Articles

Synthesis of Water Soluble Sulfur-Bridged Molybdenum Dimers with Substituted Cyclopentadienyl Ligands

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The ester substituted cyclopentadienyl ligand $C_5H_4CO_2CH_3^-$ was used in the synthesis of dinuclear molybdenum complexes with bridging sulfur ligands. New derivatives include $[MeO_2C-CpMoSC_2H_4S]_2$, **3**, $[MeO_2C-CpMoSCHCPhS]_2$, **4**, and $[MeO_2C-CpMo)_2(S_2CH_2)(SC_2H_4S)]$, **7**. Analogous dinuclear complexes with one ester substituted and one unsubstituted Cp ligand have also been isolated and characterized. The base hydrolysis reaction of **7** leads to the formation of the water soluble derivative $(NaO_2C-CpMo(\mu-S))_2S_2CH_2$, **9**. A second water soluble derivative containing three carboxylate substituents, $(NaO_2C-CpMo(\mu-S))_2S_2C(H)CO_2Na$, **11**, was also synthesized and characterized. The formyl substituted cyclopentadienyl ligand was used in the preparation of new dinuclear molybdenum derivatives, including $(OHC-CpMoSC_2H_4S]_2$, **13**, and $[OHC-CpMoSC_2H_2S]_2$, **14**. Spectroscopic data for the new complexes are presented. The reactivity of the new series of complexes has been surveyed and found to be qualitatively similar to that of the unsubstituted cyclopentadienyl derivatives. The new products will permit a more detailed study of solvent and substituent effects on sulfur ligand reactivity.

Introduction

The dinuclear cyclopentadienylmolybdenum complex $(CpMo(\mu-S))_2S_2CH_2$, **1**, has shown an unusually broad range of reactivity.[1-5] Two classes of reactions that have the potential for further development in practical applications are the reversible olefin complexations to **1**[1] and the reversible activation of hydrogen by **1**.[3] We have been interested in determining how electronic effects of substituents on the cyclopentadienyl ligands might alter the equilibrium constants in these reactions in order to obtain a more detailed mechanistic understanding.

The pentamethylcyclopentadienyl (Cp*) analogues of **1** and related derivatives have been synthesized.[4-7] While this series of complexes shows similar reactivities, the Cp* complexes appear to be less reactive than the C_5H_5 derivatives in some cases. For example, most olefins do not appear to form an adduct with $(Cp^*Mo(\mu-S))_2S_2CH_2$.[8] Both steric and electronic factors appear to play a role in determining the reactivity differences of the molybdenum sulfide derivatives as the Cp ligand is changed to Cp*.

The effect of Cp electron withdrawing groups on reactivity has not been explored for the molybdenum sulfide systems and has generally been less studied in organometallic derivatives.[9] We were interested in investigating the effect of such electron withdrawing substituents on the sulfide ligand reactivity toward olefins and hydrogen. Such substituents also have the potential for changing solubility characteristics of the complexes. In this paper we report the synthesis and characterization of carbonyl containing Cp derivatives of the molybdenum sulfide dimers, including cyclopentadienyl esters, aldehydes, and water soluble carboxylate salts.

Results and Discussion

Syntheses of $(MeO_2C-CpMo)_2S_4$ Structures. The reaction of dimethyl carbonate with sodium cyclopentadienide was carried out as reported previously[10] to prepare the ester substituted ligand. The reaction of $[MeO_2C-Cp]^-$ with molybdenum hexacarbonyl to produce $[MeO_2C-CpMo(CO)_3]_2$ was carried out according to the procedure developed for NaCp.[11] We have used this carbonyl dimer to prepare tetrasulfido-bridged molybdenum dimers by procedures which are quite analogous to those reported by us for the Cp and MeCp derivatives.[6,7] For example, the thermal reaction of the ester substituted carbonyl dimer with excess elemental sulfur led to the formation of an insoluble, carbonyl-free material, presumably $[MeO_2C-CpMoS_x]_n$, which reacted under 2-3 atm of H_2

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

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

(3) Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; Rakowski, DuBois, M. *Organometallics* **1986**, *5*, 951.

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

(5) Farmer, M. M.; Haltiwanger, R. C.; Kvietok, F.; Rakowski DuBois, M. *Organometallics* **1991**, *10*, 4066.

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

(7) Rakowski DuBois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

(8) Rakowski DuBois, M.; Koval, C.; Maciejewski, M. Manuscript in preparation.

(9) (a) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. (b) Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607. (c) Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986**, *108*, 6219. (d) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228. (e) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6942.

(10) (a) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196. (b) Macomber, D. W.; Rausch, M. D. *J. Organomet. Chem.* **1983**, *258*, 331.

(11) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 107.

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Scheme 1

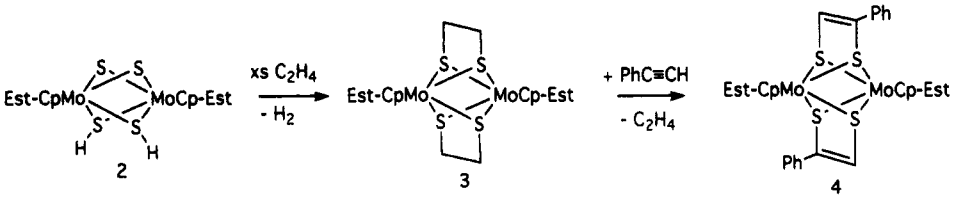


Table 1. ^{1}H NMR Data for New Complexes

complex	R–Cp	R	other
$[MeO_2C–CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, **2**	6.82 (m,[a] 4H)	3.70 (s, 6H)	−1.40 (s, SH)
$CDCl_3$, 300 MHz	6.40 (m, 4H)		−1.53 (s, SH)
$MeO_2C–CpMo(SC_2H_4S)_2MoCp$, **3a**	5.5 (m, 2H)	3.42 (s, 3H)	1.6 (m, 4H, C_2H_4)
C_6D_6, 200 MHz	4.8 (m, 2H)		1.4 (m, 4H, C_2H_4)
	4.8 (s, 5H)		
$[MeO_2C–CpMoSC_2H_4S]_2$, **3**	5.43 (m, 4H)	3.38 (s, 6H)	1.58 (s, 8H, C_2H_4)
C_6D_6, 200 MHz	4.75 (m, 4H)		
$MeO_2C–CpMo(SCHCPhS)_2MoCp$, **4a**	6.2 (m, 2H)	3.18 (s, 3H)	6.68 (s, 2H, SCH)
$CDCl_3$, 200 MHz	5.9 (m, 2H)		7.5–7.1 (m, 10H, Ph)
	6.0 (s, 5H)		
$[MeO_2C–CpMo(SCHCPhS)]_2$, **4**	6.16 (m, 4H)	3.16 (s, 6H)	6.67 (s, 2H, SCH)
$CDCl_3$, 200 MHz	5.92 (m, 4H)		7.3–7.2 (m, 10H, Ph)
$(MeO_2C–CpMo)(\mu\text{-}S)_2(S_2CH_2)MoCp$, **5a**	6.84 (t, 2H)	3.78 (s, 3H)	2.60 (dd, 2H, S_2CH_2)
$CDCl_3$, 300 MHz	6.59 (t, 2H)		
	6.59 (s, 5H)		
$(MeO_2C–CpMo\text{-}\mu\text{-}S)_2S_2CH_2$, **5**	6.9 (br m, 4H)	3.78 (s, 6H)	2.58 (s, 2H, S_2CH_2)
$CDCl_3$, 300 MHz	6.6 (br m, 4H)		
$(MeO_2C–CpMo)_2(S_2CH_2)_2$, **6**	6.22 (m, 4H)	3.58 (s, 6H)	6.03 (s, 4H, S_2CH_2)
$CDCl_3$, 300 MHz	5.88 (m, 4H)		
$(MeO_2C–CpMo)(S_2CH_2)(SC_2H_4S)MoCp$, **7a**	6.8 (m, 2H)	3.42 (s, 3H)	1.37 (m, 2H, C_2H_4)
$CDCl_3$, 200 MHz	5.1 (m, 2H)		1.62 (m, 2H, C_2H_4)
	5.1 (s, 5H)		5.48 (d, 1H, S_2CH_2)
			5.75 (d, 1H, S_2CH_2)
$(MeO_2C–CpMo)_2(S_2CH_2)(SC_2H_4S)$, **7**	5.76 (m, 4H)	3.62 (s, 6H)	1.84 (s, 4H, C_2H_4)
$CDCl_3$, 200 MHz	5.53 (m, 4H)		5.7 (s, 2H, S_2CH_2)
$[(MeO_2C–CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SMe)]OTF$, **8**	7.28 (t, 4H)	3.80 (s, 6H)	1.63 (s, 3H, SMe)
$CDCl_3$, 200 MHz	7.11 (t, 4H)		4.30 (s, 2H, S_2CH_2)
$(NaO_2C–CpMo\text{-}\mu\text{-}S)_2S_2CH_2$, **9**	6.66 (t, 4H)		2.64 (s, 2H, S_2CH_2)
D_2O, 300 MHz	6.47 (t, 4H)		
$(HO_2C–CpMo\text{-}\mu\text{-}S)_2S_2CH_2$	6.85 (t, 4H)		2.74 (s, 2H, S_2CH_2)
DMSO-d_6, 250 MHz	6.66 (t, 4H)		
$(MeO_2C–CpMo)_2(SC_2H_4S)(S_2CHCO_2Me)$, **10**	5.74 (m, 2H)	3.72 (s, 3H)	6.43 (s, 1H, S_2CH)
$CDCl_3$, 300 MHz	5.71 (m, 2H)	3.64 (s, 3H)	1.88 (m, 4H, C_2H_4)
	5.58 (m, 4H)	3.60 (s, 3H)	
$(NaO_2C–CpMo\text{-}\mu\text{-}S)_2S_2CHCO_2Na$, **11**	6.63 (t, 2H)		3.26 (s, 1H, S_2CH)
D_2O, 300 MHz	6.56 (t, 2H)		
	6.47 (t, 2H)		
	6.31 (t, 2H)		
$(HO_2C–CpMo\text{-}\mu\text{-}S)_2S_2CHCO_2H$	6.88 (t, 2H)		3.70 (s, 1H, S_2CH)
DMSO-d_6, 300 MHz	6.72 (t, 4H)		13.0 (b, OH)
	6.58 (t, 2H)		
$(CHO–CpMo)_2(SCH_2CH_2S)_2$, **13**	5.35 (s, 8H)	9.29 (s, 2H)	1.90 (s, 8H, C_2H_4)
$CDCl_3$, 300 MHz			
$(CHO–CpMo)_2(SCHCHS)_2$, **14**	6.15 (t, 4H)	9.21 (s, 2H)	6.50 (s, 4H, C_2H_2)
$CDCl_3$, 200 MHz	6.08 (t, 4H)		

