Table I provides a summary of the equilibrium constants obtained for formation of the mixed anhydrides and divanadate. The chemical shifts obtained for the species are also shown.

Although it is not surprising that the mixed anhydrides of vanadate with pyrophosphate, phosphate, and arsenate reported have formed in aqueous solution, there appear to be no other reports of such species. Complexes of the structure $VOPO_4$ have been studied in nonaqueous phases,[16] and numerous crystal structure determinations of large cluster complexes containing vanadium(V) and phosphorus(V) have been published;[17] but these species have little in common with the simple mixed anhydrides described above.

From the summary in Table I of equilibrium constants for formation of the mixed anhydrides, it is apparent that there is little difference in the stability of the two mixed anhydrides toward hydrolysis, while divanadate is from 10 to 100 times more stable toward hydrolysis. From the free energy of hydrolysis of inorganic pyrophosphate of -8 kcal/mol at pH 7.0,[18] the equilibrium constant for formation of pyrophosphate from phosphate is 1.3×10^{-6} M^{-1}. It is interesting to note that the equilibrium constant for formation of divanadate exceeds by a factor of about 10^8 that for formation of the analogous pyrophosphate. Even formation of the mixed phosphate-vanadate anhydride is more than 10^6 times more favored than is formation of pyrophosphate. At present we can provide no explanation for these large differences in stability toward hydrolysis.

The rapid and relatively favorable formation of mixed anhydrides of phosphate and vanadate makes it reasonable to consider whether such species can interact with biological systems in spite of the normally low physiological vanadium concentrations.[4] In preliminary studies to explore this possibility, it has been observed that when adenosine monophosphate (AMP) is present, added vanadate causes an increase in the rate at which pyruvate kinase converts phosphoenolpyruvate to pyruvate.[19] This result is consistent with the nonenzymic formation of the mixed anhydride AMP-vanadate, which is presumably accepted as a substrate by pyruvate kinase. The formation of mixed phosphate/vanadate anhydrides is also relevant to the inhibition of myosin ATPase by adenosine diphosphate plus vanadate.[20-22]

Acknowledgment. Thanks are greatfully extended to the Natural Sciences and Engineering Research Council of Canada for its support of this work, in the form of grants to A.S.T. and M.J.G., to the Heart Foundation of British Columbia, and to the Medical Research Council of Canada, for its support of M.J.G.

Registry No. $HP_2O_7^{3-}$, 42499-21-8; $H_2PO_4^-$, 14066-20-7; $H_2AsO_4^-$, 16518-47-1; Na_2HVO_4, 59826-07-2; $H_2O_4V^-$, 34786-97-5; $O_3POPO_2OVO_3H^{4-}$, 103884-10-2; $(O_3POPO_3)_2V(OH)_2^{5-}$, 103904-05-8; $HO_3VOVO_3H^{2-}$, 103884-11-3; $HO_3VOVO_2OVO_2OVO_3H^{4-}$, 103884-12-4; $HO_3POVO_3H^{2-}$, 103884-13-5; $O_3POVO_3H^{3-}$, 103884-14-6; $HO_3AsOVO_3H^{2-}$, 103903-97-5.

Supplementary Material Available: Figure 1S showing the ratio of concentration of monomeric tetrahedral vanadate species to the square root of vanadate dimer concentration and tables giving the concentrations of various vanadate species determined as a function of pyrophosphate and phosphate concentration (3 pages). Ordering information is given on any current masthead page.

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Activation of Hydrogen by Cationic Cyclopentadienyl Molybdenum Dimers with Sulfido Ligands. 1. Cationic Complexes Derived from Protonation of 1,2-Alkenedithiolate Ligands

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Abstract: The reaction of phenylacetylene with the sulfido ligands in $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$ ($Cp = C_5H_5$) results in the formation of a phenylacetylene adduct of formulation $(CpMo)_2(S_2CH_2)(SC(Ph)C(H)S)$, **1**. Complex **1** reacts with a protic acid (CF_3CO_2H, HBF_4, $HOSO_2CF_3$) to form a protonated cationic derivative which exists in solution as an equilibrium mixture of isomers, **2A** and **2B**. Single crystals of the triflate salt of **2A** have been grown from an acetonitrile/hexane solution. The molecule crystallizes in space group $P\bar{1}$ with $a = 7.2255$ (14) Å, $b = 11.9950$ (20) Å, $c = 14.6744$ (24) Å, $\alpha = 86.452$ (13)°, $\beta = 77.922$ (15)°, $\gamma = 79.570$ (14)°. The X-ray diffraction study establishes that protonation results in cleavage of one carbon-sulfur bond of the alkenedithiolate ligand to form $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph)CH_2)]^+$. The bridging α-phenylvinylthiolate ligand in **2A** is oriented in an equatorial configuration with the double bond twisted out of the plane of the sulfur atoms. ^1H and ^{13}C NMR data suggest that the structure of **2B** involves a protonated, 1,2-dithiolate ligand in which both carbon-sulfur bonds remain intact, $[(CpMo)_2(S_2CH_2)(\mu\text{-}SC(Ph)CH_2S)]^+$. Complex **2** (**A** and **B**) is deprotonated by triethylamine and stronger bases to form **1**. Less basic nucleophiles, such as methanol or chloride or nitrite ion, react with **2** (**A** and **B**) to cleave the carbon-sulfur bond(s) of the thiolate ligand and form substituted sytrenes. Complex **2** (**A** and **B**) reacts with hydrogen at room temperature to form a neutral molybdenum(III) dimer $(CpMo)_2(S_2CH_2)(S_2C(Ph)Me)$, **4**. Observations on this unusual hydrogen activation process are discussed.

Cyclopentadienylmolybdenum(III) dimers with alkenedithiolate ligands have been found to react with hydrogen under mild conditions to form the cis alkene or alkene adduct as shown in reaction 1.[1] An important feature of this reaction is that it

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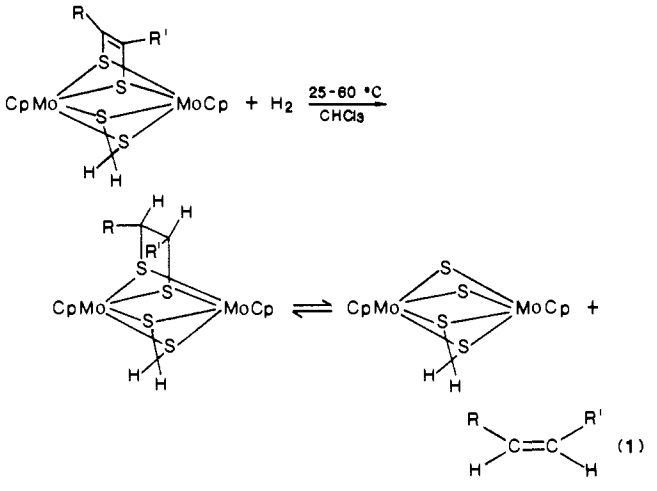
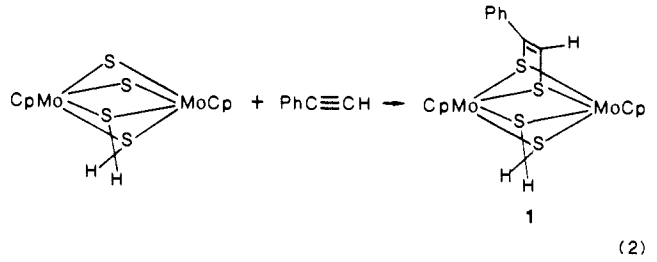


(1)

proceeds as shown only in chloroform. In order for the reaction to take place in other solvents, a catalytic amount of protic acid must be added. In addition, kinetic studies of reaction 1 (R = R′ = Ph) have established that the rate in chloroform is promoted by protic acids.[2] These observations prompted us to investigate the stoichiometric reactions of the alkenedithiolate bridged dimers (where R = R′ = Ph or CH_3 and R = H, R′ = Ph) with protic acids (CF_3CO_2H, HBF_4, $HOSO_2CF_3$). The protonation reaction of the phenylacetylene adduct (R = Ph, R′ = H) has been characterized most thoroughly and is the major subject of this paper. We report here the spectral data, structural characterization, and reactivity of the protonated phenylacetylene adduct. The unusual ability of this cationic derivative to activate molecular hydrogen is discussed with reference to the hydrogenation of the neutral alkyne adducts. Protonation of the dimeric complex has also been found to activate the dithiolate ligand toward reactions with nucleophiles, and a new pathway for the conversion of an alkyne to substituted alkenes has been characterized.

