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Activation of Hydrogen by Cationic Cyclopentadienyl Molybdenum Dimers with Sulfido Ligands. 2. Cationic Complexes Derived from Reactions with Vinyl Halides

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Abstract: The reaction of $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ (Cp = C_5H_5) with β-bromostyrene results in the formation of a β-phenylalkenylthiolate bridged cationic complex $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(H)C(H)Ph)]Br$, I. The product has been characterized by spectral methods and by an X-ray diffraction study. I crystallized in space group $P2_1/c$ with a = 13.325 (2) Å, b = 15.868 (7) Å, c= 25.901 (11) Å, and β = 98.30 (3)°. The *trans*-vinylthiolate ligand is oriented in an equatorial configuration away from the sulfido ligand in the dimer. Complex I reacts with reducing agents to form a mixed valence molybdenum(III)/molybdenum(IV) derivative which rapidly disproportionates to $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ and a new molybdenum(III) dimer with two vinylthiolate ligands of the formula $(CpMo)_2(S_2CH_2)(\mu\text{-}SCHC(H)Ph)_2$, III. Complex I reacts with hydrogen at 40 °C to form ethylbenzene and $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$. Intermediates in this hydrogenolysis reaction have been detected by NMR and have been synthesized by alternate routes. They include the cation $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(H)(Me)Ph)]Br$, IV, and the neutral complex $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH(Me)Ph)_2$, V. Possible reaction pathways for the formation of these intermediates are discussed.

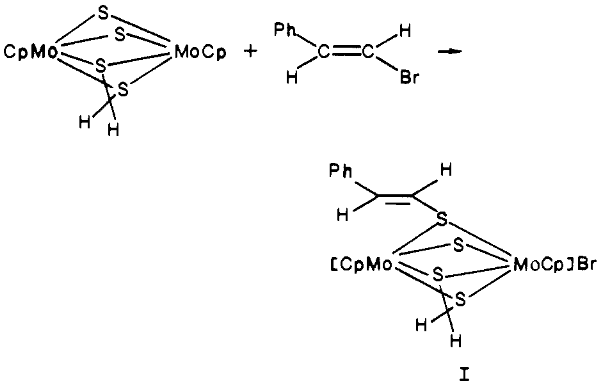
In the preceding paper we described the characterization and reaction chemisty of a cationic cyclopentadienyl molybdenum dimer with a bridging α-phenylvinylthiolate ligand.[1] In this paper we report the synthesis, structural characterization, and reaction chemistry of an isomeric form of this cation which contains a bridging β-phenylvinylthiolate ligand $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCHC(H)Ph)]Br$, I. Although gross structural features of I are similar to the previously characterized isomer, the reactivities of the two cations are significantly different.

Complex I is synthesized by the reaction of β-bromostyrene with $(CpMo\mu\text{-}S)_2S_2CH_2$. The alkylation of sulfur ligands by alkyl halides is a well-established procedure, and an analogous reaction of the molybdenum dimer with methyl iodide has been reported previously.[2] However few examples of the reaction of vinyl halides with coordinated thiolato or sulfido ligands have been reported. The reaction of β-bromostyrene with cuprous mercaptides has been found to yield vinylthio ethers.[3] In the absence of a metal complex vinyl halides have been reacted with sodium thiolates in hexamethylphosphoramide to produce vinylsulfides.[4] The reactivity of the bridging sulfido ligands in the molybdenum dimer reported here provides an interesting parallel with the reactivity of certain low valent metal complexes which undergo an oxidative addition of β-bromostyrene with retention of configuration.[5]

Our initial rationale for investigating complex I was based on our observations that $(CpMo\mu\text{-}S)_2S_2CH_2$ catalyzed the hydrogenolysis of alkenylhalides and that I was an intermediate in the catalytic conversion of β-bromostyrene to ethyl benzene. We describe here the unique reactivity of I with molecular hydrogen, which ultimately results in carbon–sulfur bond hydrogenolysis. Reactions of I with reducing agents and nucleophiles have been found to yield new products which are also discussed here.

Results and Discussion

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCHC(H)Ph)]Br$. The molybdenum dimer $(CpMo\mu\text{-}S)_2S_2CH_2$ reacts at room temperature with β-bromostyrene to form a cationic complex with a β-phenylvinylthiolate ligand, complex I (eq 1). The product is



(1)

I

isolated in 80% yield as an analytically pure purple powder which is moderately air stable and soluble in methanol, chloroform, and methylene chloride. Analysis of the product, I, by proton NMR indicates the presence of only one isomer in which the vinyl protons have a coupling constant of 15.4 Hz, consistent with a trans configuration. NMR data for the reactant β-bromostyrene likewise shows the trans isomer to be the predominant species.

The reaction of vinyl bromides with $(CpMo\mu\text{-}S)_2S_2CH_2$ appears to be quite general. For example, 2-bromo-2-butene reacts with the molybdenum dimer to form a butenyl thiolate bridged cation which is in equilibrium with a second isomer. The products have NMR spectral characteristics which are identical with those reported in the preceding paper for the protonated 2-butyne adduct.[1]

X-ray Diffraction Study of I. An X-ray diffraction study of I was undertaken in order to determine the orientation of the alkenylthiolate ligand with respect to the other sulfur ligands of the dimer. Single crystals of the bromide salt were grown from a saturated undried chloroform solution. The complex crystallizes in space group $P2_1/c$ with 8 molecules per unit cell. The unit cell also contains eight chloroform and four water molecules. Two molecules of the molybdenum dimer, A and B, are present in each asymmetric unit. A perspective drawing is shown in Figure 1, and selected bond distances and angles are presented in Table I. Positional and thermal parameters are included in Table II.

The gross structural features of molecules A and B are quite similar. In both molecules, the β-phenylvinylthiolate ligand is oriented away from the sulfideo ligand (S1) in what has been previously labeled an equatorial configuration.[6] The two mole-

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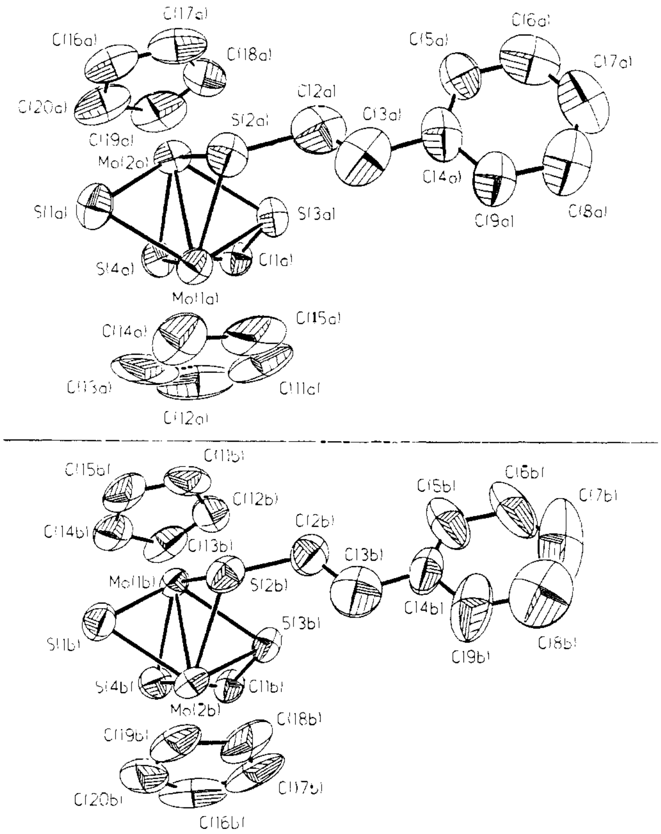


Figure 1. Perspective drawing and numbering scheme for (a) Molecule A (top) and (b) molecule B (bottom) of [(CpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SCHC(Ph)H)]Br, I. Thermal ellipsoids are drawn at the 50% probability level.

Table I. Selected Bond Distances and Angles for [(CpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SC(H)C(H)Ph)]Br

	molecule A	molecule B
	Distances, Å	
Mo$_1$–Mo$_2$	2.599 (2)	2.606 (2)
Mo$_1$–S$_1$	2.301 (5)	2.304 (4)
Mo$_1$–S$_2$	2.480 (4)	2.441 (5)
Mo$_1$–S$_3$	2.463 (5)	2.470 (4)
Mo$_1$–S$_4$	2.455 (4)	2.451 (5)
Mo$_2$–S$_1$	2.288 (5)	2.309 (4)
Mo$_2$–S$_2$	2.466 (5)	2.475 (5)
Mo$_2$–S$_3$	2.469 (4)	2.462 (4)
Mo$_2$–S$_4$	2.451 (4)	2.461 (5)
S$_2$–C$_2$	1.851 (22)	1.807 (18)
S$_3$–C$_1$	1.842 (14)	1.853 (15)
S$_4$–C$_1$	1.813 (15)	1.824 (15)
C$_2$–C$_3$	1.156 (28)	1.371 (32)
C$_3$–C$_4$	1.573 (25)	1.509 (25)
S$_3$···S$_4$	2.712	2.725
S$_1$···S$_2$	2.891	2.881
S$_2$···S$_3$	2.982	2.979
S$_4$···S$_1$	2.955	2.944
	Angles, deg	
Mo$_1$–S$_1$–Mo$_2$	69.0 (1)	68.8 (1)
Mo$_1$–S$_2$–Mo$_2$	63.4 (1)	64.0 (1)
Mo$_1$–S$_3$–Mo$_2$	63.6 (1)	63.8 (1)
Mo$_1$–S$_4$–Mo$_2$	64.0 (1)	64.1 (1)
S$_1$–Mo$_1$–S$_2$	74.3 (2)	74.7 (2)
S$_3$–C$_1$–S$_4$	95.8 (6)	95.6 (7)
Mo$_1$–S$_2$–C$_2$	117.7 (5)	109.9 (6)
Mo$_2$–S$_2$–C$_2$	111.8 (6)	116.9 (6)
S$_2$–C$_2$–C$_3$	119.7 (18)	116.4 (15)
C$_2$–C$_3$–C$_4$	122.4 (19)	116.7 (19)