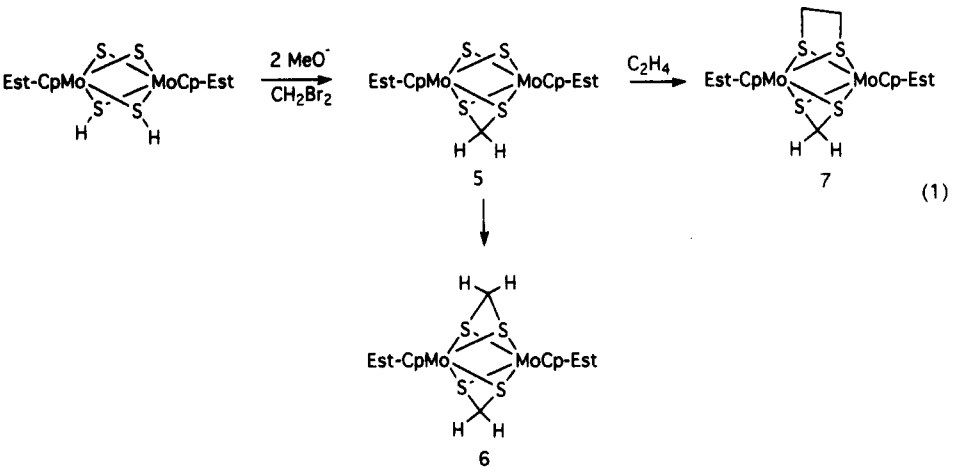
[a] Multiplicities: t for Cp hydrogens indicates a pseudotriplet; s = singlet, d = doublet, m = multiplet, dd = doublet of doublets.

pressure to form $[(MeO_2C–CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, **2**. The latter complex was identified by spectroscopic data.

The reactivity of **2** with unsaturated molecules appeared to be completely analogous to that characterized previously for $[R–CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, R = H, Me, Me_5. For example the reaction of **2** with ethylene resulted in the formation of a bis(ethanedithiolate) complex $[MeO_2C–CpMoSC_2H_4S]_2$, **3** (see Scheme 1). We have shown for the R = H system that hydrogen is eliminated in this reaction.[6] Further reaction of **3** with phenylacetylene resulted in ethylene displacement and the formation of $[MeO_2C–CpMoSCHCPhS]_2$, **4**. Complexes **3** and **4** were purified and isolated by chromatography. In some reaction runs, a second minor product, **3a** or **4a**, was isolated in the chromatography experiments. These were identified as the corresponding dimers with one ester substituted and one unsubstituted Cp ligand. They are formed in cases where there was an incomplete reaction in the initial substitution reaction of Cp. ^{1}H NMR data for the alkane- and alkenedithiolate complexes are included in Table 1, and other characterization data and microanalyses for representative complexes from the series are given in the Experimental Section.

The ester–Cp derivatives were primarily of interest to us because of their potential for further derivatization, which, for example, might lead to covalent attachment to polymers or to water soluble complexes. However, the electronic characteristics of these complexes were investigated briefly. The strength of the inductive effect of the electron-withdrawing ester substituent can be assessed by comparing the cyclic voltammetric data of these complexes with those of the unsubstituted analogues. For

Scheme 2



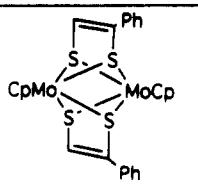
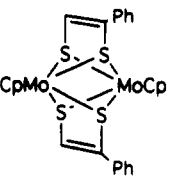
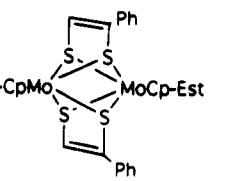
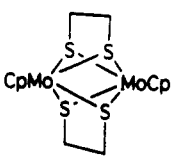
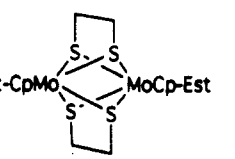
example, comparison of peak potentials for the initial reversible oxidation in the bis(phenylethenedithiolate) complexes has shown that incorporation of an ester substituent into one of the Cp ligands shifts the potential to a more anodic value by ~135 mV. Comparison of this monoester derivative **4a** with the diester complex **4** showed a similar anodic shift in potential (~160 mV) for the first oxidation of the latter complex. Data are summarized in Table 2.

Synthesis of $[(MeO_2C–CpMo)_2(S_2CH_2)(SC_2H_4S)]$. The methanedithiolate derivatives of the Cp and MeCp dimers have displayed very versatile reaction chemistry, and the synthesis of the analogous complex with ester substituted Cp ligands was therefore attempted. Deprotonation of **2** in the presence of dibromomethane produced the desired product $(MeO_2C–CpMo(\mu\text{-}S))_2S_2CH_2$, **5**, identified by NMR data, but the product did not appear to be very stable under these conditions and attempts to isolate this complex were unsuccessful. In addition, a second product, identified as $[MeO_2C–CpMoS_2CH_2]_2$, **6**, was also formed in significant yield; see eq 1. The formation of a product with two methanedithiolate ligands may occur by methoxide reduction of **5**, and nucleophilic attack of this reduced species on dibromomethane. In order to minimize the production of **6**, the reaction with dibromomethane was carried out in the presence of ethylene. Under these conditions the ethylene adduct of **5** was trapped as $(MeO_2C–CpMo)_2(S_2CH_2)(SC_2H_4S)$, **7**, before **5** underwent further reaction with dibromomethane, eq 1. Complex **7** was isolated in 44% yield under these conditions, but **6** was still produced as a side product in reaction 1 in about 20% yield. Under circumstances in which the Cp ligand was incompletely substituted, we were also able to isolate low yields (10%) of $(MeO_2C–CpMo)(S_2CH_2)(SC_2H_4S)$-MoCp, **7a**. These products were characterized by the usual spectroscopic techniques (see Experimental Section).

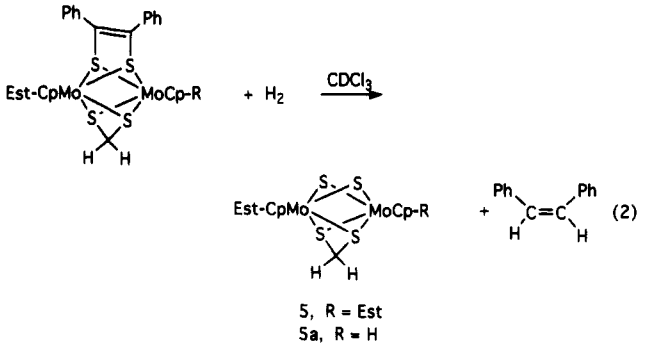
Other derivatives of the methanedithiolate complex were also synthesized and characterized. For example, reaction of **7** with diphenylacetylene led to the formation of $(EstCpMo)_2(S_2CH_2)(SCPhCPhS)$. An identical reaction was observed for the mixed ligand (Cp/EstCp) analogue of **7**. These diphenylacetylene adducts in chloroform solution reacted with 1 atm of hydrogen to form $(RCpMo(\mu\text{-}S))_2S_2CH_2$ and *cis*-stilbene, eq 2. Similar reactions have been reported for the parent C_5H_5 complex.[1] The reaction of the mixed ligand complex proceeded more rapidly and cleanly than that of the bis(ester-Cp) complex. The complex $(EstCpMo(\mu\text{-}S))_2S_2CH_2$, **5**, was not successfully isolated in the direct synthesis described above, and it appeared to have limited stability under the conditions of reaction 2 as well. Partial decomposition of **5** was observed during the hydrogenation reaction.

