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Studies of the Protonation and Oxidation of Sulfido Ligands in Dinuclear Molybdenum Complexes

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Synthetic procedures are described for the preparation of cationic derivatives of the formula $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$, where $Cp' = C_5H_5$ (a), C_5H_4Me (b), or C_5Me_5 (c). Spectroscopic data for the protonated complexes are reported, and pK_a values for the μ-SH ligands have been determined in acetonitrile. Oxidation of the protonated complexes results in the formation of a dicationic derivative of the formula $[(Cp'Mo(\mu\text{-}S))_2S_2CH_2]_2^{2+}$, 2. Both the triflate and tetrafluoroborate salts of **2b** have been characterized by X-ray diffraction studies. The triflate salt crystallized in space group $C2/c$ with $a = 35.498$ (10) Å, $b = 14.823$ (7) Å, $c = 17.246$ (5) Å, and $\beta = 115.51$ (2)°. The tetrafluoroborate salt crystallized in space group $P2_1/n$ with $a = 11.476$ (5) Å, $b = 13.843$ (6) Å, $c = 12.577$ (4) Å, and $\beta = 112.97$ (3)°. The structures confirm that two dinuclear units have interacted through formation of a S–S bond between μ-sulfido ligands. The reaction of hydrogen (1 atm) with 2 at room temperature resulted in the hydrogenolysis of the intermolecular S–S bond and the formation of 1. Other reactions of 2 have been characterized that indicate that 2 functions as an effective hydrogen atom acceptor.

Introduction

The reactivity of molybdenum complexes with hydrosulfido ligands has been investigated because of their potential relevance to the reaction chemistry of the hydrotreating catalysts. Surface S–H sites have been proposed to be involved in hydrogenation and hydrogenolysis reactions;[1,2] postulates have also appeared on the involvement of these sites in reactions promoted by Brønsted acids.[3,4] A fundamental study of factors that influence the acidity of SH ligands in discrete molybdenum complexes should help in understanding the potential reactivity of SH sites on surface catalysts. In previous studies, we have investigated the acidity and reactivity of bridging SH ligands in neutral complexes of Mo(IV) and Mo(III).[5,6] In this report we describe the syntheses of a series of cationic Mo(IV) derivatives with μ-SH ligands, their spectroscopic characterizations, and a determination of their pK_a values in acetonitrile. Our studies indicate that the cations are quite strongly acidic relative to neutral thiols and metallothiols, and this characteristic appears to play a major role in the novel chemistry observed for these derivatives.[7,8] The protonated cations are readily oxidized to form tetranuclear derivatives. The reactivities of the oxidized products have been compared to those of the S–H complexes. An unusual characteristic of the tetranuclear derivatives is their ability to activate molecular hydrogen.

Results and Discussion

Syntheses of Protonated Cations. The addition of anhydrous triflic or tetrafluoroboric acid (1–2 equiv) to the molybdenum(IV) complex $(CpMo(\mu\text{-}S))_2S_2CH_2$ in CH_2Cl_2 or CH_3CN caused an immediate color change from blue to red. Addition of anhydrous ether resulted in the precipitation of the cationic complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]X$, **1a**, as a microcrystalline, air-sensitive solid. A similar procedure was followed to produce the analogous protonated cation with methylcyclopentadienyl ligands, **1b**. The synthesis of the protonated pentamethylcyclopentadienyl derivative, **1c**, by this route resulted in a mixture of protonated and oxidized species that was difficult to separate. An alternate route for the preparation of **1c** in pure form is discussed in a following section.

The protonated cation **1a** could also be synthesized from the addition of 2 equiv of gaseous HBr, but the bromide salt was only sparingly soluble in organic solvents.[9] NMR data suggested that a large excess (ca. 10 equiv) of a weaker anhydrous acid, such as trifluoroacetic acid, was necessary to complete the formation of the protonated cation **1b** in chloroform solution.[10] The synthesis of a coordinated SH ligand by the protonation of anionic metal–sulfido complexes has been reported for several systems,[11-14] but protonation of the sulfido ligand in a neutral complex appears to be a rather unusual reaction that is limited to relatively basic systems.[15,16]

The protonated derivatives have been characterized by spectroscopic methods and by their reaction chemistry. The ^1H NMR spectrum of **1a** and **1b** each have a Cp resonance near 7.0 ppm and a S_2CH_2 resonance near 4.0 ppm. These chemical shifts occur downfield relative to those of the neutral unprotonated derivative (6.5 and 2.7 ppm).[17] Similarly the chemical shift of the Me_5C_5 ligand

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Table I. Electronic Absorption Data for Protonated, Deprotonated, and Oxidized Complexes in CH_3CN

complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$[(CpMo)_2S_2CH_2(\mu\text{-}S)(\mu\text{-}SH)]^+$, **1a**	464	870
	521	920
	840	1700
$[(MeCpMo)_2S_2CH_2(\mu\text{-}S)(\mu\text{-}SH)]^+$, **1b**	479	760
	532	890
	843	2320
$[(Me_5CpMo)_2S_2CH_2(\mu\text{-}S)(\mu\text{-}SH)]^+$ **1c**	532	860
	870	1330
$(CpMo(\mu\text{-}S))_2S_2CH_2$	588	2100
	722	2200
$(MeCpMo(\mu\text{-}S))_2S_2CH_2$	590	2000
	730	2300
$(Me_5CpMo(\mu\text{-}S))_2S_2CH_2$	390 (s)	
	423 (s)	
	580	2050
	754	2860
$[(CpMo(\mu\text{-}S))_2S_2CH_2]_2^{2+}$, **2a**	486	2510
	860	2660
$[(MeCpMo(\mu\text{-}S))S_2CH_2]_2^{2+}$, **2b**	496	2300
	865	2900
$[(Me_5CpMo(\mu\text{-}S))_2S_2CH_2]_2^{2+}$, **2c**	544	1640
	885	2700

in the protonated complex at 2.35 ppm is downfield relative to that of the neutral derivative at 2.28 ppm. In the presence of excess water the complexes are completely deprotonated. In the presence of a weak base or a trace amount of water, a rapid equilibrium is observed between the protonated and deprotonated complexes, and average chemical shifts are observed at positions between the extremes noted above. The SH proton in these complexes has not been observed in the NMR spectrum at room temperature. Rapid exchange between two adjacent sulfido ligands or with a trace amount of water in the solvent may broaden this resonance. In the NMR spectrum of **1b** at −90 °C in dry CD_2Cl_2, a broad resonance was observed at −0.72 ppm, which was assigned to the SH proton. In the infrared spectrum an absorption at 2436 cm^{-1} is consistent with the formulation of a sulfur protonated cation. In the cyclic voltammogram of **1a** an irreversible reduction was observed at −0.65 V vs the ferrocene couple. Additional quasireversible waves were also observed at −0.19 V (an oxidation) and at −1.80 V (a reduction). The latter waves were assigned to the deprotonated complex $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ (vide infra), and their amplitude was coupled to the initial irreversible reduction of **1a**, suggesting that $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ is rapidly produced upon the reduction of **1a**.

The visible spectra of the triflate salts of the protonated cations **1a–c** have been recorded in dry acetonitrile, and the data are summarized in Table I. The maxima near 500 and 840 nm are characteristic of sulfido-substituted cations of this type.[18] Each of the protonated cations was found to obey Beer's law over a concentration range 1×10^{-4}–1×10^{-2} M in acetonitrile. The visible spectral data for the deprotonated derivatives are also included in the table. Beer's law behavior was verified for the deprotonated derivatives over a similar concentration range in dry acetonitrile.

