(6)	3632 (14)	887 (15)	7847 (9)	133 (9)*
C(7)	3787 (18)	−693 (15)	7218 (12)	151 (11)*
C(11)	1493 (12)	−166 (9)	2309 (7)	72 (5)*
C(12)	1677 (13)	−858 (9)	2951 (9)	82 (5)*
C(13)	631 (15)	−932 (10)	3232 (9)	94 (7)*
C(14)	−139 (12)	−266 (11)	2723 (9)	84 (6)*
C(15)	368 (13)	221 (10)	2150 (8)	83 (6)*
C(21)	3238 (23)	3019 (13)	6073 (14)	133 (11)*
C(22)	3131 (22)	3472 (14)	5301 (17)	110 (11)*
C(23)	2089 (35)	3729 (14)	4866 (14)	146 (16)*
C(24)	1388 (18)	3442 (15)	5321 (20)	128 (11)*
C(25)	2069 (27)	2982 (12)	6136 (14)	124 (11)*
S(5)†	3153 (8)	8385 (5)	−544 (4)	164 (5)*
C(8)†	2595 (12)	8249 (8)	415 (8)	109 (13)*
F(1)†	1782 (14)	7568 (10)	201 (15)	322 (28)*
F(2)†	3474 (17)	7994 (15)	1174 (7)	272 (19)*
F(3)†	2141 (20)	9065 (9)	572 (13)	257 (22)*
O(1)†	3544 (12)	7471 (7)	−682 (11)	140 (10)*
O(2)†	4132 (11)	9064 (9)	−141 (11)	149 (10)*
O(3)†	2207 (12)	8806 (13)	−1250 (8)	198 (14)*
S(5′)†	2217 (21)	8380 (18)	−148 (15)	142 (7)
C(8′)†	3200 (58)	9185 (49)	710 (43)	126 (26)

[a] Atoms have occupancies of 1.0 except as marked with †: S(5), 0.70; C(8), 0.70; F(1), 0.70; F(2), 0.70; F(3), 0.70; O(1), 0.70; O(2), 0.70; O(3), 0.70; S(5′), 0.30; C(8′), 0.30. [b] For values marked with *, the equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The reaction of the neutral acetylene adduct (CpMo)$_2$(S$_2$CH$_2$)(SCHCHS) with methyl triflate (eq 8) formed an analogous product that was characterized by spectroscopic data. Two isomers of the product were



(8)

4

observed in the ^{1}H NMR spectrum. We believe the two isomers are related by inversion at the thioether sulfur atom. Models indicate that one of the coordination positions on this sulfur atom is more sterically hindered than the second, and in the *tert*-butyl analogue the more sterically hindered isomer is not observed. The two independent pathways that have led to this structural type are consistent with the proposal that a symmetrical thiolate–thioether derivative is a common intermediate.

Summary and Conclusions. Olefins undergo a relatively weak, reversible interaction with the sulfur ligands of thiolate-bridged cations of the formula [(CpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SR)]$^+$. The resulting olefin adduct contains a bridging thiolate–thioether ligand. Such adducts

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(14) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014.

(15) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

(16) The equation for the plane defined by S(1), S(2), and S(3) is $0.406x + 10.747y + 8.828z = 5.2811$, where *x*, *y*, and *z* are fractional cell coordinates. Other selected deviations from this plane are as follows: Mo(1), −1.371 Å; Mo(2), +1.371 Å; C(1), −0.006 Å; C(2), −1.044 Å; C(3), −0.778 Å; C(4), +1.555 Å.

(17) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

(18) Lopez, L. L.; Rakowski DuBois, M. Unpublished results.

Table V. Temperature Dependence of K_{eq} for Reaction 3

temp, K	K_{eq}, 10^4 M	temp, K	K_{eq}, 10^4 M
293	3.2	313	7.8
313	6.7	293	4.2
343	57		

provide a model for the proposed, but undetected, intermediates in the insertion reactions of olefins into the S–H bond of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$.