The reaction of **7** with methyl triflate led to the clean formation of a cationic methanethiolate complex **8**, which was isolated and characterized spectroscopically. This cation reacted with hydrogen in the presence of pyridine to form the neutral complex $(EstCpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SH)$, eq 3. This hydrogen activation proceeded under

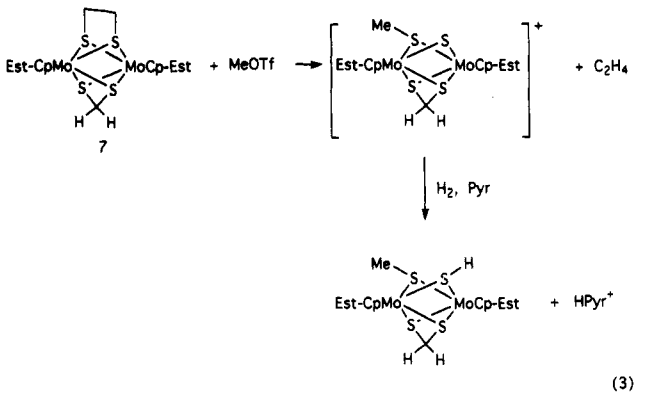
Table 2. Redox Potentials for Oxidations of Molybdenum Dimers

	$E_{p/2}$, V vs ferrocene[a]	ΔE_p, mV
	–0.175[b] 0.48[c]	70 irrev
	–0.04 0.45	94 irrev
	0.12 0.56	82 130
	–0.28[d] 0.37	60 70
	–0.020[e] 0.72	82 80

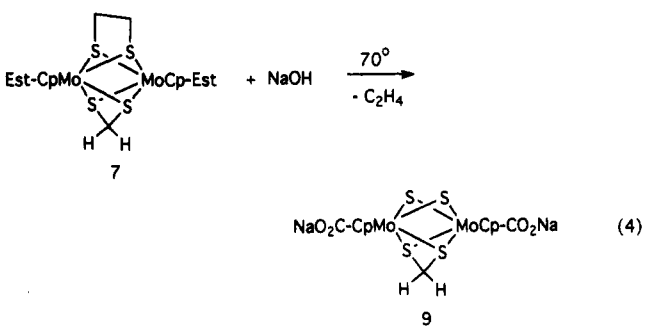
[a] Potentials determined in CH_2Cl_2/0.1 M n-Bu_4NPF_6 at a scan rate of 100 mV/s. [b] Scan rate, 300 mV/s. [c] Peak potentials reported for irreversible waves. [d] Solvent, CH_3CN. In CH_2Cl_2 the first wave occurred at the same potential, but the second was obscured by electrode adsorption. [e] Scan rate, 1000 mV/s.



conditions (3 days, room temperature) similar to those of the analogous methyl–Cp cation.[12]



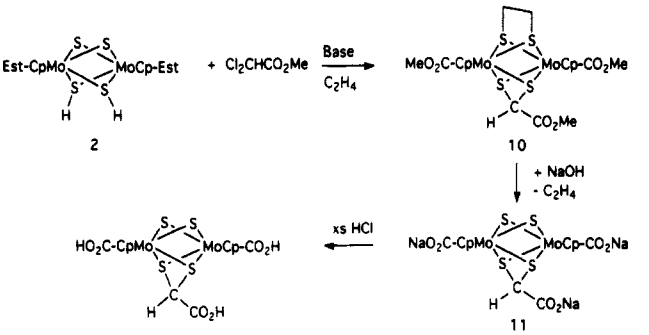
Synthesis of $(NaO_2C–CpMo(\mu\text{-}S))_2S_2CH_2$, 9. The hydrolysis of the ester substituents on the cyclopentadienyl ligands of **7** was carried out in order to obtain a water soluble derivative. A slurry of complex **7** in methanol/water was reacted with excess NaOH at 70 °C. The reaction proceeded slowly over a period of ~1 week to form a deep blue solution. Elution of this product with methanol/water on a basic alumina column led to the isolation of $(NaO_2C–CpMoS)_2S_2CH_2$, **9**, in 65% yield; see eq 4. In addition to the base hydrolysis of the ester



substituents, ethylene elimination from the ethanedithiolate ligand of **7** also occurred during this reaction. This type of thermal lability of olefins from dithiolate ligands has been established previously for related organic soluble complexes.[1]

Complex **9** was characterized by spectroscopic methods. The ^1H NMR spectrum in D_2O showed two pseudotriplets for the protons on the Cp rings and a singlet at 2.6 ppm assigned to the methanedithiolate ligand (see Table 1). In the infrared spectrum, the asymmetric carboxylate stretch was observed at 1570 cm^{-1} and two bands were observed in the region of the symmetric stretch at 1382 and 1345 cm^{-1}. The cyclic voltammogram of **9** in H_2O (0.15 M NaCl) at a glassy carbon electrode showed a fairly reversible reduction at –0.92 V vs SCE (ΔE = 120 mV) and a largely irreversible oxidation at 0.38 V ($\Delta E \simeq$ 300 mV). Additional irreversible waves at 0.8 and 1.0 V were attributed to oxidation of the carboxylate substituents.[13] The quasi reversible oxidation and reduction of **9** show anodic shifts relative to similar waves reported for $(MeCpMo(\mu\text{-}S))_2S_2CH_2$ at +0.27 and –1.30 V vs SCE in acetonitrile.[2] This is presumably a reflection of the electron-withdrawing ability of the carboxylate substituents.

Scheme 3



The solubility of **9** in water was found to be ca. 0.18 M at 20 °C. Acidification of an aqueous solution of **9** with excess HCl led to immediate precipitation of a dark green molybdenum complex. The isolated complex was found to be completely insoluble in water. The NMR spectrum in DMSO-d_6 was very similar to the spectrum of **9** in D_2O, but resonances were shifted 0.1–0.2 ppm downfield. The product is formulated as the neutral complex $(HO_2C–CpMo(\mu\text{-}S))_2S_2CH_2$. When a slurry of the neutral complex in water was titrated with NaOH, a single inflection point was observed after addition of ca. 2 equiv of base. The data suggested that the two carboxylate substituents are deprotonated independently, i.e., at the same pH. From the titration data a pK_a of 6.25 was determined for the protonated complex, corresponding to a K_B of 1.8×10^{-8} for **9**. The pK_a is ca 2 orders of magnitude larger than pK_a's determined for related carbonyl derivatives $(Cp–CO_2H)W(CO)_3Me$ (pK_a = 4.5)[10b] and $(CpCO_2H)_2W_2(CO)_6$ (pK_a = 4.5).[9b] The decrease in acidity for the molybdenum sulfur dimer is consistent with the replacement of π-accepting carbonyl ligands by sulfur donors.

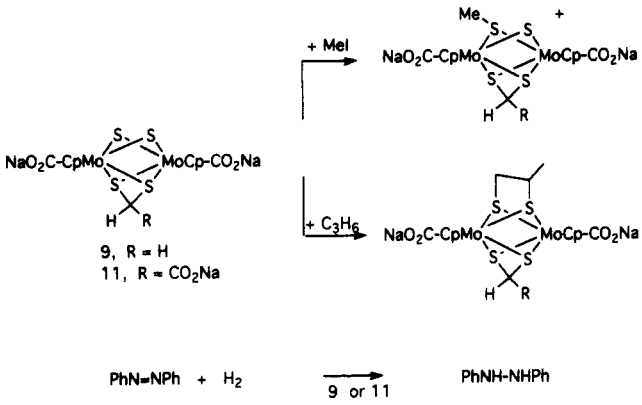
Synthesis of $(NaO_2C\text{-}CpMo(\mu\text{-}S))_2S_2CHCO_2Na$, 11. In order to enhance the water solubility of the carboxylate substituted derivative **9**, we have explored the possibility of introducing a third carboxylate group into the complex as a substituent on the methanedithiolate ligand. The deprotonation of $[(MeO_2C–CpMo)(\mu\text{-}S)(\mu\text{-}SH)]_2$, **2**, in the presence of methyl dichloroacetate led to the formation of the triester substituted complex $(MeO_2C–CpMo(\mu\text{-}S))_2(S_2CHCO_2Me)$, Scheme 3. Excess ethylene was bubbled through the solution, and the product was isolated as the more stable ethanedithiolate complex, $(MeO_2C–CpMo)_2(SC_2H_4S)(S_2CHCO_2Me)$, **10**. Complex **10** was chromatographed and identified by NMR spectroscopy and then used without further purification in the following hydrolysis reaction.