Results and Discussion

Synthesis of the Phenylacetylene Adduct. Cyclopentadienylmolybdenum dimers with bridging alkenedithiolate ligands have been synthesized previously by the reaction of excess alkyne with $(CpMo\mu\text{-}S)_2S_2CH_2$.[1] Although the phenylacetylene adduct **1** has not been reported previously, its synthesis proceeded in good yield according to the usual procedure (reaction 2). Spectral data



(2)

reported in the Experimental Section are consistent with the gross structure shown above, which is similar to those of other alkyne adducts reported previously. Cyclic voltammetry on **1** has established that the complex undergoes two quasireversible one-electron oxidations at 0.18 and 0.55 V vs. SCE. The redox behavior is also similar to that observed for the previously reported alkyne adducts.[2,3]

Protonation of the Phenylacetylene Adduct: Characterization of the Major Isomer. An NMR study of the reaction of **1** with 1–2 equiv of trifluoroacetic acid in chloroform revealed that protonation was complete within minutes. Two products were formed in an approximate 4:1 ratio. Identical products were

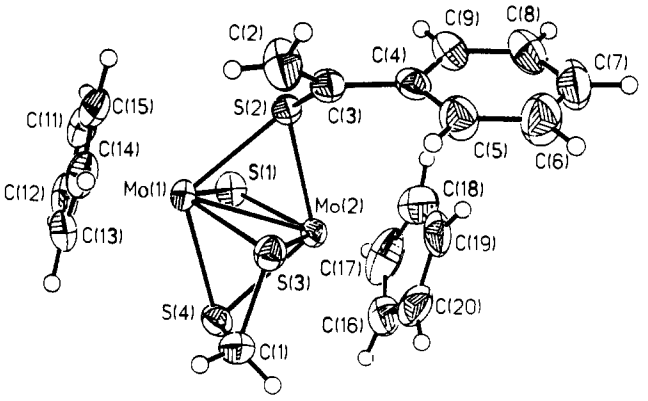
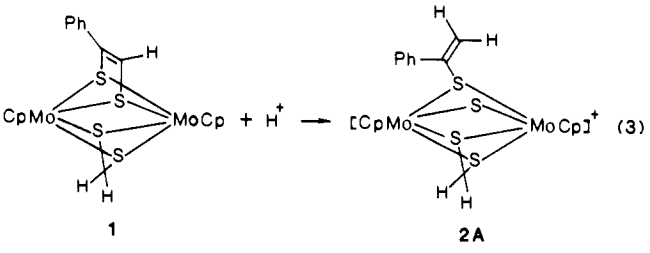


Figure 1. Perspective drawing and numbering scheme for the cation of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph)CH_2)]SO_3CF_3$, **2A**. Thermal ellipsoids are drawn at the 50% probability level.

Table I. Selected Intramolecular Distances and Angles for $[(C_5H_5Mo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph)CH_2)]SO_3CF_3$

Distances, Å			
Mo_1–Mo_2	2.613 (1)	S_2–C_3	1.798 (4)
Mo_1–S_1	2.305 (1)	S_3–C_1	1.830 (4)
Mo_1–S_2	2.463 (1)	S_4–C_1	1.810 (4)
Mo_1–S_3	2.470 (1)	C_2–C_3	1.325 (5)
Mo_1–S_4	2.464 (1)	C_3–C_4	1.474 (5)
Mo_2–S_1	2.304 (1)	S_3–S_4	2.708 (3)
Mo_2–S_2	2.470 (1)	S_1–S_2	2.888 (3)
Mo_2–S_3	2.466 (1)	S_2–S_3	2.995 (3)
Mo_2–S_4	2.448 (1)	S_4–S_1	2.939 (3)
Angles, deg			
Mo_1–S_1–Mo_2	69.1 (0)	S_3–C_1–S_4	96.1 (2)
Mo_1–S_2–Mo_2	64.0 (0)	Mo_1–S_2–C_3	116.6 (1)
Mo_1–S_3–Mo_2	63.9 (0)	Mo_2–S_2–C_3	112.3 (1)
Mo_1–S_4–Mo_2	64.3 (0)	S_2–C_3–C_2	121.0 (3)
S_1–Mo_1–S_2	74.5 (0)	C_2–C_3–C_4	123.9 (4)

formed in a ratio of 3:1 in the reaction with tetrafluoroboric acid in acetonitrile. In these protonation experiments, we observed by NMR that the minor product, **2B**, was formed initially while the resonances of the major product, **2A**, grew in more slowly. A crystalline cationic purple brown complex has been isolated as the trifluoromethanesulfonate salt from the reaction of $HOSO_2CF_3$ with **1** in acetonitrile. NMR data on a fresh solution of these crystals indicate that they correspond to the major product observed in the NMR experiments, **2A**. The spectral data identify this complex as a vinylthiolate bridged derivative, eq 3. In the



(3)

^1H NMR spectrum of **2A**, an AX pattern in the vinyl region with doublets at 5.55 and 4.95 ppm ($J_{H\text{-}H}$ = 0.7 Hz) is consistent with the proposed structure with geminal vinyl protons. ^{13}C NMR data also confirm the presence of a CH_2 group with a downfield shift (125.7 ppm) in addition to the methylene group of the methanedithiolate ligand (50.5 ppm).

An X-ray diffraction study of a single crystal of the triflate salt of **2A** was undertaken to confirm the structure deduced from spectral assignments and to determine the orientation of the alkenyl thiolate ligand. A perspective drawing of the cation is shown in Figure 1, and selected bond distances and angles are presented in Table I. Positional and thermal parameters are included in Table II. The cation crystallizes in space group $P\bar{1}$ with C_1 symmetry. The structure confirms that isomer A of the protonated