The reaction chemistry of the cations has been studied. Products resulting from S–H addition of alkenes and alkynes have been characterized. The results of our investigations of reactions of **1a** with alkenes are reported in detail in a separate publication.[19] The nature of the insertion products provides additional evidence for the formulation of the protonated cations.

Table II. pK_a Values for Triflate Salts of Protonated Complexes in CH_3CN

$[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$	8.3 ± 1
$[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$	8.4 ± 1
$[(Me_5CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]^+$	10.3 ± 2

Determination of pK_a Values for 1. The reaction of **1a** with 2,4-dichloroaniline was monitored by visible spectroscopy; relative amounts of **1a** and of its deprotonated form were determined by using known extinction coefficients for each complex at wavelengths of 500 and 722 nm. The equilibrium constant was determined for this acid–base reaction, and this value and the known pK_a of dichloroanilinium ion in acetonitrile[20] were then used to calculate the pK_a values for the protonated cation. The procedure has been described in detail by Norton and co-workers, who have determined pK_a values for a series of transition-metal hydride complexes in acetonitrile solution.[20–22] Similar procedures were followed for complexes **1b** and **1c**. The calculated values are shown in Table II.

The pK_a values for the Cp and MeCp derivatives are similar, but a significant increase in pK_a is observed for the Me_5Cp complex. This is consistent with the expectation that a more electron donating ligand increases the delocalized electron density over the Mo_2S_4 core of the molecule and therefore decreases the acidity of the SH ligand. The difference in metal hydride acidity in $CpMo(CO)_3H$ and $Me_5CpMo(CO)_3H$ was found by Norton and co-workers to be ca. 3.2 pK_a units.[20] The effect of the more electron donating ligand on the pK_a of the bridging SH ligands is somewhat smaller (ca. 2 pK_a units) as might be expected for a proton located on an adjacent ligand rather than on the metal ion.

The acidities of **1a** and **1b** in acetonitrile are quite similar to that of HCl in this solvent.[20] The data are consistent with our observation that the protonated molybdenum dimers appear to behave as strong acids in mixed aqueous solvents. The pK_a values for the bridging SH ligands in structurally related neutral molybdenum complexes have not been determined quantitatively. NMR studies of the addition of bases to the Mo(IV) complex $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ in nonaqueous solvents indicated that proton exchange occurred in the presence of 4 equiv of triethylamine and complete deprotonation occurred with methoxide ion.[5] The aqueous pK_a of the SH ligand was therefore estimated to be in the range 10–18. The reaction of the Mo(III) complex $(MeCpMo)_2S_2CH_2(\mu\text{-}SMe)(\mu\text{-}SH)$ with a series of bases has been studied by monitoring a reaction of the deprotonated analogue with acetylene. The latter reaction, which was characteristic of the anion only, was not observed in the presence of excess triethylamine or proton sponge (1,8-bis(dimethylamino)naphthalene) but was observed in the presence of an equivalent of methoxide.[6] The positive charge on the dinuclear complexes reported in this study appears to dramatically alter the acidity of the SH ligand in the dimers.

Synthesis and Characterization of Oxidized Cations. When the protonated cation **1a** was exposed to air, an oxidation occurred to form the cationic derivative with the empirical formula $[(CpMo(\mu S))_2S_2CH_2]^+$, **2a**. Alternatively, the cation could be synthesized in ca. 90% yield

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Table III. Selected Bond Distances (Å) for Salts of 2b

	triflate salt			BF_4 salt
Mo–Mo	2.608 (1) (1–2)	2.615 (3) (3–4)	2.613 (3) (3′–4′)	2.624 (4)
Mo–S	2.463 (3) (1–1)	2.434 (6) (3–7)	2.419 (7) (3′–7′)	2.467 (6) (1–1)
Mo–S	2.463 (3) (2–1)	2.450 (6) (4–7)	2.439 (7) (4′–7′)	2.471 (6) (2–1)
Mo–S	2.458 (3) (1–2)	2.439 (6) (3–8)	2.455 (6) (3′–8′)	2.435 (7) (1–2)
Mo–S	2.446 (3) (2–2)	2.452 (6) (4–8)	2.445 (5) (4′–8′)	2.440 (8) (2–2)
Mo–S	2.305 (3) (1–3)	2.292 (6) (3–6)	2.300 (6) (3′–6′)	2.301 (7) (1–3)
Mo–S	2.310 (3) (2–3)	2.288 (7) (4–6)	2.305 (8) (4′–6′)	2.299 (7) (2–3)
Mo–S	2.449 (2) (1–4)	2.446 (3) (3–5)	2.531 (3) (3′–5)	2.487 (6) (1–4)
Mo–S	2.472 (2) (2–4)	2.436 (4) (4–5)	2.482 (3) (4′–5)	2.480 (6) (2–4)
S–S		2.147 (4)		2.169 (9) ($4–4_A$)
S–C	1.811 (12) (1–1)	1.706 (33) (7–2)	1.805 (25) (7′–2′)	1.859 (21) (1–1)
S–C	1.801 (14) (2–1)	1.867 (34) (8–2)	1.862 (24) (8′–2′)	1.769 (23) (2–1)

by the reaction of $(CpMo(\mu S))_2S_2CH_2$ with 1 equiv of an oxidizing agent such as $NOBF_4$ or Ph_3CBF_4. Similar oxidations were observed for **1b** and **1c**.

In our initial work with the protonated complexes **1a** and **1b**, we did not recognize their sensitivity to oxidation. The oxidized complexes were red-purple microcrystalline products that were similar in appearance to the protonated derivatives. More surprisingly, the oxidized derivatives did not display the paramagnetic characteristics expected for a mixed-valence Mo(IV)/Mo(V) complex. The NMR spectra of the oxidized products at room temperature were very similar to that of 1. For example, in the spectrum of **2a**, sharp singlets were observed at 6.98 and 4.10 ppm for the Cp and methanedithiolate ligands, respectively. The ^{13}C NMR spectra of **1b** and **2b** were also similar (see Experimental Section). The pentamethylcyclopentadienyl derivatives **1c** and **2c** were also difficult to distinguish in our initial studies because we were unable to separate the mixture of these two compounds that formed in the reaction with protic acid. The reaction of $(Me_5CpMo(\mu\text{-}S))_2S_2CH_2$ with $NOBF_4$ gave a pure sample of **2c**, which was shown to be diamagnetic by solution magnetic susceptibility studies.[23] An intermolecular interaction between two dimers was proposed to account for the diamagnetic nature of these oxidation products, and tetranuclear products of the formula $[(Cp'Mo(\mu\text{-}S))_2(S_2CH_2)]_2^{2+}$ were therefore postulated.

The elemental analyses and, in most cases, the mass spectra for the oxidized cations were not significantly different from those of the analogous protonated complexes. The FAB mass spectrum of the triflate salt of **2c**, however, did provide evidence for a tetrameric formulation. An envelope of peaks centered at m/z 1360 was consistent with the mass of a tetranuclear dication plus one triflate anion. We have occasionally observed the incorporation of anions in the FAB mass spectra of other cationic derivatives. The visible spectra of 1 and 2 showed distinct differences, which are summarized in Table I and illustrated in Figure 1.

The cyclic voltammograms of the oxidized product **2a** and of the neutral complex $(CpMo(\mu\text{-}S))_2S_2CH_2$ each showed, at a scan rate of 400 mV/s, a near reversible wave at −0.19 V vs the ferrocene couple. **2a** was initially reduced at this potential, while $(CpMo(\mu\text{-}S))_2S_2CH_2$ was oxidized. Both complexes also underwent a quasireversible reduction at −1.80 V. The data suggest that the dimer–tetramer interconversion may be very rapid, and a more detailed electrochemical study of these systems would be of interest.