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for [(CpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SC(H)C(H)Ph)]Br

atom	*x*	*y*	*z*	*U*[a]
Mo(1a)	1995 (1)	1634 (1)	4492 (1)	51 (1)
Mo(2a)	3373 (1)	1539 (1)	3879 (1)	52 (1)
S(1a)	3221 (3)	2637 (3)	4435 (2)	65 (2)
S(2a)	3639 (3)	915 (3)	4760 (2)	66 (2)
S(3a)	2042 (3)	456 (3)	3877 (2)	58 (2)
S(4a)	1665 (3)	2075 (3)	3574 (2)	55 (1)
C(1a)	1205 (10)	1035 (10)	3369 (6)	54 (6)
C(2a)	3655 (13)	−251 (14)	4736 (7)	97 (9)
C(3a)	3264 (13)	−633 (14)	5031 (7)	102 (9)
C(4a)	3318 (11)	−1623 (7)	5061 (5)	81 (8)
C(5a)	3939 (11)	−2115 (7)	4792 (5)	72 (8)
C(6a)	3942 (11)	−2989 (7)	4846 (5)	101 (11)
C(7a)	3324 (11)	−3372 (7)	5169 (5)	105 (10)
C(8a)	2703 (11)	−2881 (7)	5438 (5)	98 (10)
C(9a)	2699 (11)	−2006 (7)	5384 (5)	80 (8)
C(11a)	492 (15)	1154 (16)	4769 (10)	108 (12)
C(12a)	312 (15)	1991 (16)	4585 (10)	136 (15)
C(13a)	978 (15)	2534 (16)	4909 (10)	132 (14)
C(14a)	1569 (15)	2032 (16)	5293 (10)	96 (10)
C(15a)	1269 (15)	1179 (16)	5206 (10)	116 (13)
C(16a)	4953 (9)	1994 (13)	3715 (5)	89 (10)
C(17a)	4968 (9)	1099 (13)	3714 (5)	97 (11)
C(18a)	4237 (9)	816 (13)	3296 (5)	112 (12)
C(19a)	3770 (9)	1536 (13)	3039 (5)	108 (11)
C(20a)	4212 (9)	2264 (13)	3298 (5)	103 (10)
Mo(1b)	1161 (1)	7760 (1)	3373 (1)	48 (1)
Mo(2b)	2258 (1)	7823 (1)	2618 (1)	52 (1)
S(1b)	2812 (3)	8235 (3)	3467 (2)	64 (2)
S(2b)	1128 (3)	8989 (3)	2804 (2)	63 (2)
S(3b)	531 (3)	7233 (3)	2488 (2)	56 (1)
S(4b)	2113 (3)	6535 (3)	3131 (2)	61 (2)
C(1b)	1020 (11)	6168 (9)	2680 (6)	57 (6)
C(2b)	−88 (14)	9060 (11)	2395 (7)	81 (8)
C(3b)	−70 (16)	9187 (12)	1873 (10)	110 (11)
C(4b)	−1077 (11)	9342 (9)	1539 (6)	94 (10)
C(5b)	−2053 (11)	9315 (9)	1674 (6)	110 (11)
C(6b)	−2885 (11)	9529 (9)	1308 (6)	139 (14)
C(7b)	−2743 (11)	9772 (9)	806 (6)	224 (24)
C(8b)	−1767 (11)	9800 (9)	670 (6)	154 (17)
C(9b)	−934 (11)	9585 (9)	1037 (6)	129 (12)
C(11b)	−51 (13)	8368 (9)	3820 (6)	87 (9)
C(12b)	−407 (13)	7550 (9)	3664 (6)	78 (8)
C(13b)	290 (13)	6953 (9)	3918 (6)	80 (8)
C(14b)	1077 (13)	7402 (9)	4231 (6)	85 (9)
C(15b)	866 (13)	8276 (9)	4170 (6)	95 (10)
C(16b)	3250 (19)	7111 (8)	2090 (9)	119 (13)
C(17b)	2474 (19)	7535 (8)	1754 (9)	115 (12)
C(18b)	2609 (19)	8415 (8)	1836 (9)	103 (11)
C(19b)	3468 (19)	8536 (8)	2222 (9)	88 (9)
C(20b)	3864 (19)	7730 (8)	2379 (9)	92 (9)
Br(1)	1467 (1)	5414 (1)	1307 (1)	80 (1)
Br(2)	1902 (2)	10814 (1)	1952 (1)	96 (1)
Cl(1a)	3985 (4)	4562 (5)	2340 (3)	137 (3)
Cl(2a)	2917 (5)	3045 (5)	1956 (3)	156 (4)
Cl(3a)	4232 (6)	3861 (5)	1340 (4)	171 (5)
C(10a)	3346 (13)	4024 (13)	1789 (7)	93 (9)
Cl(1b)	4236 (6)	9822 (5)	1186 (4)	177 (5)
Cl(2b)	5084 (6)	11335 (6)	1554 (4)	191 (5)
Cl(3b)	3601 (6)	11328 (8)	670 (3)	229 (6)
C(10b)	3940 (16)	10902 (15)	1281 (9)	120 (11)
O(1)	1416 (34)	10051 (30)	774 (18)	521 (39)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonal U_{ij} tensor.

cules differ in the orientation of the vinylthiolate ligand. In both cases the double bond is twisted out of the plane of the four bridging sulfur atoms; in molecule A the dihedral angle between the planes defined by the four sulfur atoms and by S$_2$, C$_2$, C$_3$, and C$_4$ is 77.6°, while in molecule B the dihedral angle is 93.6°. The angle between the plane of the phenyl ring and that of the double bond is 11.5° in A and 8.7° in B. The major differences between A and B involve the bond distances within the respective vinylthiolate ligands. The C$_2$–C$_3$ distance in molecule A appears to be exceptionally short, while in molecule B a significantly longer C$_2$–C$_3$ distance is accompanied by relative decreases in the S$_2$–C$_2$ and C$_3$–C$_4$ distances. Because there are relatively large errors associated with these measurements, upper and lower limits for the C$_2$–C$_3$ distances were calculated taking thermal motion into account.[7] This treatment resulted in the range of 1.156–1.516

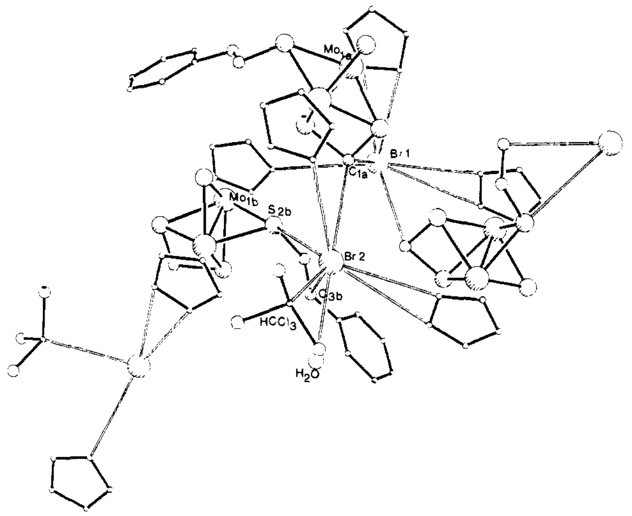


Figure 2. Nonbonding contacts of the bromide anions in the molecular structure of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCHC(Ph)H)]Br$, I.

Table III. Nonbonding Interaction Distances[a] for Bromide Counterions

Br1		Br2	
atoms	distance (Å)	atoms	distance (Å)
	Molecule A		
Br1-C1A	3.900	Br2-C1A	3.930
Br1-C11A	3.723	Br2-C19A	3.663
Br1-C12A	3.955		
	Molecule B		
Br1-C1B	3.879	Br2-S2B	3.869
Br1-C11B	3.746	Br2-C3B	3.667
Br1-C15B	3.792	Br2-C12B	3.632
Br1-C16B	3.952	Br2-C13B	3.870
Br1-C17B	3.744		
	Chloroform/Water		
Br1-C10A	3.435	Br2-C10B	3.431
		Br2-O1	3.258

[a] Distances which are within the sums of respective van der Waals radii.

Å for C_2–C_3 in molecule A and 1.371–1.641 Å in molecule B. Consideration of these limits allows for a more reasonable C_2–C_3 double bond length in molecule A. However, the trend toward a longer C_2–C_3 distance in B is still observed within these rather broad limits.

The differences in bond distances in the vinylthiolate ligands of A and B appear to arise from extensive close contacts between each cation and the bromide anions. As shown in Figure 2, both bromides interact with molecule A through the methylene group of the methanedithiolate ligand and through certain carbon atoms of the cyclopentadienyl ligands. All of these interactions appear to involve the hydrogen atoms of the C–H bonds. The nonbonding interaction distances are listed in Table III. In molecule B, Br_1 undergoes a similar hydrogen-bonding interaction with the methanedithiolate ligand, but Br_2 interacts with S_2 and C_3 of the vinylthiolate ligand. The Br_2–S_2 distance of 3.89 Å and the Br_2–C_3 distance of 3.67 Å are both within the sum of van der Waals radii for the atom pairs. It seems likely that this interaction accounts for the apparent difference in electronic distributions indicated in the vinylthiolate ligand of B compared to A. Additional interactions of the bromide ions with the molecules of chloroform and water incorporated into the crystal lattice are also observed; these are indicated in Table III.