A similar alkenethiolate–thioether complex appears to be formed in the initial interaction of acetylene with the thiolate-bridged cations. However, these structures undergo a rearrangement that results in a formal insertion of the C–C double bond into a Mo–S bond of the thioether bridge. Our studies suggest that the thioether bridge in these cyclopentadienylmolybdenum systems is relatively unstable with respect to Mo–S and C–S bond cleavage. We are particularly interested in extending these studies to related complexes with cyclic thioethers as bridging ligands, since such systems may provide information on the mechanisms of ring cleavage promoted by molybdenum sulfide catalysts.

Experimental Section

Complexes 1 and 2 were prepared as described previously.[1,19] Alkenes and allene were purchased from commercial suppliers and used without purification. Acetylene was passed through a −78 °C trap two times to remove the acetone stabilizer. Methyl triflate was purchased from Aldrich. Acetonitrile and dichloromethane were distilled from CaH_2 and P_2O_5, respectively, and stored over 4-Å molecular sieves. Reactions were carried out under a nitrogen or olefin atmosphere with standard Schlenkware.

Proton NMR spectra were recorded at 200 MHz on a Chemagnetics A-200 instrument or at 300 MHz on a Varian Gemini-300 spectrometer. Carbon-13 NMR spectra were recorded at 62.9 MHz on a Bruker WM-250 instrument. Chemical shifts are reported in ppm and are referenced to $SiMe_4$ by using the solvent signal as a secondary reference. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

Thermally Induced Elimination of 2-Methylpropene from the Cation of 2, $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCMe_3)]^+$. Compound 2 (0.016 g) was dissolved in 1.0 mL of CD_3CN in an NMR tube. The solution was freeze–pump–thaw degassed, 1 atm of N_2 was transferred to the tube, and the tube was flame-sealed. NMR spectra of the solution were recorded as the temperature in the spectrometer probe was varied from 293 to 343 K and back down to 293 K. The sample was equilibrated for 5–15 min at each temperature. K_{eq}'s for the deinsertion reaction were calculated by using the known initial concentration of 2 and integration values of appropriate resonances of 2, 1, and 2-methylpropene. Data, given in Table V, suggest K_{eq} at a given temperature is bracketed by the reported values of K approached from high and low temperatures. A plot of ln K_{eq} vs $1/T$ was linear with a correlation coefficient of 0.99. The slope and intercept were used to calculate values of ΔH and ΔS.

Reaction of Ethene with $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3)_3)]CF_3SO_3$ (2). Complex 2 (20 mg, 0.030 mmol) was dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube, and the solution was degassed in three freeze–pump–thaw cycles. Ethene (4.5 equiv) was transferred to the tube, and the tube was sealed under vacuum at −196 °C. The initial ^1H NMR spectrum was collected after 5 min at ambient temperature. An 86% yield of the ethene adduct of the 2-methyl-2-propanethiolate complex $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SCH_2CH_2SC(CH_3)_3)]CF_3SO_3$ was detected. ^1H NMR (200 MHz, CD_2Cl_2): 6.01 (s, S_2CH_2); 5.90 (s, Cp); 2.92, 1.95 (AA′XX′, SCH_2CH_2S); 1.27 (s, $SC(CH_3)_3$). After 1.4 days at ambient temperature this complex had diminished to 39%, and $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2CH_3)]CF_3SO_3$[2] had formed in 53% yield. The same reaction was carried out in CD_3CN with similar results.