X-ray Diffraction Studies of Salts of $[(MeCpMo(\mu\text{-}S))_2S_2CH_2]_2^{2+}$. Single crystals of the triflate salt of **2b** were obtained by slow diffusion of ether into an acetonitrile solution. The complex crystallized in space group *C*2/*c*.

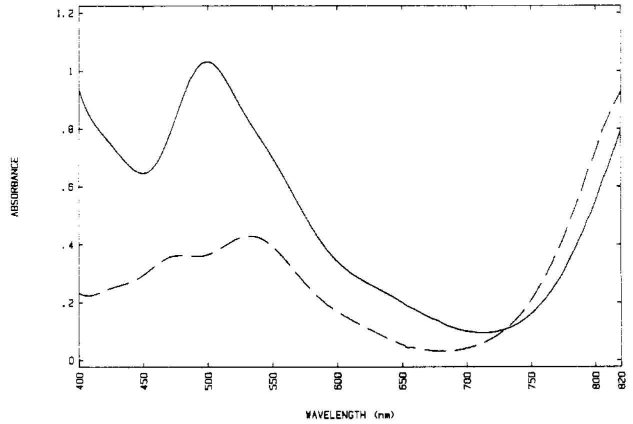

Figure 1. Portion of the visible spectrum of **1b** (- - -) and of **2b** (—) in CH_3CN. Both solutions are (4–5) × 10^{-4} M.

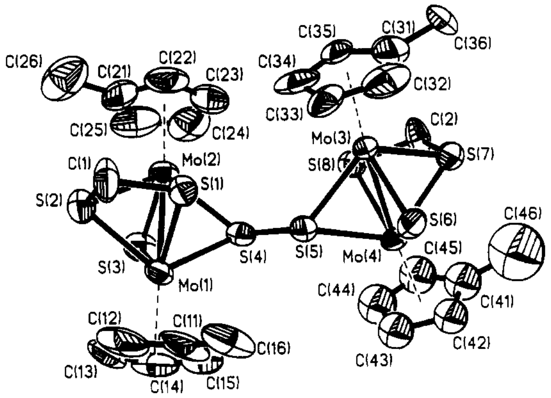

Figure 2. Perspective drawing and numbering scheme for the cation of $[(MeCpMo(\mu\text{-}S))_2S_2CH_2]_2(SO_3CF_3)_2$. Only one of the two disordered positions of the Mo_3, Mo_4 dinuclear unit is shown. Thermal ellipsoids are shown at the 50% probability level.

Table IV. Selected Bond Angles (deg) for the Triflate Salt of 2b

Mo(2)–Mo(1)–S(1)	58.0 (1)	Mo(2)–Mo(1)–S(2)	57.7 (1)
Mo(2)–Mo(1)–S(3)	55.7 (1)	Mo(2)–Mo(1)–S(4)	58.4 (1)
S(1)–Mo(1)–S(3)	113.7 (1)	S(1)–Mo(1)–S(2)	67.1 (1)
S(2)–Mo(1)–S(4)	115.7 (1)	S(1)–Mo(1)–S(4)	75.1 (1)
S(3)–Mo(1)–S(4)	73.7 (1)	S(2)–Mo(1)–S(3)	76.6 (1)
Mo(1)–Mo(2)–S(2)	58.1 (1)	Mo(1)–Mo(2)–S(1)	58.0 (1)
Mo(1)–Mo(2)–S(4)	57.6 (1)	Mo(1)–Mo(2)–S(3)	55.5 (1)
S(1)–Mo(2)–S(2)	67.2 (1)	S(1)–Mo(2)–S(3)	113.5 (1)
S(1)–Mo(2)–S(4)	74.7 (1)	S(2)–Mo(2)–S(4)	115.4 (1)
S(2)–Mo(2)–S(3)	76.8 (1)	S(3)–Mo(2)–S(4)	73.2 (1)
Mo(1)–S(1)–Mo(2)	63.9 (1)	Mo(1)–S(2)–Mo(2)	64.2 (1)
Mo(2)–S(1)–C(1)	90.2 (4)	Mo(1)–S(1)–C(1)	90.0 (4)
Mo(1)–S(2)–C(1)	90.4 (4)	Mo(2)–S(2)–C(1)	90.9 (4)
Mo(1)–S(3)–Mo(2)	68.8 (1)	Mo(1)–S(4)–Mo(2)	64.0 (1)
Mo(1)–S(4)–S(5)	106.4 (1)	Mo(2)–S(4)–S(5)	118.5 (1)
S(1)–C(1)–S(2)	97.6 (5)		

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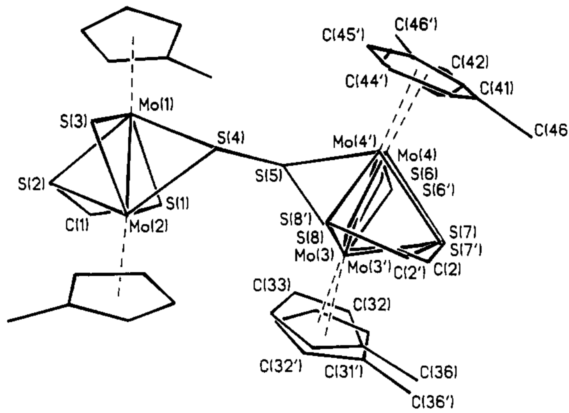

Figure 3. Line drawing of the structure of the cation of $[(MeCpMo(\mu\text{-}S))_2S_2CH_2]_2(SO_3CF_3)_2$ illustrating the nature of the disorder observed for the Mo_3, Mo_4 dinuclear unit.

The structure determined from data collected at −40 °C showed that the dication consists of two $(CpMo(\mu\text{-}S))_2S_2CH_2$ molecules linked through a single bond between μ-sulfido ligands. A perspective drawing and numbering scheme for one orientation (see below) of the dication are shown in Figure 2. Selected bond distances and angles for the cations are presented in Tables III and IV. The structure involved serious disorder problems. One of the two dinuclear units in the cation was disordered as a result of a rotation of the dinuclear unit about the sulfido bridge (S(5)) linked to the second dimer. For the sake of clarity, only one orientation of the disordered dinuclear unit is included in the ORTEP plot of Figure 2. The nature of the disorder is illustrated in the line plot of Figure 3. The disorder was modeled by including the dinuclear unit in two positions, each with 50% occupancy, with displacements in the range 0.7–1.2 Å for each of the rotated atoms. In addition to this problem, the two triflate anions were significantly disordered.

Because refinement of the data was limited by these problems, we attempted to grow single crystals of the BF_4 salt of **2b**. Several batches of crystals were obtained by slow evaporation of acetonitrile solutions and by diffusion of an ether into acetonitrile solutions. In each case similar crystals were obtained; none of these crystals was of sufficient quality to justify extensive data collection. However, a short data set was collected on a crystal isolated from diethyl ether/acetonitrile. The BF_4 salt crystallized in the space group $P2_1/n$. The structure obtained was very similar to that determined for the triflate salt. Disorder of a dinuclear $(CpMo(\mu\text{-}S))_2S_2CH_2$ unit was not observed in the structure of the BF_4 salt. Selected bond distances for this structure are compared with those of the triflate salt in Table III. Other structural data for this salt are included in the supplementary material (see the paragraph at the end of the paper).