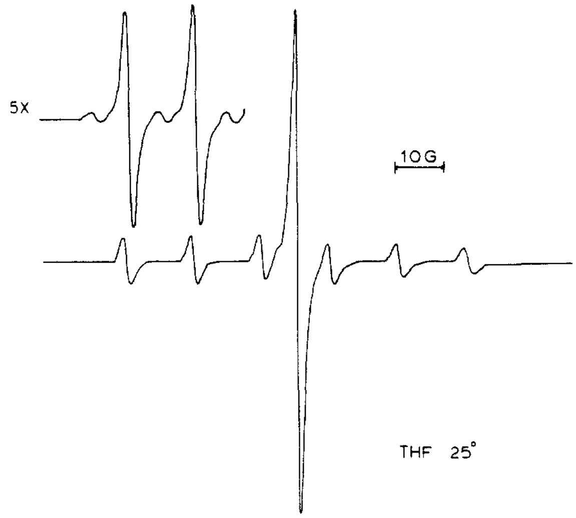
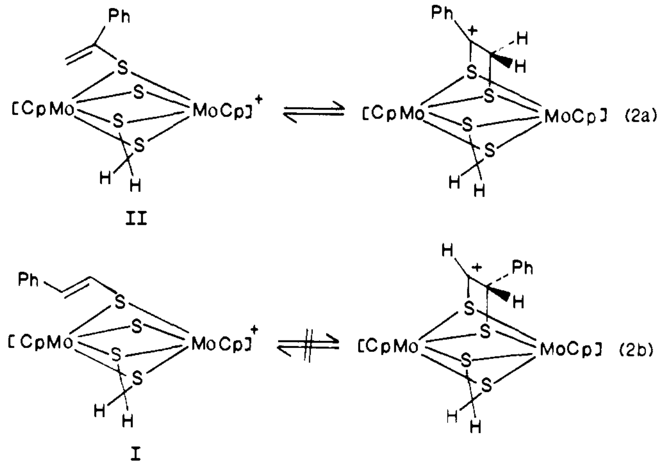


Figure 3. X-band EPR spectrum of $[(CpMo)_2(S_2CH_2(\mu\text{-}S)(\mu\text{-}SCHC(Ph)H]$ generated by the reduction of I ($\sim 10^{-5}$ M) by 1 equiv of K/graphite in THF at 25 °C. Inset shows a portion of the 11-line hyperfine coupling pattern with two $Mo_{I=5/2}$. EPR parameters: $g = 1.992$, $A_{(Mo)} = 14.0$ G.

Bond distances and angles in the $Cp_2Mo_2S_4$ core of each of the cations in structure I are very similar to those observed for the related dimer $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]I$[2] and for the isomeric cation with an α-phenylvinylthiolate ligand, II, reported in the preceding paper.[1] The orientations of the vinylthiolate ligands within cations I and II are also quite comparable.

An important difference between the two cations concerns their behavior in solution. Derivative II with the α-phenylvinylthiolate ligand is in equilibrium with a second cation at room temperature (reaction 2a).[1] The transformation to the proposed structure of the equilibrium component involves a facile rotation about the C–S bond of the vinylthiolate ligand and inversion about S_2. The reverse processes must be involved in the synthesis of cation II by protonation of the phenylacetylene adduct.



In contrast, complex I with the β-phenylvinylthiolate ligand shows no evidence, on the basis of the room temperature NMR spectrum, for an analogous equilibrium, e.g., reaction 2b. Neither are significant changes observed in the NMR spectrum over a temperature range of 25–75 °C in CD_3CN or of 25 to −50 °C in $CDCl_3$.[8] An inspection of simple molecular models does not suggest significant differences between isomers I and II in potential steric interactions involved in conformational changes in the vinylthiolate ligands. The difference in room temperature solution

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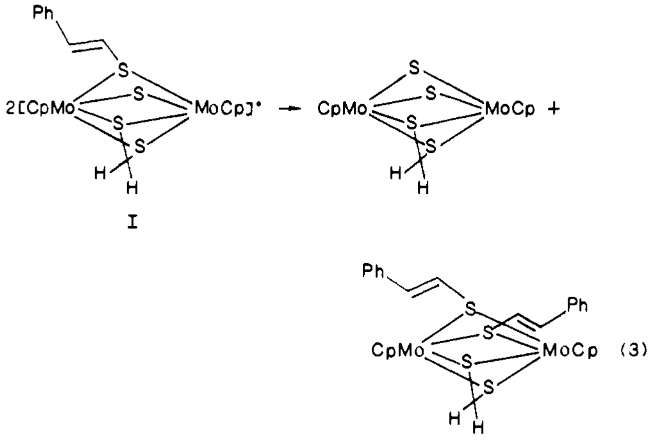
(7) Parallel and perpendicular root mean square amplitudes were calculated for all atoms bonded to C_2 and C_3 and were used to estimate the lower limit, riding model, and upper limit bond length corrections by the method of Johnson (Johnson, C. K. In *Crystallographic Computing*, Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 220–226).

(8) The ^{1}H NMR spectrum of I at −50 °C shows no change in the cyclopentadienyl resonance, as would be expected for reaction 2b, but new resonances in the vinyl region are observed. This fluxional process has not yet been completely characterized, but it may involve isomers of I resulting from inversion at S_2 or rotation about S_2–C_1.

behavior is probably related in part to the lower stability of the carbonium ion which would result in equilibrium 2b relative to that in 2a. This reasoning is also consistent with our observation that protonation of the phenylacetylene adduct occurs regioselectively at the unsubstituted carbon atom. The absence of the second equilibrium component in solutions of I may account for some of the marked differeces in chemical reactivity which are observed between I and II. These are discussed below.

Redox Behavior of I. The cyclic voltammetry of I reveals two reversible one-electron reductions at −0.26 and −1.13 V vs. SCE. The potentials are closely related to those of other thiolate-bridged cations characterized in this study and in previous work.[1,2] When 1 equiv of potassium graphite is stirred with I in dilute THF solution, the mixed valence dimer resulting from a one-electron reduction is detected by EPR spectroscopy. The spectrum, Figure 3, shows the hyperfine coupling which is consistent with delocalization of the unpaired electron over both molybdenum ions.[9] The mixed valence derivative has not been isolated because it readily undergoes a disproportionation to an equimolar mixture of Mo(III) and Mo(IV) derivatives as shown in eq 3. The known methanedithiolate bridged derivative is readily identified from spectral data.[10] The new Mo(III) dimer with two bridging vinylthiolate ligands, III, has been isolated in 45% yield (theoretical yield, 50%) and characterized by spectral data and elemental analyses. The mass spectrum shows a parent ion consistent with the proposed structure. ^{1}H NMR data show the AB pattern of trans vinyl protons in which the coupling constant of 15.2 Hz is similar to that observed for cation I. However, the integrated intensity is consistent with the presence of two vinylthiolate ligands. The chemical shift of the Cp resonance, 5.68 ppm, is characteristic of a neutral molybdenum(III) dimer.[2,10]



I

III

(3)

A stable tetrameric product has also been isolated from reactions involving the mixed valence dimer. Yields have ranged from 0 to 15%. The tetrameric formulation has been verified by FAB mass spectroscopy, but the structure of the complex has not yet been established. Since the product does not undergo further reaction to form the molybdenum(III) and -(IV) products of reaction 3, it does not appear to be an intermediate in that reaction. The analogous mixed valence dimer with a methylthiolate ligand[2] undergoes similar intermolecular reactions. Tetramer formation in the latter system has been found to be promoted by light.[11]

Reactions of I with Bases and Nucleophiles. The protonated phenylacetylene adduct, described in the preceding paper, was found to be deprotonated by basic nucleophiles and to undergo C–S bond cleavage at room temperature in the presence of several nonbasic nucleophiles.[1] Cation I displays significantly different reactivity. No reactions are observed between I and the nonbasic nucleophiles methanol and chloride ion at room temperature. In our characterization of the reactions of several more basic nucleophiles with I, no evidence for deprotonation of the cation was observed. The lower acidity of I relative to II seems consistent with the absence of a solution equilibrium involving a carbonium

Table IV. Crystal Data and Details of the Structure Determination for $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(H)C(H)Ph)]Br$

Crystal Data	
formula	$C_{19}H_{19}Mo_2S_4Br\cdot CHCl_3\cdot {}^1/_2H_2O$
mw (amu)	775.77
space group	$P2_1/c$
cryst system	monoclinic
a (Å)[a]	13.325 (2)
b (Å)	15.868 (7)
c (Å)	25.901 (11)
α (deg)	90.0
β (deg)	98.30 (3)
γ (deg)	90.0
vol (Å^3)	5419 (3)
obsd density (g/cm^3)[b]	1.903
Z	8
calcd density (g/cm^3)	1.902
F(000)	3023
μ (cm^{-1})	29.7
cryst habit	trianglr parallelepiped
cryst color	dark maroon
Data Collection and Reduction	
diffractmtr	Nicolet P3F
radiatn (Å)	Mo Kα (0.71069)
takeoff angle for graphite monochrmtr (deg)	4.0
temp (deg K)	294–296
cryst dimensns (mm)	0.3 × 0.3 × 0.45
scan technique	θ–2θ
2θ, min–max (deg)	3.0–45.0
hkl values scanned	$\pm h,+k,\pm l$
scan speed (deg/min)	6.0–60.0
scan range, deg below $K\alpha_1$ and above $K\alpha_2$	0.9–1.1
backgrnd	stationary cryst – stationary cntr background time = $^1/_2$ scan time
check reflctns	(−3, 0, 4), (−2, 1, −4), (−6, 2, 1), (−1, −1, −2)
freq	every 96 measrmnts
variatn	net 7.0% decay
no. of reflctns measd	18113
no. of unique reflectns	7101
agreement factor during averaging	0.024 before absorptn corrctn
no. of obsd reflctns	3563
σ criterion	$F > 6^*\sigma(F)$
absorptn corrctn[c]	empirical
transmissn factors, max, min	(0.125, 0.091)
Structure Determination and Refinement	
method of phase determntn	direct method
programs[d]	SHELXTL
scattering factors[e]	neutral atoms
R and R_w	0.058, 0.066
weight	$1.0/(\sigma^2(F) + 0.0006^*F^*F)$
no. of params	490
ratio of obsrvtns to params	7.3/1
goodness of fit	1.461
max shift/error	−0.045 for U_{23} of C17B
av shift/error	0.013
residual electron density e/Å^3	1.13 1.1 Å from Mo1A[f]

