maintained at 0 °C. The resulting mixture was extracted with cold pentane and filtered through Celite into another Schlenk tube which had been cooled to 0 °C. The pentane was removed under vacuum at 0 °C to give initially a dark red oil which on prolonged standing under vacuum turned into 0.11 g (10%) of a red-brown oily solid. Attempts to crystallize this compound from a small amount of pentane at −78 °C were unsuccessful: ^{1}H NMR (C_6D_6 at −5 °C) δ 0.08 [s, 18 H, $Si(CH_3)_3$], 2.16 [s, 15 H, $C_5(CH_3)_5$]; IR (hexane) $\nu_{C\equiv C}$ 1915 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{33}CuSi$: C, 58.56; H, 9.01, Cu, 17.21. Found: C, 55.56; H, 8.93; Cu, 20.1.

Reaction of (η^5-Cyclopentadienyl)[η^2-bis(trimethylsilyl)acetylene]copper with Triphenylphosphine. In a small Schlenk tube were place lithium cyclopentadienide (0.24 g, 3.3 mmol) and [η^2-bis(trimethylsilyl)-acetylene]chlorocopper(I) dimer (0.67 g, 1.25 mmol). The tube was cooled to −10 °C, and ca. 10 mL of THF was added. The mixture was stirred between −10 and 0 °C for 2 h. At 0 °C, triphenylphosphine (0.65 g, 2.5 mmol) was then added and the mixture stirred for 1 h while being warmed to 25 °C. The THF was removed under vacuum and the resulting residue extracted with ethyl ether. The combined ether extracts were filtered through Celite, and the filtrate was concentrated under vacuum. The Schlenk tube was cooled to −78 °C to produce white crystals. The crystals were washed with cold pentane and dried under vacuum to give 0.33 g (34%) of (η^5-cyclopentadienyl)(triphenylphosphine)copper, whose properties were identical with those of an authentic sample.

Reaction of (η^5-Pentamethylcyclopentadienyl)[η^2-bis(trimethylsilyl)-acetylene]copper with Triphenylphosphine. In a small Schlenk tube were placed lithium pentamethylcyclopentadienide (0.28 g, 2.0 mmol) and [η^2-bis(trimethylsilyl)acetylene]chlorocopper(I) dimer (0.48 g, 0.9 mmol). The tube was cooled to −10 °C, and 10 mL of THF was added. The mixture was stirred for 2 h between −10 and 0 °C. At 0 °C, triphenylphosphine (0.45 g, 1.7 mmol) was then added and the mixture stirred for 30 min at 25 °C. The THF was removed under vacuum and the resulting residue extracted with ethyl ether. The combined ether extracts were filtered through Celite and decolorizing carbon, and the filtrate was concentrated under vacuum. The Schlenk tube was cooled to −78 °C to produce white crystals. The latter were dried under vacuum to give 0.12 g (15%) of (η^5-pentamethylcyclopentadienyl)(triphenylphosphine)copper, whose properties were identical with those of an authentic sample.

Acknowledgment is made to the National Science Foundation and to the Donors to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research program.

Registry No. 11, 86024-09-1; **12**, 86024-10-4; **13**, 86045-48-9; **14**, 69446-48-6; **15**, 77997-76-3; **16**, 86024-11-5; **17**, 86024-12-6; $[ClCuPPh_3]_4$, 50409-58-0; $[ClCuPEt_3]_4$, 55606-52-5; CuCl, 7758-89-6; lithium cyclopentadienide, 16733-97-4; lithium pentamethylcyclopentadienide, 51905-34-1; (η^5-cyclopentadienyl)(triphenylphosphine)copper, 31781-67-6.

Synthesis of Inequivalently Bridged Cyclopentadienyl Dimers of Molybdenum and a Comparison of Their Reactivities with Unsaturated Molecules and with Hydrogen

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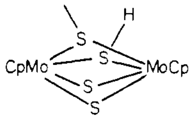
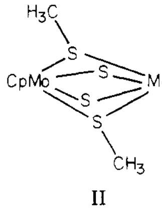
Abstract: A series of dimeric cyclopentadienyl complexes of molybdenum which are bridged by two inequivalent dithiolate ligands have been synthesized. The new complexes include $(CpMo)_2(S_2CH_2)(SC_2H_4S)$, IVa, $(CpMo)_2(S_2C(CH_3)_2)(SC_2H_4S)$, IVb, $(Cp'Mo)_2(S_2CS)(SC_2H_4S)$, V, and $(CpMo)_2(SCHCPhS)(SC_2H_4S)$, VI ($Cp = C_5H_5$, $Cp' = CH_3C_5H_4$). The relative tendencies of the ethanedithiolate ligands to eliminate ethylene have been compared for the above series. The studies establish that the ligand lability is influenced by the nature of the other dithiolate bridge as well as by substituents on the cyclopentadienyl ligands. Alkynes and cumulenes react with the ethanedithiolate ligands in IV–VI to displace ethylene and form derivatives with unsaturated dithiolate bridges. Some of these unsaturated complexes can be hydrogenated under the mild conditions of 1–2 atm of H_2 at 60 °C. The reactions result in the stoichiometric reduction of alkynes to *cis*-alkenes, allenes to alkenes, and ketenes to aldehydes. The relationship between hydrocarbon lability in the dithiolate ligands and hydrogenation activity is discussed. Two X-ray diffraction studies of complexes which contain a η^2-μ-1,1-alkanedithiolate ligand have been completed. The acetylene adduct $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$ crystallizes in space group $P2_1/c$ with a = 7.855 (2) Å, b = 8.433 (2) Å, c = 13.428 (3) Å, and β = 104.61 (2)°. The methylated derivative $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$ crystallizes in space group *Pbcn* with a = 17.143 (4) Å, b = 12.023 (2) Å, and c = 8.931 (2) Å. Structural parameters for these dimers are compared with those of other cyclopentadienylmolybdenum dimers with bridging thiolate ligands.

Cyclopentadienylmolybdenum complexes of the formula $[CpMo(\mu\text{-}S)(\mu\text{-}SR)]_2$ (R = H or alkyl) have been reported previously,[2] but the different stereochemistries which are possible for the bridging ligands in these complexes have made it difficult to compare reactivities. For example, in the hydrosulfido complex, the two bridging sulfido ligands form a reactive site which interacts with a variety of unsaturated molecules. This reactivity suggests that the complex contains a cis orientation of sulfido ligands (e.g., I) or can readily rearrange to this type of isomer. In contrast the sulfido ligands in the complex $[CpMo(\mu\text{-}S)(\mu\text{-}SCH_3)]_2$ do not react with ethylene or acetylene under similar mild conditions, suggesting that only trans isomers of this complex are formed (e.g., II).



I



II

We are interested in establishing how a range of structural and electronic effects influence the reactivity of two bridging sulfido ligands which are constrained in a cis configuration. Such an

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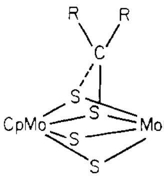
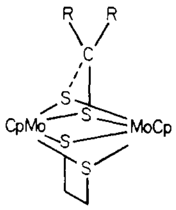
[1] Alfred P. Sloan Research Fellow, 1981–1983. Camille and Henry Dreyfus Teacher Scholar, 1981–1986.

[2] Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

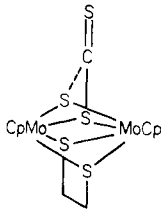
investigation has required the synthesis of a series of dimeric complexes in which (1) two of the bridging positions are occupied by a *dithiolate* ligand which is nonlabile and (2) the other two bridging sulfur atoms react with unsaturated molecules. In this paper we report the syntheses and characterization of several new derivatives of this type, including the Mo(IV) complexes with unsubstituted sulfido ligands, III, and the ethylene adducts IV–VI.



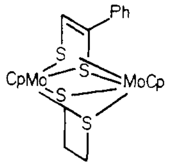
IIIa, R = H
b, R = CH_3



IVa, R = H
b, R = CH_3



V



VI

A series of competition reactions have been characterized in order to determine the relative reactivities of these complexes. The data indicate that the reactivity of the ethanedithiolate ligand changes significantly as the nature of the other bridging ligand in the complex is varied, with the sulfur atoms in IVb forming the most labile adduct with ethylene. The lability within a dithiolate ligand appears to be an important factor in the development of hydrogenation activity for these systems, which is also discussed in this paper. Unsaturated adducts of IIIa and IIIb react with hydrogen under mild homogeneous conditions. The reactions result in the stoichiometric reduction of alkynes to *cis*-alkenes, allenes to alkenes, and ketenes to aldehydes. The structural characterizations of two derivatives which contain the η^2-μ-methanedithiolate ligand are also discussed.