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Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) $\times 10^3$) for $[(C_5H_5Mo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph)CH_2)]SO_3CF_3$

atom	x	y	z	U[a]
Mo(1)	6970 (1)	7550 (1)	8725 (1)	29 (1)
Mo(2)	5994 (1)	8802 (1)	7325 (1)	30 (1)
S(1)	9007 (1)	8509 (1)	7676 (1)	40 (1)
S(2)	7153 (1)	6745 (1)	7197 (1)	32 (1)
S(3)	3647 (1)	7908 (1)	8465 (1)	36 (1)
S(4)	5440 (1)	9548 (1)	8892 (1)	41 (1)
S(5)	11372 (2)	7720 (1)	11825 (1)	50 (1)
F(1)	8140 (4)	6962 (3)	12315 (2)	98 (2)
F(2)	9114 (5)	7519 (3)	13435 (2)	95 (1)
F(3)	10494 (5)	5957 (3)	12837 (3)	102 (2)
O(1)	12880 (5)	7741 (3)	12309 (3)	82 (2)
O(2)	10219 (6)	8759 (3)	11633 (3)	89 (2)
O(3)	11963 (5)	6970 (3)	11044 (2)	74 (1)
C(1)	3071 (5)	9167 (3)	9178 (3)	47 (1)
C(2)	4756 (7)	5205 (4)	7744 (3)	58 (2)
C(3)	5282 (5)	5976 (3)	7103 (2)	37 (1)
C(4)	4518 (5)	6209 (3)	6241 (2)	36 (1)
C(5)	2569 (6)	6367 (4)	6277 (3)	52 (1)
C(6)	1830 (7)	6627 (4)	5486 (3)	68 (2)
C(7)	3049 (7)	6713 (4)	4630 (3)	64 (2)
C(8)	4984 (7)	6552 (4)	4579 (3)	55 (1)
C(9)	5731 (5)	6298 (3)	5375 (2)	43 (1)
C(10)	9721 (6)	6974 (4)	12620 (3)	58 (2)
C(11)	9397 (6)	6435 (4)	9361 (3)	54 (1)
C(12)	8620 (7)	7385 (4)	9922 (3)	58 (2)
C(13)	6702 (7)	7299 (4)	10319 (3)	55 (1)
C(14)	6292 (6)	6307 (3)	10005 (3)	50 (1)
C(15)	7950 (6)	5782 (3)	9414 (3)	51 (1)
C(16)	5076 (7)	10624 (3)	6729 (3)	60 (2)
C(17)	6764 (8)	10165 (4)	6179 (4)	82 (2)
C(18)	6407 (10)	9204 (4)	5745 (3)	86 (2)
C(19)	4506 (8)	9120 (4)	6061 (3)	66 (2)
C(20)	3688 (7)	10004 (3)	6670 (3)	59 (2)

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

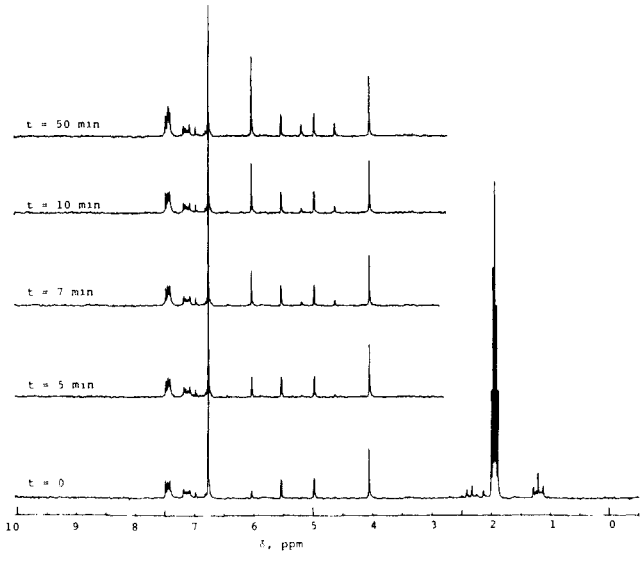
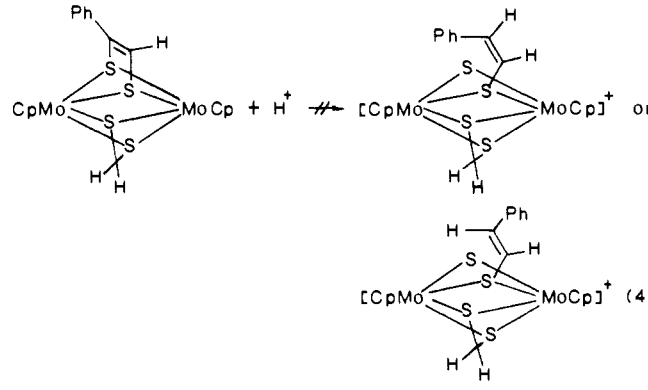


Figure 2. 90-MHz ^1H NMR spectrum of a crystalline sample of the triflate salt of **2A** in CD_3CN as a function of time. Resonances which grow in at 6.04, 5.13, and 4.61 ppm are assigned to **2B**. These appear as singlets even on an expanded scale. Resonances above 3 ppm result from solvent and solvent impurities.

derivative contains an α-phenylalkenylthiolate ligand. The orientation of the thiolate substituent relative to the dithiolate bridge of the starting neutral adduct indicates that both a rotation around the C–S bond (S_2–C_3) and inversion at the sulfur atom (S_2) have occurred upon protonation. The vinyl group is directed away from the sulfido bridge (S_1) in an equatorial configuration and is twisted out of the plane defined by the sulfur atoms. The dihedral angle between the latter plane and the plane defined by S_2, C_2, C_3, and C_4 is 79.0°. The phenyl ring is significantly rotated out of the plane of the double bond; a dihedral angle of 135° is observed between these two planes. The C_2–C_3 distance in the alkenylthiolate ligand is typical of a carbon–carbon double bond, while the S_2–C_3 distance corresponds to a normal single S–C bond. The small bite of the methanedithiolate ligand results in a short distance between S_3 and S_4, 2.71 Å, which has been observed previously.[1,4] The distance between S_1 and S_2 in **2A**, 2.89 Å, is significantly shorter than the van der Waals contact distance but is similar to the average distance between unconstrained sulfur atoms in the tetrasulfur bridged molybdenum cation $[CpMo(SCH_3)_2]_2^+$.[5] A weak bonding interaction between S_1 and S_2 cannot be ruled out. Other bond distances and angles in the $Cp_2Mo_2S_4$ core of the cation are similar to those observed in related structures.[3,6]

Characterization of the Minor Protonation Product 2B. The NMR spectral data for the protonated phenylacetylene adduct do not show evidence for the presence of the isomeric forms of **2A** which would result from protonation of the substituted carbon atom in the alkenedithiolate ligand (eq 4). In particular no

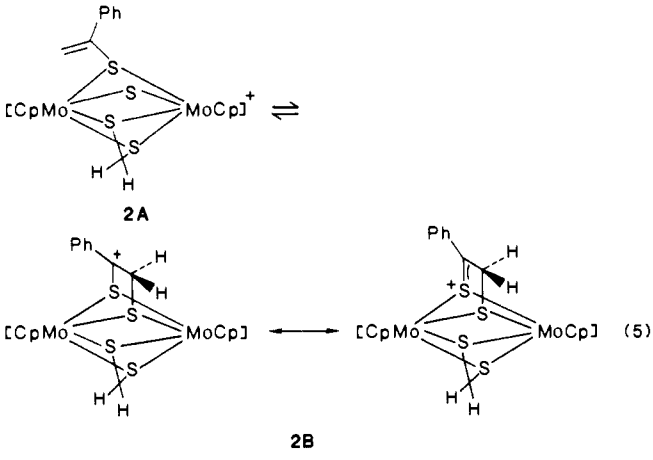


evidence for an AB pattern in the vinyl region of the spectrum is observed. The isomer with the *trans*-β-phenylalkenylthiolate ligand has been isolated by an alternate synthetic route and has been shown to have different NMR characteristics than those of the products discussed here.[6] When pure crystals of the triflate salt of **2A** are dissolved in acetonitrile-d_3, the ^1H NMR spectrum begins to show evidence for the second minor product, **2B**, almost immediately. The initial rate of formation of **2B** has been followed by NMR (Figure 2) and has been found to proceed with a half life of approximately 10 min at room temperature.[7a] No further change in the spectrum is observed after product **2B** has reached its maximum concentration. Similarly, **2B**, which is initially formed in the protonation experiments (vide supra), isomerizes to form **2A** in the same relative concentrations. The data indicate that **2** exists as an equilibrium mixture of products in solution.

