were recorded on a Hitachi Model 295 infrared spectrophotometer, ^1H NMR spectra on a Japan Electron Optics Laboratory (JEOL) Model JNM-PS-100 spectrometer, and ^{31}P and ^{13}C NMR spectra on a JEOL Model JNM-PFT-PS-100 Fourier transform spectrometer.

Melting Point and Decomposition Point. They were measured under vacuum. No color change was observed at the melting point, whereas the complex generally turned black with emergence of bubbles at the decomposition point.

Reactions of the Complexes with CO. The gas in a Schlenk type flask containing 41 mg (0.10 mmol) of **1a** dispersed in 3 mL of diethyl ether was evacuated, and then CO was introduced into the flask. Stirring of the mixture for 3 h gave a white precipitate, which was separated by filtration and found to be $Ni(P(c\text{-}Hx)_3)(CO)_3$ from its IR spectrum.[9b,31] α-Pyrrolidone (7.5 μL, 0.098 mmol) was added to the solution as an internal standard, and the amount of succinimide formed by the reaction was determined on the basis of a relative peak area of succinimide to that of α-pyrrolidone in the gas chromatogram and a relative sensitivity of succinimide to that of α-pyrrolidone. The reactions of other complexes with CO were carried out in similar manners.

Thermolysis of Nickel-Containing Cyclic Amide Complexes. A Schlenk type flask containing 45 mg (0.11 mmol) of **1b** was connected to a vacuum line, and the gas in the flask was evacuated. The flask was immersed in an oil bath, which was heated to 230 °C. The color of the complex turned black at the temperature, and sublimination of a white solid was observed. After 1 h the flask was cooled to room temperature, and the GLC analysis of the sublimed product indicated the liberation of 0.069 mmol (63%) of methacrylamide. Thermolysis of **1g** (41 mg, 0.076 mmol) at 230 °C for 1 h gave methacrylamide (0.062 mmol, 82%). The thermolyses of other complexes were carried out in similar manners.

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Characterization of Reactions of Hydrogen with Coordinated Sulfido Ligands

M. Rakowski DuBois,* M. C. VanDerveer, D. L. DuBois, R. C. Haltiwanger, and W. K. Miller

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

Abstract: Complexes of the formula $[(CH_3)_nC_5H_{5-n}Mo(S)SH]_2$, where $n = 0$, 1, and 5, have been prepared by the reaction of hydrogen with several different cyclopentadienylmolybdenum derivatives containing sulfido ligands. These include the insoluble polymeric products $[Me_nCpMoS_x]_y$, resulting from the reaction of elemental sulfur with $[Me_nCpMo(CO)_3]_2$. Excess sulfur in these species is converted to hydrogen sulfide during the course of the reaction with hydrogen. The hydrosulfido complexes have been characterized by spectral methods, and several reactions of these complexes have been studied. The complex $[MeCpMo(S)SH]_2$ catalyzes HD exchange between H_2 and D_2 as well as between H_2 and D_2O. The reduction of elemental sulfur to hydrogen sulfide by H_2 is catalyzed by the SH complexes under mild homogeneous conditions. Ethylene and acetylene react with the complexes to displace hydrogen from the SH ligands and form derivatives with bridging dithiolate ligands. Alkyl- and arylthiols react with the SH complexes to form H_2S and derivatives of the formula $[Me_nCpMo(S)SR]_2$ where R = CH_3, C_2H_5, $i\text{-}C_3H_7$, and C_6H_5. Spectral data suggest that these complexes have the same gross structures as the SH compounds. A single crystal of the derivative with $n = 1$ and R = CH_3 has been characterized by an X-ray diffraction study. The compound crystallizes in the space group $P2_1/c$ with the cell dimensions $a = 7.794$ (3) Å, $b = 14.184$ (7) Å, $c = 7.805$ (2) Å, and $\beta = 100.03$ (3)°. All four sulfur atoms in the complex occupy positions bridging the two metal ions. The *S*-methyl groups are oriented on trans sulfur atoms so as to form a centrosymmetric isomer. The relationship between the chemistry of these new complexes and aspects of proposed mechanisms of the hydrodesulfurization catalysts are discussed.

Introduction

The hydrodesulfurization reaction, which involves the hydrogenolysis of organosulfur compounds, e.g., reactions 1–3, is an

$$RSH + H_2 \rightarrow RH + H_2S \quad (1)$$

$$RSR + 2H_2 \rightarrow 2RH + H_2S \quad (2)$$

$$RSSR + 3H_2 \rightarrow 2RH + 2H_2S \quad (3)$$

important catalytic process in the purification of petroleum products.[1,2] The heterogeneous systems which catalyze these reactions most often contain sulfided molybdenum and cobalt species supported on alumina. The surface composition of the catalysts[3–9] and the sites which participate in catalytic activity[3,9–13] have been the subjects of extensive studies. It is generally agreed that a molybdenum sulfide surface is the catalytic site for the hydrogenolysis reaction.[9–13] On the basis of kinetic and other studies, several workers have proposed mechanisms for the hydrogenolysis of thiophene which involve two types of sites on the sulfided catalyst surface.[10–13] One site is a coordination vacancy on the molybdenum ion which permits interaction of the organosulfur compound with the metal. The second type of sites are the surface sulfide ligands which are proposed to react with molecular hydrogen to form hydrosulfido ligands. The hydrogenolysis reaction involving carbon–sulfur bond rupture and hydrogen atom transfer is proposed to occur between the species adsorbed on these sites.