Determination of K_{eq} for the Reactions of Alkenes with $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3)_3)]CF_3SO_3$ (2). Complex 2 (12 mg, 0.018 mmol) was dissolved in 1.0 mL of CD_2Cl_2 in a NMR tube, and the solution was freeze–pump–thaw degassed. Ethene (ca. 3 equiv) was transferred to the tube, and the tube was sealed under vacuum at −196 °C. The solution was warmed to 20 °C for 144 min, and then a series of eight ^1H NMR spectra were recorded at 20 °C over a period of 3 h to ensure that the reaction had reached equilibrium. Concentrations of 2, the ethene adduct $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SCH_2CH_2SC(CH_3)_3)]CF_3SO_3$, and ethene were determined by using integration values and the known initial concentration of 2.[20] Values of K_{eq} varied randomly from 92 to 105 M^{-1} with an average value of 96 M^{-1}. The temperature was then changed to −10 °C and raised to 40 °C, and lower and upper limits of K_{eq} at these temperatures were determined: K_{eq} (−10 °C) $\geq$ 160 M^{-1}; K_{eq} (40 °C) $\leq$ 30 M^{-1}.[20]

Similar procedures were followed to characterize the reaction of 2 with other alkenes. ^1H NMR of the propene adduct, $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SCH(CH_3)CH_2SC(CH_3)_3)]CF_3SO_3$ (300 MHz, CD_2Cl_2): 5.99 (AB, S_2CH_2); 5.92, 5.90 (s, Cp); 3.42, 2.22, 2.10 (m, $SC\mathit{H}(Me)C\mathit{H}_2S$); 1.92 (m, $SCH(C\mathit{H}_3)CH_2S$); 1.22 (s, $SC(CH_3)_3$). K_{eq} (0 °C) = 9.6 ± 0.3 M^{-1}. The solution was warmed to 20 °C for 25 min. K_{eq} (20 °C) $\leq$ 4.1 M^{-1}.[20]

^1H NMR of the 1-butene adduct, $[(CpMo)_2(S_2CH_2)(SCH(CH_2CH_3)CH_2SC(CH_3)_3)]SO_3CF_3$ (300 MHz, CD_2Cl_2): 5.98 (br, S_2CH_2); 5.90 (Cp); 1.22 (s, $SC(CH_3)_3$); other resonances obscured by excess 1-butene. K_{eq} (0 °C) $\simeq$ 9.

A similar procedure was followed for the reaction of 2 with 2-methylpropene, except that a large excess (~80 equiv) of 2-methylpropene was used. The solution was kept in an isopropyl alcohol/liquid N_2 bath (−35 to −40 °C) for 5 days. The ^1H NMR spectrum was recorded at −40 °C, and evidence for the olefin adduct of 2 was observed in <10% yield. ^1H NMR of $[(CpMo)_2(S_2CH_2)(SC(CH_3)_2CH_2SC(CH_3)_3)]SO_3CF_3$ (300 MHz, CD_2Cl_2): 5.93 (s, Cp); 6.01 (s, S_2CH_2); 1.19 (CMe_3); other resonances obscured because of the formation of oligomers of 2-methylpropene.

Reaction of $(CpMo)_2(S_2CH_2)(SCH_2CH_2S)$ with Methyl Triflate. The above complex[1] (15 mg, 0.030 mmol) and methyl triflate (4 μL, 0.035 mmol) were dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube. The tube was sealed under vacuum at −196 °C, and the reaction was monitored by ^1H NMR spectroscopy. After 30 min at ambient temperature the reaction was complete, forming ethene and $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]CF_3SO_3$. ^1H NMR ($CDCl_3$): 6.95 (s, Cp); 4.09 (s, S_2CH_2); 1.68 (s, Me). The iodide salt of the observed cation has been reported previously,[21] and spectroscopic data are similar.

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(CH_3){=}CH_2)]SO_3CF_3$ (5). Complex 1 (28 mg, 0.046 mmol) was dissolved in 0.8 mL of CD_3CN in a NMR tube. Allene (1 equiv) was transferred to the tube, and the tube was sealed under vacuum at −196 °C. After 11 h at ambient temperature, no free allene remained and the insertion product 5 had formed quantitatively. The complex was not isolated, but NMR data were compared to those obtained previously when the complex was synthesized by another route.[22] ^1H NMR (200 MHz, CD_3CN): 7.01 (s, Cp); 4.08 (s, S_2CH_2); 5.24, 4.68 (AX, CH_2); 1.72, (s, Me).