[a] Cell dimensions were determined by least-squares fit of the setting angles of 20 reflections with 2θ in the range of 5.0–20.0. [b] By flotation methods in 1,3-dibromopropane–iodobenzene. [c] Based on 4 scan data measured for 10 reflections with varying values of 2θ, using 36 ten-degree steps in 4. The internal agreement for these 360 reflections was 0.024 before correction and 0.018 after. [d] Sheldrick, G. M. SHELXTL, *A Program for Crystal Structure Determination*: Nicolet Analytical Instruments: Madison, WI, 1983; Version 4.1. [e] *International Tables for X-ray Crystallography*: Kynoch Press: Birmingham, England, 1974; Vol. 4. [f] All of the top 10 peaks are less than 1.25 Å from a heavy (Mo or Br) atom.

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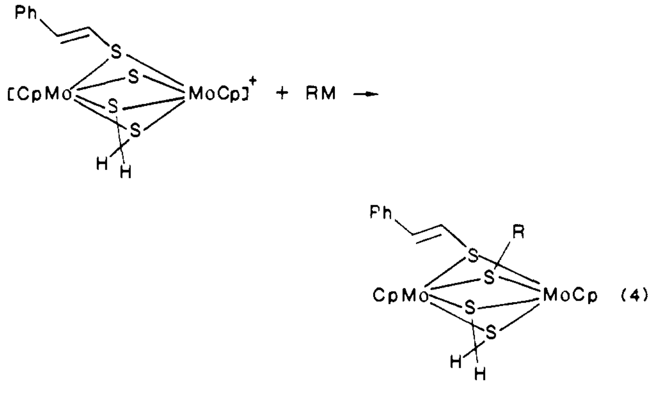
(9) Casewit, C. J.; Rakowski DuBois, M. *Inorg. Chem.* **1986**, *25*, 74.

(10) McKenna, M; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

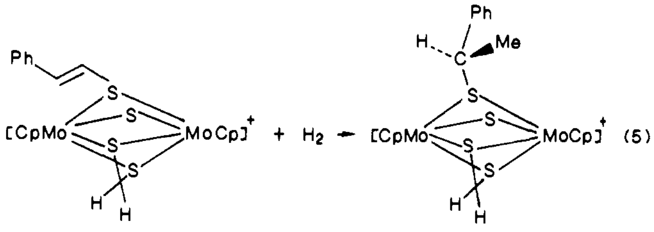
(11) Casewit, C. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 5482.

ion structure as discussed above. The addition of triethylamine, methoxide, or methylthiolate anion, or the hydride ion, to I in chloroform or THF results in the formation of the neutral disproportionation products shown in reaction 3. Each of these nucleophiles therefore appears to be acting as a reducing agent for complex I in a thermodynamically controlled reaction. In contrast, in the reactions of cation I with several carbon nucleophiles, sulfur–carbon bond formation is kinetically favored over electron transfer, and neutral bis(thiolate) bridged derivatives of Mo(III) are formed (eq 4). Characterization data for these new derivatives are presented in the Experimental Section.



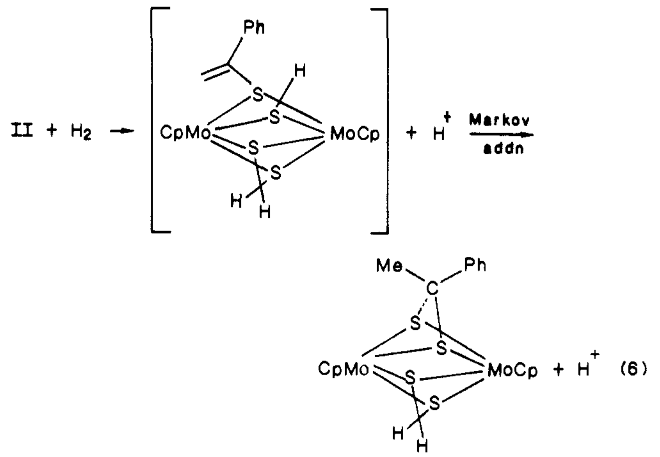
RM = CH_3Li, C_6H_5ZnCl, CH_3CH_2MgBr

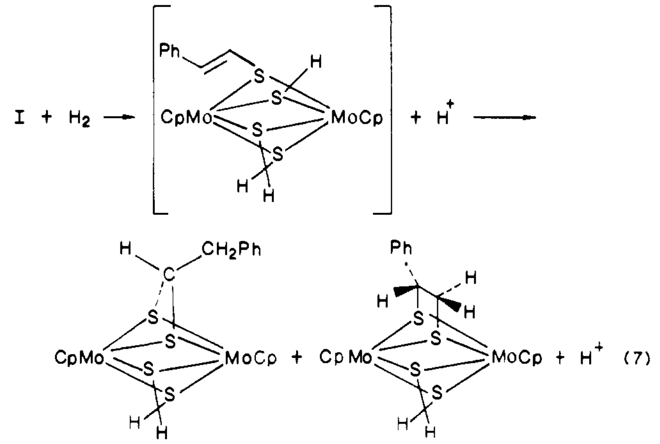
Reactivity of I with Hydrogen. The catalytic hydrogenation of β-bromostyrene to ethylbenzene has been observed in the presence of $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ in chloroform solution at 70 °C (1–2 atm of hydrogen). NMR studies of a solution containing 3 equiv of substrate per mol of catalyst establish that the reaction proceeds through the initial formation of I. A second intermediate was also observed at a latter stage of the reaction and was tentatively identified as complex IV, eq 5. The identity of IV has been confirmed by its independent synthesis from $(CpMoS)_2S_2CH_2$ and (1-bromoethyl)benzene. The product, which is isolated as an analytically pure purple powder in 88% yield, shows ^1H NMR characteristics which are identical with those of the intermediate detected in the hydrogenation reaction. A characteristic methyl doublet at 1.47 ppm and a quartet at 2.95 ppm are observed as expected for the new ligand. The chiral carbon center in the molecule results in inequivalent cyclopentadienyl ligands which are represented by singlets at 6.37 and 7.07 ppm. Chemical shifts for cyclopentadienyl ligands near 7 ppm are characteristic of cationic derivatives in this series of molybdenum dimers.[1,2] The mass spectrum of IV shows a parent ion for the cation and a fragmentation pattern consistent with the proposed formulation. Cyclic voltammetric data show two reversible reductions at −0.32 and −1.21 V vs. SCE which are also typical of cationic derivatives of this structural class.[1,2,8]