Although we are unable to unambiguously assign a structure to **2B**, the NMR spectrum, which is shown in Figure 2, is consistent with a protonated product in which the carbon–sulfur bond remains intact (eq 5). NMR data indicate that the molecule contains a mirror plane which passes through the sulfur atoms. In addition to the singlet observed for the Cp protons at 6.04 ppm, two additional singlets, each of relative intensity 2, are observed at 5.18 and 4.61 ppm. These are tentatively assigned to the methylene groups which are present in each of the dithiolate ligands of **2B**. The ^{13}C (DEPT) spectrum of the equilibrium mixture confirms the presence of two CH_2 groups at 47.8 and 64.9 ppm in the minor isomer. A weak resonance at 152 ppm in the ^{13}C spectrum is tentatively assigned to the Ph–*C* atom. Other ^{13}C assignments are listed in the Experimental Section.

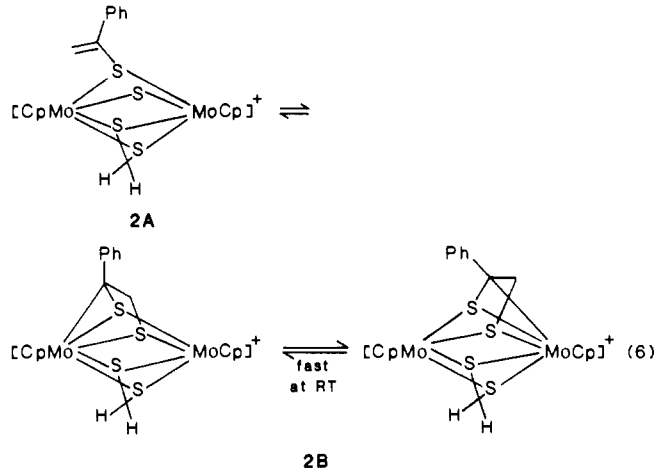
An investigation of the low-temperature ^1H NMR spectrum for the mixture of isomers **2A** and **2B** (triflate salt) reveals fluxional processes. The resonances for isomer **2A** and the relative

(4) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.
(5) Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7470.
(6) Weberg, R. T.; Haltiwanger, R. C.; Laurie, J. C. V.; Rakowski DuBois, M. *J. Am. Chem. Soc.*, the folling paper in this issue.



2A **2B** (5)

intensities of resonances for A and B remain unchanged as the temperature is decreased to −85 °C in $(CD_3)_2CO$.[7b] However the Cp resonance for the minor isomer, **2B**, broadens, coalesces at −60 °C, and subsequently splits into two singlets of approximately equal intensity. The protons in each of the methylene groups also become inequivalent and two AX patterns are observed with doublets at 4.12 and 5.43 ppm (J = 13 Hz) and ~5.2 and 5.77 ppm (J = 9 Hz) (Figure 3). The free energy of activation for this fluxional process derived from coalescence temperatures is calculated to be 45 kJ/mol.[7c] The interaction of the triflate anion with the carbonium ion of the ligand could account for the observed inequivalencies at low temperature.[8] However, an investigation of the fluxional behavior of the tetrafluoroborate salt in the same solvent revealed that coalescence occurred at the same temperature as observed for the triflate system. The nucleophilic behavior of these two anions might be expected to vary detectably. An alternate possibility for the fluxional behavior is suggested in equation 6 in which each molybdenum ion interacts



2A **2B** (6)

with the positively charged ligand. This rather unusual donation of an electron pair from a molybdenum ion to a positively charged dithiolate ligand in dinuclear complexes of this class has been observed previously in cations characterized by X-ray diffraction studies.[9]

Protonation of Other Alkyne Adducts. The facile protonation of the phenylacetylene adduct **1** has been compared to the reactions of other alkyne adducts with acid. The addition of 1 equiv of

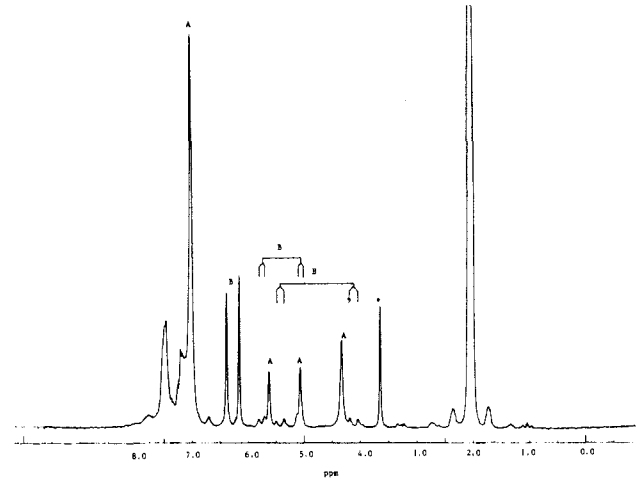
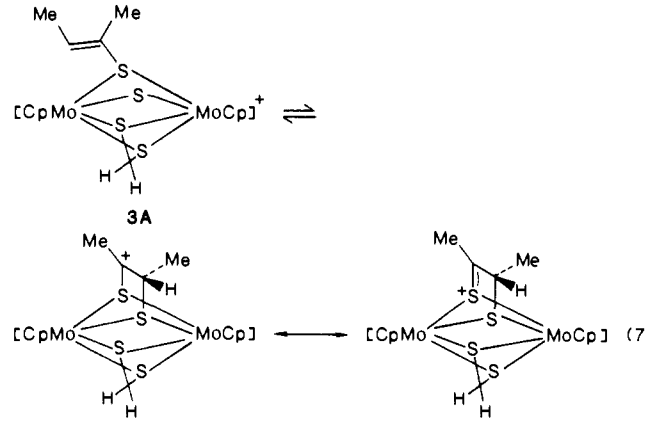


Figure 3. 90-MHz ^1H NMR spectrum of **2A** + **B** (triflate salt) in $(CD_3)_2CO$ at −88 °C. AX patterns assigned to the methylene protons of **2B** are indicated by lines. The doublet at 5.2 ppm is partially obscured by a resonance of **2A**. Coupling has been confirmed by homonuclear decoupling experiments. The resonance marked by an asterisk is a solvent impurity, probably water.

trifluoroacetic acid to the 2-butyne or diphenylacetylene adduct results in the immediate disappearance of the NMR spectrum of each complex although no color change is observed. Low-temperature (−50 °C) NMR studies of the diphenylacetylene adduct failed to resolve any resonances.[2] After 4–6 h reaction time, the spectra of the alkyne adducts plus acid show the characteristics of diamagnetic protonated derivatives. The nature of the initial interaction of the proton with the dimers, which results in the disappearance of the NMR spectrum, is not known at the present time. Nor is it clear why the formation of the final products proceeds so much more slowly than the protonation of the phenylacetylene adduct.