Attempted Reactions of Ethene with Other Thiolate Cations. Complex 5 (20 mg, 0.030 mmol) was dissolved in 0.8 mL of CD_3CN in a NMR tube, and the solution was degassed. Ethene (2.5 equiv) was transferred to the tube, and the tube was sealed under vacuum at −196 °C. No reaction was observed by NMR spectrometry after 5 days at ambient temperature. A similar procedure was followed with the methanethiolate cation. No ethene adduct was detected. With the 2-propanethiolate cation, 4 equiv of ethene was added to a CD_2Cl_2 solution, and the

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(19) Birnbaum, J.; Godziela, G.; Maciejewski, M.; Tonker, T. L.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 394.

(20) In these equilibrium studies the assumption was made that the complexes were completely dissolved in solution at all temperatures. If the starting molybdenum complex were incompletely dissolved, true equilibrium constants would be somewhat higher than those calculated.

(21) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.

(22) Laurie, J. C. V.; Rakowski DuBois, M. Unpublished results.

Table VI. Crystal Data, Data Collection Conditions, and Solution and Refinement Details for 3 and 4

	complex 3	complex 4		complex 3	complex 4
Crystal Data					
empirical formula	$C_{17}H_{21}S_4Mo_2{\cdot}SO_3CF_3{\cdot}0.5CH_2Cl_2$	$C_{18}H_{21}O_3F_3S_5Mo_2$	V, Å^3	5193 (3)	2373 (2)
color; habit	burnt orange parallelepipeds	dark maroon parallelepipeds	formula units/cell, Z	8	4
			formula wt	737.0	694.5
cryst dimens, mm	0.08 × 0.15 × 0.22	0.38 × 0.40 × 0.45	density (calcd), g/cm^3	1.885	1.944
space group[a]	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	abs coeff, mm^{-1}	1.475	1.497
unit cell dimens[b]			F(000), e	2920	1376
a, Å	15.498 (6)	11.983 (7)			
b, Å	14.132 (6)	13.839 (6)			
c, Å	24.130 (10)	15.200 (6)			
β, deg	100.68 (3)	109.71 (4)			
Data Collection					
diffractometer used	Siemens P3/F	Siemens P3/F	bkgd measurements	stationary cryst and stationary counter at beginning and end of scan, each for 50% of total scan time	stationary cryst and stationary counter at beginning and end of scan, each for 50% of total scan time
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)			
temp, °C	22–24	22–24			
monochromator	highly oriented graphite cryst	highly oriented graphite cryst	std rflns	3 measd every 47 rflns	3 meas every 97 rflns
			index ranges	$-16 \le h \le 1, -15 \le k \le 0, -25 \le l \le 26$	$-14 \le h \le 14, 0 \le k \le 16, -17 \le l \le 17$
mosaic character,[c] deg	0.30	0.32	no. of rflns collected	7792	8746
2θ range, deg	3.0–45.0	3.0–50.0	no. of unique rflns[d]	6815 (R_{int} = 4.75%)	4214 (R_{int} = 7.48%)
scan type	θ–2θ	θ–2θ			
scan speed, deg/min	variable; 4.00–60.00	variable; 2.02–58.59	no. of obsd rflns	2653 ($F > 6.0\sigma(F)$)	2787 ($F > 6.0\sigma(F)$)
			abs cor	semiempirical	semiempirical
scan range, deg	from 1.00 below 2θ for $K\alpha_1$ to 1.00 above 2θ for $K\alpha_2$	from 1.10 below 2θ for $K\alpha_1$ to 1.10 above 2θ for $K\alpha_2$	min/max transmissn	0.7497/0.8018	0.6750/0.8300
Solution and Refinement					
system used[e]	Nicolet SHELXTLPLUS (MicroVAX II)	Siemens SHELXTLPLUS (MicroVAX II)	final residuals (obsd data), %	$R = 7.25, R_w = 8.30$	$R = 6.17, R_w = 8.25$
soln	direct methods	direct methods	residuals (all data), %	$R = 16.50, R_w = 11.00$	$R = 8.72, R_w = 9.70$
refinement method[f]	full-matrix least-squares	full-matrix least-squares	goodness of fit	1.48	1.48
scattering factors	neutral atoms[g]	neutral atoms[g]	largest and mean Δ/σ	0.004, 0.000	0.791, 0.037
extinction cor	not applicable	not applicable	data-to-param ratio	8.1:1	9.7:1
H atoms	not included in model[h]	riding model, fixed isotropic U	largest diff peak, e/Å^3	1.06	1.60
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.0010F^2]$	$w = 1.0/[\sigma^2(F) + 0.0010F^2]$	largest diff hole, e/Å^3	−0.77	−1.24