Results and Discussion

Syntheses of Inequivalently Bridged Complexes. The deprotonation of $[CpMo(S)SH]_2$ with 2 equiv of sodium methoxide in the presence of excess dibromomethane results in the formation of a dimer with a bridging methanedithiolate ligand. Analytical and spectral data are consistent with the formulation $(CpMoS)_2S_2CH_2$. Because the infrared spectrum of the product shows no absorptions characteristic of terminal sulfido ligands,[3] structure III is assigned. We have attempted the synthesis of other complexes with the $Cp_2Mo_2S_4$ core and a single dithiolate bridge by an extension of the procedure described above. However, reactions of the deprotonated hydrosulfido complex with 1,2-dibromoethane or with 2,2-dibromopropane did not lead to characterizable products with a single bridging 1,2- or 2,2-dithiolate ligand. The complex $(CpMoS)_2S_2C(CH_3)_2$, IIIB, has been synthesized by a less direct route involving a hydrogenation reaction which has been discussed elsewhere.[4]

Several alkene adducts of III have been synthesized. A color change is apparent within seconds after excess olefin is added to IIIa or IIIB in dichloromethane solution. The reaction is reversed when the solution is evacuated, purged with nitrogen, or simply exposed to the atmosphere for several minutes. NMR data confirm that the olefin interaction occurs with the sulfido ligands in the dimers. Chemical shifts for the resulting alkanedithiolate ligands are very similar to those reported for other dithiolate-bridged dimers of molybdenum.[5] A very large downfield shift in the NMR resonance of the methylene group of the methanedithiolate ligand is observed when adduct formation occurs. For example, this resonance occurs at 2.68 ppm in the spectrum of IIIa and at 6.09 ppm in the spectrum of IVa. Similar spectral shifts occur when the sulfido ligands in IIIa interact with other unsaturated molecules, and this serves as a useful indicator of adduct formation. However, the changes in electronic environment that cause this shift are not readily determined. Although such downfield shifts are often associated with an increase in acidity,[6] the methanedithiolate ligand in the adducts does not exhibit acidic character. For example, the stepwise addition of butyllithium and methyl iodide to an alkyne adduct of III, $(CpMo)_2(S_2CH_2)(SCR{=}CRS)$, results only in the methylation of the cyclopentadienyl ligand.

Table I

A. Equilibrium Constants for Reaction 1 at 26 °C

alkene	K, M^{-1}
ethylene	$>3 \times 10^4$
trans-2-butene	$(3 \pm 1) \times 10^2$
cis-2-butene	17 ± 2
cis-2-hexene	3.8 ± 0.2
cis-stilbene	<1

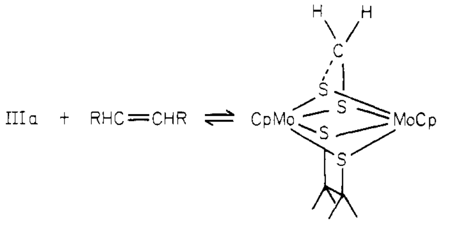
B. Percent Formation of IV in Reaction 2 at Room Temperature

reactant	% IVa	
	Cp	Cp′
IVb	70^a	
V	9^b	<3
VI	30^c	<3
$[CpMoSC_2H_4S]_2$	22^d	<3

[a] K_{eq} for this reaction has been determined to be 6.25 (5) at 30 °C. [b] VII is not observed spectrally because of paramagnetism, but the product is believed to be stable in solution since the percent formation shows a *reversible* dependence on temperature. [c] At 25 °C, ~45% of VI disproportionates to $[CpMoSC_2H_4S]_2$ and $[CpMoSCHCPhS]_2$ over a period of ~8 weeks. The former disproportionation product contributes to the formation of IV. See last entry in table. [d] The reversibility of this reaction has not been established.

The reaction of the hydrosulfido complex with thiophosgene results in the elimination of HCl and the formation of a product with a μ-trithiocarbonate ligand. The Mo(IV) complex $(Cp'MoS)_2S_2CS$ appears to be paramagnetic and has not been well characterized. However diamagnetic adducts of this complex with acetylene and ethylene are readily isolated (e.g., structure V). Strong absorptions near 1020 cm^{-1} in the infrared spectra of these complexes are assigned to $\nu_{C{=}S}$,[7] and other spectral and analytical data are consistent with the proposed formulations. The inequivalently bridged complex VI has been synthesized by the addition of 1 equiv of phenylacetylene to the bis(ethanedithiolate)-bridged dimer[5] and purified by column chromatography.

Comparisons of Alkene Adducts. The relative stabilities of a series of olefin adducts of III have been compared by measuring equilibrium constants for the following reaction at 26 °C (Table I). The equilibrium appears to be largely influenced by the steric



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[3] Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

[4] Miller, D. J.; Haltiwanger, R. C.; Rakowski DuBois, M. "Proceedings of 4th International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Ed.; Climax Molybdenum Co.: Ann Arbor, MI, 1982; p 384.

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

[6] Dyer, J. R. "Applications of Absorption Spectroscopy of Organic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1965; p 99.

[7] Reference 6, p 74.

Table II. ^{1}H NMR Data for Adducts of $[(CH_3)_nC_5H_{5-n}MoS]_2S_2CR_2$ [a]

n	R	reactant	C_5H_5 or C_5H_4 [b]	S_2CH_2 [b]	$S_2C(CH_3)_2$ [b]	CH_3-Cp [b]	other resonances
0	H	ethene	5.48	6.09			1.74 (s, 4, C_2H_4)
0	CH_3	ethene	5.38		1.51		1.76 (s, 4, C_2H_4)
1	H	ethene	5.26	6.15 (br)		1.95	1.67 (s, 4, C_2H_4)
0	H	propene	5.49, 5.57	6.08			1.16 (m, 4, $(CH(CH_3)S)$) 2.11 (m, 2, SCH_2)
0	H	acetylene	5.91	6.28			6.56 (s, 2, SC_2H_2S)
1	H	acetylene	5.76	6.27		2.10	6.57 (s, 2, SC_2H_2S)
0	CH_3	acetylene	5.85		1.40		6.68 (s, 2, SC_2H_2S)
0	H	2-butyne [c]	5.56	5.90			1.30 (s, 6, CH_3)
1	H	2-butyne [c]	5.61	6.05		1.94	1.38 (s, 6, CH_3)
0	H	2-hexyne [c]	5.58	5.92			0.64 (t, 3, CH_3) 1.20 (m, 2, CH_2) 1.34 (s, 3, $C{=}CCH_3$) 1.76 (t, 2, $C{=}CCH_2$)
1	H	diphenylacetylene [c]	5.62	6.00		1.95	6.95 (2m, 10, C_6H_5)
0	H	diphenylacetylene	5.95	6.31			6.98 (2m, 10, C_6H_5)
0	CH_3	allene	5.42	*d*	1.49		2.62 (m, 2, SCH_2C) 5.26, 5.73 (2m, 2, $H_2C{=}CS$)
0	H	methylallene	5.48	6.08			1.54 (d, $CH_3C{=}C$) 2.42 (br s, 2, SCH_2) 6.5 (br m, 1, $SC{=}CH$)
0	CH_3	ketene	5.65	*d*	1.52		2.83 (s, 2, SCH_2)
0	CH_3	diphenylketene	5.31	*d*	1.52		7.2 (m, 10, C_6H_5)

[a] Ppm in $CDCl_3$. [b] Singlets. [c] Ppm in C_6D_6. [d] Very broad or not observed.

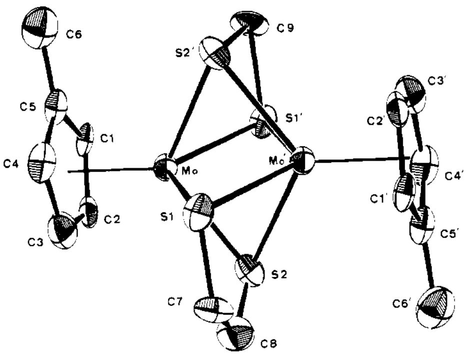
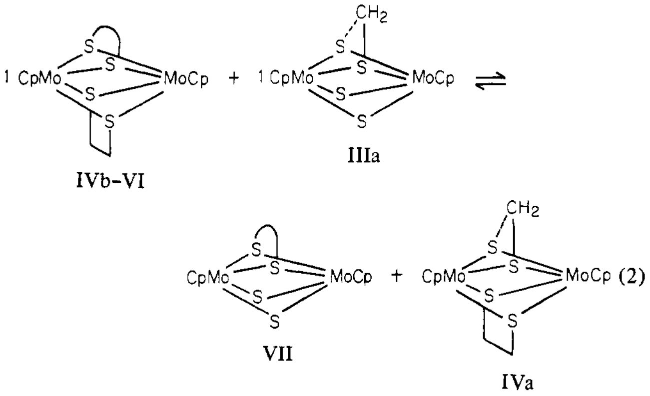


Figure 1. A perspective drawing of $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$. Only one of the two disordered sets of dithiolate carbon atoms is shown.

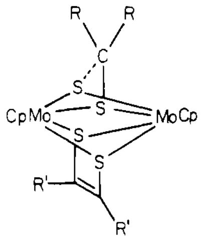
bulk of the alkene. The values range from very large for R = H (no dissociation of the adduct is detected) to very small for R = phenyl (no adduct formation is detected). We have also compared the relative olefin affinities in a series of ethylene adducts in which the other dithiolate ligand has been varied (reaction 2).