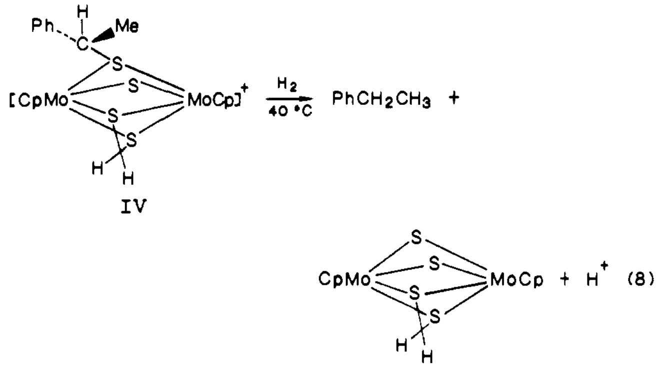
I IV

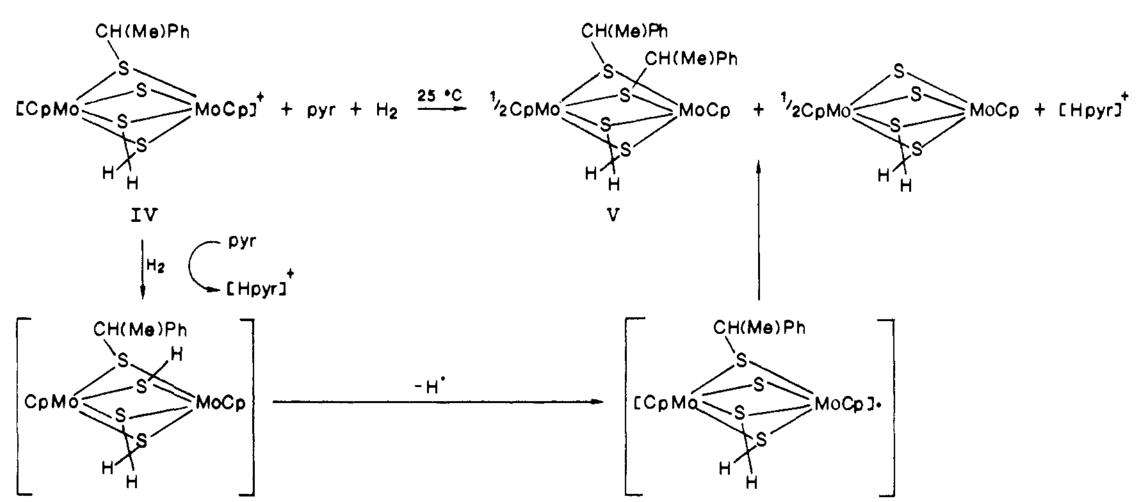
The reaction of I with hydrogen, shown in eq 5, contrasts markedly with that of the isomeric protonated phenylacetylene adduct which reacts to form a neutral complex with a 1,1-dithiolate ligand, reaction 6. It seems likely that the two cations I and II initially react with hydrogen in similar ways and that both reactions proceed through initial formal hydride addition to form an intermediate with an S–H ligand.[1] The different products of reactions 5 and 6 may be a result of a different orientation of intramolecular addition of the S–H ligand to the carbon–carbon double bond. In reaction 7, the 1,2-dithiolate product is expected to be favored sterically over the unobserved 1,1-dithiolate bridged derivative since the benzyl substituent in the latter extends toward a cyclopentadienyl ligand of the dimer. We have established in independent experiments that the 1,2-dithiolate product undergoes a further reaction with acid to form the observed product, complex IV.[12] As indicated, hydrobromic acid is proposed to be present in the reaction system of eq 7 as a result of the interaction of cation I with molecular hydrogen.





Reactivity of IV with Hydrogen. Complex IV reacts with an atmosphere of hydrogen in chloroform solution at 40 °C to form ethylbenzene as shown in reaction 8. Because the hydrogenolysis products are consistent with the overall heterolytic cleavage of the hydrogen molecule, we have attempted to determine the effect of base on the course of reaction 8. The addition of an equivalent of pyridine to this reaction resulted in the rapid formation at room temperature of neutral Mo(III) and Mo(IV) products which are derived from the reduction of the cation and the disproportionation of the neutral mixed valence dimer. The products observed in this base-promoted reaction of IV with H_2 are shown in eq 9. The observations that (1) pyridinium ion is formed in reaction 9 and that (2) no reaction between IV and pyridine occurs under these conditions in the absence of hydrogen suggest that a heterolytic

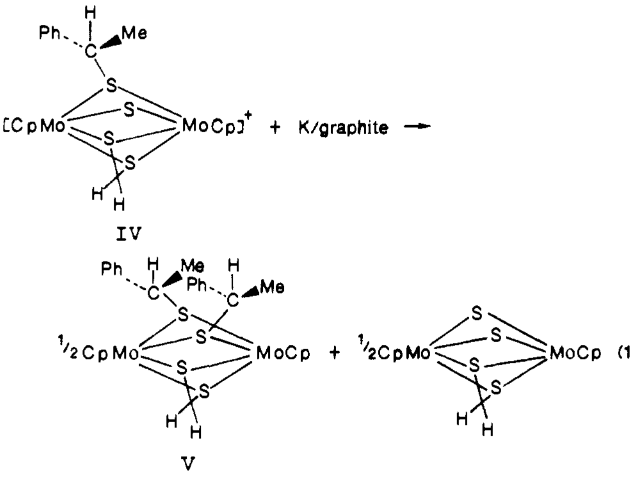




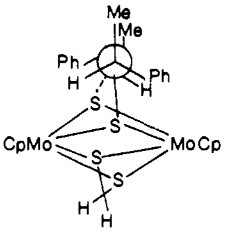
(9)

cleavage of the hydrogen molecule precedes the reduction of the dimer (reaction 9). In the above scheme we have shown, for the sake of clarity, the *formal* loss of a hydrogen atom from an intermediate S–H complex. A likely pathway for this transformation involves electron transfer from the hydrosulfido complex to cation IV followed by deprotonation of the oxidized intermediate.

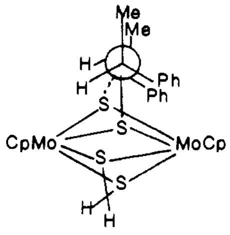
The identity of the final molybdenum(III) product in reaction 9 with two phenylethylthiolate ligands, V, has been confirmed. The complex has been synthesized by an alternate reduction reaction, reaction 10, isolated as a brown powder in 41% yield (theoretical yield, 50%) and characterized by spectral data. The product exhibits a complicated ^{1}H NMR spectrum which indicates the presence of two diastereoisomers (Figure 4). For example, two sets of cyclopentadienyl resonances are observed in a ratio of 2:3, a singlet at 5.19 ppm and a pair of singlets at 4.65 and 5.78 ppm. Other resonances are assigned in the Experimental Section. The data are consistent with two possible orientations of the two chiral carbon centers in the molecule, such as those shown below,[13] in which isomer B accounts for the inequivalent cyclopentadienyl ligands.



(10)



VA



VB

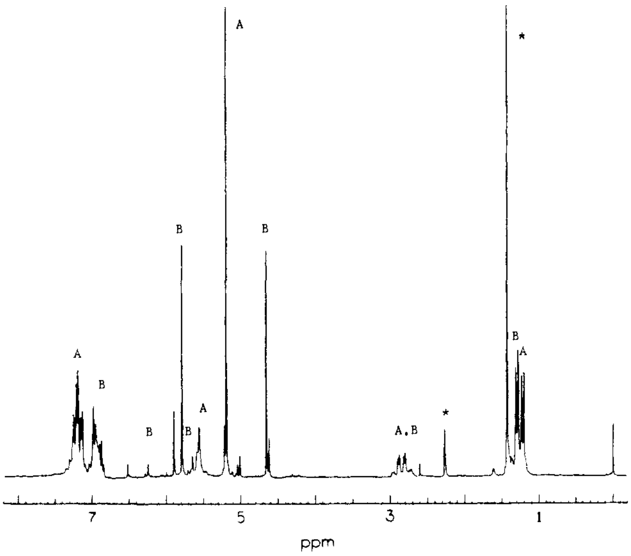
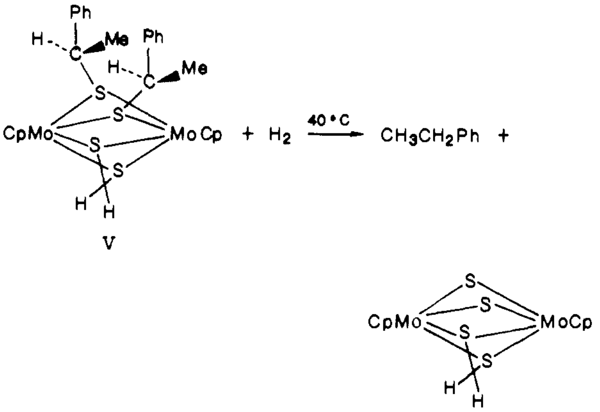


Figure 4. 90-MHz ^{1}H NMR spectrum of $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH(Ph)Me)_2$, V. Resonances corresponding to diastereosmers A and B are indicated. Assignments are made in the Experimental Section. Resonances marked by asterisks are from solvent impurities.

Although the neutral molybdenum(III) complex V does not appear to react with hydrogen under the room temperature conditions of reaction 9, the complex is slowly hydrogenolyzed in chloroform solution at 40 °C to form ethylbenzene (reaction 11). The rate of the reaction is qualitatively similar to that of the hydrogenolysis of the cation IV at this temperature. In fact,



(11)

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(12) The 1,2-dithiolate bridged product is in equilibrium with $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ and free styrene in solution.[10] Hydrobromic acid readily adds to styrene to form 1-bromoethylbenzene. As reported above, this organic halide reacts with the molybdeum dimer to form cation IV.

(13) For the sake of clarity, Newman projections are shown for isomers of complex V which contain both thiolate substituents in axial positions. It is likely that the substituents are actually in equatorial positions in order to minimize unfavorable steric interactions.

when the reaction of IV with hydrogen at 40 °C is monitored by NMR, resonances which are consistent with the presence of small amounts of complex V are observed. It therefore appears that the reduction and disproportionation of cation IV may be intermediate steps in the unusual carbon–sulfur bond hydrogenolysis reaction of eq 8. It has not been established at this time, however, that this is the only pathway which is operative in the catalytic reduction of β-bromostyrene in these systems.

The reaction of a tetrakis(thiolate)-bridged molybdenum(III) dimer, such as V, with hydrogen has not been observed previously, and in fact was considered unlikely because of the absence of sulfido ligands as potential reactive sites.[14] The addition of an equivalent of $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$, which has been found to function as a hydrogen transfer reagent in other intermolecular reactions,[11] did not have a significant effect on the initial rate of reaction 11. Further studies on the reactivity of V and related derivatives with hydrogen are in progress.