[a] *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, Holland, Boston, 1983; Vol. A. [b] Cell dimensions were determined by a least-squares fit of the setting angles for 25 reflections with 2θ in the range 17.3–22.9° for 3 and 25–28.7° for 4. Angle tolerances for centering, 2θ, ω, and χ: 0.02, 0.01, and 0.04. [c] Crystal mosaic character was determined from the width at half-height of ω scans. [d] $R_{int} = [\sum N(\sum w(F_{mean} - F)^2/\sum(N-1)\sum wF^2]^{1/2}$. [e] Sheldrick, G. M. SHELXTL-PLUS, A Program For Crystal Determination; Nicolet Analytical Instruments: Madison, WI, 1988; Version 3.4. [f] The quantity minimized in the full-matrix least-squares procedures is $\sum w(|F_o| - |F_c|)^2$:

$$R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_w = R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$$

[g] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. [h] Since the final difference map had no peaks that corresponded to possible hydrogen atom positions, no hydrogen atoms were included.

temperature was maintained at −10 to 0 °C for 7 weeks. No reaction was detected by NMR spectroscopy.

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SC({=}CH_2)CH_2SC(CH_3)({=}CH_2))]SO_3CF_3$ (3). Complex 5 was prepared as described with use of excess allene (ca. 20 equiv). Complex 5 reacted further with the excess allene, and after 3 days at ambient temperature the reaction was complete, forming the allene adduct $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SC({=}CH_2)CH_2SC(CH_3)({=}CH_2))]CF_3SO_3$ (3) in quantitative yield. ^1H NMR (300 MHz, CD_2Cl_2): major isomer (87%) 6.12 (s, S_2CH_2), 5.95 (s, Cp), 5.93, 5.64 (m, $SC({=}CH_2)CH_2S$), 5.59, 5.20 (m, $S({=}CH_2)Me$), 3.81 (m, $SC({=}CH_2)CH_2S$), 2.08 (m, CH_3); minor isomer (13%) 6.15 (s, S_2CH_2), 5.96 (s, Cp), 2.67 (m, $SC({=}CH_2)CH_2S$), 2.05 (m, CH_3), 6.1, 5.9, 5.7, 5.3 (m, vinyl protons). ^{13}C NMR with tentative assignments (75.4 MHz, CD_2Cl_2): 138.54, 138.50 ($SC({=}CH_2)CH_2SC(CH_3)({=}CH_2)$); 126.2 ($SC({=}CH_2)CH_2SR$); 116.5 ($SCRR'CS(CH_3)({=}CH_2)$); 94.8 (Cp); 87.4 ($SC({=}CH_2)CH_2SR$); 43.7 ($S_2CH_2$); 21.2 ($CH_3$). MS (FAB): m/e 545 (P), 505 (P − C_3H_4), 464 (P − C_3H_4 − C_3H_5). Anal. Calcd for $C_{18}H_{21}Mo_2S_5O_3F_3$: C, 31.13; H, 3.05; S, 23.08. Found: C, 30.97; H, 3.13; S, 23.10.