Despite the difficulties in the structure refinements, the data answered the major questions that prompted this X-ray diffraction study. The structures established that the oxidized dinuclear cation undergoes an intermolecular interaction with a second cation through formation of a S–S bond between sulfido ligands. The formation of S–S bonds that link two dinuclear metallosulfur units has been reported previously in the oxidation of $[(CO)_6Fe_2(\mu\text{-}S)(\mu\text{-}SR)]^-$ [24] and in the spontaneous dehydrogenation and dimerization of $[(CO)_6Fe_2(\mu\text{-}S)(\mu\text{-}SH)]^-$.[25] The S_4–S_5 distance (2.147 (4) Å) in the cation of **2b** is longer than that observed for a single S–S bond in elemental sulfur (2.037 (5) Å)[26] and longer than that reported for an intradimer S–S bond in a related dinuclear molybdenum complex (2.095 (7) Å).[27] The disulfide distance in **2b** is intermediate to the values found for the disulfide bonds in the two tetranuclear iron systems: 2.108 (3) Å for $[(CO)_6Fe(\mu\text{-}SR)(\mu\text{-}S)]_2$[24] and 2.164 (2) Å for $[(CO)_6Fe_2S_2]_2^{2-}$.[25] The relatively long bond in the latter system was attributed to a delocalized bonding scheme that involved all four sulfido atoms. In the cyclopentadienylmolybdenum system, the distance between μ-sulfido ligands S_4 and S_3 within a single dinuclear unit, 2.85 Å, is also consistent with a partial bonding interaction between these atoms. Similar distances have been observed in dinuclear molybdenum complexes.[28]

The relatively long distance for S_4–S_5 in **2b** may be attributable, at least in part, to the steric interactions involved in tetramer formation. For the triflate salt, the dihedral angles between the vectors defined by Mo_1–Mo_2 and Mo_3–Mo_4 or M_3'–Mo_4' were 54° and 50°, respectively; this represents the twist angle between the two dimers. For the BF_4 salt the twist angle was 180°. The MeCp ligands were distorted from the parallel orientation usually found in the dinuclear complexes, and Mo–Mo–$Cp_{centroid}$ angles in the range 172–177° were observed in the structures of the dication. The internuclear distances and angles within the Mo_2S_4 cores of **2b** in both structures were similar to those observed in previous structures of dinuclear derivatives.[28]

Comparisons of Reactions of the Oxidized Cations, 2, with Those of the Protonated Cations, 1. Since the physical properties and NMR data for **1** and **2** were very similar, we found that an easy chemical test for distinguishing between the protonated and oxidized cations was useful. One such test was based on their reactivity with 2,4-dichloroaniline. Unlike the solutions of the protonated complexes, which rapidly changed to the deep blue color of $(Cp'Mo(\mu\text{-}S))_2S_2CH_2$ upon addition of this base, the oxidized cations did not react. However, some stronger bases, e.g., ammonium hydroxide, did react with the oxidized cations to form the corresponding dinuclear neutral derivatives. When the reaction of **2a** with excess NH_4OH was monitored by visible spectroscopy, the initial yield of $(CpMo(\mu\text{-}S))_2S_2CH_2$ was consistently in the range 45–50%. This yield suggests that the base (OH^- shows greater thiophilicity than amines)[29] heterolytically cleaves the S–S bond of **2** (eq 1). Heterolytic cleavage of organic disulfides by base is a known reaction.[29] The potential cationic product in this reaction, which had an absorbance near 500 nm, underwent further decomposition and was not characterized.

The reactions of olefins with **1a** and **2a** have also been compared and found to very different. Ethylene inserted into the SH bond of **1a** to form the diamagnetic purple cation $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC_2H_5)]^+$. When **2a** was stirred in the presence of excess ethylene, rapid formation of an olive-green precipitate was observed that was characterized as $[(CpMo)_2(S_2CH_2)(SC_2H_4S)]^+$. A strong EPR

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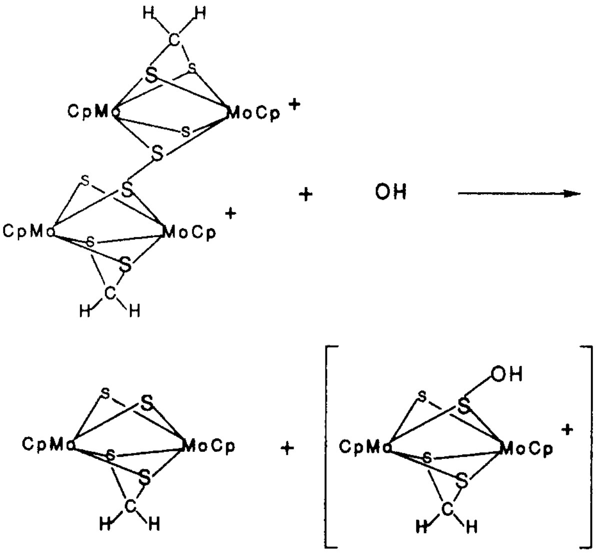
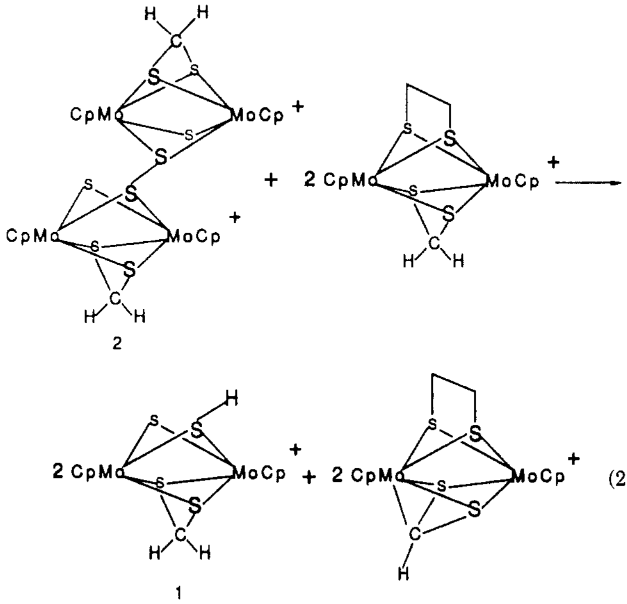


(1)

signal was observed for the product which indicated that the S–S bond between dimers was broken during the course of the adduct formation with ethylene. Since NMR data could not be obtained, the identity of $[(CpMo)_2(S_2CH_2)(SC_2H_4S)]^+$ was established by a comparison of its cyclic voltammogram with that of the known neutral derivative $(CpMo)_2(S_2CH_2)(SC_2H_4S)$.[17] A quasireversible oxidation at +0.48 V vs the ferrocene couple was observed for both compounds. The cation was reduced quasireversibly at −0.30 V, while the corresponding neutral complex underwent an oxidation at this potential. The data support our proposal that the two complexes are structural analogues related by a single-electron transfer. Mass spectral data and elemental analyses further supported the formulation of the cation.

Hydrogen-Transfer Reactions. As we mentioned above, the NMR spectra of the protonated and oxidized cations were very similar,[30] but pure samples of each cation could be distinguished by the chemical shift of the methanedithiolate ligand. However, when an equimolar mixture of **1a** and **2a** in dry CD_3CN was characterized by 200-MHz NMR, only a single sharp set of resonances was observed. The resonance of the S_2CH_2 ligand at 4.05 ppm was midway between the expected chemical shifts of this ligand in **1a** (4.00 ppm) and **2a** (4.10 ppm). The data indicate that rapid interconversion between **1a** and **2a** is occurring. Although the details of this interconversion are not understood, rapid hydrogen atom transfer appears to be involved. We have, therefore, briefly studied the reactivity of **2a** as a hydrogen atom acceptor with other potential donors.