Despite the mechanistic proposals for the hydrodesulfurization catalysts described above, the reaction of molecular hydrogen with coordinated sulfido ligands in discrete metal complexes to form SH ligands or H_2S has not been observed previously. Known hydrosulfido complexes have most often been prepared by metathesis reactions with HS^- salts or with H_2S.[14–23] Hydrolysis

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Table I. Spectral Data for $[(CH_3)_nC_5H_{5-n}Mo(S)SH]_2$

compd	IR,[a] cm^{-1} ν_{S-H}	IR,[a] cm^{-1} ν_{Mo-S}	NMR,[b] ppm	visible,[c] nm	$\epsilon \times 10^{-3}$, M^{-1} cm^{-1}	mass spec, *m/e*
$[C_5H_5Mo(S)SH]_2$	2410 vw	422 m	−1.44, −1.50 (2s, 2, SH)	694	1.8	450 P − H_2
			6.40 (s, 10, Cp)	511	3.3	419 P − SH
				387	1.4	386 P − 2SH
				315	sh	
$[CH_3C_5H_4Mo(S)SH]_2$	2410 w	427 m	−1.53, −1.60 (2s, 2, SH)	700	2.5	480 P
			2.31 (s, 6, CH_3)	510	3.9	465 P − CH_3
			6.24 (s, 8, Cp)	390	1.7	447 P − SH
				310	sh	414 P − 2SH
$[(CH_3)_5C_5Mo(S)SH]_2$	2410 m	421 m	−2.01, −2.09 (2s, 2, SH)	731	2.1	592 P
			2.24 (s, 30, CH_3)	499	3.2	577 P − CH_3
				437	1.3	560 P − S
				340	sh	542 P − CH_3-SH
						526 P − 2SH

[a] Nujol mulls. [b] Solvent $CDCl_3$. [c] Solvent $CHCl_3$.

of sulfur-containing ligands has also resulted in the formation of SH complexes.[24–29] We report in this paper that elemental hydrogen is dissociated by interaction with the sulfido ligands in several cyclopentadienyl- and methyl-substituted cyclopentadienylmolybdenum complexes, including the simple dimer $[CH_3C_5H_4MoS_2]_2$.[31] The product of each reaction is a dimeric complex with hydrosulfido ligands with the formula $[(CH_3)_nC_5H_{5-n}Mo(S)SH]_2$. The results of our studies of the reactions of the hydrosulfido complexes with hydrogen, with unsaturated molecules, and with some organosulfur compounds are also reported here.

Results and Discussion

Syntheses and Characterization of Complexes. It has been reported previously that the reaction of bis(cyclopentadienylmolybdenum tricarbonyl) with elemental sulfur produced a carbonyl-free solid which could not be purified or identified because of its insoluble nature.[32] We have found that introducing methyl substitution on the cyclopentadienyl ligands enables one to isolate some soluble complexes from this reaction,[31] but a large fraction of the products remains insoluble with variable sulfur content. A chloroform slurry of this insoluble material containing either C_5H_5, $CH_3C_5H_4$, or $(CH_3)_5C_5$ ligands reacts under an atmosphere of hydrogen at 25–75 °C. Almost all solid dissolves to give an intensely colored purple solution. A molybdenum product with the formulation $[(CH_3)_nC_5H_{5-n}Mo(S)SH]_2$ (where $n = 0$, 1, or 5) is isolated from each reaction. Hydrogen sulfide, identified by gas chromatography and mass spectroscopy, is the second product in this reaction. The soluble cyclopentadienylmolybdenum complexes with sulfido and disulfido ligands, $[(CH_3)_nC_5H_{5-n}MoS_2]_2$[31] and $[(CH_3)_5C_5MoS_5]_2$,[31] also react with hydrogen to form the dimeric products with mercaptan ligands formulated above.

Table II. Typical Turnover Frequency Day^{-1} for the Catalytic Hydrogenation of Sulfur[a]

catalyst:[b] $[Me_nCpMo(S)SH]_2$	temp, °C	mol of H_2S produced/mol of catalyst
$n = 1$	25	10
$n = 1$	75	300
$n = 1$	100[c]	800
$n = 0$	75	40
$n = 5$	75	400

[a] Catalytic activity is not constant throughout the period. Rates appear to increase as the solution becomes homogeneous. [b] Catalyst concentration was approximately 10^{-3} M in chloroform, and hydrogen pressure was 1 atm at 77 K. Temperatures are ±3 °C, and turnover frequencies are typical values for these temperature ranges in an initial 24-h period. [c] 1:1 vol $CHCl_3$/toluene was the solvent.

The spectral data for the new derivatives, which are given in Table I, are consistent with the formulation of hydrosulfido complexes. In each NMR spectrum two resonances ~1.5 ppm upfield from Me_4Si are assigned to the SH ligands. The chemical shifts are similar to those of mercaptan ligands in other metal complexes.[15–17,19] These resonances are associated with two different isomers of the complex because they have unequal intensities, ~2:3. No evidence for exchange between these isomers was observed in variable-temperature NMR studies of $[(CH_3)_5C_5Mo(S)SH]_2$ up to 90 °C. In each infrared spectrum of the SH complexes, a broad weak band at 2410 cm^{-1} is assigned to ν_{S-H}. The absorption at 420 cm^{-1} has a lower frequency than those reported for terminally bonded sulfido ligands in molybdenum(V) complexes[33,34] and may be associated with a $M-S_{bridge}$ vibration. The mass spectra of the complexes have envelopes corresponding to the parent ions, and the fragmentation patterns correspond to loss of hydrosulfido and sulfido ligands. The spectral data do not define the structures of these complexes. On the basis of X-ray diffraction data for the structurally related complex $[CH_3C_5H_4Mo(S)SCH_3]_2$, which we will discuss later in this paper, we propose that the hydrosulfido complexes have all four sulfur atoms in bridging positions. While the NMR spectra provide evidence for only two isomers, a number of isomers are possible for a tetrasulfur-bridged structure. Two possible trans isomers, I and II, are related by inversion at a sulfur atom, shown viewed down the M–M vector. Likewise three cis isomers are possible.