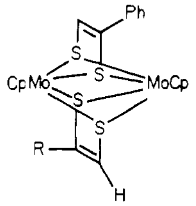
IVb-VI IIIa VII IVa

Although product VII is not observed spectrally in every case, the reactivities of the adducts have been compared by determining the relative concentration of IVa which is formed in a sealed tube reaction. The data, which are summarized in Table IB, establish that the Cp derivatives have a higher affinity for ethylene than those with MeCp ligands and that for a series with a given Cp ligand, IVb loses ethylene most readily. The complex chemistry of VI (see footnote c, Table I) makes it difficult to directly compare its olefin affinity with others in the series. However, there is an especially marked difference in the affinities of IV and V, and this appears to relate to other differences observed in the chemical activity of these systems (vida infra).

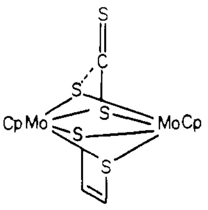
Alkyne Adducts. A series of unsaturated adducts have been synthesized by the reaction of III–VI with alkynes, e.g., VIII–X.



VIIIa, R = H, R' = H, C_6H_5, CH_3
b, R = CH_3, R' = H



IX, R = H, Ph



X

Characterization data are included in the Experimental Section and in Table II. The alkyne adducts are considerably more stable than those derived from alkenes. The dissociation of free alkyne is not detected spectrally for any of the inequivalently bridged complexes, even when the adduct involves a bulky molecule such as diphenylacetylene. However, an exchange of the sulfur-"coordinated" alkyne with excess free acetylene has been characterized for VIII. For example, the 2-hexyne adduct of VIII reacts with excess diphenylacetylene in $CHCl_3$ at 60 °C to form $(CpMo)_2(S_2CH_2)(SC(C_6H_5)C(C_6H_5)S)$. Such exchange reactions have not been observed for X. If we assume that the observed exchange reactions occur via a dissociative mechanism similar to that characterized previously for related Mo dimers,[8] the ordering

Table III. Positional and Thermal Parameters for the Atoms of $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)^a$

atom	x	y	z	$U_{11}{}^b$	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	0.14165 (4)	0.08014 (3)	0.05227 (2)	0.0237 (2)	0.0372 (2)	0.0277 (2)	−0.0031 (1)	0.0083 (1)	−0.0027 (1)
S(1)	0.1564 (1)	−0.2038 (1)	0.01373 (9)	0.0323 (5)	0.0450 (5)	0.0580 (6)	−0.0102 (5)	0.0133 (4)	0.0049 (4)
S(2)	−0.0397 (2)	−0.0688 (1)	0.13675 (8)	0.0432 (6)	0.0820 (8)	0.0319 (5)	0.0013 (5)	0.0137 (4)	−0.0201 (5)
C(1)	0.2574 (5)	0.2823 (5)	0.1639 (3)	0.041 (2)	0.042 (2)	0.042 (2)	−0.014 (2)	0.009 (2)	−0.005 (2)
C(2)	0.3003 (6)	0.3036 (5)	0.0707 (3)	0.047 (2)	0.051 (2)	0.052 (3)	−0.008 (2)	0.016 (2)	−0.019 (2)
C(3)	0.4186 (5)	0.1794 (6)	0.0658 (3)	0.032 (2)	0.072 (3)	0.047 (2)	−0.015 (2)	0.014 (2)	−0.017 (2)
C(4)	0.4486 (5)	0.0853 (5)	0.1535 (3)	0.026 (2)	0.065 (3)	0.045 (2)	−0.016 (2)	0.004 (2)	−0.001 (2)
C(5)	0.3516 (5)	0.1486 (5)	0.2152 (3)	0.031 (2)	0.050 (2)	0.036 (2)	−0.013 (2)	0.003 (1)	−0.003 (2)
C(6)	0.3513 (7)	0.0860 (7)	0.3175 (4)	0.048 (3)	0.082 (4)	0.036 (2)	−0.002 (2)	0.003 (2)	0.010 (2)
C(7)	0.168 (2)	−0.289 (2)	0.127 (2)	0.039 (8)	0.028 (5)	0.087 (9)	0.011 (5)	0.018 (6)	0.004 (5)
C(8)	0.076 (1)	−0.228 (1)	0.1825 (8)	0.045 (5)	0.041 (5)	0.037 (5)	0.008 (4)	0.007 (4)	−0.003 (4)
C(9)	0.113 (2)	−0.266 (2)	0.140 (1)	0.05 (1)	0.050 (9)	0.047 (9)	0.026 (7)	0.006 (7)	0.005 (7)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
H(1)	0.1682 (5)	0.3561 (5)	0.1896 (3)	0.066 (7)	H(5)	0.25 (1)	0.097 (7)	0.326 (6)	0.11 (1)
H(2)	0.2515 (6)	0.3971 (5)	0.0148 (3)	0.066 (7)	H(6)	0.434 (8)	0.154 (7)	0.376 (5)	0.11 (1)
H(3)	0.4757 (5)	0.1615 (6)	0.0050 (3)	0.066 (7)	H(7)	0.383 (9)	−0.047 (7)	0.335 (5)	0.11 (1)
H(4)	0.5324 (5)	−0.0193 (5)	0.1708 (3)	0.066 (7)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-0.25(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The quantities given in the table are in units of Å^2.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)^a$

A. Bond Distances			
Mo–Mo	2.601 (1)	S(2)–C(8)	1.631 (11)
Mo–S(1)	2.464 (1)	S(1)′–C(9)	1.948 (16)
Mo–S(2)	2.456 (1)	S(2)′–C(9)	2.046 (15)
Mo–$C_{Cp(av)}$	2.305 (4)	C(5)–C(6)	1.502 (7)
S(1)–C(7)	1.682 (21)	C(7)–C(8)	1.316 (17)
		C–$C_{Cp(av)}$	1.415 (6)
B. Bond Angles			
S(1)–Mo–S(2)	71.30 (4)	S(1)′–C(9)–S(2)′	91.7 (6)
S(2)–Mo–S(2)′	116.1 (1)	S(1)–C(7)–C(8)	119.8 (13)
Mo–S(2)–Mo′	63.90 (4)	S(2)–C(8)–C(7)	116.0 (12)
Mo–S(1)–C(7)	102.0 (6)	C(4)–C(5)–C(6)	126.3 (4)
Mo–S(2)–C(8)	105.4 (4)	C(1)–C(5)–C(6)	126.2 (4)
Mo–S(1)–C(9)	92.1 (5)	C–C–$C_{Cp(av)}$	108.0 (4)
Mo–S(2)′–C(9)	90.0 (4)		

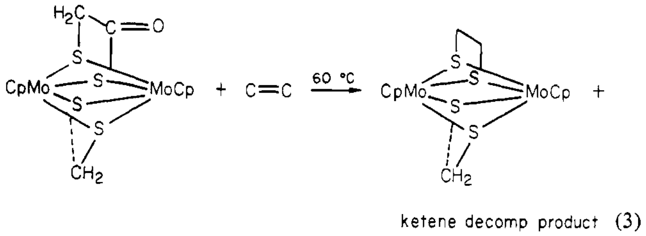
[a] The treatment of the disorder of the two dithiolate ligands is discussed in the Experimental Section.

of the adduct lability for alkynes appears to be similar to that observed for the alkene adducts, i.e., VIII > X.

We have undertaken an X-ray diffraction study of $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$ in order to determine whether unusual structural features are present which would account for the reactivity of these adducts. A perspective view of the molecule is shown in Figure 1, and structural parameters and selected bond distances and angles are given in Tables III and IV, respectively. The study confirms the gross structure of the complex. However, the compound crystallizes about a center of inversion with the two dithiolate bridges disordered. This unfortunately prevents an accurate determination of individual distances and angles in the $Mo_2S_4R_4$ core. More detailed structural information has been obtained from an X-ray diffraction study of a related derivative which is discussed below.

Cumulene Adducts. Preliminary studies indicated that the alkyne adducts VIII can be hydrogenated under mild conditions. These hydrogenations are discussed in more detail in the following section. In order to investigate the scope of this reduction activity, we have synthesized a series of additional unsaturated adducts by the reaction of IIIa or IIIB with cumulenes. Allene, methylallene, ketene, and diphenylketene each react with III to form an adduct in which an olefinic bond interacts with the sulfido ligands. Spectral data confirm the nature of the products. Strong absorptions at 1602 and 1664 cm^{-1} in the infrared spectra of the allene and ketene adduct, respectively, are assigned to the stretching vibrations of isolated C═C and C═O bonds, respectively, in the newly formed dithiolate ligands. In the ^{1}H NMR of the allene adduct the hydrogens in the 1-propene-2,3-dithiolate ligand form an A_2XY system; assignments of these resonances are confirmed by spin-decoupling experiments. The NMR spectrum of the isolated methylallene adduct is characteristic of a complex with a 2-butene-3,4-dithiolate ligand. Both isomers of this ligand, in which the methyl group is either cis or trans to the sulfur atom, have been detected in the reaction mixture by NMR, but only one isomer (stereochemistry unassigned) is present in the final product.

The labilities of the cumulene adducts of III appear to be similar to those of the related alkyne complexes. No dissociative equilibria analogous to reaction 1 are observed, even for the bulkiest adduct with diphenylketene, but some exchange reactions with excess alkenes have been characterized, e.g., reaction 3.