Complex **10** was hydrolyzed by refluxing it in a MeOH/H_2O solution of KOH. Excess hydroxide was neutralized

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

(13) *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York: 1978; Vol. XII, pp 267–270.

Scheme 4



with $NaHCO_3$ and column chromatography of the blue product permitted the isolation of $(NaO_2CCpMo(\mu\text{-}S))_2S_2CHCO_2Na$, 11, in ~60% yield. The solubility of 11 in water at 20 °C was found to be 0.23 M, slightly greater than that of 9. Spectroscopic data for 11 are consistent with the proposed formulation and are included in the Experimental Section. In particular, the ^1H NMR spectrum of 11 shows evidence for inequivalent cyclopentadienyl ligands which result from substitution of the methanedithiolate carbon (see Table 1). The cyclic voltammetry of 11 was similar to, but less reversible than that of 9, with a reduction wave at −0.99 V vs SCE and the first irreversible oxidation at +0.40 V.

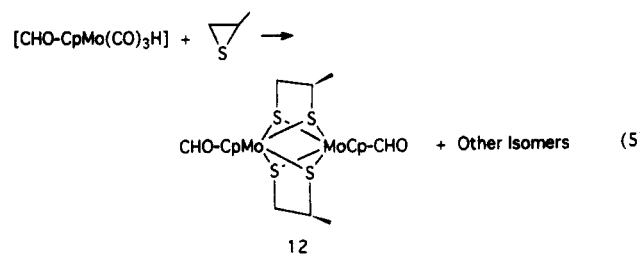
The reaction of 11 with excess HCl produced a product insoluble in water. Spectroscopic data and microanalyses suggested that all three carboxylates were protonated. This was confirmed by a titration of the protonated derivative with NaOH. A single inflection point was observed in the titration curve after 3 equiv of base was added. The pH at the equivalent point was 8.30, and an overall pK_a of 4.73 was calculated. Our failure to detect separate end points for the $Cp\text{–}CO_2H$ and the S_2CHCO_2H acids suggests that the ionization constants for the two acid types are similar ($K_{a1}/K_{a2} < 10^4$).[14] The protonated form of 11 shows a lower average pK_a than that of 9. This is attributed to the contribution of the dithiolate carboxy acid, which is expected to be more acidic than the Cp substituted acids.

Reactivity of Water Soluble Complexes. The reactivity of $(NaO_2CCpMo(\mu\text{-}S))_2S_2CHR$, where R = H, 9, or R = CO_2Na, 11, in aqueous solution was similar to that of the organic soluble parent compound $(CpMo(\mu\text{-}S))_2S_2CH_2$; see Scheme 4. For example, the μ-sulfido ligands were nucleophilic and could be alkylated with organic halides. The addition of methyl iodide to 9 in aqueous solution produced $[(NaO_2CCpMo)_2(\mu\text{-}S)(\mu\text{-}SMe)(S_2CH_2)]I$, which was isolated and characterized spectroscopically. No evidence was observed for the formation of the methyl ester product in this reaction. The alkylated product in the solid state could also be formulated as a zwitterion resulting from elimination of NaI, but attempts to obtain single crystals of this product were unsuccessful.

The sulfide ligands in 9 and 11 reacted reversibly with olefins in aqueous solution to form products with alkanedithiolate ligands; examples of these adducts have been isolated and characterized. Both 9 and 11 retained the intriguing ability of the parent complex to activate molecular hydrogen. For example, the complexes served as catalysts or catalyst precursors for the hydrogenation of azobenzene in a two phase aqueous/benzene solvent system. More detailed characterization of the reversible olefin binding and hydrogen activation reactions in aqueous solutions will be discussed in subsequent papers.

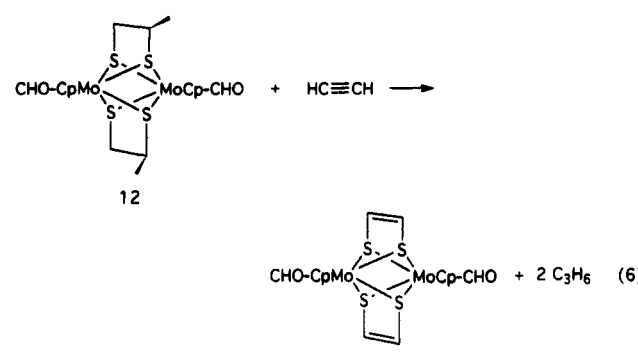
Synthesis of $(CHO\text{–}CpMo)_2S_4$ Derivatives. A related Cp substituent which has interesting potential for further derivatization is the formyl group. The formyl substituted complex $[CHO\text{–}CpMo(CO)_3]_2$ was synthesized from $CHO\text{–}Cp^-$ [10] and $Mo(CO)_6$, and the further reaction chemistry of this complex with sulfur sources was investigated. The reaction route used previously for the synthesis of $[(R\text{–}CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ was unsuccessful in the case where R = CHO. While refluxing of the carbonyl dimer with elemental sulfur did lead to the formation of an insoluble carbonyl-free product, no further reaction of this material with hydrogen was observed.

An alternate route to the dinuclear CHO–Cp molybdenum derivatives with four bridging sulfur ligands was therefore employed. The hydride complex $OHC\text{–}CpMo(CO)_3H$ was synthesized according to the procedure reported for the C_5H_5 analogue[11] and then reacted with propylene sulfide. This reaction led to the formation of isomers of the bis(propanedithiolate) complex $[CHO\text{–}CpMoSCH_2CHMeS]_2$, 12, eq 5. Four isomers are expected



because of the different orientations possible for the propanedithiolate ligands, and evidence for these was observed in the ^1H NMR spectrum. Further reaction of this complex with ethylene or acetylene gave ethane- and ethenedithiolate complexes, respectively, which were isolated by chromatography and characterized by spectroscopic methods. Secondary products were also isolated which contained only one formyl substituted Cp ligand. The characterization data for these complexes are included in the Experimental Section.

The alkene exchange reactions of 12 were significantly slower than those of the unsubstituted Cp system under similar conditions. For example, the reaction of 12 with acetylene to form $[CHO\text{–}CpMoSC_2H_2S]_2$, 14, and propene, eq 6, required stirring at 50 °C for 2 weeks, while with the

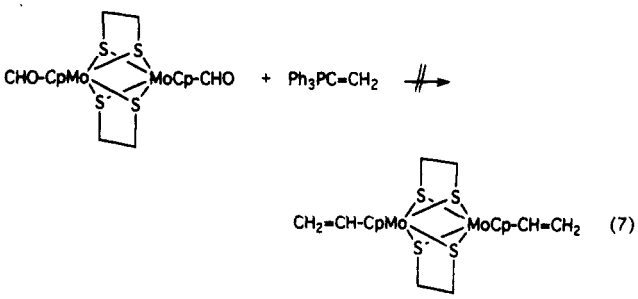


C_5H_5 derivative the reaction was complete within 2 days

(14) Fritz, J. S.; Schenk, G. H., Jr. *Quantitative Analytical Chemistry*, 2nd ed.; Allyn and Bacon: Boston: 1969; p 167.

at 25 °C. For the latter system, the rate of this exchange reaction was found to be limited by propene dissociation from the starting reagent,[6] and a similar dissociative mechanism is assumed for the reactions of **12**. The electron-withdrawing effect of the formyl substituent, therefore, appears to promote stronger olefin binding to the sulfido ligands relative to the Cp system. A more detailed study of how substituents affect the rates of olefin binding and dissociation in these dimers is in progress and will be reported in a separate paper.

The reactions of $[CHO–CpMoSC_2H_4S]_2$, **13**, and $[CHO–CpMoSC_2H_2S]_2$, **14**, with the ylide reagent $Ph_3P{=}CH_2$ were carried out under various reaction conditions[15] in attempts to prepare the vinyl substituted Cp derivatives, eq 7. These products are of interest because of the utility



(7)

of vinyl–Cp complexes in preparing organometallic polymer materials.[16] However, the reactions with the ylide reagent proved to be quite complex and we were unable to identify the desired complexes $[CH_2{=}CHCpMoSCH_nCH_nS]_2$ (n = 1, 2) in these reactions. Further studies of the reactivities of the formyl–Cp derivatives are planned.