Reactions of $[Me_nCpMo(S)SH]_2$ with Hydrogen. When $[CH_3C_5H_4Mo(S)SH]_2$ is stirred under 1–2 atm of hydrogen at 100 °C in toluene, trace amounts of hydrogen sulfide are detected,

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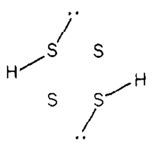

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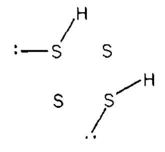


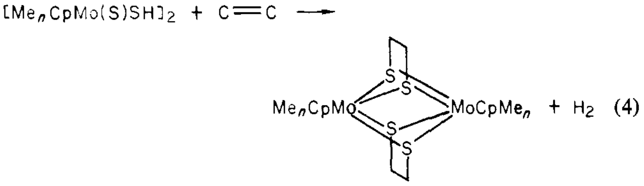
II

but most of the complex can be recovered unchanged. There is no evidence that the addition of a second molecule of hydrogen to the two remaining sulfido ligands in $[CH_3C_5H_4Mo(S)SH]_2$ produces a stable complex. However, the SH complex does catalyze the formation of HD when stirred in benzene solution at 25 °C under an atmosphere of a hydrogen/deuterium mixture. It is likely that this exchange reaction proceeds through a reduced intermediate with two SH and two SD ligands. Under an atmosphere of hydrogen at room temperature the complex $[CH_3C_5H_4Mo(S)SH]_2$ also catalyzes HD exchange with D_2O. This result suggests that protonation of the sulfido ligands or deprotonation of the SH ligands occurs to produce an intermediate with a mixture of SH and SD ligands.

The hydrosulfido complexes catalyze the reduction of elemental sulfur to hydrogen sulfide. The reaction proceeds in $CHCl_3$ solution under pressures of 1–3 atm H_2 and at a temperature of 75 °C. As the reaction proceeds all solids dissolve and the solution becomes homogeneous. The derivatives with methyl-substituted cyclopentadienyl ligands are more active than $[C_5H_5Mo(S)SH]_2$. Typical turnover frequencies per day for batch reactions in the presence of excess H_2 and S_8 are given in Table II. In a reaction with $[(CH_3)_5C_5Mo(S)SH]_2$ in which the hydrogen supply was periodically renewed, no catalyst decomposition was evident after 3000 turnovers.

The conditions required for the catalytic system described here are remarkably mild. In the absence of a catalyst, hydrogen can be bubbled into liquid sulfur at 450–600 °C to form 98–100% H_2S.[35] A number of metal sulfides, including ZnS, MoS_2, and WS_2, have been reported to serve as heterogeneous catalysts for this hydrogenation; these require temperatures ranging from 180–420 °C.[36,37] It is interesting to note that elemental sulfur is an impurity in petroleum products, and a standard Mo–Co hydrodesulfurization catalyst has also been patented as a catalyst for sulfur hydrogenation.[37] This system functions at 260–350 °C and 8 atm H_2.

Reactions of $[Me_nCpMo(S)SH]_2$ with Unsaturated Molecules. The hydrosulfido complexes react quantitatively with excess ethylene at 1 atm and 25 °C. A hydrogen molecule is eliminated from the SH ligands, and this product has been detected by gas chromatography. The organometallic product is the complex with two ethanedithiolate bridges (reaction 4) which has been characterized previously.[38] The hydrosulfido complexes also react with acetylene to eliminate hydrogen and form the ethenedithiolate-bridged complex. A second possible reaction route which would result in the same molybdenum complex would involve S–H addition to the alkyne and subsequent replacement of the resulting hydrocarbon bridge by excess alkyne (reactions 5 and 6). Bridge replacement reactions of this type have been characterized previously for these dimeric molybdenum complexes.[38] However, ethylene, which would be a product of this sequence, was not detected in the reaction products. The presence of base, which is known to catalyze the addition of thiols to acetylenes,[39] did not change the nature of the products.



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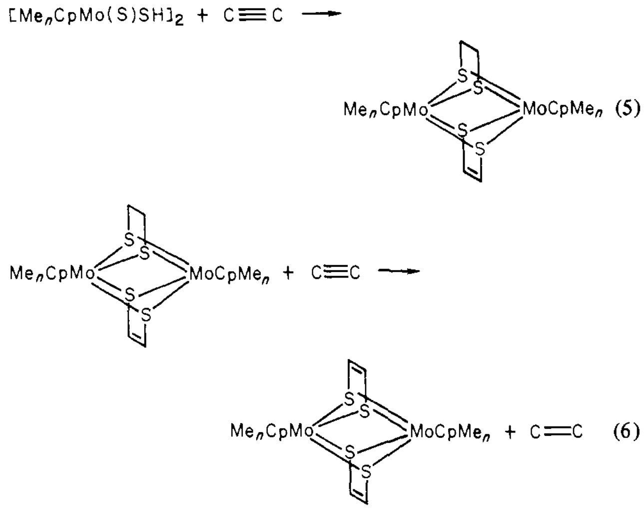
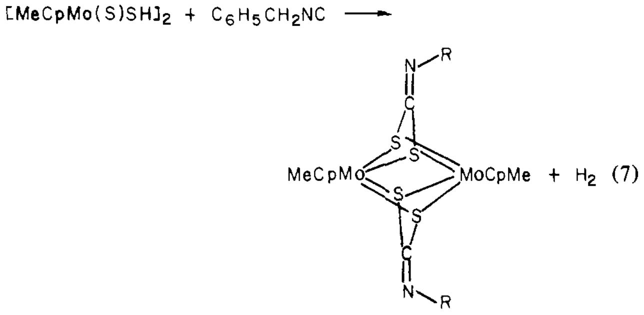