(3)

Hydrogenations of Unsaturated Adducts. All of the adducts of III which involve unsaturated dithiolate ligands can be hydrogenated under mild conditions. For example, each of the alkyne adducts VIIIa reacts with hydrogen (1–2 atm) at 55–65 °C to form the corresponding alkene. The methanedithiolate ligand does not react with hydrogen under the mild conditions used in these studies; the molybdenum-containing products are therefore IIIa and its olefin adduct IVa. Although III is reformed in the process, the reaction does not proceed in a continuous catalytic cycle, apparently because excess substrate inhibits the hydrogenation. The product alkenes have been characterized by NMR and/or gas chromatography. Despite the greater stability of the trans products (Table I), the reductions of the disubstituted alkyne adducts are stereoselective processes in which only the *cis*-alkenes or alkene adducts are produced. A number of heterogeneous and homogeneous catalysts for the reduction of alkynes to *cis*-alkenes by various reducing agents are known,[9-13] including the molyb-

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Table V. Positional and Thermal Parameters for the Atoms of $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$

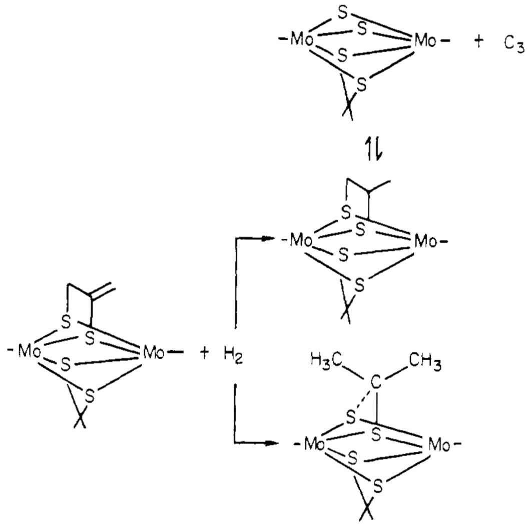
atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo(1)	0.06323 (2)	0.24951 (2)	−0.32996 (3)	0.0317 (2)	0.0314 (2)	0.0269 (2)	0.0053 (1)	0.00314 (9)	0.0040 (1)
S(1)	0.04318 (7)	0.11705 (8)	−0.1254 (1)	0.0594 (6)	0.0394 (5)	0.0374 (5)	0.0097 (4)	0.0043 (5)	0.0071 (5)
S(2)	0.04510 (6)	0.37639 (8)	−0.1178 (1)	0.0398 (5)	0.0407 (5)	0.0334 (5)	−0.0052 (4)	−0.0065 (4)	−0.0071 (4)
C(1)	0.00000	0.0134 (5)	−0.25000	0.080 (4)	0.037 (3)	0.040 (3)	0.0000 (*)	0.013 (3)	0.0000 (*)
C(2)	0.0963 (3)	0.3344 (5)	0.0519 (5)	0.077 (4)	0.082 (4)	0.044 (2)	0.000 (3)	−0.030 (2)	−0.014 (3)
C(11)	0.1424 (3)	0.3354 (4)	−0.5080 (5)	0.052 (3)	0.059 (3)	0.052 (2)	0.024 (2)	0.021 (2)	0.007 (2)
C(12)	0.1175 (3)	0.2295 (4)	−0.5577 (5)	0.065 (3)	0.062 (3)	0.039 (2)	0.006 (2)	0.022 (2)	0.004 (2)
C(13)	0.1495 (3)	0.1493 (4)	−0.4590 (6)	0.061 (3)	0.048 (2)	0.067 (3)	0.004 (2)	0.032 (2)	0.013 (2)
C(14)	0.1940 (3)	0.2081 (4)	−0.3495 (7)	0.037 (2)	0.052 (2)	0.078 (3)	0.013 (3)	0.010 (2)	0.013 (2)
C(15)	0.1904 (2)	0.3227 (4)	−0.3811 (6)	0.034 (2)	0.060 (3)	0.073 (3)	0.023 (2)	0.015 (2)	0.005 (2)
C(16)	0.2310 (3)	0.4122 (5)	−0.2954 (7)	0.044 (2)	0.072 (4)	0.111 (5)	0.018 (3)	−0.007 (3)	−0.019 (3)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
H(1)	0.04280	−0.0358 (5)	−0.30459	0.071 (7)	H(13)	0.1410 (3)	0.0603 (4)	−0.4641 (6)	0.071 (7)
H(2A)	0.0763 (3)	0.3914 (5)	0.1372 (5)	0.11 (1)	H(14)	0.2256 (3)	0.1709 (4)	−0.2577 (7)	0.071 (7)
H(2B)	0.1566 (3)	0.3517 (5)	0.0261 (5)	0.11 (1)	H(16A)	0.1976 (3)	0.4864 (5)	−0.3181 (7)	0.11 (1)
H(2C)	0.0909 (3)	0.2501 (5)	0.0923 (5)	0.11 (1)	H(16B)	0.2900 (3)	0.4232 (5)	−0.3352 (7)	0.11 (1)
H(11)	0.1281 (3)	0.4139 (4)	−0.5598 (5)	0.071 (7)	H(16C)	0.2319 (3)	0.3968 (5)	−0.1762 (7)	0.11 (1)
H(12)	0.0811 (3)	0.2131 (4)	−0.6538 (5)	0.071 (7)					

[a] The form of the anisotropic thermal ellipsoid is given in Table III.

denum–sulfur containing enzyme nitrogenase.[14] The coordination of substrate by sulfur atoms in the present systems suggests that these stoichiometric hydrogenations proceed by a mechanism which is fundamentally different from those characterized for other homogeneous transition-metal complexes.

The unsaturated ligands in the cumulene adducts of III are hydrogenated under similar mild conditions. In the reduction of the ketene adduct $(CpMo)_2[S_2C(CH_3)_2][SCH_2C(O)S]$, acetaldehyde is the only organic product detected. However, during the reduction of the diphenylketene adduct which forms diphenylacetaldehyde, a competing reaction takes place which produces diphenylacetic acid. This product probably arises from dissociation of the bulky ketene molecule from the sulfur ligands and its subsequent reaction with trace amounts of moisture in the solvent.[15] The allene adduct is hydrogenated to form primarily propene and its adduct, but a molybdenum complex which contains a rearranged 2,2-propanedithiolate ligand is also formed in ~15% yield (reaction 4). The hydrogenation of the methylallene adduct produces exclusively *cis*-2-butene and its adduct.



(4)

Relatively few reports of homogeneous transition-metal systems which effect the reduction of allenes and ketenes have appeared in the literature. Nitrogenase is a notable metalloenzyme system which is capable of utilizing water and reducing equivalents to convert allene to propene.[16] Synthetic allene complexes of Rh and Ru have been involved in the reduction of this cumulene by reaction with hydrogen and by the stepwise addition of protons and hydride ions, respectively.[17,18] A cyclopentadienylmanganese dicarbonyl complex of diphenylketene has been synthesized and found to react with hydrogen at high pressures (740 atm) to form the corresponding aldehyde and alcohol.[19] The systems reported here effect the hydrogenation of these cumulenes under exceptionally mild conditions. Furthermore, the molybdenum complexes can be recovered in good yields after the hydrogenations and recycled in the adduct formation and reduction reactions.

A side reaction prevents the quantitative recovery of III or IV from the hydrogenations. At temperatures of 60–70 °C in chlorinated solvents, III reacts slowly under a hydrogen atmosphere to form a complex with a new methanedithiolate ligand, $(CpMo)_2(S_2CH_2)(S_2CR_2)$. The formulation is consistent with spectral data and with elemental analyses. This complex is observed as a minor product in the hydrogenations of some of the adducts. In the absence of an alkyne or cumulene, yields of the new dimer as high as 90% have been isolated. This precludes a methylene transfer resulting from a bimolecular interaction of molybdenum dimers. Since the product is not formed under similar reaction conditions in benzene or tetrahydrofuran, it appears that chloroform is involved in this very unusual transformation.

The hydrogenation of IX, R = H, has been carried out at 25 °C under 1 atm of H_2 in $CDCl_3$ in a sealed NMR tube. Spectral data indicate that at this temperature only the bulkier alkenedithiolate ligand is reduced, forming $(CpMo)_2(SCH_2C(H)PhS)(SC_2H_2S)$. This dimer slowly decomposes to form free styrene and unidentified molybdenum products. After the solution is heated at 60 °C for 24 h, resonances for the saturated dimer $[CpMoSC_2H_4S]_2$ can be identified in the spectrum.

In contrast to the facile hydrogenations of VIII and IX, complex X is not reduced under similar conditions. The difference in lability involving the alkenedithiolate ligands in these systems (discussed above) suggests that the dissociation of the alkyne is necessary for hydrogenation activity. Our observation that the hydrogenation reactions are inhibited by the presence of excess substrate is also consistent with the proposal of an initial dissociative equilibrium. We propose that an equilibrium which produces unsubstituted cis μ-sulfido ligands is necessary for the

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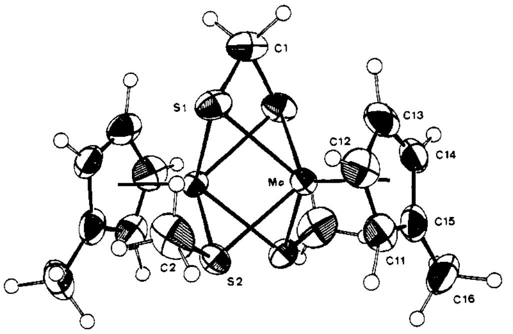

Figure 2. A perspective drawing of $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$.