The room temperature ^1H NMR spectra of the final products are consistent with structures analogous to those of **2**. For example, in the ^1H NMR spectrum of the protonated 2-butyne adduct (BF_4^- salt) in $(CD_3)_2CO$, two products are apparent in approximately equal ratios. For isomer **3A** two methyl resonances are observed at 1.67 and 1.55 ppm. The latter is a doublet with $J_{H\text{-}CH_3}$ = 6.7 Hz. A quartet assigned to the vinyl proton is observed at 5.30 ppm, and two singlets at 7.19 and 4.29 ppm correspond to the protons of equivalent cyclopentadienyl ligands and the methanedithiolate ligand, respectively. Spectral features of the second product, **3B**, are consistent with a structure with a protonated 1,2-dithiolate ligand, similar to that proposed for the phenylacetylene system (reaction 7). In particular, the doublet



3A **3B** (7)

and singlet in the methyl region of the spectrum and the inequivalencies of the Cp ligands and of the protons of the methanedithiolate ligand support the proposed structure of **3B**. No fluxional behavior was detected by ^1H NMR for the triflate salt of **3** in $(CD_3)_2CO$ over a temperature range of −70 to +25 °C

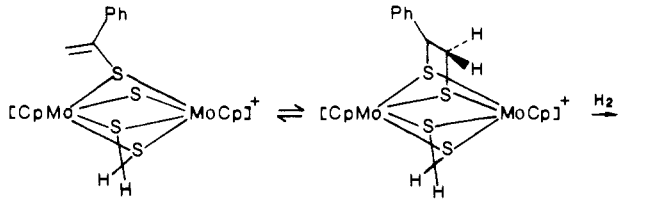
(7) (a) Data were treated as appropriate for a reversible reaction: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*: McGraw Hill: New York, 1981; p 42. (b) In variable temperature NMR studies in CD_3CN, the relative concentration of **2A** increases as the temperature is increased to 80 °C, but coalescence of the resonances of the two isomers is not observed. (c) Gunther, H. *NMR Spectroscopy*: *An Introduction*; translated by Gleason, R. W. Wiley: New York, 1980; p. 243.

(8) As suggested by a referee, the triflate ion is capable of acting as a weak nucleophile.

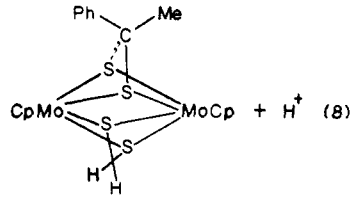
(9) Coons, D. E.; Wright, L. L.; Haltiwanger, R. C.; Rakowski DuBois, M., manuscript submitted for publication.

or for the bromide salt of **3** in CD_3CN from 25 to 85 °C.

Reaction of the Protonated Phenylacetylene Adduct with Hydrogen. The equilibrium mixture of isomers of the protonated phenylacetylene adduct, **2**, reacts slowly with an atmosphere of hydrogen at room temperature. The product of the reaction is a neutral molybdenum(III) complex with a 1,1-dithiolate ligand **4** (reaction 8). The product of this reaction has been isolated



2A 2B

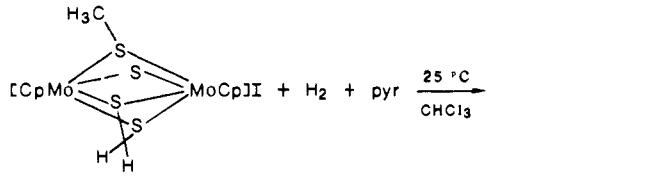


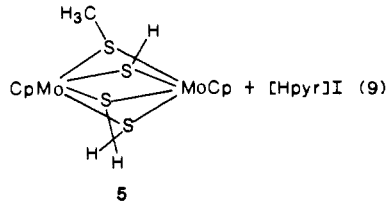
4

in 70% yield and characterized by conventional spectral methods. Mass spectral data and elemental analyses are consistent with the formulation, and NMR data support the proposed structure. In the proton NMR spectrum, for example, two singlets at 5.30 and 5.97 ppm confirm the presence of inequivalent cyclopentadienyl ligands. The methyl resonance is a singlet at 1.66 ppm, and an AB pattern at 6.48 ppm is assigned to the protons of the methanedithiolate ligand.

The activation of hydrogen by cationic sulfido bridged dimers of molybdenum has not been reported previously. The overall process appears to involve a heterolytic cleavage of the hydrogen molecule, although the site and mechanism of the initial hydrogen activation by dimer **2** have not been established. No intermediates are detected by NMR during the course of reaction 8. Attempts to determine whether this reaction is promoted by the presence of a proton acceptor which is more basic than $CF_3CO_2^-$ or BF_4^- have been unsuccessful. The addition of an equivalent of triethylamine or pyridine to a solution of **2** results in deprotonation and bond cleavage reactions, respectively, in the absence of hydrogen. These are described below.

Further information on the activation of hydrogen by cationic molybdenum dimers has been sought by a study of the reactivity of the simpler derivative $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S)]I$[3] with hydrogen. The reaction proceeds in the presence of pyridine to form the products shown in eq 9. The pyridinium ion has been



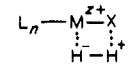


5

identified by NMR and IR spectroscopy. Complex **5** has been previously synthesized by an alternate route, and a complete characterization study has been reported in a separate paper.[10]

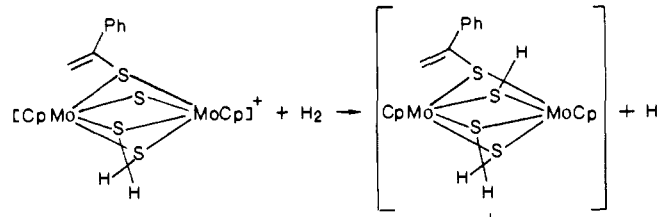
(10) Casewit, C. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 5482–5489.

Although these studies do not establish the initial site and mechanism of hydrogen activation, they do demonstrate that a proton is produced in the reaction with molecular hydrogen and that the bridging sulfido ligand participates in the final coordination of hydrogen. The reaction identifies a novel feature in that the ultimate formal hydride addition occurs at the ligand rather than at the metal ion, as has been previously observed (formula I).[11] Reaction 9 is consistent with our observation that other

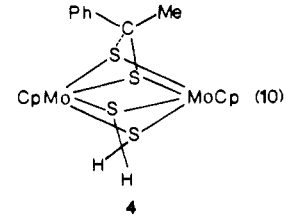


I

nucleophiles, e.g., methyllithium, also react with the sulfido ligand in this cationic dimer.[3] On the basis of these studies, the formation of an analogous intermediate by complex **2A** is tentatively proposed (reaction 10). Insertion of the double bond of the alkenyl thiolate



2A



4

ligand into the S–H bond of such an intermediate would result in the formation of the final observed product. When reaction 10 is carried out under deuterium, the ^1H NMR spectra of the product **4** suggest that there is approximately one deuterium atom incorporated into the methyl group. Although the initial interaction of **2A** with hydrogen could be reversible, the deuteration experiment indicates that the proposed insertion step of the reaction does not have a significant reverse contribution under these conditions.

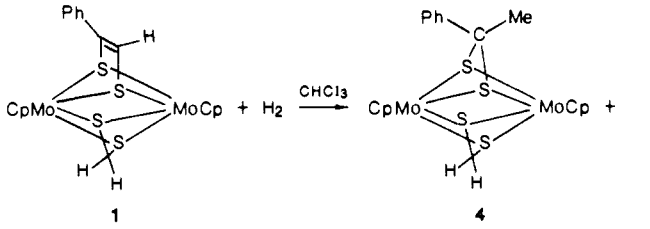
On the basis of the proposed mechanism, an alternate way of synthesizing the 1,1-dithiolate bridged product was devised. The reaction of the triflate salt of the protonated adduct **2** with triethylsilane at room temperature in acetonitrile led to the formation of complex **4** in 70% yield. Triethylsilane has been used previously as a hydride source for protonated molecules in "ionic hydrogenation" reactions.[12] More nucleophilic hydride reagents react in a different way with the protonated salt **2**, as discussed below.