Summary and Conclusions. New derivatives of the cyclopentadienylmolybdenum complexes with bridging sulfur ligands have been synthesized that incorporate ester, carboxylate, or formyl substituents into the Cp ligands. The dimers with carboxylate substituents were found to be soluble and stable in neutral and basic aqueous solutions. Electrochemical data provided evidence for the electron-withdrawing effects of the Cp substituents, but these inductive effects were relatively small. The reactivities of the sulfur ligands in the new complexes were found to be qualitatively similar to those of previously studied $Cp_2Mo_2S_4$ derivatives. For example, reactions of the sulfur ligands with alkenes and with hydrogen were identified. Preliminary studies indicate that the electron-withdrawing Cp substituents lead to enhanced acceptor properties of the bridging sulfur ligands. The new complexes reported here provide the basis for further development of the aqueous chemistry of molybdenum sulfur complexes in the areas of small molecule activation and catalysis.

Experimental Section

The syntheses of $C_5H_4CO_2Me^-$ and $C_5H_4CHO^-$ were carried out by published procedures.[10] Organic solvents were dried by conventional methods; deionized water was used in aqueous syntheses. In the electrochemical measurements, platinum disk and glassy carbon electrodes were used as working electrodes in nonaqueous and aqueous systems, respectively. In nonaqueous solvents the reference electrode was a copper wire, and ferrocene was used as an internal standard. The reference electrode for aqueous solutions was the saturated calomel electrode (SCE). Voltammograms of the aqueous solutions were recorded at scan rates of 50 mV/s. Faster scans were significantly less reversible. It was necessary to clean the electrode between scans to obtain reproducible potentials.

Synthesis of $[MeO_2C–CpMo(CO)_3]_2$. Sodium hydride (2.5 g, 0.1 mol) was added against a flow of nitrogen to a solution of freshly cracked cyclopentadiene (10 mL, 0.12 mol) in dry, degassed THF (300 mL). This solution was allowed to stir under nitrogen at oil bubbler pressure. When all gas evolution had ceased (ca. 10 h), degassed dimethyl carbonate (27 mL, 0.3 mol) was added via syringe.[10] This solution was refluxed for 48 h. After this time period, the pink solution was allowed to cool to room temperature and molybdenum hexacarbonyl (30 g, 0.11 mol) was added against a flow of nitrogen to the solution. This mixture was refluxed for 3 days. After this time period, a degassed solution of iron(III) sulfate pentahydrate (40 g) in water (500 mL) and acetic acid (30 mL) were added to the yellow-orange THF solution via cannula over a 1-h period. The resultant slurry was allowed to stir until gas evolution had ceased, and then the flask was placed in an ice bath and allowed to sit for 30 min. The red, crystalline solid $[MeO_2CCpMo(CO)_3]_2$ was filtered from the solution through a coarse porosity fritted funnel. The solid on the filter was washed with two 20-mL portions of water, two 10-mL portions of methanol, and two 20-mL portions of pentane. Yield: 80%, Purity: 80%. ^1H NMR (300 MHz, C_6D_6): δ 5.48 (br s, 4H), 4.57 (br s, 4H), 3.34 (br s, 6H). ^{13}C NMR (75 MHz, C_6D_6): δ 165 (CO_2CH_3), 97.2 (C_5H_4), 91.9 (C_5H_4), 51.6 (CO_2CH_3). IR (Nujol) (cm^{-1}): 3116 (w, Cp–H), 2926 (w, CH_3), 1967 (s, MoCO), 1915 (s, MoCO), 1888 (s, MoCO), 1717 (m, CO), 1410 (w, Cp).

Synthesis of $[MeO_2C–CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$, 2. Sulfur (5.1 g, 20.0 mmol) was added to a solution of $[MeO_2C–CpMo(CO)_3]_2$ (12.1 g, 20.0 mmol) in toluene (600 mL) in a one-neck, 1000-mL flask fitted with reflux condenser. The resulting slurry was refluxed under nitrogen for 3 days. The black solution was then filtered through a medium porosity fritted funnel, and the black solid was washed with 200 mL of dichloromethane or until the washings became colorless. The dried black-purple solid was then combined with 400 mL of dichloromethane, and the slurry was heated (50 °C) under hydrogen pressure (40 psi) in a Parr hydrogenation apparatus. After 3 days the apparatus was vented in a hood. **CAUTION**: H_2S is released. (An aqueous $CuSO_4$ solution can be used to trap the H_2S.) The red purple solution was filtered through a bed of Celite (1 in. thick) on a coarse porosity fritted funnel. The filter bed was washed with 100 mL of dichloromethane or until the washings were colorless. The solvent was removed from the filtrate by rotoevaporation to yield a purple powder, **2**. Yield: 8 g, 75%. IR (KBr) (cm^{-1}): 3100, 2944, 2300 (vw, SH), 1717 (s, CO), 1473 (m, Cp), 1193 (s, C–O–CH_3). Mass spec (FAB$^+$): m/z = 567 (P, 100), 536 (P – OCH_3, 50), 509 (P – CO_2CH_3, 40). NMR evidence for the analogous Cp/ester–Cp complex was observed in some cases.

Formation of $[(MeO_2CCpMo)_2(SC_2H_4S)_2]$, 3. A solution of **2** (0.21 g, 3.7×10^{-4} mol) in dichloromethane (40 mL) was freeze–pump–thaw degassed two times in a 500-mL flask with a Teflon stopcock. The flask was charged with 1.5 atm of ethylene. The solution was stirred for 3 days at room temperature. The resulting brown solution was filtered through Celite (1-in. bed), and the Celite was washed with dichloromethane until the rinses were colorless. The brown filtrate was then concentrated on a rotary evaporator to about 20 mL and loaded onto an alumina column. An initial gold band was eluted with dichloromethane. Once this band had eluted, a trailing copper colored band was eluted with dichloromethane/acetonitrile (3/1). The initial band was determined to be $[(MeO_2CCpMo)(SC_2H_4S)_2(CpMo)]$, **3a**. The compound was isolated by evaporation of the solvent by rotary evaporation. Yield: 12%. Anal. Calcd for $C_{16}H_{20}O_2S_4Mo_2$: C, 34.04; H, 3.57; S, 22.71. Found: C, 34.04; H, 3.34; S, 22.36. The second band was determined to be $[(MeO_2CCpMo)_2(SC_2H_4S)_2]$, **3**. This fraction was also isolated by removal of the solvent by

(15) Macomber, D. W.; Rausch, M. D.; Jayarzaman, T. V.; Preister, R. D.; Pittman, C. U. *J. Organomet. Chem.* **1981**, *205*, 353.

(16) (a) Gibson, C. P.; Bern, D. S.; Falloon, S. B.; Hitchens, T. K.; Cortopassi, J. E. *Organometallics* **1992**, *11*, 1742. (b) *Advances in Organometallic and Inorganic Polymer Science*; Carraher, C. G., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds.; Marcel Dekker: New York, 1982.

rotary evaporation. Yield: 45%. Anal. Calcd for $C_{18}H_{22}O_4S_4Mo_2$: C, 34.73; H, 3.56; S, 20.60. Found: C, 34.76; H, 3.54; S, 20.69.

Formation of $(MeO_2CCpMo)(SCHCPhS)_2(CpMo)$, 4a. A gold solution of **3a** (0.050 g, 7.0×10^{-5} mol) in dichloromethane (5 mL) was treated with excess phenylacetylene (0.091 g, 8.9×10^{-4} mol). The solution was allowed to stir under static vacuum at 50 °C for 3 days. During this time period, the solution turned green. The product was isolated by elution on an alumina column. The first fraction $[(MeO_2CCpMo)(SCHCPhS)_2(CpMo)]$, **4a**, was eluted with dichloromethane and isolated by evaporation of solvent. Yield: 85%. MS (FAB^+): m/z = 710 (P, 40), 608 (P − HC_2Ph, 50), 508 (P − $2HC_2Ph$, 100).

Formation of $[(MeO_2CCpMo)_2(SCHCPhS)_2]$, 4. A red solution of **3** (0.050 g, 6.5×10^{-5} mol) in dichloromethane (5 mL) was treated with excess phenylacetylene (0.091 g, 8.9×10^{-4} mol). The solution was allowed to stir under static vacuum at 50 °C for 3 days. During this time period, the solution turned green. The product was isolated by elution on an alumina column. The first fraction $[(MeO_2CCpMo)_2(S_2CHCPh)_2]$ was eluted with dichloromethane/acetonitrile (4:1). Yield: 85%.