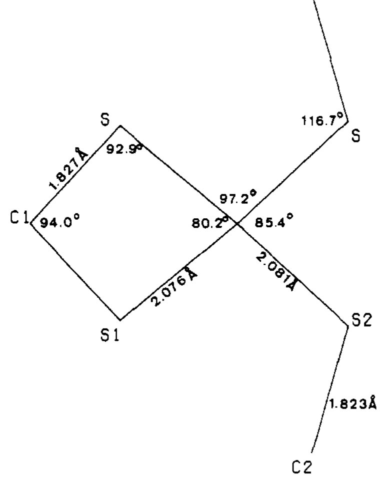

Figure 3. A two-dimensional view down the M–M vector of $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$ with projected bond distances and angles for the bridging ligands. Cp′ ligands have been omitted for clarity.

activation of hydrogen in these systems. Detailed kinetic and mechanistic studies of a hydrogenation reaction have been carried out, and the results will be presented elsewhere.[20]

X-ray Diffraction Study of an Alkylated Derivative of III. During the course of mechanistic studies we have established that the sulfido ligands in III also react with electrophilic and nucleophilic alkylating agents. For example, the cation $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]^+$ can be isolated from the reaction of IIIa with excess methyl iodide. The addition of methyllithium to this cation leads to the formation of the neutral Mo(III) dimer with two methylthiolate ligands. The development of this chemistry will be described in a separate paper.[21] However the isolation of $(CpMo)_2(S_2CH_2)(SCH_3)_2$, XI, as single crystals has enabled us to complete an ordered X-ray diffraction study of a molybdenum derivative with a η^2-μ-methanedithiolate ligand. The structural data serve to complete our characterization of derivatives of III and are therefore included here. Complex XI crystallizes in space group *Pbcn*. The molecule contains a twofold rotational axis which bisects the metal–metal vector and passes through the carbon of the methanedithiolate ligand. A perspective view of the structure is shown in Figure 2, and structural parameters and selected bond distances and angles are summarized in Tables V and VI, respectively. Projected bond lengths and angles for the Mo_2S_4 core are presented in Figure 3, an idealized view down the metal–metal vector. Many structural features of XI, including the Mo–Mo and Mo–S distances and the Mo–S–Mo angles are similar to those observed for bis(dithiolate)-bridged complexes of Mo(III).[4,22,23] We expected that the relatively small bite of the methanedithiolate ligand would compress the S_1–Mo–S_1' angle in this dimer relative to those in 1,2-alkanedithiolate complexes, and this is indeed observed; the angle is 7–9° smaller than those observed in other structures. In addition, the S_1–C_1–S_1' and C_1–S_1–Mo angles in the chelate are compressed relative to the ideal tetrahedral values as might be expected for a four-membered metallocyclic unit. Both the S_1–C_1–S_1' angle and the S_1–S_1' distance are very similar to those reported for the μ-methanedithiolate ligand in the iron dimer $CH_2S_2Fe_2(CO)_6$ (94.55 (3)° and 2.673 (2) Å, respectively).[24]

Table VI. Selected Bond Distances (Å) and Angles (deg) for $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$

	A. Bond Distances		
Mo–Mo′ [a]	2.596 (1)	S(1)–C(1)	1.827 (4)
Mo–S(1)	2.448 (1)	S(2)–C(2)	1.823 (4)
Mo–S(2)	2.453 (1)	C(15)–C(16)	1.494 (7)
Mo–$C_{Cp(av)}$	2.301 (4)	C–$C_{Cp(av)}$	1.415 (7)
S(1)···S(2)	3.119 (2)	S(2)···S(2)′	2.823 (2)
S(1)···S(1)′	2.673 (2)		
	B. Bond Angles		
S(1)–Mo–S(2)	79.10 (4)	Mo–S(1)–C(1)	92.6 (1)
S(1)–Mo–S(1)′	66.1 (1)	Mo–S(2)–C(2)	114.2 (2)
S(2)–Mo–S(2)′	70.30 (4)	S(1)–C(1)–S(1)′	94.0 (3)
Mo–S(1)–Mo′	64.00 (4)	C(11)–C(15)–C(16)	127.4 (5)
Mo–S(2)–Mo′	64.00 (4)	C(14)–C(15)–C(16)	125.6 (5)
		C–C–$C_{Cp(av)}$	108.0 (4)

[a] Atoms in symmetry position $-x, y, z - 1/2$ are marked with a prime. All other atoms are at positions given in Table V.

It is interesting to compare the S–S distances in XI with those observed for related molybdenum dimers. In the complex $[CpMo(SCH_3)_2]_2$, in which the sulfur atoms are not constrained by hydrocarbon bridges, the average S–S distance is 2.96 Å.[23] In neutral cyclopentadienylmolybdenum dimers with 1,2-alkenedithiolate bridges, the angles at the sp^2-hybridized carbon atoms cause a lengthening in the intraligand S–S distance to 3.0 Å, and the interligand distance between sulfur atoms is decreased to 2.91–2.93 Å.[22] A different type of distortion in the sulfur atom positions is observed for the present complex. The distance between the sulfur atoms of the methanedithiolate ligand of 2.67 Å is the shortest observed in the series of dithiolate-bridged dimers and is well within the range for which intraligand S–S bonding interactions have been proposed.[25] It is interesting that the distance between the sulfur atoms in the methylthiolate ligands of XI is also significantly shorter than that observed in $[CpMo(SCH_3)_2]_2$. No significant intermolecular interactions are observed for the alkyl groups of these ligands which would account for the short S–S distance, and a weak bonding interaction between these sulfur atoms may be present.

Summary. In dimeric complexes with the $Cp_2Mo_2(\mu\text{-}S)_4$ core, the nature of one bridging dithiolate ligand affects the reactivity at the other two sulfur bridges. Reactions which involve an exchange of the hydrocarbon portion of a bridging alkanedithiolate ligand are much more facile when the other ligand in the dimer is methanedithiolate than when the other ligand is μ-trithiocarbonate. The ability of the dimers to react with hydrogen appears to be related to this hydrocarbon lability. Unsaturated adducts of complexes with the methanedithiolate ligand are readily hydrogenated while no reduction is observed for adducts involving the trithiocarbonate ligand. The comparative studies in this paper suggest that the reactivity of sulfido ligands in these dimers can be significantly tuned by synthetic modifications.

Experimental Section

Materials. Dicyclopentadienylhexacarbonylmolybdenum and the methylcyclopentadienyl analogue were purchased from Alfa or synthesized by a published procedure.[26] Reagent grade alkenes and alkynes

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were used without further purification. Allene was purchased from Liquid Carbonic, and methylallene was purchased from Wiley Organics. Ketene[27] and diphenylketene[28] were synthesized by published procedures. Thiophosgene was obtained from Aldrich, and a methyllithium solution (low halide content) was purchased from Alfa. For most reactions the solvents were dried according to the following procedures: chloroform and dichloromethane were distilled from P_2O_5 or passed through an activated alumina column, benzene was distilled from calcium hydride, and tetrahydrofuran was distilled from $LiAlH_4$.

Physical Measurements. ^1H NMR spectra were measured at 90 MHz on a Varian 390 spectrometer. The 25- and 22.5-MHz ^{13}C NMR spectra were obtained with a JEOL PFT-100 spectrometer with a Nicolet Model 1080 data system and with a JEOL FX90-Q spectrometer, respectively. ^1H and ^{13}C chemical shifts were measured relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer. Mass spectra were obtained at 70-eV electron energies with a Varian MAT CH-5 spectrometer. Elemental analyses were provided by Spang Laboratories. A Varian 920 gas chromatograph with a thermal conductivity detector was used with a Porapak N column for the identification of most organic products. The analysis for butenes was done on a Hewlett-Packard gas chromatograph, Model 5880 A. A 30-m cross-linked silicone liquid phase fused silica capillary column (J & W Scientific, DB-5) was employed, and the oven was temperature programmed from −70 to +220 °C at 8°/min.

X-ray Crystallography. Crystals of $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$ and $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$ suitable for X-ray analysis were obtained by slow evaporation of THF and benzene solutions, respectively. Intensity data for both structures were collected on a Syntex P$\bar{1}$ autodiffractometer at ambient temperature, ca. 293 K, using θ–2θ scanning techniques with scan rates ranging from 2.0 to 24.0°/min. Mo Kα radiation, monochromatized by a graphite crystal in the incident beam, was used throughout the experiments. Examination of systematic absences observed on the diffractometer led to the space group assignments. Cell constants were obtained by least-squares refinement of 15 centered reflections. Further details of the parameters used during data collection are tabulated in Table VII.