(5)

(6)

$[CH_3C_5H_4Mo(S)SH]_2$ also reacts quantitatively with benzyl isocyanide to form the complex with dithiocarbonimidate bridges (reaction 7). The analogous complex with unsubstituted cyclopentadienyl ligands has been prepared previously by a different method.[40] We have reported previously that no interaction of carbon monoxide with the sulfur ligands in the dithiocarbonimidate complexes has been detected.[40] Similarly, no reaction occurred when the SH complex was purged with CO for 24 h.



(7)

Reactions of $[Me_nCpMo(S)SH]_2$ with Thiols. Alkyl and aryl thiols undergo an exchange reaction with the SH ligands in $[Me_nCpMo(S)SH]_2$ ($n = 0, 1$)[41] according to reaction 8. These

$$[Me_nCpMo(S)SH]_2 + 2RSH \rightarrow [Me_nCpMo(S)SR]_2 + 2H_2S \quad (8)$$

reactions are normally carried out under an atmosphere of hydrogen. In the absence of H_2 some insoluble side products are produced, possibly due to loss of H_2 from the SH ligands and subsequent polymerization. Although some reactions involving facile carbon–sulfur and hydrogen–sulfur bond ruptures have been characterized for these dimeric systems, we have confirmed that in reaction 8 metal–sulfur bonds are broken. Mass spectral data indicate that the labeled compound $[CH_3C_5H_4Mo(^{34}S)^{34}SH]_2$ reacts with C_2H_5SH to form $[CH_3C_5H_4Mo(^{34}S)SC_2H_5]_2$ and $H_2{}^{34}S$. Similar thiolate-exchange reactions have been well characterized in other systems,[42,43] including the iron–sulfur cubane derivatives.[44]

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Table III. Spectral Data for $[(CH_3)_nC_5H_{5-n}Mo(S)SR]_2$, $n = 1, 0$

compd	IR,[a] cm^{-1} ν_{Mo-S}	NMR,[b] ppm	visible,[c] nm	$\epsilon \times 10^{-3}$, $M^{-1}\ cm^{-1}$	mass spec, *m/e*
$[CH_3C_5H_4Mo(S)SCH_3]_2$	418	1.05, 1.56 (s, 6, SCH_3)	687	2.8	508, P
		2.40 (s, 6, CH_3)	506	5.2	493, P – CH_3
		6.34 (m, 8, Cp)	397	1.3	478, P – $2CH_3$
			330	sh	
$[CH_3C_5H_4Mo(S)SC_2H_5]_2$	426	0.65 (2 t, 6, CH_3)	687	2.1	536, P
		1.50 (2 q, 4, $-CH_2-$)	514	3.9	507, P – C_2H_5
		2.46 (2 s, 6, CH_3Cp)	398	1.6	478, P – $2C_2H_5$
		6.38 (m, 8, Cp)	320	sh	
$[CH_3C_5H_4Mo(S)S\text{-}i\text{-}C_3H_7]_2$	420	0.70 (2 d, 12, CH_3)	685	2.6	
		1.90 (m, 2, CH)	514	4.7	564, P
		2.50, 2.55 (2 s, 6, CH_3)	395	1.4	521, P – C_3H_7
		6.41 (m, 8, Cp)	310	sh	478, P – $2C_3H_7$
$[CH_3C_5H_4Mo(S)SC_6H_5]_2$	488	2.46 (s, 6, CH_3)	684	2.7	632, P
	442	6.51 (2 m, 8, Cp)	510	5.2	555, P – C_6H_5
		7.27 (3 m, 10, C_6H_5)	402	sh	489, P – $S_2C_6H_5$
			350	sh	445, P – $S(C_6H_5)_2$
					413, P – $2SC_2H_5$
$[C_5H_5Mo(S)SC_2H_5]_2$	422	0.61 (t, 6, CH_3)	675	2.5	508, P
		1.47 (q, 4, CH_2)	510	5.1	479, P – C_2H_5
		6.48 (s, 10, Cp)	382	1.4	450, P – $2C_2H_5$
			320	sh	

[a] Nujol mulls. [b] Solvent $CDCl_3$. [c] Solvent $CHCl_3$.

Table IV. Positional and Thermal Parameters for the Atoms of $[CH_3C_5H_4Mo(S)SCH_3]_2$