Synthesis of $(MeO_2C–CpMo)_2(S_2CH_2)(SC_2H_4S)$, 7. Over a period of 15 min, freshly prepared sodium methoxide (0.38 g, 7×10^{-3} mol) in methanol (5 mL) was added to a purple solution of **2** (2.0 g, 3.5×10^{-3} mol) and dibromomethane (250 μL, 3.5×10^{-3} mol) in dry degassed THF (120 mL). The blue-green solution was allowed to stir under nitrogen at room temperature for 1 h. After this time period, ethylene was bubbled through the solution for 5 min, and an immediate color change to brown was observed. The solution was then filtered through a Celite bed (1 in. thick), the filtrate was evaporated, and the resulting solid was extracted with dichloromethane. The brown solution was filtered again, concentrated to about 20 mL, and loaded onto a neutral alumina column (ca. 70 mL). In come cases, an initial, small orange fraction was eluted with dichloromethane. This product was identified as $(MeO_2CCpMo)(S_2CH_2)(SC_2H_4S)(MoCp)$, **7a**. Yield: 10%. ^1H NMR (200 MHz, $CDCl_3$): δ 6.8 (m, 2H, C_5H_4), 5.11 (m, 2H, C_5H_4), 5.11 (s, 5H, C_5H_5), 5.75 (d, 1H, S_2CH_2), 5.48 (d, 1H, S_2CH_2), 3.42 (s, 3H, OCH_3), 1.62, (m, 2H, $S_2C_2H_4$), 1.37 (m, 2H, $S_2C_2H_4$). IR (KBr) (cm^{-1}): 3083 (w), 2952 (w), 1705 (s), 1465 (m), 1272 (ms), 1136 (m), 1037 (mw), 967 (mw). A second, large orange fraction was eluted from the column with dichloromethane/acetonitrile (3:1). The solvent was removed from this second fraction by rotoevaporation to give $(MeO_2CCpMo)_2)(S_2CH_2)(SC_2H_4S)$, **7**, as rust colored crystals. Yield: 30%. ^1H NMR: Table 1.

Formation of $[(MeO_2CCpMo)_2(S_2CH_2)(SC(Ph)C(Ph)S)]$. A mixture of **7** and **7a** (6.6×10^{-5} mol, 39 mg) was dissolved in dichloromethane (20 mL), and diphenylacetylene (0.50 g, 2.8×10^{-3} mol) was added. The reaction was stirred for 10 days at room temperature. After this time period, the solution was a brown-green color. Two green products were isolated by elution on an alumina column with acetonitrile/dichloromethane (1:10). The first band was $(MeO_2CCpMo)(S_2CH_2)(SC(Ph)C(Ph)S)$-$(MoCp)$. Yield: 32%. ^1H NMR (200 MHz, $CDCl_3$): δ 7.1 (m, 6H, Ph), 6.75 (m, 4H, Ph), 6.25 (m, 2H, C_5H_4), 5.92 (m, 2H, C_5H_4), 5.90 (s, 5H, C_5H_5), 6.25 (dd, 2H, S_2CH_2), 3.50 (s, 3H, OCH_3). IR (KBr) (cm^{-1}): 3102 (w, Cp–H stretch), 2952, 2895 (w, alkyl stretch), 1705 (s, CO stretch), 1460 (m, Cp double bond vibrations), 1277 (ms, C–OCH_3 vibration), 1141 (m), 1028 (mw). The second band was the title compound. Yield: 65%. ^1H NMR (200 MHz, $CDCl_3$): δ 7.08 (m, 6H, Ph), 6.93 (m, 4H, Ph), 6.24 (m, 4H, C_5H_4), 5.95 (m, 4H, C_5H_4), 5.97 (s, 2H, S_2CH_2), 3.51 (s, 6H, OCH_3). IR (KBr) (cm^{-1}): 3112 (w, Cp–H stretch), 2952, 2906 (w, alkyl stretch), 1702 (s, CO stretch), 1458 (m, Cp double bond vibrations), 1276 (s, C–O–CH_3 vibration), 1081 (mw).

Reactions of Diphenylacetylene Adducts with Hydrogen. A solution of $[(MeO_2CCpMo)(S_2CH_2)(SC(Ph)C(Ph)S)(CpMo)]$ (8 mg) in chloroform-d_1 (0.7 mL) was transferred to a flame sealable NMR tube. The solution was freeze–thaw degassed (3×) and then frozen at −196 °C. The tube was charged with 150 mmHg of hydrogen gas at −196 °C and then flame sealed. The reaction mixture was kept at room temperature and monitored by ^1H NMR spectroscopy. After 1 day, 60% of the starting material had been converted to $[(MeO_2CCpMo)(S_2CH_2)(\mu\text{-}S)_2$-$(CpMo)]$, **5a**, and *cis*-stillbene. After 4 days the reaction was complete. Yield: >95%.

An identical procedure was followed for the reaction of $[(MeO_2$-$CCpMo)_2(S_2CH_2)(SC(Ph)C(Ph)S)]$ with hydrogen. After 4 days at room temperature, a ^1H NMR spectrum revealed that no reaction had occurred yet. After the reaction mixture was further heated for 4 days at 50 °C, some reaction had occurred (ca. 20%). Most of the product $[(MeO_2CCpMo)_2(S_2CH_2)(\mu\text{-}S)_2]$, **5**, had decomposed. After 20 days of rapid agitation at room temperature, most of the starting material had been converted to **5** and *cis*-stilbene. Purity: <50%.

Formation of $[(MeO_2CCpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]$-OTF, 8. An orange-red solution of **7** (130 mg, 2.1×10^{-4} mol) in distilled dichloromethane (30 mL) was treated with methyl trifluoromethanesulfonate (MeOTF) (18 μL, 2.4×10^{-4} mol) under nitrogen at room temperature. The Schlenk flask was evacuated to remove any liberated gasses. After 12 days, the darker red solution was layered with degassed diethyl ether (45 mL). Crystallization was apparent within a couple of hours. After 1 month of diffusion at room temperature, the maroon crystals of the product were isolated by removal of the solution via a cannula. Yield: 90%. MS (FAB^+): m/z = 595 (P − OTF, 100), 580 (P − OTF − CH_3, 20), 566 (P − OTF − CH_3 − CH_2, 15). Anal. Calcd for $C_{17}H_{19}S_5Mo_2F_3$: C, 27.41; H, 2.55; S, 21.52. Found: C, 27.54; H, 2.45; S, 21.68.

Formation of $[(MeO_2CCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SCH_3)]$. A solution of **8** (7 mg, 9×10^{-6} mol) and pyridine (15 μL, 2×10^{-4} mol) in CD_2Cl_2 (0.7 mL) was loaded into a flame sealable NMR tube. The purple solution was freeze–thaw degassed three times and charged with 300 mmHg of H_2 at −196 °C. The tube was flame sealed and thawed. An initial ^1H NMR spectrum revealed that the resonances of the starting material had broadened or disappeared. The reaction was allowed to proceed at room temperature for 3 days. During this time broad resonances of $[(MeO_2CCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SCH_3)]$ appeared. The tube was heated at 50 °C for 3 days without much change in the ^1H NMR. The spectrum sharpened when recorded at −80 °C. ^1H NMR (300 MHz, CD_2Cl_2 (−80 °C)): δ 5.8 (m, 8H, Cp), 5.45 (s, 2H, S_2CH_2), 3.51 (s, 6H, OCH_3), 1.41 (s, 3H, SCH_3), −1.18 (s, 1H, SH).

Synthesis of $(NaO_2C–CpMo(\mu\text{-}S))_2S_2CH_2$, 9. A solution of potassium hydroxide (300 mg, $5. \times 10^{-3}$ mol) in water (10 mL) was added to a red-brown suspension of $[(MeO_2C–CpMo)_2(S_2$-$CH_2)(SC_2H_4S)]$ (600 mg, 1×10^{-3} mol) in methanol (100 mL). The solution was stirred at reflux in a 70 °C oil bath for 7 days. The reaction was finished when the final solution color was royal-blue with no red-brown solid left. The excess potassium hydroxide was neutralized by adding sodium bicarbonate (ca. 1 g, 0.012 mol) and stirring at room temperature under nitrogen for 2 days. The resulting blue solution was filtered from the undissolved solids through a Whatman No. 1 qualitative filter paper. The solvent was then removed by rotoevaporation to yield a light-blue solid. The blue solid was loaded onto a basic alumina column (Brockman I, pH 9.5), and a blue band was eluted with methanol/water (5:1). Only the first two thirds of the band was collected. The solvent was removed to give $(NaO_2CCpMo$-$(\mu\text{-}S))_2S_2CH_2$, **9**. Yield: 0.40 g, 65%. ^{13}C NMR (75 MHz, D_2O): δ 33.3 (S_2CH_2), 101.4, 101.8, 102.6 (C_5H_4), 171.5 (CO_2^-). Vis spectrum (H_2O): 512 nm (ε = 1300 M^{-1} cm^{-1}), 586 nm (ε = 1450 M^{-1} cm^{-1}), 742 nm (ε = 1790 M^{-1} cm^{-1}). IR (KBr) (cm^{-1}): 3071 (w), 2924 (w), 1570 (s), 1460 (m), 1382 (s), 1345 (ms), 1095 (mw), 794 (m). CV, 0.15 M NaCl in H_2O (V vs SCE): E_{pa} = 0.38 (ΔE_p = 0.3 V), 0.80, 1.0 (irr), $E_{p/2}$ = −0.92 (ΔE_p = 0.12 V). Anal. Calcd for $C_{13}H_{10}O_4S_4Mo_2Na_2$: C, 26.18; H, 1.69; S, 21.50. Found: C, 25.95; H, 1.74; S, 21.51.