One of the original questions which prompted this work was the role of acid in the hydrogenation of alkyne adducts, reaction 1. When the neutral phenylacetylene adduct is reacted with hydrogen in chloroform, the methylphenyl-1,1-dithiolate bridged complex **4** is the major product. The reduced 1,2-dithiolate bridged derivative, the styrene adduct **6**, is also observed in approximately 30% yield[13] (reaction 11). Complex **6** does not isomerize to **4** in the presence of acid. The course of the reduction of the phenylacetylene adduct therefore differs significantly from those of the other alkyne adducts, which proceed quantitatively as shown in reaction 1.[1] The difference in products may be a result of the different rates of formation of the protonated derivatives

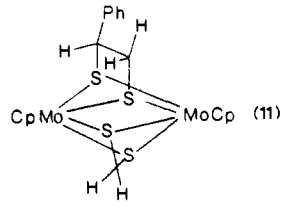
(11) (a) Halpern, J. *Adv. Catal.* **1959**, *11*, 301. (b) Henrici-Olive, G.; Olive, S. *J. Mol. Catal.* **1975–76**, *1*, 121. (c) Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *32*, 1.

(12) Loim, N. M., et. al. *Synthesis* **1974**, 633.

(13) The styrene adduct is in equilibrium with free styrene and $(CpMo\text{-}\mu\text{-}S)_2S_2CH_2$.[1] The 30% yield includes both the styrene adduct and the dissociated species.



1 4

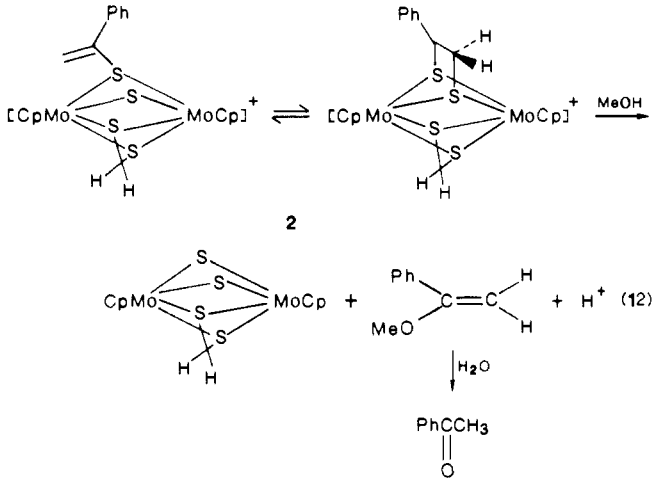


6

as the nature of alkyne substituents is varied (vide supra). In the hydrogenation of the phenylacetylene adduct, it seems likely that the formation of the 1,1-dithiolate bridged product **4** proceeds through the intermediacy of the protonated derivative **2** and is therefore catalyzed by trace amounts of acid in the chloroform. In fact, the addition of 0.1 equiv of CF_3CO_2H to reaction 11 results in the formation of a single product, complex **4**. In contrast, the formation of the styrene adduct in the absence of added acid appears to involve a different, and as yet unidentified, pathway. Studies of the reactions of the other protonated alkyne adducts with hydrogen reveal a complex chemistry which shows a marked dependence on alkyne substituents. A discussion of this work is beyond the scope of the present paper and will be presented elsewhere.[14]

Reactivity of 2A and 2B with Nucleophiles. The protonated phenylacetylene adduct **2** has been found to be reactive toward nucleophiles. For example, the addition of an equivalent of triethylamine to the trifluoroacetate salt of **2** in chloroform regenerates the neutral phenylacetylene adduct. The fact that the alkenylthiolate bridged derivative is in equilibrium with an isomeric form proposed to have some carbonium ion character (see reaction 5) accounts for the unexpectedly high acidity of the cation. Deprotonation of **2** also occurs with stronger bases, such as methyllithium or sodium hydride in THF solution.

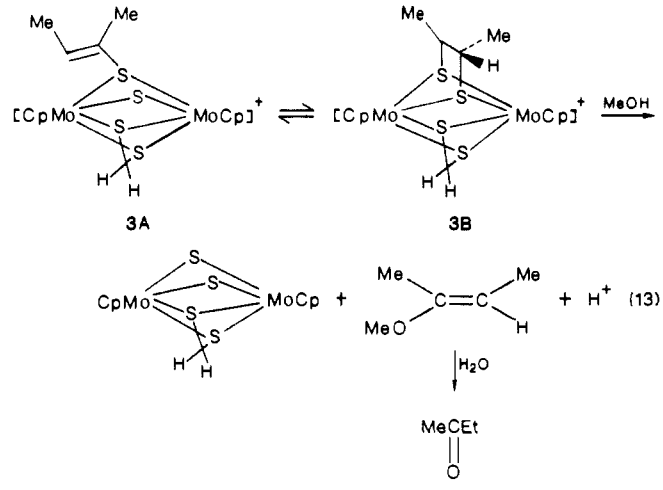
Less basic nucleophiles follow a different reaction pathway. For example, addition of excess methanol to an acetonitrile solution of the tetrafluoroborate salt of **2A** and **2B** results in cleavage of the C–S bond(s) of the thiolate ligand to form the neutral molybdenum dimer $(CpMoS)_2S_2CH_2$ (reaction 12). α-Methoxystyrene is detected by GC/MS soon after the reaction is initiated. Under the reaction conditions, this product is rapidly hydrolyzed to acetophenone, which has been identified by NMR and MS. In contrast, the reaction between the cation **2** and water under similar conditions requires 2 weeks to generate significant amounts of acetophenone.



2

The protonated complex **2** (BF_4 salt) also reacted with chloride and nitrite anions which were added to acetonitrile solutions of **2** as bis(triphenylphosphine)iminium (PPN) salts. In each case a high yield of the methanedithiolate bridged complex is precipitated from solution, indicating a facile cleavage of the carbon–sulfur bond(s) of the protonated thiolate ligand. The organic products of these reactions, nitrostyrene and chlorostyrene, have been characterized by GC/MS techniques. In the reaction with the nitrite ion, only β-nitrostyrene is observed;[15] the reaction with chloride ion also produces some of the β regioisomer. The stereochemistries of the β-substituted styrene products have not yet been determined. We cannot presently propose detailed mechanistic features for these reactions with nucleophiles. The reaction with the nitrite ion is complete within the time period of the equilibration between **2A** and **2B**, implying that both isomers must react with this anion. The other reactions reported here are generally slower than the equilibration process.

As we described above, the alkenedithiolate bridged derivatives are synthesized by the reaction of the appropriate molybdenum dimer with the free alkynes. The stepwise cleavage of the carbon–sulfur bonds of the alkenedithiolate ligand by acid and by nucleophiles therefore represents a new route to alkyne addition reactions. We are interested in comparing the characteristics of this reaction pathway to the nucleophilic additions to alkynes which are catalyzed by high valent and cationic metal complexes.[16] Questions which are under current investigation in our laboratories include the effect of other alkyne substituents on the nucleophilic substitution process. We have identified a similar type of reaction for the protonated butyne adduct **3** (reaction 13), suggesting that



3A 3B

the substitution process can be extended to less activated alkynes. We are also interested in investigating the reactivities of additional types of nucleophiles, in understanding the factors which control the regio- and stereochemistry of the product alkenes, and in determining whether these differ from those of previously characterized alkyne addition reactions.

Experimental Section

Materials. The molybdenum dimer $(CpMo\mu\text{-}S)_2S_2CH_2$ and the alkyne adducts $(CpMo)_2(S_2CH_2)(SC(R)=C(R)S)$, R = CH_3 and Ph, were synthesized as described in the literature.[1] $HBF_4 \cdot Et_2O$ was purchased from Alfa. The bis(triphenylphosphine)iminium salts $PPN(NO_2)$ and PPN(Cl) were purchased from Aldrich.