Reactions of Allene with Other Thiolate Cations. $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]SO_3CF_3$ (0.100 g, 0.16 mmol) was dissolved in 5 mL of CH_2Cl_2, the solution was freeze–pump–thaw degassed, and allene (~5 equiv) was condensed into the reaction mixture. The flask was sealed and kept at −50 °C for 1 week and then stirred at room temperature for 2 weeks. The solvent was removed, and the resulting orange product, $[(CpMo)_2(S_2CH_2)(SC(CH_2)CH_2SCH_3)]SO_3CF_3$, was chromatographed on an Al_2O_3 column with a 10/1 mixture of CH_3CN/EtOH. Further purification was accomplished through recrystallization from a CH_2Cl_2 solution by hexane diffusion: yield 55%. Two isomers were observed in the ^1H NMR spectrum in roughly equal concentrations. ^{1}H NMR (CD_2Cl_2): 6.21, 6.20 (2 s, S_2CH_2); 5.91, 5.90 (2 s, Cp); 5.83, 5.52 (2 s, $SCCH_2$); 3.62 (s, SCH_2); 2.74, 2.69 (2 s, SCH_3). MS (FAB): *m/e* 519 (P), 504 (P − CH_3), 479 (P − C_3H_4), 464 (P − CH_3 − C_3H_4), 432 (P − $CH_3SC_3H_4$). Anal. Calcd: C, 28.60; H, 2.85; S, 23.87. Found: C, 28.66; H, 2.96; S, 23.75.

Complex 2 (0.010 g, 0.015 mmol) was dissolved in CD_3CN, the solution was freeze–pump–thaw degassed, and 2–4 equiv of allene was distilled into the solution under vacuum. The NMR tube was sealed and kept at room temperature, and the reaction was monitored by NMR spectroscopy over a period of several days. The reaction proceeded slowly to form 3, which was identified by NMR spectroscopy.

Thermal Reactivity of [(CpMo)$_2$(μ-S_2CH_2)(μ-SC(=CH_2)(CH_2SC(CH_3)(=CH_2))]CF_3SO_3 (3). Complex 3 (20 mg, 0.029 mmol) was dissolved in 0.8 mL of CD_2Cl_2 in a NMR tube, and the tube was sealed under vacuum at −196 °C. The reaction mixture was heated at 70 °C for 12 days. [(CpMo)$_2$(μ-S_2CH_2)(μ-S)(μ-SC(CH_3)(=CH_2))]CF_3SO_3 (5) was the major product formed (ca. 50–60% yield). The remaining complex was unidentified: ^{1}H NMR (200 MHz, CD_2Cl_2) 6.00, 5.32 (2 s, Cp), other resonances obscured by those of the above cation; MS (FAB) *m/e* 545 (P). ^{1}H NMR analysis of the volatiles detected ~50–60% yield of allene, 2-chloropropene, and propene in a ca. 3/2/1 ratio, respectively. Results from GCMS analysis of the volatiles were consistent with these assignments.

Synthesis of [(CpMo)(SCH=CHSC(CH_3)$_3$)(S_2CH_2)(MoCp)]SO_3CF_3 (4). Complex 2 (63 mg, 0.089 mmol) was dissolved in 8 mL of CH_2Cl_2, the solution was freeze–pump–thaw degassed, and acetylene (~3 equiv) was transferred to the solution under vacuum. The reaction was stirred at 0 °C for 8 h and at room temperature for 4 h. The solvent was removed, and the orange-brown solid was recrystallized from CH_3CN/Et_2O to give orange crystals of 4, yield 60%. ^{1}H NMR (300 MHz, CD_2Cl_2): 5.98, 5.56 (s, Cp); 6.12, 5.16 (AX, S_2CH_2, J = 8.5 Hz); 5.39, 3.84 (AX, SCH=CHS, J = 3.9 Hz); 1.25 (s, SC(CH_3)$_3$). MS (FAB): *m/e* 547 (P), 490 (P − C(CH_3)$_3$), 444 (P − C(CH_3)$_3$ − SCH_2), 418 (P − C(CH_3)$_3$ − SCH_2 − HC=CH). Anal. Calcd for $C_{18}H_{23}Mo_2S_5O_3F_3$: C, 31.01; H, 3.33; S, 23.00. Found: C, 30.61; H, 3.45; S, 22.74.