Summary. The reaction of β-bromostyrene with $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ results in the formation of a cationic complex with a bridging β-phenylvinylthiolate ligand, I. The cation I undergoes a complex reduction chemistry, both with electron donors and with molecular hydrogen. Our investigations of the reactions of I with hydrogen under mild conditions have led to the identification of intermediates in the catalytic conversion of bromostyrene to ethylbenzene promoted by $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$. The studies indicate that the reductive cleavage of the carbon–halogen bond proceeds through the stepwise formation and hydrogenolysis of carbon–sulfur bonds. These complexes significantly expand the scope of homogeneous systems which effect carbon–sulfur bond hydrogenolysis.[15] They serve as useful models for probing mechanistic possibilities of the heterogeneous molybdenum sulfide surfaces used in hydrotreating catalysts;[16] in particular, the reactivity of the cationic complexes offers insight into the possible role of acid promoters in the heterogeneous systems.[17]

Experimental Section

^1H and ^{13}C NMR instrumentation are described in the preceding paper.[1] Mass spectra were measured on a VG Analytical 7070EQ-HF tandem mass spectrometer by using FAB or EI techniques. In the FAB spectra, thioglycerol was used as the matrix. EPR spectra were recorded on a Varian E-109 X-band spectrometer. Cyclic voltammetry was carried out as described previously.[1] Potentials were checked against the ferrocene couple with a potential of +0.42 V vs. SCE. The solvent in the electrochemical studies was dry acetonitrile with 0.1 M $(n\text{-}Bu)_4NBF_4$ as supporting electrolyte. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

$(CpMo\mu\text{-}S)_2S_2CH_2$ was synthesized following literature methods.[10] Dichloromethane was distilled from P_2O_5 under nitrogen. THF was distilled from CaH_2 under nitrogen. Acetonitrile was distilled from P_2O_5 and then from NaH under N_2 before storage in a nitrogen atmosphere glove box. Chloroform was passed through an alumina column before use. Zinc chloride was dried by reflux in thionyl chloride. All other reagents and solvents were used as received. Potassium graphite was purchased from Alfa. Schlenk techniques were used in the synthetic procedures, and all products were stored under nitrogen.

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCHCH(Ph))]Br$, I. $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ (200 mg, 0.48 mmol) was dissolved in 40 mL of THF in a 100-mL Schlenk flask fitted with a rubber septum. After a nitrogen flush, β-bromostyrene (0.1 mL, 0.8 mmol) was added by syringe under nitrogen at room temperature. The solution was stirred at room temperature for 2 h. At this point, the product, which is insoluble in THF, was present as a dark precipitate. Solvent was removed under vacuum, and the remaining dark solid was redissolved in methanol and filtered through a fine frit in air to remove a small amount of starting material. Solvent was removed from the resulting burgundy solution to give a purple solid. This was redissolved in dichloromethane and filtered on a medium frit to remove a brown solid. Excess hexanes were then added to precipitate the product as a pastel purple microcrystalline solid. The product was filtered and washed with hexanes until the washings were colorless. Since the product is slightly air sensitive it was stored in an inert atmosphere glove box: yield 257 mg (80%); MS (FAB) 567 (P of cation), 521 ($P\text{-}SCH_2$), 418 ($P\text{-}SCH_2\text{-}CHCH(Ph)$), 386, 355, 323; ^1H NMR ($CDCl_3$) δ (ppm) 7.26 (m, 5, phenyl), 7.04 (s, 10, Cp), 6.63 (d, 1, J = 15 Hz, $SC\mathit{H}{=}$), 5.77 (d, 1, J = 15 Hz, $SCHC\mathit{H}Ph$), 4.81 (s, 2, S_2CH_2); ^{13}C NMR ($CDCl_3$) δ (ppm) 142.8 ($S{-}C{=}$), 134.2 ($C{-}C_{Ph}$), 129.5, 129.0, 126.8 (Ph), 122.2 ($={C}{-}Ph$), 103.9 (Cp), 51.6 (S_2CH_2); $E_{1/2}$, V vs. SCE −0.26 (ΔE_p = 84 mV), −1.13 (ΔE_p = 80 mV), E_a = +0.82 (irrev), +1.04 (ΔE_p = 140 mV). Anal. Calcd for $C_{19}H_{19}BrMo_2S_4$: C, 35.25; H, 2.96; S, 19.81. Found: C, 34.98; H, 3.07; S, 19.69.

X-ray Diffraction Study of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCHCH(Ph))]Br$, I. Crystals were obtained by slow evaporation of a chloroform solution of I. Details of the crystal data, experimental conditions, and a summary of solution and refinement details are given in Table IV.

In the model used for the block-cascade least-squares refinement, all phenyl and cyclopentadienyl rings were treated as rigid groups. Hydrogen atoms were not included. The thermal parameters of all the atoms including the highly disordered oxygen of the H_2O solvate were treated anisotropically.

Attempted Reactions of I with Nonbasic Nucleophiles. Complex I (80 mg, 0.12 mmol) was combined with 5 mL of CH_3CN and 10 mL of CH_3OH. The purple solution was degassed and stirred under nitrogen at room temperature. No reaction occurred over 4 days, nor was any reaction observed after heating at 40 °C for 2 days.

Pyridine (1 equiv) was added to I in $CDCl_3$ at 25 °C. Monitoring the reaction by NMR showed no evidence for reaction over a period of several days.

Synthesis of $(CpMo)_2(S_2CH_2)(\mu\text{-}SCHCH(Ph))_2$, III, by Reaction of I with Sodium Methoxide. Complex I (83.0 mg, 0.13 mmol) and solid sodium methoxide (7.5 mg, 0.14 mmol) were combined with 10 mL of THF. After the slurry was degassed, it was stirred under N_2 at 40 °C. After 2 days, the color had changed to a dark blue-green. Solvent was collected by vacuum distillation. No organic products were detected in the solvent by NMR. Complex III was extracted with diethyl ether and purified on an alumina column with dichloromethane eluent: yield 40 mg (46%); ^1H NMR ($CDCl_3$) δ (ppm) 5.62 (s, 2, S_2CH_2), 6.68 (s, 10, Cp), 6.06 (d, 1, J = 15.2 Hz, CH), 6.56 (d, 1, J = 15.2 Hz, CH), 7.16 (m, 5, Ph); mass spectrum (EI), m/e (assignment) 672 (P^+), 626 ($P^+ - SCH_2$), 568 ($P^+ - CHCH(Ph)$), 521 ($P^+ - CHCH(Ph), - SCH_2$), 464 ($P^+ - 2CHCH(Ph)$), 418 ($P^+ - 2CHCH(Ph), - SCH_2$). Anal. Calcd for $C_{27}H_{26}Mo_2S_4$: C, 48.36; H, 3.91; S, 19.12. Found: C, 47.92; H, 3.97; S, 19.23.

Reaction of I with $NaSCH_3$. Complex I (16 mg, 0.024 mmol) and solid sodium methylthiolate (2.0 mg, 0.024 mmol) were placed in an NMR tube as a slurry in deuterated THF. The slurry was degassed, sealed under N_2, and heated at 40 °C. After 2 weeks, the solution color had changed to a blue-green, and the spectra were identical with those recorded for the analogous experiment with sodium methoxide.

Reaction of I with $(CH_3CH_2)_3N$. Complex I (48 mg, 0.074 mmol) was dissolved in 35 mL of methylene chloride in a 100-mL Schlenk flask. After a nitrogen purge, triethylamine (0.3 μL, 0.074 mmol) was added by syringe. The burgundy solution was stirred under nitrogen at room temperature for 12 h. Solvent was removed to give a red-brown solid. This was washed with methanol, and the remaining solid was purified by chromatography on alumina with methylene chloride eluent. Complex III and the previously reported complex $(CpMo\ \mu\text{-}S_2CH_2)_2$[10] were the major products. $(CpMo\mu\text{-}S)_2S_2CH_2$ was also observed. The methanol soluble portion was also chromatographed. This consisted mainly of unreacted starting material.

Reaction of I with $NaBH_4$. Complex I (16 mg, 0.025 mmol) and $NaBH_4$ (1.4 mg, 0.037 mmol) were placed in an NMR tube with 0.5 mL of THF-d_8. After degassing, the slurry was sealed under nitrogen. the reaction proceeded at room temperature to give complex III and $(CpMo\mu\text{-}S)_2S_2CH_2$. No SH resonances were observed throughout the experiment.

Reaction of I with CH_3CH_2MgBr. Complex I (100 mg, 0.16 mmol) in 40 mL of THF was placed in a 100-mL Schlenk flask fitted with a rubber septum. After a nitrogen flush, the slurry was cooled to −78 °C, and CH_3CH_2MgBr in THF solution (0.1 mL, 1.5 equiv) was added by syringe. Within 1 min the solution color turned red-brown. The solution was slowly warmed to room temperature with stirring. After 1 h solvent was removed under vacuum. Chromatography on alumina with methylene chloride eluant yielded $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_2CH_3)(\mu\text{-}SCHCH(Ph))$: yield 64 mg (68%); ^1H NMR ($CDCl_3$) δ (ppm) 0.89 (t, 3, CH_3), 1.82 (q, 2, SCH_2), 5.58 (s, 2, S_2CH_2), 5.69 (s, 10, Cp), 6.06 (d, 1, J = 15.2 Hz, β-H), 6.56 (d, 1, J = 15.2 Hz, α-H), 7.17 (m, 5, Ph); mass spectrum (EI), m/e (assignment) 596 (P), 567 ($P - C_2H_5$), 521 ($P - C_2H_5, -SCH_2$), 493 ($P - CHCH(Ph)$), 465 ($P - C_2H_5, -CHCH(Ph)$,

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(14) DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1981**, *103*, 3429.

(15) Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 3710.

(16) (a) For a recent review, see: Grange, P. *Catal. Rev. - Sci. Eng.* **1980**, *21*, 135. Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (b) Massoth, F. E. *J. Catal.* **1977**, *47*, 316. (c) Kilanowski, D. R.; Teeuwen, H.; de Beer, V. H. J.; Gates, B. C.; Schuit, G. C. A.; Kwart, H. *J. Catal.* **1978**, *55*, 129. (d) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128.

(17) (a) Valyon, J.; Schneider, R. L.; Hall, W. K. *J. Catal.* **1984**, *85*, 277. (b) Segawa, K.; Hall, W. K. *J. Catal.* **1982**, *76*, 133; **1982**, *77*, 221.