The structure of $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$ was solved by using the heavy-atom method and Fourier techniques.[29] Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.038$ and $wR = [\sum w(|F_o| - |F_c|]^2/\sum w(F_o)^2 = 0.047$.[35]

The positions of the molybdenum and sulfur atoms of $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$ were located by using direct methods, MULTAN 78.[30] After least-squares refinement of these atoms a subsequent three-dimensional fourier map clearly revealed the positions of the methylcyclopentadiene carbons but not those of the bridging carbon atoms. Since the dimer is on a center of inversion, these atoms are disordered. After further least-squares refinement with the molybdenum and sulfur atoms anisotropic, the next difference Fourier revealed what could be interpreted as the positions of the carbons of the 1,2-ethenedithiolate group. The carbon of the methanedithiolate ligand was not resolved. After least-squares refinement was carried out with the distance between these two carbons fixed at 1.31 Å, a difference Fourier revealed the location of the carbon of the methanedithiolate ligand. Final full-matrix least-squares refinement with the distance constraint removed and with all non-hydrogen atoms anisotropic converged with $R = 0.028$ and $wR = 0.033$.[35]

Syntheses. Reactions were carried out under a nitrogen atmosphere, but products were isolated in air unless otherwise noted.

$(CpMoS)_2[S_2C(CH_3)_2]$. The synthesis and characterization of this complex has been reported previously.[4]

$(CpMoS)_2S_2CH_2$. $(CpMoS)_2(SH)_2$[2] (0.75 mmol) was dissolved in THF. CH_2Br_2 (1.0 mmol) and a freshly prepared solution of $NaOCH_3$ (1.50 mmol) in methanol (5 mL) were added. The resulting blue solution was stirred for 40 min at 25 °C, the solvent was evaporated, and the remaining solid was extracted with CH_2Cl_2. Evaporation of the CH_2Cl_2 produced the crude deep blue product which was recrystallized from CH_2Cl_2/toluene. The complex was stored under nitrogen: yield 60%; ^1H NMR ($CDCl_3$) δ(Cp) 2.68 (s, 2, CH_2), 6.55 (s, 10, Cp); δ(Cp′) 2.28 (s, 6, CH_3), 2.53 (s, 2, CH_2), 6.27 (s, 10, Cp); ^{13}C NMR ($CDCl_3$) (results of gated decoupling experiments are included in parentheses) δ(Cp′) 16.91 (CH_3, q, $J_{C-H} = 128$ Hz), 33.51 (CH_2, t, $J_{C-H} = 156$ Hz), 97.58, 100.59, 117.86 ($C_5H_4^-$, multiplets); mass spectrum, *m/e* (relative intensity) Cp 464 (19, P^+), 450 (11, $Cp_2Mo_2S_4^+$), 418 (100, $Cp_2Mo_2S_3^+$), Cp′ 492 (74, P^+), 478 (12, $Cp_2Mo_2S_4^+$), 460 (12, $P^+ - S$), 446 (100, $Cp_2Mo_2S_3^+$). Anal. Calcd for $C_{18}H_{16}S_4Mo_2$ (Cp′): C, 31.71; H, 3.28; S, 26.04. Found: C, 31.92; H, 3.28; S, 26.12.

Table VII. Crystallographic Parameters

	$(Cp'Mo)_2$-$(S_2CH_2)(SCH_3)_2$	$(Cp'Mo)_2$-$(S_2CH_2)(SC_2H_2S)$
Crystal Data		
M_r, amu	522.49	518.45
space group	*Pbcn*	*P*2_1/*c*
a, Å	17.143 (4)	7.855 (2)
b, Å	12.023 (2)	8.433 (2)
c, Å	8.931 (2)	13.428 (3)
α, deg	90.0	90.0
β, deg	90.0	104.61 (2)
γ, deg	90.0	90.0
vol, Å^3	1840.9 (7)	860.8 (3)
d_{calcd}, g cm^{-3}	1.89	2.00
Z	4	2
F(000)	1032	512
μ(Mo Kα), cm^{-1}	17.6	19.1
cryst size, mm	0.3 × 0.4 × 0.5	0.2 × 0.2 × 0.25
Experimental Data		
min 2θ, deg	3.0	3.0
max 2θ, deg	70.0	55.0
scan range	from 0.8° below 2θ for Kα_1 to 0.8° above 2θ for Kα_2	
bkgd mode	stationary crystal, stationary counter	
bkgd time/scan time	0.5	0.5
no. of stds measd	4	4
freq of std measurement	every 96 reflections	
no. of data points		
measd	8260	4097
unique measd	4087	1980
obsd [$F_o^2 > 3\sigma(F_o^2)$]	2224	1601
final residuals		
R	0.038	0.028
R_w	0.047	0.033

$(Cp'Mo)_2(S_2CS)(SC_2H_2S)$. $[Cp'Mo(S)SH]_2$[2] (0.31 g, 0.65 mmol) was dissolved in freshly distilled THF, and Cl_2CS (55 μL, 0.74 mmol) was added. The solution was stirred at 25 °C for ~90 min. A color change from purple to brown was observed. The solution was degassed, and 1 atm of acetylene was added. After the solution was stirred for ~24 h at 25 °C, the solvent was evaporated and the crude product was purified by chromatography through an alumina column. Elution with CH_2Cl_2 produced first a yellow band ($[Cp'MoSC_2H_2S]_2$) and an orange band ($[Cp'MoS_2CS]_2$). The last red brown fraction was the desired product: yield 0.17 g (48%); ^1H NMR ($CDCl_3$) δ 2.07 (s, 6, CH_3), 5.44 (m, 8, Cp), 6.58 (s, 2, CH_2); IR (Nujol) $\nu_{C=S}$ 1020 cm^{-1}; mass spectrum, *m/e* (relative intensity) 548 (P^+), 446 (base $Cp_2Mo_2S_3^+$). Anal. Calcd for $C_{15}H_{16}S_5Mo_2$: C, 32.85; H, 2.94; S, 29.23. Found: C, 32.96; H, 2.88; S, 29.20.

$(CpMo)_2(SC_2H_4S)(SCHCPhS)$. $[CpMoSC_2H_4S]_2$[5] (1.81 g, 3.57 mmol) was dissolved in CH_2Cl_2, and 0.4 mL (3.57 mmol) of phenylacetylene was added. After the solution was stirred at 25 °C for 4 days, the crude product was isolated by evaporating the solvent. The product was purified by chromatography on an alumina column. Elution with hexane/methylene chloride (3:1) produced first a yellow band ($[CpMoSCHCPhS]_2$). The second turquoise band was the desired product: yield 25%; ^1H NMR (C_6D_6) δ 1.55 (4, SC_2H_4S), 5.30 (s, 10, C_5H_5), 6.76 (s, 1, SC*H*CPhS), 7.25 (m, 6, Ph); mass spectrum, *m/e* 580 (P^+), 552 ($P - C_2H_4$). Anal. Calcd for $C_{20}H_{20}S_4Mo_2$: C, 41.38; H, 3.47; S, 22.09. Found: C, 41.29; H, 3.37; S, 22.12.

$(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$. $(Cp'MoS)_2S_2CH_2$ (0.176 g, 0.36 mmol) was dissolved in freshly distilled THF, and 1 equiv of CH_3Li was added. After the solution was stirred for 10 min, CH_3I (0.22 mL, 0.36 mmol) was added, and stirring was continued for 1 h. The solvent was evaporated, and the resulting solid was chromatographed on an alumina column with CH_2Cl_2. The first yellow brown band was collected and recrystallized from THF: yield 0.050 g (27%) (alternate higher yield syntheses will be discussed elsewhere[21]); ^1H NMR ($CDCl_3$) δ 1.30, 1.47 (s, 6, SCH_3), 2.07, 2.18 (s, 6, CH_3Cp), 5.48 (s, 8, Cp), 5.60 (br s, 2,

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CH_2); mass spectrum, *m/e* (relative intensity) 522 (33, P^+), 507 (47, $P^+ - CH_3$), 492 (2, $P^+ - 2CH_3$), 461 (55, $P^+ - CH_3$, SCH_2), 446 (100, $Cp_2Mo_2S_3^+$).

$(CpMoS)_2S_2CR_2$ + Alkenes (R = H, CH_3). A CH_2Cl_2 or $CHCl_3$ solution of the molybdenum dimer (~0.4 mmol) was stirred with excess ethene, propene, or butene for 1 h. The brown products were isolated by using an alkene purge to evaporate the solvent. ^1H NMR data for those adducts which are relatively stable in solution are included in Table II. Mass spectrum: parent ions are not observed; *m/e* for P − alkene and subsequent fragmentation patterns are characteristic. Anal. Calcd for $C_{15}H_{20}S_4Mo_2$ ($(Cp'Mo)_2(S_2CH_2)(SC_2H_4S)$): C, 34.62; H, 3.87; S, 24.64. Found: C, 34.47; H, 3.71; S, 24.64.