Synthesis of [(CpMo)(S_2CH_2)(SCH=CHSCH_3)(MoCp)]SO_3CF_3. (CpMo)$_2S_2CH_2$(SCHCHS)[1] (0.050 g, 0.10 mmol) and $CH_3SO_3CF_3$ (15 μL, 0.13 mmol) were combined in 10 mL of CH_2Cl_2, and the solution was stirred at room temperature for 16 h. The color changed from green to brown. No further visible change was apparent after 5 days. The solvent was removed, and the remaining solid was recrystallized from CH_3CN/Et_2O to give a brown microcrystalline product, yield 0.050 g (76%). ^{1}H NMR (300 MHz, $CDCl_3$): isomer A 6.02, 5.42 (2 s, Cp), 5.11 (d, J = 8.3 Hz, S_2CH_2) 4.86, 4.27 (2 d, J = 4.4 Hz, CH=CH), 1.88 (s, Me); isomer B 6.00, 5.44 (2 s, Cp), 5.21 (d, J = 8.5 Hz, S_2CH_2), 5.39, 4.14 (2 d, J = 3.9 Hz, CH=CH), 1.96 (s, CH_3). The second doublet expected for the S_2CH_2 protons of each isomer is thought to be obscured by Cp resonances near 6 ppm. In CD_3CN the second doublet was observed at 6.15 and 5.93 ppm for each isomer, respectively.

Crystal Structure Determinations of 3 and 4. Compound 3 crystallized from CH_2Cl_2 at 0 °C with two independent molecules of the complex and one molecule of solvation per asymmetric unit. The positions of the molybdenum–sulfur cores were located by using direct methods. Other atoms were located with use of structure factor and Fourier calculations. The disordered CH_2Cl_2 and $CF_3SO_3^-$ moieties were refined with bond distance constraints.[23] The cyclopentadienyl rings were refined as idealized pentagons with C–C distances of 1.42 Å. Since no difference peaks corresponding to possible hydrogen atom positions were observed in difference maps, no hydrogens were included in the final model. For the final cycles of full-matrix, least-squares calculations, all molybdenum and sulfur atoms and the chlorines of the disordered CH_2Cl_2 were refined with anisotropic thermal parameters. All other atoms were refined isotropically. The largest shift/error on the final refinement was for the x/a positional coordinate of the methylene carbon in the disordered CH_2Cl_2. The largest difference peak was 1.1 Å for Mo(1′) and 1.5 Å for S(4′). Details of the crystal data, experimental conditions, and a summary of solution and refinement information are given in Table VI, which also has the same information for compound 4.

Compound 4 crystallized from CH_3CN/Et_2O at room temperature. The structure was solved as above. The triflate anion exhibited serious disorder and was refined with distance constraints as described above. Electron density difference maps revealed the positions of some of the hydrogen atoms. All hydrogen atoms were included in idealized geometries riding on the atom to which they were attached with isotropic displacement parameters set equal to 1.2 times those of the latter. For the final cycles of full-matrix, least-squares refinement, all non-hydrogen atoms except for the lower occupancy disordered triflate atoms were refined with anisotropic displacement parameters. The largest shift/error in this final refinement was for the isotropic displacement parameter for the lower occupancy disordered triflate carbon. The highest residual electron density peak was in the region of the disordered triflate.

Acknowledgment. This work was supported by grants from the National Science Foundation and from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

Supplementary Material Available: Complete tables of bond distances and angles for 3 and 4 (9 pages); listings of observed and calculated structure factors for 3 and 4 (36 pages). Ordering information is given on any current masthead page.

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(23) The bond distance constraints, given as distances in angstroms (allowed esd's), are as follows: CH_2Cl_2, C–Cl = 1.77 (1), Cl···Cl = 2.93 (1); $CF_3SO_3^-$, S–C = 1.81 (1), S–O = 1.41 (1), C–F = 1.32 (1), O···O = 2.38 (1), F···F = 2.14 (1), C···O = 2.55 (1), S···F = 2.59 (1).