Formation of $(HO_2C–CpMo(\mu\text{-}S))_2S_2CH_2$. Diluted (10% v/v) hydrochloric acid (ca. 1.0 mL) was dripped into a stirred, blue solution of **9** (0.050 g, 8.4×10^{-5} mol) in water (ca. 15 mL) until the blue color ceased to persist. The resulting forest-green solid was filtered through a 0.45-μm membrane filter, rinsed with

three portions of water (20 mL each), and dried *in vacuo*. Yield: ca. 100%. IR (KBr) (cm^{-1}): 3300–2500 (bw, CO_2H), 3093 (w, ν_{C-H}), 1672 (s, ν_{CO}), 1479 (ms, COH), 1409 (mw, Cp), 1371 (mw), 1296 (ms), 920 (mw). Vis spectrum (DMSO): 475 nm ($\epsilon = 6.48 \times 10^2$ M^{-1} cm^{-1}), 590 nm ($\epsilon = 2.81 \times 10^2$ M^{-1} cm^{-1}), 730 nm ($\epsilon = 2.89 \times 10^2$ M^{-1} cm^{-1}). Anal. Calcd for $C_{13}H_{12}O_4S_4Mo_2$: C, 28.26; H, 2.19; S, 23.21. Found: C, 28.16; H, 2.29; S, 22.93.

Synthesis of [$(NaO_2C-CpMo)_2(S_2CH_2)(\mu-S)(\mu-SMe)$]I. Iodomethane (20 μL, 3×10^{-4} mol) was added against a flow of nitrogen to a solution of **9** (0.120 g, 2.1×10^{-4} mol) in degassed water (ca. 10 mL). The solution was allowed to stir under nitrogen at room temperature for 1 day. The solvent was then removed from the deep-maroon solution by rotoevaporation to afford a maroon solid. ^1H NMR (250 MHz, D_2O): δ 7.04 (dd, $J_{H-H} = 4.5$ Hz, $J_{H-H} = 2.3$ Hz, 2H, C_5H_4), 7.00 (dd, $J_{H-H} = 4.5$ Hz, $J_{H-H} = 2.3$ Hz, 2H, C_5H_4), 6.85 (pseudo-t, $J_{H-H} = 2.4$ Hz, 4H, C_5H_4), 3.94 (s, 2H, S_2CH_2), 1.46 (s, 3H, SCH_3). IR (KBr) (cm^{-1}): 3093 (w), 2920 (w), 1596 (s), 1462 (m), 1385 (vs), 1348 (s). Anal. Calcd for $C_{14}H_{13}IO_4S_4Mo_2Na_2$: C, 22.77; H, 1.77; S, 17.37. Found: C, 22.11; H, 1.98; S, 16.74.

Synthesis of $(MeO_2CCpMo)_2(SC_2H_4S)(S_2CHCO_2Me)$, 10. $[(MeO_2CCpMo)(S)(SH)]_2$ (2.0 g, 3.5×10^{-3} mol) was dissolved in 125 mL of dry N_2 saturated THF. To this purple solution was added $Cl_2CHCO_2CH_3$ (0.37 mL, 3.5×10^{-3} mol), followed by a solution of NaOMe (7.1×10^{-3} mol of Na (0.161 g) in 6 mL of MeOH) dropwise over 20 min. The deep-green solution was stirred at room temperature for 2 h. At this stage ethylene was bubbled through the solution for 5 min, giving a red-brown solution. The solution was filtered through a Celite bed (1 in.). The filter bed was washed with 2 × 20 mL of THF. Solvent was removed from the filtrate by rotoevaporation to give a dark-brown solid. The solid was extracted with CH_2Cl_2 and filtered again through a Celite bed (1 in.). The red-brown filtrate was concentrated by rotoevaporation to ~30 mL and then loaded onto a neutral alumina column. An initial small yellow-orange fraction was eluted with CH_2Cl_2 and discarded. A second red-orange fraction was eluted with CH_2Cl_2/CH_3CN (3:1). The solvent was removed to give a brown-red solid. Yield: 0.85 g, 35%. The ^1H NMR spectrum in $CDCl_3$ shows that the product is ca. 95% pure.

Synthesis of [$(NaO_2CCpMo(\mu-S))_2(S_2CHCO_2Na)$], 11. $[(MeO_2CCpMo)_2(SC_2H_4S)(S_2CHO_2Me)]$ (0.82 g, 1.2×10^{-3} mol) was suspended in 140 mL of CH_3OH. A solution of KOH (0.42 g) in 10 mL of H_2O was added. The mixture was refluxed for 7 days, resulting in a blue-green solution. At this stage $NaHCO_3$ (1.4 g) was added to the solution, and the mixture was further stirred for 2 days. The blue-green solution was gravity filtered using a Whatman No. 1 filter paper. Solvent was rotoevaporated from the blue solution to give a blue solid. The blue solid was loaded onto a basic alumina column via methanol extractions. A small light blue band eluted with $MeOH/H_2O$ (2:1). A second blue band eluted with $MeOH/H_2O$ (1:1). The solvent was rotoevaporated from this large fraction to give a dark blue solid. Yield: 0.55 g, 69%. IR (KBr) (cm^{-1}): 3400 (b), 1578 (ν_{CO}, asym), 1463 (m), 1388, 1352 (s), 802 (m). Vis spec, nm (H_2O): 742, 594, 512 (sh), 374. CV, 0.15 M NaCl in H_2O (V vs SCE): $E_{pa} = 0.40$, 0.80, 1.0 (irr), $E_{pc} = -1.02$. Anal. Calcd for $C_{14}H_9O_6S_4Na_3Mo_2$: C, 25.39; H, 1.37; S, 19.36. Found: C, 25.36; H, 1.60; S, 18.77.

Formation of $(HO_2C-CpMo(\mu-S))_2S_2CHCO_2H$. HCl (10%, v/v) was added dropwise to a solution of **11** (0.07 g, 1.0×10^{-4} mol) in water (ca. 15 mL) until the blue color ceased to persist. The resulting green solid was filtered through a 0.45-μm membrane filter, rinsed with 3 × 20 mL of H_2O, and dried in vacuo. Yield: >90%. IR (KBr) (cm^{-1}): 1677 (vs, ν_{CO}), 1477 (s, COH), 1411 (m, Cp), 1384 (m), 1293 (s). Anal. Calcd for $C_{14}H_{12}O_6S_4Mo_2$: C, 28.20; H, 2.02; S, 21.50. Found: C, 28.07; H, 2.04; S, 20.57.

Titration of $(HO_2C-CpMo(\mu-S))_2S_2CHR$, R = H or CO_2H. $(HO_2C-CpMo(\mu-S))_2S_2CHCO_2H$ (0.040 g, 6.7×10^{-5} mol) was slurried in 25 mL of water. The slurry was titrated with NaOH (0.098 M), and the pH was monitored with a Orion Research Model 701A digital pH meter. The slurry was stirred for 30 min after each addition of base in order to permit the pH to stabilize. The equivalence point (pH = 8.3) was reached after addition of 2.04 mL of base. All solid had dissolved. A similar procedure was followed in the titration of $(HO_2C-CpMo(\mu-S))_2S_2CH_2$ (0.066 g, 1.19×10^{-4} mol) with NaOH (0.099 M), but the slurry was stirred for only 5–10 min after each addition of base. The equivalence point (pH 8.9) was reached after addition of 2.79 mL of base.