Physical Measurements. ^1H NMR spectra were recorded at 90 MHz on a JEOL FX 90 Q spectrometer, and ^{13}C NMR spectra were obtained

(14) Duncan, L.; Laurie, J. C. V.; Weberg, R. T.; Rakowski DuBois, M., manuscript in preparation.

(15) α-Nitrostyrene is known to rearrange to β-nitrostyrene under basic conditions: Leseticky, L.; Fidler, V.; Prochazka, M. *Collect. Czech. Commun.* **1973**, *38*, 459.

(16) (a) Nicolas, K. M.; Nestle, M. O.; Seyferth, D. *Transition Metal Organometallics II*; Academic Press: New York, 1978, p 1. (b) Coates, G. E. *Organometallic Compounds*, 3rd ed.; Methuen: New York, 1967.

at 62.9 MHz on a Bruker WM250 spectrometer. Mass spectra (electron impact and FAB) were recorded on a VG 7070 EQ-HF tandem mass spectrometer. Cyclic voltammetric studies were carried out in a conventional three cell system with platinum wires as working and counter electrodes. The reference electrode, a SCE, was separated from the test solution by a bridged tube with a Vycor frit. Potentials were determined with a Princeton Applied Research Model 174A polarographic analyzer at scan rates of 50 or 100 mV/s. Elemental analyses were determined by Spang Laboratory.

X-ray Diffraction Study of $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph)=CH_2)]SO_3CF_3$, 2A. Crystals were obtained by slow evaporation of an acetonitrile/hexane solution of **2**. Details of the crystal data, experimental conditions, and a summary of solution and refinement details are given in Table III.

In the model used for the final block-cascade least-squares refinement, all non-hydrogen atoms thermal parameters were treated anisotropically. The hydrogens attached to the cyclopentadienyl rings were included in riding idealized positions. The hydrogens of the bridging methylene group and of the terminal carbon of the ethylene were not constrained.

Syntheses. Reactions were carried out under a nitrogen atmosphere with standard Schlenk ware. Products were isolated in air unless otherwise noted.

$(CpMo)_2(S_2CH_2)[S(Ph)C=C(H)S]$, 1. $(CpMo\mu\text{-}S)_2S_2CH_2$ (1.00 g, 2.15 mmol) was dissolved in 70 mL of THF, and phenyl acetylene (0.27 mL, 2.58 mmol) was added. The solution was stirred under nitrogen for 1.5 h at room temperature. The reaction mixture was filtered, and the filtrate was rotoevaporated. The recovered green solid was recrystallized from toluene and washed with a small amount of diethyl ether: yield 60%. The solid was further purified by dissolving in CH_2Cl_2 and chromatographing on alumina with a 1:10 hexane/CH_2Cl_2 solvent mixture: ^1H NMR ($CDCl_3$) δ 7.12 (br s, 5, phenyl), 6.74 (s, 1, CH), 6.33 (s, 2, CH_2), 6.05 ppm (s, 10, Ph); ^{13}C NMR ($CDCl_3$) δ 128.2–124.4 ppm (phenyl), 95.8 ppm (CH), 93.7 (Cp), 92.9 ppm (CH_2); IR (Nujol) 1565 cm^{-1}, $\nu_{C=C}$); mass spectrum, m/e (rel intensity) 566 (P^+), 552 ($P^+ - CH_2$), 520 ($P^+ - SCH_2$), 464 ($(CpMoS)_2(S_2CH_2)^+$), 450 ($(CpMoS_2)_2^+$), 418 ($[(CpMo)_2S_3]^+$). Electrochemical data in CH_3CN/0.1 M n-Bu_4NBF_4, $E_{1/2}$, V vs. SCE, +0.18 (ΔE_p = 90 mV), +0.55 (ΔE_p = 80 mV). Anal. Calcd for $C_{19}H_{18}S_4Mo_2$: C, 40.28; H, 3.18. Found: C, 40.88; H, 3.35.

In the mass spectrum of the product, an additional envelope observed at 654 corresponds to the molecular ion for $[CpMo(SCH=C(Ph)S)]_2$. It is not known whether this derivative is a side product in the synthetic reaction or whether it is formed upon electron impact in the spectrometer. No evidence for this product is detected in further reactions of **1**.

Protonation of $[(CpMo)_2(S_2CH_2)(\mu\text{-}SRC=CR'S)]$ (R = Ph, R' = H; R = R' Ph; R = R' = Me). To a green solution of the alkyne adduct $(CpMo)_2(S_2CH_2)(SRC=CR'S)$ (~0.2 mmol) in chloroform (5–8 mL) was added a slight excess of $HBF\cdot Et_2O$ (~22 μL, 0.21 mmol). The reaction mixtures were stirred at room temperature for 1–4 h. The resultant purple or green solutions were filtered, the volume of solvent was reduced to about 3 mL, and diethyl ether (10 mL) was added. The purple or green salts were filtered in air, washed with diethyl ether (3–5 mL), and dried in vacuo.

$[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph)=CH_2)]BF_4$, 2A: Purple solid, yield (**2A** + **2B**) 0.239 g, 96%; ^1H NMR (CD_3CN) δ 7.43 (m, 5, Ph), 6.77 (s, 10, Cp), 5.55 [d, J(HH) 0.7 Hz, 1, =CH], 4.95 [d, J(HH) 0.7 Hz, 1, =CH], 4.05 ppm (s, 2, S_2CH_2); ^{13}C NMR, DEPT (for $CF_3CO_2^-$ salt in $CDCl_3$) δ 50.5 (S_2CH_2), 103.4 (Cp), 125.7 (=CH_2), 126.4, 128.7, 129.0 (C–H_{Ph}), 140.5 (C–C_{Ph}), 143.5 (S–C), 115.5 (CF_3, J_{C-F} = 238 Hz), 159.8 ppm ($CF_3CO_2^-$, J_{CCF} = 38 Hz). **$(CpMo)_2(S_2CH_2)(SC(Ph)CH_2S)]BF_4$, 2B**: ^1H NMR (CD_3CN) δ 7.43 (m, 5, Ph), 6.04 (s, 10, Cp), 5.18 (br s, 2, S_2CH_2), 4.61 ppm (br s, 2, CH_2); ^{13}C NMR (for $CF_3CO_2^-$ salt in $CDCl_3$) δ 47.8, 64.9 (CH_2), 97.9 (Cp, br), 127–130 (C–H_{Ph}), 132.4 (C–C_{Ph}), 151.4 ppm (S–C); mass spectrum, **2A** + **B** m/e (rel intensity) 567 (P^+), 464 (P^+ –PhC=CH_2), 450 $[(CpMo)_2S_4^+]$, 433 $[(CpMoS)_2SCH_2^+]$, 418 [base $(CpMo)_2S_3^+$]. Anal. of **2A** + **B** Calcd for $C_{19}H_{19}BF_4S_4Mo_2$: C, 34.87: H, 2.94; S, 19.60. Found: C, 34.62; H, 3.06; S, 19.44.