$(CpMoS)_2S_2CH_2$ + Alkynes. The molybdenum dimer (~1 mmol) was dissolved in freshly distilled THF, excess alkyne (10–25 mmol) was added, and the solution was stirred at 25 °C for 1–2 h. (The reaction with 2-butyne was stirred at 0 °C.) The reaction mixture was filtered, and the filtrate was evaporated to dryness. The resulting green product was recrystallized from toluene and washed with diethyl ether: yields 50–80%; ^1H NMR data are listed in Table II; ^{13}C NMR ($CDCl_3$) (results of gated decoupling experiments are included in parentheses) $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$ δ 16.38 (CH_3, q, $J_{C-H} = 128$ Hz), 90.10, 95.35, 112.87 (MeCp, m), 92.19 (CH_2, t observed by off-resonance decoupling), 147.38 (C_2H_2, d of d, $J_{C-H} = 182$ Hz, $J_{C=C-H} = 6.1$ Hz); mass spectrum characteristic fragmentation pattern, parent ion, parent − SCH_2, parent − alkyne, $Cp_2Mo_2S_3^+$ (base); IR (Nujol) $(CpMo)_2(S_2CH_2)(SC_2H_2S)$ $\nu_{C=C}$ 1560 cm^{-1}, $\nu_{C=C}$ is not observed for the disubstituted alkyne adducts. Anal. Calcd for $C_{15}H_{18}Mo_2S_4$ ($(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$): C, 34.75; H, 3.50; S, 24.74. Found: C, 34.79; H, 3.38; S, 24.75. Calcd for $C_{25}H_{22}Mo_2S_4$ ($(CpMo)_2(S_2CH_2)(SC(C_6H_5)C(C_6H_5)S)$): C, 46.73; H, 3.45; S, 19.96. Found: C, 46.53; H, 3.42; S, 19.88.

Allene Adducts. $(CpMo)_2[S_2C(CH_3)_2][SCH_2C(S)CH_2]$. One atmosphere of allene was added to a degassed solution of $(CpMoS)_2S_2C(CH_3)_2$ (~0.10 g) in 30 mL of $CHCl_3$ in a 150-mL flask. The solution was stirred for 12 h, then filtered, and evaporated to dryness. The resulting brown product was pure by NMR criteria: ^1H NMR data are given in Table II; IR (Nujol) $\nu_{C=C}$ 1602 cm^{-1}; mass spectrum, *m/e* (relative intensity) 532 (13, P^+), 492 (4, P − C_3H_4), 458 (24, P − C_3H_6S), 450 (8, $Cp_2Mo_2S_4^+$), 418 (100, $Cp_2Mo_2S_3^+$).

$(CpMo)_2(S_2CH_2)[SCH_2C(S)C(H)CH_3]$. To 0.17 g (0.37 mmol) of $(CpMoS)_2S_2CH_2$ dissolved in 15 mL of dry, degassed THF was added 70 mL (0.44 mmol) of methylallene. After 2 h of stirring at room temperature, the orange solution was filtered to remove a small quantity of brown solid and then rotoevaporated to dryness to obtain the orange-brown product in a 58% yield: ^1H NMR data are reported in Table II; mass spectrum, *m/e* (relative intensity) 518 (80, P^+), 472 (22, $P^+ - SCH_2$) 418 (100, $Cp_2Mo_2S_3^+$).

Ketene Adducts. $(CpMo)_2[S_2C(CH_3)_2][SCH_2C(O)S]$. A $CHCl_3$ solution (~30 mL) of $(CpMoS)_2[S_2C(CH_3)_2]$ (0.27 g, 0.55 mmol) in a 150-mL flask was evacuated in two freeze–pump–thaw cycles, and 1 atm of ketene/acetone was added. The color immediately changed from blue to red. After being stirred at 25 °C for 75 min, the solution was filtered and the filtrate flash evaporated. The resulting solid was washed with diethyl ether and methanol and extracted with dichloromethane. Evaporation of the extract gave a pure sample of the red brown product: yield 0.17 g (59%); IR $\nu_{C=O}$ 1664 cm^{-1} (strong); ^1H NMR data are reported in Table II; mass spectrum, *m/e* (relative intensity) 534 (4, P^+); 492 (15, $P^+ - C_2H_2O$), 450 (3, $Cp_2Mo_2S_4^+$); 418 (100, $Cp_2Mo_2S_3^+$). Anal. Calcd for $C_{15}H_{18}OS_4Mo_2$: C, 33.71; H, 3.39; S, 24.00. Found: C, 34.01; H, 3.59; S, 24.25.

$(CpMo)_2[S_2C(CH_3)_2][S(Ph)_2CC(O)S]$. Diphenylketene (0.075 mL, 0.43 mmol) was added to a degassed $CHCl_3$ solution of $(CpMoS)_2[S_2C(CH_3)_2]$ (0.10 g, 0.21 mmol). The solution was stirred and the filtrate evaporated to produce an oil. The addition of ether induced the formation of a brown solid which was washed with small amounts of ether, heptane, and carbon tetrachloride: yield 0.036 g (24%); IR $\nu_{C=O}$ 1661 cm^{-1} (strong); ^1H NMR data are reported in Table II; mass spectrum, no parent ion was observed, $P^+ - Ph_2C_2O$ and subsequent fragmentation patterns were observed.

$(CpMo)_2(S_2CH_2)[S_2C(CH_3)_2]$. Hydrogen (1 atm) was added to a degassed solution of $(CpMoS)_2[S_2C(CH_3)_2]$ in dry $CHCl_3$ or CH_2Cl_2 at −196 °C. The solution was heated to 60 °C for a period of 7–14 days until the color of the solution changed from blue to brown. After being cooled, the solution was filtered and evaporated. The resulting residue was purified by elution through an alumina column with benzene and collection of the first brown band: yields varied from 60 to 90%; ^1H NMR ($CDCl_3$) δ 1.47 (s, 6, CH_3), 5.89 (s, 10, Cp), 6.49 (br s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 38.8 (CH_3), 91.9 (Cp), 98.3 (S_2CH_2), 115.8 (S_2C); mass spectrum, *m/e* (relative intensity) 506 (42, P^+); 492 (4, P − CH_2), 464 (7, P − C_3H_6); 432 (88, P − C_3H_6S), 418 (43, $Cp_2Mo_2S_3^+$), 386 (100, $Cp_2Mo_2S_2^+$). Anal. Calcd for $C_{14}H_{18}S_4Mo_2$: C, 33.20; H, 3.58; S, 25.32. Found: C, 33.29; H, 3.61; S, 25.28.

$(CpMo)_2(S_2CH_2)_2$. $(CpMoS)_2S_2CH_2$ was reacted with hydrogen for 4 days in a procedure similar to that described above: ^1H NMR ($CDCl_3$) δ 5.92 (s, 10, Cp), 6.32 (s, 4, SCH_2S); mass spectrum, *m/e* (relative intensity) 478 (71, P^+), 464 (7, P − CH_2), 432 (64, P − CH_2S), 418 (38, $Cp_2Mo_2S_3^+$), 386 (100, $Cp_2Mo_2S_2^+$).

Deprotonation of $(CpMo)_2(S_2CH_2)(SCPhCPhS)$. Freshly distilled THF was added to the above complex (0.20 g, 0.31 mmol) under N_2. Distilled tetramethylethylenediamine (1.25 equiv) and *n*-butyllithium in hexane (1.25 equiv) were syringed into the solution at −78 °C. After being stirred 1 h, the solution was warmed to 0 °C and distilled CH_3I (1.25 equiv) was added by syringe. The solution was stirred at 25 °C for 12 h. Chromatography of the recovered solid (CH_2Cl_2 on Al_2O_3) provided a single green band which was isolated and identified by NMR as $CpMo(S_2CH_2)(SCPhCPhS)MoCp'$: yield 78%; NMR ($CDCl_3$) δ 2.10 (s, 3, CH_3), 5.78 (s, 4, Cp'); 5.94 (s, 5, Cp), 6.24 (s, 2, S_2CH_2), 7.2 (m, 10, Ph); mass spectrum, *m/e* 656 (P), 478 (P − PhCCPh); 432 (base, $CpCp'Mo_2S_3^+$).

Hydrogenation of Alkyne Adducts and Characterization of Alkenes. The alkyne adduct (≃0.2 mmol) was dissolved in $CHCl_3$ (25 mL), the solution was degassed, and 1 atm of H_2 was added at −196 °C. The solution was stirred at 60–65 °C until the color of the solution changed from green to blue (8–20 h). Volatile products and solvent were vacuum distilled, and the remaining solid was analyzed by NMR. Molybdenum-containing products were $(CpMoS)_2S_2CH_2$ and, in some cases, alkene adducts of this dimer, which were identified by comparison with authentic samples. The organic products from the hydrogenation reactions were characterized by the following methods. Ethylene was identified by GC. Separation and identification of the butene isomers was carried out by high-resolution gas chromatography. Vacuum distillation and analysis of the volatiles showed 99.7% *cis*-2-butene, 0.2% *trans*-2-butene, and <0.1% 1-butene. No butane was detected. A binuclear silver lanthanide shift reagent was used to differentiate the isomers of 2-hexene.[31] The hydrogenation reaction was carried out in $CDCl_3$, and the volatiles were then vacuum distilled from the reaction vessel. Treatment of this solution, with the shift reagent, and examination of the ^1H NMR spectrum showed the presence of only one isomer. *cis*-2-Hexene was identified by spiking the solution with an authentic sample. *cis*- and *trans*-stilbene are readily distinguished by their ^1H NMR spectra. Only the cis isomer was observed in the hydrogenation reaction.