atom	*x*	*y*	*z*	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.12501 (7)	0.00921 (4)	0.13115 (6)	1.88 (3)	2.82 (3)	1.62 (3)	0.12 (2)	−0.60 (2)	−0.21 (2)
S(1)	0.12440 (25)	0.08291 (14)	−0.13897 (23)	2.93 (8)	3.92 (9)	2.26 (7)	−0.53 (7)	−0.29 (6)	0.33 (6)
S(11)	−0.164 (3)	0.0289 (25)	0.151 (3)	1.7 (10)	6.2 (17)	0.9 (8)	−0.8 (10)	0.1 (8)	−1.0 (10)
S(2)	−0.13822 (24)	0.11020 (14)	0.09807 (23)	2.79 (8)	3.55 (9)	2.47 (7)	0.58 (6)	−0.39 (6)	−0.54 (6)
S(22)	0.022 (4)	0.1415 (19)	−0.070 (4)	4.3 (15)	2.1 (11)	3.1 (12)	−0.9 (10)	−3.5 (11)	0.7 (9)
C(1)	0.4230 (10)	0.0115 (5)	0.2390 (10)	2.2 (3)	5.0 (4)	2.4 (3)	0.38 (26)	−1.55 (24)	−0.67 (26)
C(2)	0.3476 (10)	−0.0580 (6)	0.3299 (10)	3.1 (3)	4.3 (4)	3.0 (3)	0.47 (27)	−1.93 (26)	0.16 (28)
C(3)	0.2362 (11)	−0.0144 (6)	0.4285 (10)	3.4 (4)	6.0 (5)	1.99 (29)	−0.4 (3)	−1.66 (26)	0.03 (28)
C(4)	0.2392 (9)	0.0834 (6)	0.3986 (9)	2.7 (3)	5.0 (4)	2.31 (28)	−0.39 (27)	−1.30 (23)	−0.92 (27)
C(5)	0.3574 (9)	0.1008 (5)	0.2777 (9)	3.0 (3)	4.2 (3)	2.7 (3)	−0.76 (26)	−1.64 (25)	−0.59 (26)
C(6)	0.4114 (12)	0.1955 (6)	0.2166 (13)	5.5 (5)	4.8 (4)	6.1 (5)	−2.3 (4)	−1.5 (4)	1.0 (4)
C(7)	−0.1023 (11)	0.2309 (5)	0.0288 (10)	5.4 (5)	2.9 (3)	4.5 (4)	0.9 (3)	−0.7 (3)	−0.44 (29)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + b_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The quantities give in the table are in units of Å^2.

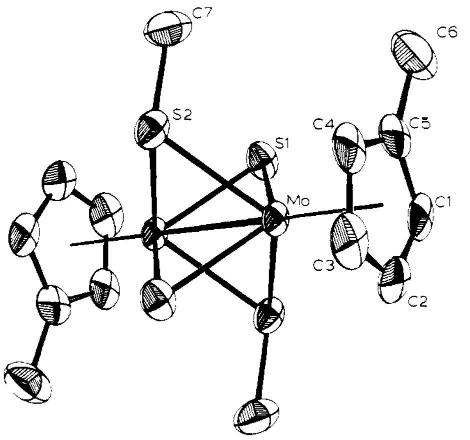

Figure 1. Perspective drawing of $[CH_3C_5H_4Mo(S)SCH_3]_2$.

Table V. Selected Bond Lengths and Angles for $[CH_3C_5H_4Mo(S)SCH_3]_2$

	A. Bond Lengths (Å)		
Mo–Mo′[a]	2.582 (1)	Mo–C_{av}[b]	2.35 (2)
Mo–S(1)′	2.352 (2)	S(2)–C(7)	1.832 (8)
Mo–S(1)	2.352 (2)	C(5)–C(6)	1.51 (1)
Mo–S(2)	2.478 (2)	C–C_{av}	1.42 (2)
Mo–S(2)′	2.479 (2)		
	B. Bond Angles (Deg)		
S(1)–Mo–S(1)′	113.42 (6)	Mo–S(2)–C(7)	113.9 (3)
S(1)–Mo–S(2)	77.14 (7)	Mo–S(2)–C(7)	113.5 (3)
S(1)–Mo–S(2)′	69.57 (8)	C(1)–C(5)–C(6)	126.6 (8)
S(2)–Mo–S(2)′	117.22 (5)	C(4)–C(5)–C(6)	126.9 (8)
Mo–S(1)–Mo′	66.58 (6)	C–C–C_{av}	108 (1)
Mo–S(2)–Mo’	62.78 (5)		

[a] Atoms in symmetry positions $\bar{x}, \bar{y}, \bar{z}$, are marked with a prime. All other atoms are at positions given in Table IV. [b] Average bond lengths are given for the cyclopentadiene ring.

A series of thiolate complexes, where R = CH_3, C_2H_5, i-C_3H_7, and C_6H_5, have been synthesized by reaction 8 and characterized. Spectral data, presented in Table III, suggest that the complexes have the same gross structural features as the starting hydrosulfido complex. A single low-energy absorption in the infrared spectrum of each alkyl derivative occurs at a frequency similar to that observed in the spectrum of $[Me_nCpMo(S)SH]_2$. The three well-defined bands in the visible spectra of the complexes are also very similar in wavelength and intensity to those of the SH complex. The NMR data again provide evidence for the presence of isomers in solution. Generally, two sets of *S*-alkyl resonances are observed in variable ratios. The ^{13}C spectrum of $[CH_3C_5H_4Mo(S)SCH_3]_2$ also shows two resonances for the SCH_3 ligands. For the major isomer in this solution, the five carbons of the cyclopentadienyl ring are inequivalent, and this is consistent with the isomer defined by X-ray diffraction data (vida infra).

Description of the Structure of $[CH_3C_5H_4Mo(S)SCH_3]_2$. An X-ray diffraction study of a single crystal of the methyl thiolate

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derivative has been completed. A perspective view of the molecule is shown in Figure 1. Structural parameters and selected bond distances and angles are given in Tables IV and V, respectively. The structure consists of discrete dimers oriented about a crystallographic inversion center. All four sulfur atoms are in bridging positions with the *S*-methyl groups oriented to give the centrosymmetric trans isomer. The four sulfur atoms form a plane perpendicular to the metal–metal vector with S–S distances of 2.758 (3) and 3.014 (3) Å. The sulfur atoms show a disorder which involves 94% of the S atoms in the positions shown (Figure 1) and 6% rotated in the same plane by 45%. Bond distances from the disordered sulfurs to the metal and to the methyl carbons are equivalent within experimental error to those for the predominant form.