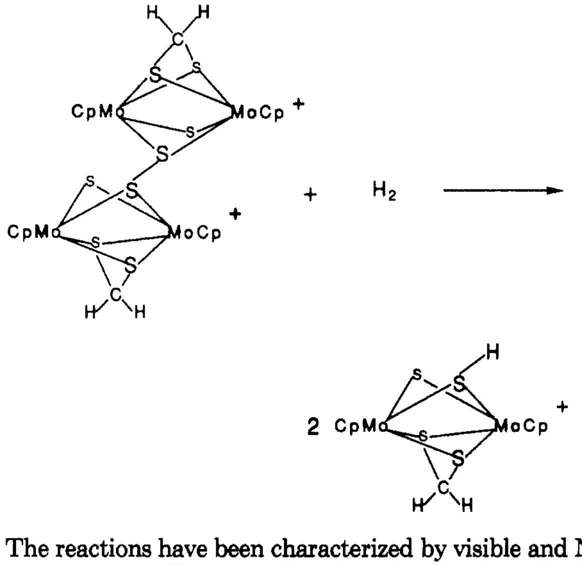
Complex **2a** reacted rapidly and quantitatively with thiophenol at room temperature to form **1a** and phenyl disulfide. The reaction of **2a** with 1,4-cyclohexadiene at room temperature also resulted in hydrogen atom abstraction to form **1a** and benzene, but the yields of these products were low (ca. 5%). The major reaction pathway appeared to involve initial interaction of a double bond of cyclohexadiene with **2a**, as described above for ethylene. Further reactions of this cyclohexadienyl adduct led to tetranuclear products. A more detailed description of the reaction chemistry of this system will be provided elsewhere.[31] A final and unexpected example of hydrogen atom transfer was observed in the reaction of **2a** with an isolated sample of the cationic ethylene adduct (eq 2).



(2)

The isolation and characterization of the ethanedithiolate bridged cation with the molybdenum carbon bond has been reported previously,[19] and the formation of this product in eq 2 was confirmed by comparison of NMR data with those of an authentic sample.

Reaction of 2 with Hydrogen. An interesting characteristic of the tetranuclear derivatives is their ability to activate molecular hydrogen. When a dichloromethane solution of **2a**, **b**, or **c** is placed under 1–2 atm of hydrogen at room temperature, the complex is converted cleanly to the corresponding protonated derivative **1a**, **b**, or **c** (eq 3).



(3)

The reactions have been characterized by visible and NMR spectroscopy. For example, when the reaction of a dilute dichloromethane solution (10^{-3}–10^{-4} M) of **2b** with 1 atm of H_2 in a sealed cell was monitored by visible spectroscopy, complete conversion to **1b** was observed within 2 h. Further evidence for the reduction of the tetranuclear complexes by hydrogen was obtained from reactivity studies. When the oxidized cations were placed under a hydrogen atmosphere, they were found to undergo reactions identical with those of 1, e.g. reactions 4 and 5.[7,8]

Reaction 3 represents a useful synthetic procedure for the preparation of the protonated derivatives **1a–c** in pure form. In particular, in the synthesis of **1c** by protonation

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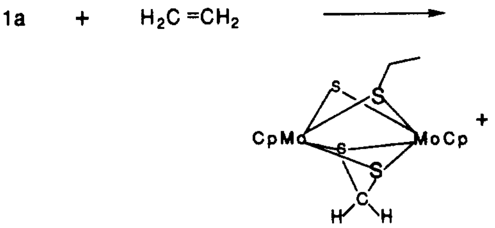
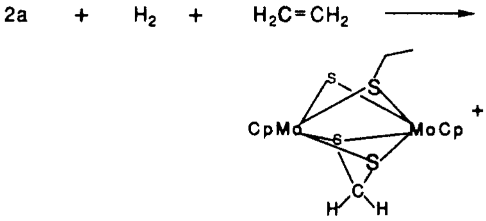
(30) Unlike the spectra of **2a,b**, the spectrum of **2c** shows evidence for two inequivalent Me_5Cp ligands and for inequivalent protons in the S_2CH_2 ligands (see Experimental Section). The spectrum suggests that there is restricted rotation about the S–S bond in **2c**.

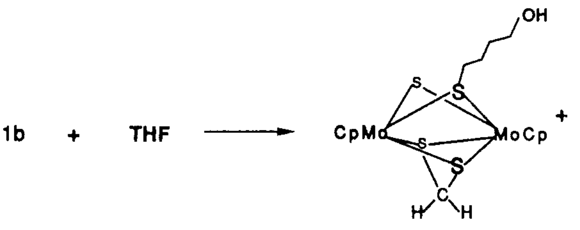
(31) Birnbaum, J.; Rakowski DuBois, M. Unpublished data.



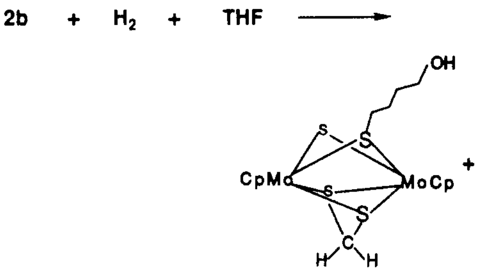
(4a)



(4b)



(5a)



(5b)

of the neutral derivative, we were unable to avoid a competing oxidation reaction, and mixtures of **1c** and **2c** were always produced. Under hydrogen this mixture is converted to **1c** in >95% purity. Although the tetranuclear complexes are analogues of organic disulfides in many respects, the reactivity of the S–S bond toward molecular hydrogen is a characteristic that appears to be unique to this and related cyclopentadienylmolybdenum structures.[5,27,32]

Experimental Section

Materials. The syntheses of $(CpMo(\mu\text{-}S))_2S_2CH_2$, $(MeCpMo(\mu\text{-}S))_2S_2CH_2$, and $[Me_5C_5Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ have been reported previously.[17,5] 2,4-Dichloroaniline, purchased from Aldrich, was recrystallized from either diethyl ether or absolute alcohol and dried under vacuum at 40 °C for 6 h. Triflic acid and $NOBF_4$ were purchased from Aldrich and used without further purification. $n\text{-}Bu_4NBF_4$ was purchased from Strem Chemicals and dried by heating to 150 °C under vacuum for 24 h. Acetonitrile was distilled from CaH_2, collected over molecular sieves, redistilled from anhydrous $CuSO_4$, and collected over molecular sieves, or was distilled from P_2O_5. Dichloromethane was distilled from P_2O_5, collected over molecular sieves, and deoxygenated by bubbling with N_2 gas. In some cases diethyl ether was distilled from sodium/benzophenone. All syntheses, reactions and spectroscopic measurements were carried out under inert conditions, either in a glovebox or by employing standard Schlenkware.

Instrumentation. Electronic spectra were recorded on a HP 8451 A diode array spectrometer or a Perkin-Elmer Lambda 9 spectrophotometer. Proton NMR spectra were recorded on a Chemagnetics A 200-MHz instrument or a Bruker WM-250 or a Varian Gemini-300 spectrometer. Carbon-13 NMR spectra were recorded on the Bruker WM-250 spectrometer. Signal positions (ppm) were referenced to $SiMe_4$ by using the solvent signal as a secondary reference. The EPR spectrum was recorded on a Varian E-109 X-band spectrometer at room temperature. The g value was referenced to solid DPPH (g = 2.0036). Mass spectra (m/z) were obtained on a *VG* Analytical 7070 EQ-HF mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Elemental analyses were performed by Spang Laboratories.

All electrochemical measurements were carried out in a N_2-purge glovebox using 0.1 M $n\text{-}Bu_4NBF_4$ in CH_3CN. Cyclic voltammograms were obtained by using a BAS 100 electrochemical analyzer with a Pt wire or Pt disk working electrode, Pt wire mesh auxiliary electrode, and Ag wire reference electrode. Potentials are reported vs the ferrocene couple (0.42 V vs SCE), which was used as an internal standard. Many of the potentials were determined by using the secondary reference $[MeCpMo(\mu\text{-}S)(\mu\text{-}SMe)]_2$,[5a] which has a reversible reduction at −1.97 V vs ferrocene. Scan rates were 400 mV/s.