Hydrogenation of Allene Adducts. $(CpMo)_2[S_2C(CH_3)_2](SC_3H_4S)$ was dissolved in $CHCl_3$, the atmosphere was evacuated, and excess hydrogen (1 atm) was added. The solution was stirred at 60–65 °C for 2 days. The color changed from red-brown to blue. Propene was detected by gas chromatography. The solvent was flash evaporated, and the remaining solid was characterized by NMR. The reaction was incomplete; 60% of the solid was starting material, ≃20% $(CpMoS)_2[S_2C(CH_3)_2]$, ≃10% $(CpMo)_2[S_2C(CH_3)_2]_2$, and ≃10% $(CpMo)_2(S_2CH_2)[S_2C(CH_3)_2]$. The methyl allene adduct in $CDCl_3$ was sealed in an NMR tube under 1–2 atm of hydrogen, and the reaction at 60 °C was monitored periodically by NMR. No intermediates were detected; products were *cis*-2-butene, $(CpMoS)_2S_2CH_2$, and the butene adduct of this dimer.

Hydrogenation of Ketene Adducts. The ketene adduct (0.172 g, 0.322 mmol) was dissolved in 20 mL of dry $DCCl_3$ in a 150-mL reaction vessel. The atmosphere was evacuated, and 1 atm of hydrogen was admitted at −196 °C. The solution was stirred at 60–70 °C for a total of 9 days. During this time a color change from red to blue was observed. The volatile fraction was vacuum distilled and analyzed by gas chromatography and ^1H NMR. Acetaldehyde was identified by comparison of spectral data with those of an authentic sample. The solid from the reaction was analyzed by ^1H NMR spectroscopy and was found to be composed of $(CpMoS)_2[S_2C(CH_3)_2]$ and $(CpMo)_2(S_2CH_2)[S_2C(CH_3)_2]$ in a 2:1 ratio. The diphenylketene adduct was reacted with hydrogen in

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a procedure identical with that described above. After 9 days the solution was filtered and the solvent was flash evaporated. Diphenylacetaldehyde and diphenylacetic acid were extracted from the resulting solid with diethyl ether and identified by NMR and IR.[32-34] The molybdenum-containing products, identified by NMR, were $(CpMoS)_2[S_2C(CH_3)]_2$ and $(CpMo)_2(S_2CH_2)[S_2C(CH_3)_2]$ in a 1:4.5 ratio.

Competition Reactions. Equimolar amounts of an ethylene adduct and $(CpMoS)_2S_2CH_2$ were dissolved in $CDCl_3$ in an NMR tube. The solution was degassed in two freeze-pump-thaw cycles, and the tube was sealed and warmed to room temperature. The NMR spectrum was recorded periodically over a period of 2 months, and the percent formation of $(CpMo)_2(SC_2H_4S)(S_2CH_2)$ was determined when no further spectral changes were observed. Results are given in Table I.

Determination of Equilibrium Constants. A $CDCl_3$ solution of known concentration in $(CpMoS)_2S_2CH_2$ was transferred to an NMR tube. One to four equivalents of *cis*- or *trans*-2-butene or *cis*-2-hexene were syringed or condensed into the tube. The NMR tubes were sealed at −195 °C. Concentrations were determined at 26 °C by integration of the ^1H NMR spectra, and equilibrium distributions were calculated when no further changes were observed (usually after 1 day, but concentrations were also checked after ~2 months). When the olefin was *cis*-stilbene or ethylene, only an upper or lower limit for the equilibrium constant could be determined. A solution of known concentration in alkyne adduct $(CpMo)_2(S_2CH_2)(SCRCRS)$, where R = Ph or H, was transferred to an NMR tube. Hydrogen was added, and the NMR tube was sealed at −195 °C. After hydrogenation was complete no adduct formation was observed for *cis*-stilbene. For the ethylene system only the adduct was formed. Limiting values were calculated by determining that a 3% solution of the missing Mo species would be observable under identical conditions.

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Registry No. $(Cp'Mo)_2(S_2CH_2)(SCH_3)_2$, 86163-39-5; $(Cp'Mo)_2(S_2CH_2)(SC_2H_2S)$, 86163-40-8; $(CpMo)_2(S_2CH_2)(SC_2H_2S)$, 86163-46-4; $(CpMo)_2(S_2CH_2)(SCPhCPhS)$, 86163-53-3; $(CpMo)_2(S_2CH_2)(SCCH_3CCH_3S)$, 86163-59-9; $(CpMo)_2(S_2CH_2)(SCCH_3C(CH_2CH_2CH_3)S)$, 86163-61-3; $(Cp'Mo)_2(S_2CH_2)(SCPhCPhS)$, 86163-62-4; $(CpMo)(S_2CH_2)(SCPhCPhS)(Cp'Mo)$, 86163-54-4; $(Cp'Mo)_2(S_2CH_2)(SCCH_3CCH_3S)$, 86163-60-2; $(CpMo)_2(S_2CH_2)(SC_2H_4S)$, 86163-55-5; $(Cp'Mo)_2(S_2CH_2)(SC_2H_4S)$, 86163-56-6; $(CpMo)_2(S_2CH_2)(SCH_2CH(CH_3)S)$, 86163-57-7; $(CpMo)_2(S_2CH_2)[SCH_2C(S)C(H)CH_3]$, 86163-48-6; $(CpMo)_2(S_2CH_2)[S_2C(CH_3)_2]$, 86163-51-1; $(CpMo)_2(S_2CH_2)_2$, 86163-52-2; $(CpMo)_2[S_2C(CH_3)_2](SC_2H_2S)$, 86163-58-8; $(CpMo)_2[S_2C(CH_3)_2](SC_2H_4S)$, 86163-63-5; $(CpMo)_2[S_2C(CH_3)_2][SCH_2C(S)CH_2]$, 86163-47-5; $(CpMo)_2[S_2C(CH_3)_2][SCH_2C(O)S]$, 86163-49-7; $(CpMo)_2[S_2C(CH_3)_2][S(Ph)_2CC(O)S]$, 86163-50-0; $(CpMo)_2(SC_2H_4S)(SCHCPhS)$, 86163-44-2; $(Cp'Mo)_2(S_2CS)(SC_2H_2S)$, 86163-43-1; $(CpMoS)_2[S_2C(CH_3)_2]$, 86163-41-9; $(CpMoS)_2S_2CH_2$, 86163-42-0; $(CpMoS)_2(SH)_2$, 75675-64-8; $(Cp'MoS)_2S_2CH_2$, 86163-45-3; $[Cp'Mo(S)SH]_2$, 75675-65-9; $[CpMoSC_2H_4S]_2$, 78186-29-9; Cl_2CS, 463-71-8; CH_2Br_2, 74-95-3; CH_3Li, 917-54-4; acetylene, 74-86-2; phenylacetylene, 536-74-3; ethene, 74-85-1; propene, 115-07-1; butene, 25167-67-3; 2-butyne, 503-17-3; allene, 463-49-0; methylallene, 590-19-2; ketene, 463-51-4; diphenylketene, 525-06-4; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; *cis*-2-hexene, 7688-21-3; *cis*-stilbene, 645-49-8.

Supplementary Material Available: Tables of observed and calculated structure amplitudes (17 pages). Ordering information is given on any current masthead page.

Synthesis of Some Polyimidazole Ligands Related to Zinc Enzymes

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Abstract: Methods have been developed for the synthesis of new ligands bearing imidazole groups. Tris(imidazolyl)ethane and tris(imidazolyl)butane derivatives have a more expanded geometry than the known tris(imidazolyl)carbinols, leading in at least one case to better binding to metals. Ligands carrying 2-phenylimidazole rings show altered properties because of the bulky phenyl substituent. Methods have been devised to prepare 4-substituted imidazole systems by a protecting group switch and to deoxygenate the carbinol groups of these ligands so as to remove ambiguity about their mode of binding.

In metalloenzymes, imidazole rings of histidine are frequently at least part of the metal-binding site. For example, in carbonic anhydrase[1] the zinc is bound to three imidazole ligands and in carboxypeptidase[2] and in thermolysin[3] the zinc is bound to two imidazole rings and a carboxylate anion, while in plastocyanine[4] copper is bound to two imidazole rings and two sulfur atoms. Because of the general occurrence of imidazole ligands in many metalloenzymes, we initiated a program a few years ago to develop good synthetic approaches to polyimidazole molecules that might mimic the binding and catalytic properties of some of these enzymes.

We reported[5] the first synthesis of ligand systems comprised of three imidazole units, in the compounds which we referred to as 2-TIC (tris(2-imidazolyl)carbinol; **1**) and 4-TIC (tris(4-imidazolyl)carbinol; **2**). Synthesis of the first type of system was achieved simply by metalation of N-protected imidazole at C-2, followed by reaction with diethyl carbonate and deprotection. In the synthesis of 4-TIC we protected imidazole both at nitrogen and at C-2 and then metalated at C-5. After reaction with diethyl

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