Application of the effective atomic number formalism to the diamagnetic molecule leads to the postulate of a double bond between Mo(IV) ions. The metal–metal distance of 2.582 (1) Å is slightly shorter than that reported for the similar Mo(III) dimers $[C_5H_5Mo(SCH_3)_2]_2$[45] and $[CH_3C_6H_5Mo(SCH_3)_2]_2^{2+}$,[46] and the M–S(R)–M angles in the Mo(IV) structure are slightly more acute. However, the M–M distance is considerably longer than those normally associated with a proposed double bond between Mo(IV) ions.[47] It has been pointed out previously that the bridging ligands in these types of molecules clearly play a role in determining the metal–metal bond distance, and this distance alone is not a reliable index of bond order.[45]

Experimental Section

Materials. Molybdenum hexacarbonyl, bis((cyclopentadienyl)molybdenum tricarbonyl) and bis((methylcyclopentadienyl)molybdenum tricarbonyl) were purchased from Strem Chemicals. Pentamethylcyclopentadiene was purchased from Aldrich.

$(CH_3)_5C_5Mo(CO)_3H$ was prepared from $LiC_5(CH_3)_5$ and $Mo(CO)_6$ in a method analogous to that reported for $C_5H_5Mo(CO)_3H$.[48] Details will be reported elsewhere.[31] Alkyl- and arylthiols (97–98%) and benzyl isocyanide were supplied by Aldrich and used without purification. Deuterium (99.5 atom %) and methyl mercaptan were purchased from Matheson. 90% enriched $^{34}S_8$ was purchased from Stohler Isotope Chemicals. Unless specified, reagent grade solvents were used without purification.

Physical Measurements. Proton NMR spectra were recorded at 90 MHz by using a Varian EM-390 spectrometer. The 25- MHz ^{13}C NMR spectrum was obtained with a JEOL PFT-100 spectrometer with a Nicolet Model 1080 data system. ^1H and ^{13}C chemical shifts are reported with reference to tetramethylsilane. Mass spectra were obtained with a Varian MAT CH-5 spectrometer. Electronic spectra were recorded on a Cary 17 spectrophotometer, and a Perkin-Elmer 337 spectrophotometer was used to obtain infrared spectra of Nujol mulls. Gas chromatographic identification of H_2S was done with a Varian 920 chromatograph with a thermal conductivity detector using a Chromisil 330 column purchased from Supelco. A Porapak N column purchased from Varian was used in the identification of hydrocarbons. H_2 was detected by using a GC equipped with an electron capture detector. The carrier gas was doped with ppm concentrations of N_2O to enhance the electron capture response for H_2.[49] Elemental analyses were determined by Spang Labs, Eagle Harbor, MI.

X-ray Crystallography. Crystals of $[CH_3C_5H_4Mo(S)SCH_3]_2$ suitable for X-ray analysis were grown by slow evaporation of a THF solution. Examination of the dark purple crystals on a Syntex P1 diffractometer operated at room temperature showed them to be monoclinic in a unit cell of dimensions $a = 7.794$ (3) Å, $b = 14.184$ (7) Å, $c = 7.805$ (2) Å, and $\beta = 100.03$ (3)°. The volume is 849.6 (6) Å^3. Systematic absences observed on the diffractometer are consistent with space group $P2_1/c$ (C_{2h}^5, no. 14). With the assumption of two molecules of the compound (mol wt 508.45) per unit cell the calculated density is 1.987 g/mL, in good agreement with the measured value of 1.988 g/mL. Intensity data were collected on a crystal (0.19 × 0.26 × 0.27 mm) by using standard procedures as programmed by Syntex. Molybdenum Kα radiation, monochromatized by a graphite crystal in the incident beam was used throughout the experiment. 1744 reflections were surveyed within a single quadrant over the range $2.0° < 2\theta < 50.0°$. Each reflection was measured by using θ–2θ scanning techniques with a minimum scan rate of 2.0°/min and scan ranges calculated to start 1.0° below 2θ for Kα_1 ($\lambda = 0.70926$ Å) and to end 1.0° above 2θ for Kα_2 ($\lambda = 0.71354$ Å). Backgrounds were measured at the begining and end of each scan. The data, monitored every 100 measurement cycles by three standard reflections, showed no significant variation. The data were corrected for Lorentz and polarization effects.[50] No correction was made for absorption, μ(Mo Kα) = 19.02 cm^{-1}.

The positions of the molybdenum and sulfur atoms were determined by using MULTAN. The remaining atoms were located by using Fourier techniques. Upon isotropic refinement,[51] the parameters converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.115$ and $wR = [\sum w(|F_o| - |F_c|]^2/\sum w(F_o)^2 = 0.142$. Additional refinement with all atoms treated anisotropically converged with $R = 0.055$ and $wR = 0.076$. Examination of the three-dimensional difference Fourier map revealed a 6% disorder in the sulfur atoms. Including the two sets of sulfur atoms in the refinement gave $R = 0.048$ and $wR = 0.063$. The standard deviation of an observation of unit weight was 2.31. All least-squares refinements were calculated by using the 1274 unique reflections that met the criterion of $F_o > 3.0\sigma(F_o)$.[51] Atomic scattering factors used were those for neutral atoms.[52] Anomalous dispersion effects were included in the scattering curves for molybdenum and sulfur.[52]