-SCH$_2$). Anal. Calcd for $C_{21}H_{24}Mo_2S_4$: C, 42.28; H, 4.06; S, 21.50. Found: C, 42.09; H, 3.92; S, 21.34.

Reaction of I with CH$_3$Li. Complex I (74 mg, 0.11 mmol) was combined with 40 mL of THF in a 100-mL Schlenk flask fitted with a rubber septum. After a nitrogen flush, 0.16 mL (~2 equiv) of CH$_3$Li in THF solution were syringed into the slurry. After 2 h, the solution was homogeneous and had changed to a red-brown color. Solvent was removed under vacuum, and the red-brown solid was chromatographed on a 10-cm alumina column with methylene chloride/hexane eluent. The first fraction was $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCHCH(Ph))$: yield 33 mg (49%) [subsequent fractions were uncharacterized decomposition products]; ^{1}H NMR (CDCl$_3$) δ (ppm) 1.51 (s, 3, SCH$_3$), 5.53 (s, 2, S$_2$CH$_2$), 5.64 (s, 10, Cp), 6.00 (d, 1, J = 15.2 Hz, β-H), 6.49 (d, 1, J = 15.2 Hz, α-H), 7.13 (m, 5, C$_6$H$_5$); mass spectrum (EI), *m/e* (assignment) 582 (P), 567 (P – CH$_3$), 522 (P – CH$_3$, -SCH$_2$), 480 (P – CHCH(Ph)), 418 (P – CH$_3$, -SCH$_2$, -CHCH(Ph)). Anal. Calcd for $C_{20}H_{22}Mo_2S_4$: C, 41.24; H, 3.81; S, 22.01. Found: C, 41.38; H, 3.73; S, 22.17.

Reaction of I with PhZnCl. Dry ZnCl$_2$ (48 mg, 0.35 mmol) was weighed in a glove box and placed in a 100-mL Schlenk flask. THF (10 mL) was added, and the solution was removed from the glove box and cooled to –77 °C. Phenyllithium (0.16 mL, ~1.5 equiv) was added by syringe through the rubber septum. The solution was warmed to room temperature for 10 min after which the temperature was returned to –77 °C. Complex I (130 mg, 0.20 mmol) was added in solid form under an N$_2$ stream, and the solution color immediately changed to red-brown. The solution was warmed slowly to room temperature and stirred for 1 h. Solvent was removed under vacuum, and the resulting red-brown solid was chromatographed on alumina with methylene chloride eluent. The first fraction proved to be $(CpMo)_2(S_2CH_2)(\mu\text{-}SPh)(\mu\text{-}SCHCH(Ph))$: yield 95 mg (74%); ^{1}H NMR (CDCl$_3$) δ (ppm) 5.48 (s, 2, S$_2$CH$_2$), 5.75 (s, 10, Cp), 6.06 (d, 1, J = 15.2 Hz, β-H), 6.64 (d, 1, J = 15.2 Hz, α-H), 6.98 (m, 5, S(Ph)), 7.20 (m, 5, Ph); mass spectrum (EI), *m/e* (assignment) 644 (P), 598 (P – SCH$_2$), 521 (P – SCH$_2$, Ph), 492 (P – SCH$_2$, -CHCH(Ph)), 418 (P – SCH$_2$, -CHCH(Ph), -(Ph)), 386 (P – S$_2$CH$_2$, -(Ph), -CHCH(Ph)). Anal. Calcd for $C_{25}H_{24}Mo_2S_4$: C, 46.58; H, 3.76; S, 19.89. Found: C, 46.64; H, 3.63; S, 19.90.

Reduction of I with Potassium Graphite. Complex I (157 mg, 0.24 mmol) was placed in a 100-mL, round-bottom flask. Further manipulations were carried out in a nitrogen atmosphere glove box. Approximately 1.3 equiv of potassium graphite (29% K) were added with 10 mL of THF. The slurry was stirred at room temperature for 20 min at which time the mixture was a homogeneous purple-brown solution. The solution was filtered through a glass wool plug, and solvent was removed under vacuum to give a brown solid. This was exposed to air and chromatographed on alumina by using methylene chloride eluent. The first fraction contained complex III: yield 36 mg (22%). A second fraction yielded a pink solid of unknown structure but with a tetrameric formulation $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCHCH(Ph))]_2$ (yield 21 mg (15%; mass spectrum (FAB), *m/e* (assignment) 1133 (P), 581 (P/2 + CH$_2$), 567 (P/2), 522 (P/2 – SCH$_2$), 433 (P/2 – SCHCH(Ph)), 419 (P/2 – SCH$_2$, -CHCH(Ph)); ^{1}H NMR (CDCl$_3$) δ (ppm) 5.58 (s, 10, Cp), 6.39 (s, 10, Cp), 7.17 (m, 10, Ph). Several unassigned resonances between 5 and 7 ppm are attributed to vinyl protons and to S$_2$CH$_2$ groups. A third blue fraction was identified by NMR as $(CpMo\text{-}\mu\text{-}S)_2S_2H_2$ which decomposed during chromatography. Methanol eluted a fourth fraction which was characterized by NMR as starting material, complex I: yield 26 mg (17%).

Catalytic Hydrogenation of β-Bromostyrene to Ethylbenzene. $(CpMo\mu\text{-}S)_2S_2CH_2$ (15 mg, 0.03 mmol) and β-bromostyrene (12 μL, 0.1 mmol) were placed in an NMR tube with 0.5 mL of CDCl$_3$. The solution was degassed and sealed under 450 mm of hydrogen. The solution color turned a burgundy-red immediately upon addition of the reagents. At this point, complex I was the only molybdenum complex observed by NMR. After 24 h at 70 °C, resonances due to complex IV and ethylbenzene were observed. After 1 week all β-bromostyrene had been converted to ethylbenzene.

Reaction of I with H$_2$. Complex I (15 mg, 0.024 mmol) was dissolved in 0.5 mL of CDCl$_3$ in an NMR tube. After degassing, the tube was sealed under 450 mm of H$_2$ and heated to 40 °C. On addition of hydrogen, NMR resonances of complex I broaden considerably. Intermediates are not readily identified during the course of the reaction. After 2 weeks the reaction was complete, and resonances of ethylbenzene and $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ were observed.

Reaction of I with H$_2$ in the Presence of Pyridine. Complex I (15 mg, 0.024 mmol) was combined with pyridine (2.2 μL, 0.027 mmol) and 0.5 mL of deuteriochloroform in an NMR tube. After degassing, the solution was sealed under 450 mm of hydrogen and placed at room temperature. Within 2 days, complex I had disappeared to give pyridinium ion, $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ and complex III. No further reaction was observed at room temperature. Upon heating to 70 °C, the reaction proceeded to give ethylbenzene and more $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$.

Synthesis of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH(Me)Ph)]Br$, IV. $(CpMo\mu\text{-}S)_2S_2CH_2$ (160 mg, 0.34 mmol) was dissolved in 40 mL of chloroform in a 100-mL Schlenk flask fitted with a rubber septum. After a nitrogen flush, 1-bromoethylbenzene (0.1 mL, 0.73 mmol) was added by syringe. The flask was placed in a 40 °C oil bath with stirring for 18–20 h over which time the color changed to a deep purple. Solvent was removed to give an oily purple product. This was redissolved in methanol and filtered to remove any starting material. Solvent was again removed and the purple product was redissolved in a minimum of methylene chloride. Hexanes were added to precipitate the product as a pastel purple microcrystaline solid. The product was washed with excess hexane and dried under vacuum: yield 0.20 g (88%); ^{1}H NMR (CDCl$_3$) δ (ppm) 1.47 (d, 3, Me), 2.95 (q, 1, SCH), 4.73 (q, 2, S$_2$CH$_2$), 6.37 + 7.07 (s, 10, Cp), 7.32 (m, 5, Ph); ^{13}C NMR DEPT (CDCl$_3$) δ (ppm) 143.4 (C–C_{Ph}), 128.9, 128.3, 126.8 (C–H_{Ph}), 103.3, 103.1 (Cp), 51.6 (S$_2$CH$_2$), 48.8 (S–*C*), 24.6 (Me); mass spectrum (FAB), *m/e* (assignment) 569 (P), 467 (P – CH(CH$_3$)(Ph)) 418 (P–SCH$_2$, -CH(Me)(Ph)); $E_{1/2}$, V vs. SCE –0.28 (ΔE_p = 75 mV), –1.17 (ΔE_p = 75 mV), E_a = +1.44 (irrev). Anal. Calcd for $C_{19}H_{21}BrMo_2S_4$: C, 35.14; H, 3.26; S, 19.75. Found: C, 35.18; H, 3.37; S, 19.84.