Synthesis of $(Me_5CpMo(\mu\text{-}S))_2S_2CH_2$.[33] $[Me_5CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (2.5 g, 4.2 mmol) was dissolved in THF (125 mL). CH_2Br_2 (0.6 mL, 8.4 mmol) and a freshly prepared solution of $NaOCH_3$ (8.4 mmol) in methanol (5 mL) were added. The resulting blue solution was stirred at room temperature for 40 min. The solvent was evaporated, and the crude blue product was chromatographed on an alumina column with $CHCl_3$. The second, blue band was collected, and the solvent was evaporated under reduced pressure; yield 1.9 g, 77%; ^1H NMR ($CDCl_3$) 2.28 (s, Me), 2.44 (s, S_2CH_2); MS (FAB), 604 (P), 559 (P − SCH_2). Anal. Calcd for $C_{21}H_{32}Mo_2S_4$: C, 41.72; H, 5.33; S, 21.21. Found: C, 41.80; H, 5.26; S, 21.02.

Synthesis of $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)](SO_3CF_3)$, Cp′ = C_5H_5 or $C_5H_4CH_3$ (1a or 1b). Under a nitrogen atmosphere, $(Cp'Mo(\mu\text{-}S))_2S_2CH_2$ (1.06 g, 2.15 mmol) was dissolved in 15 mL of freshly distilled CH_2Cl_2, and triflic acid (300 μL, 3.2 mmol) was slowly added while stirring. A color change from blue to red was observed immediately. After the solution was stirred for 5 min, 60 mL of ether was added, and the product precipitated as a deep red–purple solid. The mixture was filtered and washed three times with ether, yield 90–95%. **1a**: ^1H NMR (CD_3CN) 6.95 (s, Cp), 4.00 (s, S_2CH_2); IR (KBr) 2420 cm^{-1} (ν_{SH}); MS (FAB) 465 (P (=parent) of cation); Cyclic voltammetry: reduction, E_1 = −0.65 V, irreversible, E_2 = −1.81 V, ΔE = 360 mV (vs 290 mV for reversible reference couple under identical cell conditions with Pt wire electrode); oxidation, E = −0.18 V, ΔE = 336 mV. Scanning the reduction at −0.65 V increased the amplitude of the oxidation at −0.18 V. A second scan at −0.65 V showed significantly reduced wave amplitude. Anal. Calcd for $C_{12}H_{13}F_3Mo_2O_3S_5$: C, 23.46; H, 2.13; S, 26.09. Found: C, 23.47; H, 2.27; S, 26.18.

1b: ^1H NMR (−70 °C in CD_3CN) 6.84 (m, Cp), 6.79 (m, Cp), 3.95 (s, S_2CH_2), 2.43 (s, Me), −0.72 (s, SH); ^{13}C NMR (CD_3CN) 124.4, 105.6, 103.7 (Cp), 44.6 (S_2CH_2), 17.1 (Me); IR (KBr) 2436 cm^{-1} (ν_{SH}); MS (FAB) 645 (parent ion for salt, **1b** + SO_3CF_3).

Synthesis of $[(Me_5CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$. $(Me_5CpMo(\mu\text{-}S))_2S_2CH_2$ (2.5 mmol, 1.5 g) was dissolved in dry CH_3CN (50 mL). HSO_3CF_3 (3 mmol, 0.027 ml) was added. The resulting blue–violet solution was stirred for 15 min at 25 °C and then filtered. The solvent was concentrated to 3 mL under reduced pressure, distilled diethyl ether (25 mL) was added, and the solution was stored at −20 °C for 12 h. The blue–violet crystals, which were collected on a glass frit, were a 40:60 mixture of **1c** and **2c**, determined by visible spectroscopy (see Table I); yield 65%. This mixture was dissolved in acetonitrile, and the solution was freeze–pump–thaw degassed. Hydrogen (ca. 500 Torr) was added, and the solution was stirred at room temperature for 1 day. The conversion of **2c** to **1c** was monitored by visible spectroscopy; ^1H NMR ($CDCl_3$) 2.36 (s, 30, CH_3), 3.82 (s, 2, CH_2); IR (KBr) 2643 cm^{-1} (ν_{SH}); MS (FAB) 605 (P of cation). Anal. Calcd for $C_{22}H_{33}F_3Mo_2O_3S_5$: C, 35.02; H, 4.41; H, 21.23. Found: C, 34.76; H, 4.23; S, 20.89.

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[32] Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; Rakowski DuBois, M. *Organometallics* **1986**, *5*, 951.

[33] A similar synthesis of this compound has been reported very recently: Kubas, G. J.; Ryan, R. R.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1989**, *111*, 7823.

Synthesis of $[(Cp'Mo(\mu\text{-}S))_2(S_2CH_2)]_2(BF_4)_2$ (2a–c). Method 1. $(CpMo(\mu\text{-}S))_2S_2CH_2$ (0.19 g, 0.41 mmol) and Ph_3CBF_4 (0.42 mmol) were dissolved in 15 mL of freshly distilled CH_2Cl_2. The dark green solution was stirred for 6 h at room temperature. A fine dark precipitate slowly formed, and after 6 h the solution was yellow. The solution was filtered, and fine burgundy crystals were collected and washed with two 20-mL portions of CH_2Cl_2; yield 0.20 g, 86%.

Method 2. $(CpMo(\mu\text{-}S))_2S_2CH_2$ (0.13 g, 0.28 mmol) and $NOBF_4$ (0.40 g, 0.34 mmol) were dissolved in 10 mL of CH_2Cl_2 and stirred at room temperature for 18 h. The deep blue solution was almost colorless at the end of the reaction. The solution was filtered, and the red–burgundy crystals were recrystallized from CH_3CN/Et_2O; ^1H NMR (CD_3CN) 6.97 (s, Cp), 4.10 (s, S_2CH_2); MS (FAB) 552 ($(CpMo(\mu\text{-}S))_2S_2CH_2 + BF_4$, weak), 465 ($(CpMo(\mu\text{-}S))_2(S_2CH_2)^+$), 419 ($465 - SCH_2$). Cyclic voltammetry: reductions, $E_1 = -0.19$ V, $\Delta E = 223$ mV (vs 180 mV for the reversible reference couple under identical cell conditions); $i_c/i_a = 1$; $E_2 = -1.79$ V, $\Delta E = 247$ mV, $i_c/i_a = 2$. Cyclic voltammetry of $(CpMo(\mu\text{-}S))_2S_2CH_2$: oxidation, $E = -0.18$ V, $\Delta E = 180$ mV (vs 130 mV for reversible reference couple under identical cell conditions); $i_a/i_c = 1$; reduction, $E = -1.79$ V; $i_c/i_a = 2$. Anal. Calcd for $C_{11}H_{12}Mo_2S_4BF_4$: C, 23.97; H, 2.19; S, 23.27. Found: C, 24.05; H, 2.29; S, 23.07.