Syntheses. $[C_5H_5Mo(S)SH]_2$. The preparation of insoluble products containing cyclopentadienyl ligands, molybdenum, and sulfur, $[C_5H_5MoS_x]_y$, has been reported elsewhere.[32] In a 100-mL flask a slurry of this insoluble material (1.0 g) in $CHCl_3$ was degassed in two freeze–pump–thaw cycles and 1 atm H_2 was added at −196 °C. The flask was sealed, warmed to room temperature, and stirred for 5–7 days. The resulting hydrogen sulfide was then released from the flask. The deep purple solution was filtered rapidly in air, and the filtrate was rotoevaporated to 5–10 mL. Purple-black crystals were filtered and stored under nitrogen. Yield: 0.40 g. Anal. Calcd: C, 26.55; H, 2.68; S, 28.35. Found: C, 26.43; H, 2.55; S, 28.50.

$[CH_3C_5H_4Mo(S)SH]_2$. An analogous procedure was followed by using the insoluble material $[CH_3C_5H_4MoS_x]_y$ or the soluble complex $[CH_3C_5H_4MoS_2]_2$.[31] Reaction of H_2 with the latter complex required 10–14 days at 25 °C. Yield from 1 g of $[CH_3C_5H_4MoS_x]_y$: 0.70 g. Anal. Calcd: C, 30.00; H, 3.36; S, 26.69. Found: C, 29.93; H, 3.21; S, 26.69.

$[(CH_3)_5C_5Mo(S)SH]_2$. A similar procedure as described above was followed by using any of the following starting materials: $[(CH_3)_5C_5MoS_x]_y$,[31] $[(CH_3)_5C_5MoS_5]_2$,[31] or $[(CH_3)_5C_5MoS_2]_2$.[31] The reactions were stirred at 75–100 °C for 3–4 days, and the product was isolated under a nitrogen atmosphere. Yield from 1.0 g of $[(CH_3)_5C_5MoS_x]_y$: 0.6 g. Anal. Calcd: C, 40.54; H, 5.44 S, 21.64. Found: C, 40.21; H, 5.45; S, 21.39.

Thiol-Exchange Reactions. $[CH_3C_5H_4Mo(S)SR]_2$, R = CH_3, C_2H_5, *i*-C_3H_7, and C_6H_5. $[MeCpMo(S)SH]_2$ (0.25 g, 0.52 mmol) was dissolved in $CHCl_3$/toluene (10 mL/10 mL) and excess (5–10 mmol) RSH was added. The solutions were degassed in two freeze–pump–thaw cycles, and 1 atm of H_2 was added at −196 °C. The solutions were stirred at 80–100 °C for 48 h. H_2S was identified by GC in a sample of vapors from the reaction vessel. The products were isolated by evaporation of solvent, and for R = CH_3, C_2H_5, and C_6H_5, products were recrystallized from $CHCl_3$/THF. Hexane was used to recrystallize the isopropyl derivative. For R = CH_3, yield: 68%. Anal. Calcd: C, 33.07, H, 3.97; S, 25.22. Found: C, 32.94; H, 3.78; S, 25.08. ^{13}C NMR ($CDCl_3$): 16.89 (CH_3Cp), 17.47, 21.02 (SCH_3), 96.20, 96.63, 98.67, 99.06, 99.43, 116.15 ppm (Cp). Anal. Calcd for R = C_2H_5: C, 35.82; H, 4.52; S, 23.90. Found: C, 35.86; H, 4.38; S, 23.78. For R = *i*-C_3H_7, yield: 34%. Anal. Calcd: C, 38.29; H, 5.00; S, 22.72. Found: C, 38.12; H, 4.89; S, 22.72. For R = C_6H_5, yield: 72%. Anal. Calcd: C, 45.57; H, 3.82;

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(51) The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weighting factor, w, was defined as $1/\sigma(F_o) = 4.0F_o^2/\sigma^2(F_o^2)$. $\sigma^2(F_o^2)$ determined from counting statistics as $\sigma^2(F_o^2) = \mathrm{RLP}\{\mathrm{TSC} + \mathrm{BACK} + [P(\mathrm{TSC} - \mathrm{BACK})]^2\}$ where RLP is the reciprocal of the Lorentz and polarization correction, TSC is the total scan count, and BACK is the number of counts accumulated during background measurement during a period equivalent to the scan time. *P* was given a value of 0.04. See: Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563; Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

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S, 20.27. Found: C, 45.85; H, 3.72; S, 20.23.

$[C_5H_5Mo(S)SC_2H_5]_2$. A procedure analogous to that described above was followed. The solution was stirred at 60 °C for 48 h. The product was recrystallized from chloroform/hexane. Yield: 14%. Anal. Calcd: C, 33.08; H, 3.94; S, 25.23. Found: C, 32.81; H, 3.86; S, 25.02.