Synthesis of $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH(Me)Ph)_2$, V, by Reduction of IV. Complex IV (135 mg, 0.21 mmol) was placed in a 100-mL, round-bottom flask. In an inert atmosphere glovebox, approximately 1.5 equiv of potassium graphite and 40 mL of THF were added, and the slurry was stirred at room temperature. Within 5 min, the solution color changed to a green-black color. After 15 min, 30 mg more of IV was added to react with any anion ([IV]$^-$) that may have formed. This brought about no color change. The dark green solution was stirred at room temperature for an additional 10 h. The solution was exposed to air, and solvent was removed to give a dark product. Chromatography on alumina with methylene chloride eluent gave a yellow-brown, a blue, and a purple-brown band. The first of these is complex V. This was further purified on a second alumina column with THF eluent: yield 58 mg (41%); ^{1}H NMR (CDCl$_3$) δ (ppm) isomer A 6.95 (m, 12, Ph), 6.27, 5.62, (2 d, 2, J = 2.9 Hz, S$_2$CH$_2$), 5.78, 4.65 (2 s, 10, Cp), 2.86 (q, 1, J = 7.0 Hz, SCH), 1.27 (d, 3, J = 7.0 Hz, Me); isomer B 7.18 (m, 12, Ph), 5.55 (s, 2, S$_2$CH$_2$), 5.19 (s, 10, Cp), 2.84 (q, 1, J = 7.0 Hz, SCH), 1.24 (d, 3, J = 7.0 Hz, Me; mass spectrum (FAB), *m/e* (assignment) 675 (P), 569 (P – CH(Me)(Ph)), 465 (P – 2CH(Me)(Ph)), 419 (P – 2CH(Me)(Ph), -SCH$_2$).

Reaction of IV with Sodium Methoxide. Complex IV (14 mg, 0.022 mmol) and NaOCH$_3$ (1.2 mg, 0.022 mmol) were dissolved in 0.5 mL of CDCl$_3$ in an NMR tube. After degassing, the solution was sealed under nitrogen. After 2 days at room temperature the solution color had turned dark purple, and resonances due to complex V and $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ were apparent in the NMR spectrum. Heating at 40 °C brought about no further change. The above products were isolated by chromatographing on alumina with methylene chloride eluent.

Reaction of IV with CH$_3$Li. Complex IV (104 mg, 0.16 mmol) and 40 mL of THF were placed in a 100-mL Schlenk flask fitted with a rubber stopper. After having been flushed with nitrogen, the purple solution was cooled to –77 °C (CO$_2$/acetone). A stock THF solution of methyllithium (0.15 mL, 1.5 equiv) was added by syringe. The solution color immediately turned brown. The solution was warmed to room temperature with stirring. After 15 minutes, the solution was filtered in air, and solvent was removed to give an orange-brown solid. This was chromatographed on alumina with methylene chloride eluent to remove a single red-brown band. Solvent was removed under vacuum. The red-brown solid was redissolved in a minimum of methylene chloride and precipitated out of solution by excess hexane to give the orange-brown complex $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}SCH(Me)Ph)$: yield 64 mg (68%). Two isomers which contain an axial and equatorial methylthiolate ligand, respectively, were observed by NMR: ^{1}H NMR (CDCl$_3$) δ (ppm) 7.25, 6.94 (2 m, 5, Ph), 5.701, 5.702 (2 s, 10, Cp), 5.13, 5.11 (2 s, 10, Cp), 5.58, 5.50 (2 d, 2, J = 1.0 and 1.0 Hz, S$_2$CH$_2$), 2.86, 2.73 (2 q, 1, J = 7.0 Hz and 7.0 Hz, C*H*(Me)(Ph)), 1.58, 1.43 (2 s, 3, SMe), 1.30, 1.27 (2 d, 3, J = 7.0 and 7.0 Hz, CH(*Me*)(Ph)). Anal. Calcd for $C_{20}H_{24}Mo_2S_4$: C, 41.10; H, 4.13; S, 21.94. Found: C, 41.23; H, 4.11; S, 21.98.

Reaction of IV with H$_2$. Complex IV (13 mg, 0.020 mmol) was dissolved in 0.5 mL of CDCl$_3$ in an NMR tube. The burgundy solution was degassed and sealed under hydrogen. ^{1}H NMR resonance of IV broadened under H$_2$, and small amounts of complex V and $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ were detected. No further reaction occurred at room temperature. After having been heated at 40 °C for 3 days, the reaction went to completion to give ethylbenzene, $(CpMo\mu\text{-}S)_2S_2CH_2$, and a small amount of unidentified red-brown precipitate.

Reaction of IV with H$_2$ and Pyridine. Complex IV (14 mg, 0.022 mmol) and pyridine (1.8 μL, 0.022 mmol) were dissolved in 0.5 mL

$CDCl_3$ in an NMR tube. After degassing, the solution was sealed under hydrogen and placed at room temperature. For comparison, a second tube was prepared containing only complex IV (14 mg, 0.022 mmol) dissolved in 0.5 mL of $CDCl_3$. This solution was also degassed and sealed under hydrogen. after 6 h at room temperature, the NMR spectrum of the first solution showed that the pyridine had been converted to pyridinium ion and that the molybdenum species consisted of the methanedithiolate bridged dimer and complex V. A broad peak at 6.17 ppm was also present, but disappeared after several days. No further reaction took place over the period of 1 week–no SH resonance were observed. The blue-green solution was then placed at 40 °C. After 2 weeks, reaction was complete to give $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ and ethylbenzene with some insoluble brown solids.

After 6 h at room temperature, the NMR spectrum of the second tube showed broadened resonances of the starting complex IV and very small amounts of the methanedithiolae bridged dimer and of complex V. Heating the solution at 40 °C for 2 weeks gave the same products as observed above.

Reaction of $(CpMo)_2(S_2CH_2)(\mu\text{-}SCH(Me)Ph)_2$, V, with Hydrogen. Complex V (10 mg, 0.015 mmol) was dissolved in 0.5 mL of deuteriochloroform in an NMR tube. The solution was degassed, sealed under 450 mm of hydrogen, and placed at 40 °C. Hydrogenolysis proceeded to 62% completion in 6 days to give ethylbenzene and $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$. The reaction slowly went to completion after 1 month.

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Supplementary Material Available: Anisotropic temperature factors (1 page); calculated and observed structure factors for the crystal structure of I (21 pages). Ordering information can be found on any current masthead page.

Topological Enhancement of Basicity: Molecular Structure and Solution Study of a Monoprotonated Catenand

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Abstract: The molecular structure of a proton catenate has been determined by X-ray crystallography. It is very similar to that of the copper(I) catenate, the two 2,9-diphenyl-1,10-phenanthroline fragments being entwined, contrary to the situation in the free ligand. A detailed ^1H NMR study in solution has been performed, demonstrating the entwined topography of the system either for the mono- or the diprotonated molecule. The basicity of the catenand is several orders of magnitude higher than that of its open chain analogue, this enhancement of basicity being due to topological factors only.

Interlocked macrocyclic ligands represent a new class of coordinating molecules whose first member **1** has recently been synthesized[1] (see Chart I). The catenand **1** is able to coordinate a large variety of transition metals, low oxidation states being highly stabilized.[2-5] Other species like Li^+ form complexes with **1** in which the two 2,9-diphenyl-1,10-phenanthroline (dpp) fragments are entwined while coordinating to the cation,[5] such a topography being typical of all the catenates $\mathbf{1}.M^{n+}$ prepared up to now. We wish to report that H^+ leads also to the same type of geometry, either in the solid state—as shown by X-ray crystallography—or in solution. In addition, for topological reasons, the monoprotonated catenand is surprisingly stabilized with respect both to the free ligand and to the diprotonated species. For comparison purposes, protonation studies on the open chain analogue **2** have also been performed.

Experimental Section

Preparation of the Proton Catenate. $\mathbf{1}^1$ (50 μmol, 57 mg) is dissolved in 10 mL of CH_2Cl_2, and 4.9 μmol (4.9 mg) of $HClO_4$ in a mixture of CH_3OH and H_2O (4:1) is added at room temperature with stirring. Instantaneously, a bright lemon yellow color appears, indicating a fast protonation reaction of **1**. After standing overnight, the solvent is pumped off under vacuum. The solid residue is redissolved in CH_2Cl_2 (10 mL), and the organic phase is washed 3 times with 10 mL of distilled water. The organic layer is dried over $MgSO_4$, filtered, and evaporated. The yellow solid obtained is pure $[\mathbf{1}\cdot H^+][ClO_4^-]\cdot 2H_2O$ (64 mg, quantitative yield). The compound might be recrystallized from CH_2Cl_2–benzene, affording an analytical sample.

Analytical and spectroscopic data for $[\mathbf{1}\cdot H^+][ClO_4^-]\cdot 2H_2O$ (mp 226–228 °C). Anal. Calcd for $C_{68}H_{73}H_4O_{18}Cl$: C, 64.32; H, 5.67; N, 4.41. Found: C, 64.80; H, 5.69; N, 4.49. Electronic spectrum (CH_2Cl_2) λ_{max} in nm (ϵ) = 270 nm (57 000), 300 (48 000), and shoulder at 340 (34 000).

Incidently, the same compound was made from **1** and $Ni(ClO_4)_2\cdot 6H_2O$ in excess in CH_2Cl_2–CH_3OH (1:1). After an identical workup as that described above, a quantitative yield of $[\mathbf{1}\cdot H^+][ClO_4^-]$, $2H_2O$ is also obtained.

X-ray Study. Crystals were grown from CH_2Cl_2–benzene as bright yellow prisms: $[C_{68}H_{69}N_4O_{12}]^+[ClO_4^-]$, $2C_6H_6$; monoclinic, $P2_1/c$ a = 14.539 (9) Å, b = 20.406 (14) Å, c = 24.852 (17) Å, β = 103.86° (10), U = 7158 Å^3, Z = 4.

The 5048 observed data were collected on an automatic Philips diffractometer. The structure was solved by direct methods using a local program.[6] Two benzene molecules were located on the asymmetric unit. All H atoms appeared on difference Fourier maps. Refinement with anisotropic thermal parameters for heavy atoms and isotropic for H atoms, led to an R factor of 7.0% (R_w = 6.2%). First peak on the last difference series was 0.25 e high.

NMR Spectroscopy. Spectra were obtained by using a Bruker WP-200 operating at a ^1H resonance frequency of 200.13 MHz. Low-

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