A similar procedure was followed in the synthesis of the BF_4 salt of **2b**. The triflate salt of **2b** was consistently synthesized by adventitious air oxidation of **1b** as follows. $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ (1.06 g, 1.24 mmol) was dissolved in 10 mL of 50:50 $CHCl_3/CH_3CN$, and HSO_3CF_3 (150 μL, 1.4 equiv) was added. The solution was stirred for 2 h under N_2. The solvent was removed, and the resulting oil was redissolved in 3 mL of CH_3CN. Diethyl ether (~70 mL) was added, and the solution was allowed to stand overnight on a Schlenk line under N_2. The ether solution was decanted, and the resulting solid was dried under vacuum. The product was recrystallized from CH_3CN/Et_2O; yield 0.63 g, 80%; ^1H NMR (CD_3CN) 6.81 (s, Cp), 4.07 (s, S_2CH_2), 2.41 (s, Me); ^{13}C NMR (CD_3CN) 125.4, 106.7, 105.6 (Cp), 47.4 (S_2CH_2), 17.0 (Me); MS (FAB) 641 ($(MeCpMo(\mu\text{-}S))_2S_2CH_2 + SO_3CF_3$). Anal. Calcd for $C_{14}H_{16}F_3Mo_2O_3S_5$: C, 26.21; H, 2.51; S, 24.99. Found: C, 26.11; H, 2.62; S, 24.87.

A similar procedure with $NOBF_4$ was followed in the synthesis of **2c**. The blue–violet product was isolated by addition of diethyl ether and recrystallized from CH_2Cl_2/Et_2O; ^1H NMR ($CDCl_3$) 2.33, 2.32 (2 s, Me), 4.00, 3.93 (2 s, S_2CH_2); MS (FAB), BF_4 salt 605 ($(Me_5CpMo(\mu\text{-}S))_2S_2CH_2)^+$), SO_3CF_3 salt 1360 (P of dication + SO_3CF_3), 755 ($(Me_5CpMo(\mu\text{-}S))_2S_2CH_2 + SO_3CF_3$). Anal. Calcd for $C_{21}H_{32}Mo_2S_4BF_4$: C, 36.29; H, 4.79; S, 18.46. Found: C, 36.48; H, 4.67; S, 18.55.

Synthesis of $[(CpMo)_2(S_2CH_2)(SCH_2CH_2S)]BF_4$. Complex **2a** (0.10 g, 0.09 mmol) was dissolved in 5 mL of CH_3CN in a Schlenk flask. Ethylene (100 equiv) was condensed into the flask. Upon warming to 20 °C, the burgundy solution rapidly turned olive green. The product was precipitated from solution with Et_2O, filtered on a fine glass frit, and washed with ether; yield 0.091 g, 82%; EPR (CH_3CN) $g = 2.0064$, $A_{Mo} = 27$ G (see ref 18 for a description of EPR spectra of mixed-valence molybdenum dimers); MS (FAB) 492 (P of cation). Cyclic voltammetry: reduction, $E = -0.31$ V, $\Delta E = 192$ mV (vs 190 mV for reversible reference couple under identical cell conditions), $i_c/i_a = 1.1$; oxidation, $E = 0.45$ V, $\Delta E = 264$ mV, $i_a/i_c = 1$. Cyclic voltammetry for $(CpMo_2)(S_2CH_2)(SC_2H_4S)$: oxidation, $E_1 = -0.29$ V, $\Delta E = 214$ mV (vs 124 mV for reversible reference couple under identical cell conditions), $i_a/i_c = 1.3$, $E_2 = 0.51$ V, $\Delta E = 330$ mV, $i_a/i_c = 1$. Anal. Calcd for $C_{13}H_{16}Mo_2S_4BF_4$: C, 26.96; H, 2.78; S, 22.14. Found: C, 27.05; H, 2.81; S, 22.07.

Reaction of 2a with $[(CpMo)_2(S_2CH_2)(SC_2H_4S)]BF_4$. Complex **2a** (8 mg, 0.007 mmol) and $[(CpMo)_2(S_2CH_2)(SC_2H_4S)]BF_4$ (8.3 mg, 0.014 mmol) were dissolved in 0.8 mL of CD_3CN in an NMR tube. The tube was sealed under vacuo and the reaction was monitored at ambient temperature. After 3 days, the NMR spectrum showed that an equal molar ratio of **1a** and $[Cp\overline{Mo(S_2C}H)(SC_2H_4S)MoCp]^+$ was present;[19] ^1H NMR (CD_2Cl_2) 7.64 (s, 1, CH), 6.22 (s, 5, Cp), 5.44 (s, 5, Cp), 3.02, 3.00 (AA′BB′, 4, SC_2H_4S). Further characterization data have been reported elsewhere.[19]

Reaction of 2a with 1,4-Cyclohexadiene. Complex **2a** (0.014 g, 0.013 mmol) and 1,4-cyclohexadiene (2.7 μL, 0.029 mmol) were dissolved in CD_2Cl_2 in an NMR tube, and the reaction was monitored by NMR at ambient temperature. At early stages of the reaction, NMR evidence for **1a** and benzene was observed. Further reactions were observed that will be described elsewhere.[31] After 22 h, volatiles were distilled from the reaction solution, and benzene was further identified in this fraction by ^1H and ^{13}C NMR, yield 5%.

Reaction of 2a with Thiophenol. Complex **2a** (0.014 g, 0.013 mmol) and thiophenol (2.9 μL, 0.028 mmol) were dissolved in CD_2Cl_2 in an NMR tube, and the reaction was monitored by NMR at ambient temperature. The NMR spectrum showed the quantitative formation of **1a** and PhSSPh within 2 h.

Reaction of 2a with Ammonium Hydroxide. A stock solution of **2a** (5.37×10^{-3} M) was prepared. The stock solution (1.000 mL) and 0.0050 mL of NH_4OH (0.085 mmol) were diluted to 5.00 mL with CH_3CN. This solution was placed in a Schlenk cuvette and analyzed by visible spectroscopy. The formation of $(CpMo(\mu\text{-}S))_2S_2CH_2$ was instantaneous, and known extinction coefficients were used to calculate a yield of 50.6% after 5 min. The yield did not change significantly within the next 4 h, but after 1 day the yield of $(CpMo(\mu\text{-}S))_2S_2CH_2$ was 66%, and after 6 days the yield was 69%.

Determination of pK_a Values of 1. Acetonitrile solutions of $(Cp'Mo(\mu\text{-}S))_2S_2CH_2$ and $[(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ ($Cp' = C_5H_5$, $C_5H_4CH_3$, and $C_5(CH_3)_5$) were prepared with known concentrations over the range 1×10^{-4}–1×10^{-3} M. Visible spectra were recorded, and each of the complexes was found to obey Beer's law. Absorption maxima and extinction coefficients are given in Table I. Stock solutions of **1a**, **b**, or **c** and of 2,4-dichloroaniline were prepared in acetonitrile, and serial dilutions were prepared. Aliquots of the aniline solution were added to aliquots of the complex solution. Visible spectra were recorded, and concentrations of **1** and of its deprotonated form were determined by using the absorptions and known extinction coefficients at two wavelengths. For **1a**, wavelengths of 500 ($\epsilon = 910\ M^{-1}\ cm^{-1}$) and 722 nm ($\epsilon = 160\ M^{-1}\ cm^{-1}$) were used. For $(CpMo(\mu\text{-}S))_2S_2CH_2$ at 500 nm, $\epsilon = 860\ M^{-1}\ cm^{-1}$, and at 722 nm, $\epsilon = 2200\ M^{-1}\ cm^{-1}$. For **1b**, wavelengths of 534 ($\epsilon = 880\ M^{-1}\ cm^{-1}$) and 730 nm ($\epsilon = 202\ M^{-1}\ cm^{-1}$) were used. For $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ at 534 nm, $\epsilon = 1078\ M^{-1}\ cm^{-1}$, and at 730 nm, $\epsilon = 2280\ M^{-1}\ cm^{-1}$. For **1c**, wavelengths of 754 ($\epsilon = 504\ M^{-1}\ cm^{-1}$) and 532 nm ($\epsilon = 860\ M^{-1}\ cm^{-1}$) were used. For $(Me_5C_5Mo(\mu\text{-}S))_2S_2CH_2$ at 754 nm, $\epsilon = 2870\ M^{-1}\ cm^{-1}$, and at 532 nm, $\epsilon = 1490\ M^{-1}\ cm^{-1}$. With the concentrations determined for **1** and its deprotonated form, the equilibrium constants for the reactions of **1a**, **b**, or **c** with the aniline was calculated. These equilibrium constants and the known pK_a of 2,4-dichloroanilinium in acetonitrile (8.0)[20] were used to determine the pK_a values for **1a**, **b**, and **c** in acetonitrile. Values are listed in Table II.