Reactions with Unsaturated Molecules. $[CH_3C_5H_4Mo(S)SH]_2$ (0.20 g, 0.4 mmol) was dissolved in 25 mL of $CHCl_3$ in a 60-mL reaction vessel, the solution was degassed in two freeze-pump-thaw cycles, and the unsaturated species was added (2 atm of C=C, 1 atm of C≡C, or 2 mL of $C_6H_5CH_2NC$). The solution was stirred at room temperature for 1-2 days. In the reaction with ethylene, vapors from the reaction vessel were sampled and analyzed by GC to identify hydrogen. The product molybdenum complexes were crystallized by partial evaporation of the solvent and characterized by NMR and elemental analyses. For $[CH_3C_5H_4MoSC_2H_4S]_2$ NMR ($CDCl_3$): δ 1.69 (s, 8, C_2H_4), 2.04 (s, 6, CH_3), 4.98 (s, 8, C_5H_4). Anal. Calcd: C, 35.96; H, 4.12; S, 23.97. Found: C, 36.02; H, 4.08; S, 23.78. For $[CH_3C_5H_4MoSC_2H_2S]_2$ NMR ($CDCl_3$): δ 2.06 (s, 6, CH_3), 5.82 (br s, 8, C_5H_4), 6.49 (s, 4, C_2H_2). Anal. Calcd: C, 36.23; H, 3.42; S, 24.18. Found: C, 36.43; H, 3.37; S, 24.30. For $[CH_3C_5H_4MoS_2CNCH_2C_6H_5]_2$ NMR ($CDCl_3$): δ 1.88 (s, 6, CH_3), 4.41 (s, 4, $-CH_2-$), 5.21 (br s, 8, C_5H_4), 7.28 (s, 10, C_6H_5). Anal. Calcd: C, 47.18; H, 3.97; S, 17.99. Found: C, 46.93; H, 3.90; S, 17.89. The reaction of $[(CH_3)_5C_5Mo(S)SH]_2$ with ethylene was carried out in dry THF in an analogous manner. NMR of $[(CH_3)_5C_5MoSC_2H_4S]_2$ ($CDCl_3$): δ 1.68 (s, 8, C_2H_4), 1.80 (s, 30, CH_3). Anal. Calcd: C, 44.57; H, 5.92; S, 19.83. Found: C, 44.53; H, 5.89; S, 19.76. Reactions of the unsubstituted cyclopentadienyl derivative were analogous. Products were identified by comparison of NMR spectra with those of known samples.[38,40]

H_2/D_2 Exchange. $[CH_3C_5H_4Mo(S)SH]_2$ (0.2 g) was dissolved in dry benzene (10 mL) in a 50-mL flask, and the solution was degassed in two freeze-pump-thaw cycles. Approximately 0.75 atm of H_2 and 0.25 atm of D_2 were added, and the solution was stirred at 25 °C for 3 days. Mass spectrum analysis showed that approximately 12% of the gas was HD. A blank with no complex present was run simultaneously. No HD was detected.

H_2/D_2O Exchange. $[CH_3C_5H_4Mo(S)SH]_2$ (0.17 g) was dissolved in 10 mL of THF and 2 mL of D_2O. The solution was degassed in two freeze-pump-thaw cycles, and 1 atm of H_2 was added at -196 °C. The solution was stirred at room temperature for 5 days. Mass spectrum analysis showed 37% H_2, 16% HD, and 47% D_2. The mass spectrum of the blank, run simultaneously, showed only H_2. The molybdenum complex was recovered by evaporation of the solvent and identified by NMR. The SH ligands were partially substituted by deuterium.

Catalytic Hydrogenation of Sulfur. Sublimed sulfur (1.2 g) and $[Me_nCpMo(S)SH]_2$ (0.03-0.05 g) were accurately weighed and were slurried in 50 mL of $CHCl_3$ in a 500-mL flask. The solution was degassed in freeze-pump-thaw cycles and 1 atm H_2 was added at -196 °C. The solution was stirred for 24 h at room temperature or in an oil bath. The solvent was evaporated, and the remaining solid was weighed to determine the amount of sulfur consumed. In some cases the product H_2S was distilled on a vacuum line and weighed.

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Supplementary Material Available: Table of observed and calculated structure amplitudes (4 pages). Ordering information is given on any current masthead page.

Protonation Reactions of Molybdenum and Tungsten Dinitrogen Complexes with Halogen Acids. Hydride Hydrazido(2–) and Diazenido Complexes as Intermediate Stages of Reduction[1]

Tamotsu Takahashi, Yasushi Mizobe, Maki Sato, Yasuzo Uchida, and Masanobu Hidai*

Contribution from the Department of Industrial Chemistry, University of Tokyo, Hongo, Tokyo 113, Japan.

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Abstract: Reactions of dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) with an excess of HCl in 1,2-dimethoxyethane give hydrazine in moderate yields. This stands in sharp contrast to the formation of ammonia on treatment with H_2SO_4 in methanol. The hydrazido(2–) complex $[WBr_2(NNH_2)(PMe_2Ph)_3]$, which is obtained from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and HBr, reacts with 1 molar equiv of HCl to afford a hydride hydrazido(2–) complex $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$. The structure has been definitely determined by infrared and NMR spectra and X-ray analysis. Anion exchange with $NaBPh_4$ gives a novel diazenido complex $[WHClBr(\overset{\leftarrow}{=}N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]\cdot CH_2Cl_2$ in a low yield, in addition to $[WHClBr(NNH_2)(PMe_2Ph)_3][BPh_4]$, whose molecular structure has been determined by X-ray analysis. A mechanism for reduction of coordinated dinitrogen is proposed on the basis of these results.

Several systems are now known with which the ligating dinitrogen in well-defined complexes is converted into ammonia and hydrazine under mild conditions.[2] However, the detailed mechanism for the reduction of dinitrogen in the above systems is not well understood. Its clarification may shed some light on the mechanism of nitrogen fixation in biological systems.

Recently we have briefly reported that hydrazine is formed in moderate yield on treatment of dinitrogen complexes $[M(N_2)_2(PMe_2Ph)_4]$ or hydrazido(2–) complexes $[MBr_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W) with HCl in 1,2-dimethoxyethane (DME).[3] This is in sharp contrast to the protonation reactions with H_2SO_4 in methanol, where ammonia is mainly produced.[4]

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