Formation of $[(CHOCpMo)_2(SC_3H_6S)_2]$, 12. Sodium hydride (2.5 g, 0.10 mol) was added against a flow of nitrogen to a solution of freshly cracked cyclopentadiene (10 mL, 0.12 mol) in dry, degassed THF (300 mL). This solution was allowed to stir under nitrogen bubbler pressure. When all gas evolution had ceased (ca. 10 h), degassed ethyl formate (24 mL, 0.3 mol) was added via syringe.[10] This solution was refluxed for 5 h. After this time period, the pink solution was allowed to cool to room temperature and molybdenum hexacarbonyl (30 g, 0.11 mol) was added against a flow of nitrogen to the solution. This mixture was refluxed for 3 days. After this time period, degassed acetic acid (17.2 mL, 0.30 mol) was added via a cannula. The yellow-reddish solution was stirred for 2 h at room temperature. Degassed propylene sulfide (2 mL) was syringed into the reaction mixture and the contents of the flask were allowed to stir for 24 h. The solvent was removed from the brown solution/suspension. The solid was extracted with dichloromethane (5 × 5 mL, or until the washings were colorless) and filtered through a 1-in. bed of Celite. This solution was concentrated on a rotary evaporator (ca. 50 mL) and then loaded onto a silica gel column (4 × 20 cm). An initial red fraction was eluted with dichloromethane/hexanes (2:1). This material was discarded. A second fraction, colored brown-green, was eluted with acetonitrile/dichloromethane (5:1). The solvent was removed via rotary evaporation to yield a gold-greenish solid which was identified as a mixture of isomers of $(CHOCpMo)_2(SC_3H_6S)_2$, **12**, and $(CHOCpMo)(SC_3H_6S)_2(MoCp)$, **12a**. Yield: 3.8 g, 6%. A 1-g amount of the resulting solid was loaded onto a neutral alumina column with 5 mL of dichloromethane. An initial orange band was eluted with dichloromethane/acetonitrile (5:1) and was identified as isomers of **12a**. (Six isomers are possible.) ^1H NMR (250 MHz, $CDCl_3$): δ 9.35, 9.33, 9.30, 9.26, 9.24 (s, 1H, CpC*H*O), 5.48, 5.41, 5.30, 5.27 (m, 4H, Cp), 5.27, 5.18, (s, 5H, Cp), 2.4–2.0 (m, 4H, CH_2), 1.3–1.1 (m, 8H, $CHCH_3$). A second orange fraction was eluted with dichloromethane/acetonitrile (2:1) and was identified as the isomers of **12**. (Four isomers are possible.) They were not separated. ^1H NMR (250 MHz, $CDCl_3$): δ 9.38, 9.36, 9.34, 9.30, 9.28 (s, 2H, CpC*H*O), 5.54, 5.5, 5.46, 5.4–5.3 (m, 8H, Cp), 2.46–2.14 (m, 4H, CH_2), 1.4–1.24 (m, 2H, C*H*), 1.2 (t, 6H, CH_3).

Formation of $(CHOCpMo)_2(SCH_2CH_2S)_2$, 13. A solution of **12** and **12a** (0.2 g, 3.4×10^{-4} mol) in dichloromethane (25 mL) was treated with 1.5 atm of ethylene (0.3 mol) in a 500-mL flask fitted with a Teflon stopcock. The reaction was allowed to stir for 2 weeks at 50 °C. After this time the solution was loaded onto a neutral alumina column (2.5 cm × 15 cm). An initial orange fraction was eluted with dichloromethane. The solvent was removed via rotary evaporation to yield the product $(CHOCpMo)_2(SCH_2CH_2S)_2$, **13**. Yield: 40%. Purity: 80%. A second orange fraction was eluted with dichloromethane/acetonitrile (1:2). The solvent was removed via rotary evaporation to yield a 50:50 mixture of **13** and $(CHOCpMo)(SCH_2CH_2S)_2(CpMo)$, **13a**. Yield: 40%. ^1H NMR (300 MHz, $CDCl_3$): δ 9.25 (s, 1H, CpC*H*O), 5.29 (pseudo-t, 2H, Cp), 5.26 (pseudo-t, 2H, Cp), 5.1 (s, 5H, Cp), 1.9 (m, 4H, C_2H_4), 1.78 (m, 4H, C_2H_4).

Formation of $(CHOCpMo)_2(SCHCHS)_2$, 14. A solution of **12a** and **12** (0.20 g, 3.4×10^{-4} mol) in dichloromethane (25 mL) was treated with 0.9 atm of acetylene (0.18 mol) in a 500-mL flask fitted with a Teflon stopcock. The reaction was allowed to stir for 2 weeks at 50 °C. After this time, the solution was loaded onto a neutral alumina column (2.5 cm × 15 cm). An initial green fraction was eluted with dichloromethane. The solvent was removed via rotary evaporation to yield $[(CHOCpMo)(SCHCHS)_2(CpMo)]$, **14a**. Yield: 30%. ^1H NMR (200 MHz,

$CDCl_3$): δ 9.19 (s, 1H, CpC*H*O), 6.47 (s, 4H, C_2H_2), 6.12 (pseudo-sext, 2H, Cp), 6.03 (pseudo-sext, 2H, Cp), 5.95 (s, 5H, Cp). MS (EI): *m/z* 548 (?, 30), 532 (P, 100), 506 (P – C_2H_2, 20), 476 (P – $2C_2H_2$, 75), 450 (P – $2C_2H_2$ – CHO, 30), 418 (P – $2C_2H_2$ – CHO – S, 20), 386 (P – $2C_2H_2$ – CHO – 2S, 35). A second green fraction was eluted with dichloromethane/acetonitrile (10:1). The solvent was removed via rotary evaporation to yield **14**. Yield: 55%. MS (EI^+): *m/z* 558 (P, 100), 532 (P – C_2H_2, 20), 506 (P – $2C_2H_2$, 70), 476 (P – $2C_2H_2$ – CHO, 25), 450 (P – $2C_2H_2$ – 2CHO, 25), 418 (P – $2C_2H_2$ – 2CHO – S, 25), 386 (P – $2C_2H_2$ – 2CHO – 2S, 25).

Reaction of (CHO–CpMo)(SC_2H_4S)$_2$(MoCp), 13a, with Triphenylphosphine Methylene Ylide. (a) The ylide was prepared by adding butyllithium to a stirred suspension of methyl triphenylphosphine iodide until all the solid reacted to form a yellow solution. This solution was cooled to −78 °C and used immediately. A solution of **13a** (52 mg, 9.7×10^{-5} mol) in THF (4 mL) was treated with a solution of triphenylphosphine methylene ylide (9.7×10^{-5} mol) in THF (4 mL) at −78 °C in oven dried glassware. After 0.5 h, the solution took on a reddish color. The mixture was allowed to warm to room temperature and stirred for 12 h. After this time period the reaction was quenched with water (3 mL) and solvent was removed *in vacuo*. A solution was made of 5 mg of the resulting solid in $CDCl_3$ and transferred to a NMR tube. The tube was freeze–thaw degassed and cooled to liquid nitrogen temperature. Ethylene ($^3/_4$ atm) was transferred to the reaction mixture. The tube was then flame sealed and thawed. ^1H NMR revealed no resonances in the vinyl region except that due to ethylene. A ^{31}P NMR experiment showed that most of the phosphine was converted to Ph_2MePO (60%), Ph_3PS (25%), and Ph_3PO (15%). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 43.6 (s, Ph_3PS), 29.2 (s, Ph_2MePO), 22.5 (s, Ph_3PO).

(b) Under phase transfer conditions, a degassed solution of (CHOCpMo)$_2$(SC_2H_4)$_2$, **13** (38 mg, 7.1×10^{-5} mol), and methyl triphenylphosphonium iodide (57 mg, 1.4×10^{-4} mol) in benzene (2 mL) was reacted with a degassed sodium hydroxide solution (0.42 mL of a 5 M solution) added via a syringe. The solution was stirred under N_2 at room temperature for 3 days. TLC revealed that there was no triphenylphosphine oxide present. The reaction solution was eluted on a short alumina column, and the solvent was removed to give a brown solid. A ^1H NMR spectrum revealed that no reaction had occurred.

(c) A solution of **14** (147 mg, 2.77×10^{-4} mol) and **14a** (73 mg, 1.3×10^{-4} mol) in THF (4 mL) was treated with a solution of triphenylphosphine methylene ylide (4.5×10^{-4} mol) in THF (4 mL) at −78 °C in oven dried glassware. After 0.5 h, the color of the solution took on a reddish color. The mixture was warmed to room temperature and stirred for 24 h. TLC analysis of the reaction mixture, using alumina plates and CH_3CN/CH_2Cl_2 (1:1), indicated that the starting materials were gone. The solution was dried, extracted with CH_2Cl_2, and filtered, and the filtrate was evaporated to give a brown red solid. The ^1H NMR spectrum was broad and did not show evidence for vinyl Cp ligands. ^1H NMR (250 MHz, $CDCl_3$): δ 8.7 (m, Ph_3PO), 8.5 (m, Ph_3PO), 8.3 (m, Ph_3P), 6.6–6.4 (br, Cp), 6–5 (br, Cp), 1–2 (br), 0.71 (br).

Catalytic Reactions of 9 and 11. ($NaO_2CCpMo(\mu\text{-}S))_2S_2CH_2$, **9** (40 mg, 6.70×10^{-5} mol), was dissolved in 2 mL of water. A solution of azobenzene (300 mg, 1.6 mmol) dissolved in 3 mL of C_6D_6 was layered over the water solution in a Schlenk tube. The mixture was degassed by three freeze–pump–thaw cycles, and hydrogen gas (∼3 atm) was added to the Schlenk tube at 77 K. The sealed tube was put on a shaker for 24 h. The NMR spectrum of the C_6D_6 solution showed that 37% of the azobenzene had been hydrogenated to diphenylhydrazine.

In an analogous experiment using ($NaO_2CCpMo(\mu\text{-}S))_2(S_2CHCO_2Na)$, **11**, about 9% of the azobenzene was hydrogenated to diphenylhydrazine.

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