X-ray Diffraction Studies. Crystal data and conditions for data collection for the X-ray diffraction study of the triflate salt are given in Table V. Further details concerning the data refinement are included in the supplementary materials (Table I-S). The same information for the tetrafluoroborate salt is included in the supplementary material.

A crystal of the triflate salt was mounted on a glass fiber with epoxy resin and aligned on an automated diffractometer. On the basis of a fast 24-h data collection, the structure of the molybdenum tetramer was determined. However, the triflate anions were not accurately located, and one of the dinuclear units of the tetramer was found to be disordered. Because of these complications we decided to collect data at low temperature. The same crystal was used for the low-temperature data collection. Initially the sample was cooled to −80 °C. At this temperature, centering reflections that were well defined at room temperature were no longer measurable. ω-Scans showed that reflections that had shown ω-scan peak widths at half-height of 0.3° were split into two peaks, indicating a phase transition. Raising the temperature to −40 °C restored the original cell and ω-scan widths. Details of the experimental conditions are given in Tables V and I-S. An adequate model of the disorder of the dimer was developed by using the low-temperature data, as described in the Discussion. Unfortunately, models for the disordered triflate anions that were completely satisfactory were not developed. The two triflates

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Table V. Summary of Crystallographic Data

	$[(CH_3C_5H_4Mo(\mu\text{-}S))_2S_2CH_2]_2(SO_3CF_3)_2$	$[(CH_3C_5H_4Mo(\mu\text{-}S))_2S_2CH_2]_2(BF)_2$
fw	1282.9	1158.4
space group	*C*2/*c*	$P2_1/n$
a, Å	35.498 (10)	11.476 (5)
b, Å	14.823 (7)	13.843 (6)
c, Å	17.246 (5)	12.577 (4)
β, deg	115.51 (2)	112.97 (3)
V, Å^3	8190 (5)	1839.6 (13)
ρ(calcd), g cm^{-3}	2.081	2.091
radtn	Mo K*α* (λ = 0.71073 Å)	Mo K*α* (λ = 0.71073 Å)
temp, °C	−35	22–24
2*θ* range, deg	5.0–50.0	3.0–45.0
scan type	*ω*	Wyckoff
scan speed, deg min^{-1}	variable; 4.00–60.00	fixed; 4.00
scan range	from 0.80° below 2*θ* for Kα_1 to 0.80° above 2*θ* for Kα_2	0.60°
index ranges	$-42 \le h \le 42$	$-12 \le h \le 12$
	$0 \le k \le 17$	$-14 \le k \le 14$
	$-20 \le l \le 20$	$-13 \le l \le 12$
rflctns coll	15266	2964
unique rflctns	7225	2407
obsd rflctns	5714	1487
abs corr	semiempirical	none
min/max transm	0.6265/0.9020	
R, %	6.05	8.73
R_w, %	9.00	11.01

occupied three positions in the asymmetric unit: one was located about two different positions along the 2-fold axis, i.e., at 0, 0.32, $^3/_4$ and at 0, 0.04, $^3/_4$; and the other was at an independent position in the cell. Several different orientations for each of these triflates were found in difference maps. These were included as constrained groups in further least-squares calculations.

Because of the problems with the triflate anions, crystals of the tetrafluoroborate salt were synthesized and examined. After three crystals were mounted, all of which exhibited split peaks, a crystal was located that, while still showing split peaks, was of better quality than the previous ones. A fast data collection on this sample gave data of sufficient quality to confirm a tetranuclear structure similar to that determined for the triflate salt. Numerous attempts to obtain better crystals of the tetrafluoroborate salt were unsuccessful.

Further attempts were therefore made to improve the treatment of the disordered anions in the triflate salt. Several other orientations were added, but there was still significant electron density in the region of two of the triflates. Eight of these peaks were included in the final least-squares cycles as individual atoms rather than as constrained atoms in complete triflates. No further attempts to improve the quality of the structure seemed warranted since the tetranuclear nature of the dication had been established. Hydrogen atoms were not seen in the difference maps, so they were not included. For the final refinement, all methylcyclopentadiene groups were treated as rigid groups and all complete triflates were refined with distance restraints.

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Supplementary Material Available: For the triflate and tetrafluoroborate salts of **1b**, tables of crystal data and collection, solution, and refinement details, atomic coordinates and equivalent isotropic displacement parameters, complete bond distances and angles, and anisotropic displacement parameters (23 pages); listings of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

NMR and X-ray Studies of Penta- and Hexaborane Alkyl Derivatives Involving [3.3.1] and [3.3.2] Ring Systems

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The reaction of the $B_5H_8^-$ anion with *B*-chloro-9-borabicyclo[3.3.1]nonane (*B*-Cl-9-BBN) produces a boron bridge substituted *nido*-pentaborane, (*μ*-9-BBN)B_5H_8 (1). The solid-state structure of 1 reveals that the 9-BBN fragment retains its characteristic chair–chair conformation. In solution at room temperature the 9-BBN fragment rotates relative to the pentaborane framework. From a dynamic ^{13}C NMR experiment the free energy of activation for the rotation has been found to be 14.6 ± 0.1 kcal mol^{-1}. In diethyl ether solution this compound slowly converts to a *nido*-hexaborane derivative, 4,5-(cycloocta-1,5-diyl)B_6H_8 (2), in which the bridging boron atom has moved into the cluster. The result is the conversion of the [3.3.1] ring system of 9-BBN to a [3.3.2] bi-cycle in which two adjacent basal boron atoms of a *nido*-hexaborane cluster provide the two-atom bridge. Compound 2 is the first example of a fused borane cluster–organic bi-cycle. The solid-state structure of 2 reveals a chair–boat conformation for the [3.3.2] bicyclic ring system. In addition, two independent molecules are observed that differ primarily in the placement of the hydrogen atoms bridging the basal edges of the hexaborane fragment. Compounds 1 and 2 were characterized by ^{11}B, ^{13}C, ^1H, and ^{11}B–^{11}B COSY NMR spectroscopic studies and by single-crystal X-ray diffraction. Crystal data for 1, $C_8H_{22}B_6$, at −150 °C: triclinic, space group $P\bar{1}$, $a = 9.427$ (2) Å, $b = 10.380$ (2) Å, $c = 12.525$ (2) Å, $\alpha = 87.341$ (16)°, $\beta = 80.729$ (15)°, $\gamma = 89.86$ (2)°, $Z = 4$. Crystal data for 2, $C_8H_{22}B_6$, at −125 °C: orthorhombic, space group $P2_12_12_1$, $a = 9.077$ (3) Å, $b = 11.585$ (3) Å, $c = 22.352$ (6) Å, $Z = 8$.

Introduction

As part of our effort to gain a better understanding of the alkylation of pentaborane(9), B_5H_9 we have begun investigating reactions involving the diverse and rapidly growing number of organoborane reagents. The *B*-chloro derivative of commercially available 9-BBN, 9-borabicyclo[3.3.1]nonane, has led to the synthesis of a pentaborane derivative in which the 9-BBN boron atom bridges a pentaborane basal edge. This cluster undergoes a Lewis-base-catalyzed isomerization to a unique molecule in

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