$[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Me)=C(H)Me)]BF_4$, 3A. Purple-brown solid, yield (**3A** + **3B**): 60%; ^1H NMR [$(CD_3)_2CO$] δ 7.19 (s, 10, Cp), 5.30 (q, J(HH) 6.7 Hz, 1, =CH), 4.29 (s, 2, S_2CH_2), 1.67 (s, 3, Me), 1.55 ppm (d, J(HH) 6.7 Hz, Me); ^{13}C NMR (Br^- salt in $CDCl_3$) δ 15.1 (=C(H)*Me*), 21.2 (SC*Me*), 49.9 (S_2CH_2), 103.4 (Cp), 130.2 (S*C*Me), 135.4 ppm (=*C*(H)Me). **$[(CpMo)_2(S_2CH_2)(S(Me)C=CH(Me)S)]BF_4$, 3B**: proton NMR [$(CD_3)_2CO$] δ 6.64 (s, 5, Cp), 5.95 (s, 5, Cp), 5.00 (m, 2, S_2CH_2), 4.36 (q, J(HH) 6.3 Hz, 1 H, C–H), 2.41 (s, 3, Me), 1.00 (d, J(HH) 6.3 Hz, 3, Me); ^{13}C NMR ($CF_3SO_3^-$ salt in $CDCl_3$) 26.6, 28.3 (Me's), 53.4 (*C*(H)Me), 73.8 (S_2CH_2), 92.5, 101.5 (Cp). Anal. for **3A** + **B** Calcd for $C_{15}H_{19}BF_4S_4Mo_2$: C, 29.71; H, 3.16; S, 21.15. Found: C, 29.61; H, 3.29; S, 21.08.

Table III.

Crystal Data	
formula	$C_{20}H_{19}F_3Mo_2O_3S_5$
mw (amu)	716.03
space group	$P\bar{1}$
cryst system	triclinic
a (Å)[a]	7.2255 (14)
b (Å)	11.9950 (20)
c (Å)	14.6744 (24)
α (deg)	86.452 (13)
β (deg)	77.922 (15)
γ (deg)	79.570 (14)
vol (Å^3)	1222.75 (38)
Z	2
calcd density (g/cm^3)	1.944
F(000)	708
μ (cm^{-1})	14.52

Data Collection and Reduction	
diffrctmtr	Nicolet P3/F
radtn (Å)	Mo Kα (0.71069)
takeoff angle for graphite monochrmtr (deg)	4.0
temp (deg K)	294–296
cryst dimns (mm)	0.40 × 0.22 × 0.20
cryst color	dark burgundy
cryst habit (needles, plates)	plates
scan technique	θ–2θ
2θ, min–max (deg)	3.0, 65.0
hkl values scanned	11, 19, 23
scan speed (deg/min)	3.9–58.0
scan range, deg below $K\alpha_1$ and above $K\alpha_2$	0.9, 0.9
backgrnd	stationry cryst – stationry cntr backgrnd time = $^1/_2$ scan time
check reflctns	3, 0, 0; 0, 8, 0; 0, 0, 7; –5, –3, –6
freq	every 96 measurmnts
variatn	no overall decay
no. of reflctns measd	11565
no. of unique reflctns	8895
agreement factor during averaging	0.012
no. of obsd reflctns	5764
σ criterion	$F > 6^*\sigma(F)$
absorptn correctn[b]	empirical
transmissn factors, max, min	0.312, 0.277

Structure Determination and Refinement	
method of phase determntn	direct method
programs	SHELXTL[c]
scattering factors	neutral atoms[d]
R and R_w	0.035, 0.042
weight	$1.0/(\sigma^2(F) + 0.0004\times F\times F)$
no. of params	314
ratio of obsrvtns to params	19/1
goodness of fit	1.239
max shift/error	0.025 U_{33} of C5
ave shift/error	0.008
residual electron density e/Å	1.2 e$^-$

[a] Cell dimensions were determined by least-squares fit of the setting angles of 25 reflections with 2θ in the range of 29.8–38.6. [b] Based on 4 scan data for 10 reflections with varying values of 2θ, using 36 ten-degree steps in 4. The internal agreement for these 360 reflections was 0.021 before correction and 0.018 after. [c] Sheldrick, G. M. SHELXTL, *A Program for Crystal Structure Determination*; Nicolet Analytical Instruments: Madison, WI, 1983; Version 4.1. [d] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

$[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph)=CH(Ph)]BF_4$: green salt, yield: 0.12 g, 90%; ^1H NMR [$(CD_3)_2CO$] δ 7.50–7.02 (m, 10, Ph), 6.99 (s, 10, Cp), 5.66 (s, 1, =CH), 4.35 ppm (s, 2, S_2CH_2).

Reversible Protonation of $(CpMo)_2(S_2CH_2)[S(Ph)C=C(H)S]$. Complex **1** (0.046 g, 0.08 mmol) was dissolved in $CDCl_3$ which had previously been filtered through alumina and transferred to an NMR tube. The solution was purged with nitrogen and sealed with a rubber septum. An NMR spectrum was immediately taken. Trifluoroacetic acid (6 μL, 0.08

mmol) was syringed into the tube. The color of the solution changed from green to light brown in about 10 min. The spectrum taken during this period showed the appearance of the diamagnetic protonated complex **2**. After the color change was complete, 1 equiv of NEt_3 was syringed into the tube. The spectrum of the original neutral complex was obtained. Resonances assigned to $HNEt_3^+$ were also observed in the spectrum.

In separate experiments, MeLi (1 equiv) or NaH (3 equiv) was added to an acetonitrile solution of the protonated adduct (BF_4^- salt) under nitrogen. After stirring for an hour at room temperature, the solution was evaporated to dryness, and the green residue was chromatographed on alumina with CH_2Cl_2/hexane (50/50). The major green band was collected, and solvent was evaporated. The product was identified as **1** by NMR, yield: 80–90%.

$(CpMo)_2(S_2CH_2)(S_2C(Me)Ph)$, 4. A. From the Reaction of 2A + B with Hydrogen. The trifluoroacetate or tetrafluoroborate salt of **2** (0.10 g, 0.15 mmol) was dissolved in chloroform. The solution was degassed, and 1 atm of H_2 was added at −196 °C. The reaction was stirred at room temperature for 2 days. The solvent was rotoevaporated, and the remaining solid was chromatographed on alumina with CH_2Cl_2. The orange-red band which eluted with the solvent front was collected, and the solvent was evaporated to give the orange-tan product: Yield 70%; ^1H NMR ($CDCl_3$) δ 7.2 (m, 5, Ph), 6.48 (m, 2, CH_2), 5.97 (s, 5, Cp), 5.30 (s, 5, Cp), 1.66 ppm (s, 3, Me); mass spectrum, *m/e* (rel intensity) 568 (P^+), 476, (P^+ − Ph, Me), 464, (P^+ − C(Ph)Me), 432, (P^+ − SCPh(Me)), 418, ($[Cp_2Mo_2S_3]^+$). Anal. Calcd for $C_{19}H_{20}Mo_2S_4$: C, 40.28; H, 3.53. Found: C, 40.26, H, 3.61.

B. From the Reaction of 2A + B with Triethylsilane. To a solution of the trifluoromethanesulfonate salt of **2** (0.06 g, 0.1 mmol) in CH_3CN (5–10 mL) was added an excess (30 μL, 0.2 mmol) of triethylsilane. The solution was stirred at room temperature for 36 h. The color changed from purple to brown, and a brown precipitate was observed. The solvent was removed in vacuo, and the light brown residue was washed with a small portion of CH_3CN (3 mL) and dried in vacuo. The product $(CpMo)_2(S_2CH_2)(S_2C(Me)Ph)$ was identified by its ^1H NMR spectrum, yield 70%.

Reaction of $(CpMo)_2(S_2CH_2)[SC(H)C(Ph)S]$, 1, with Hydrogen. The alkyne adduct **1** (0.022 g, 0.04 mmol) and an internal standard, *p*-methoxybiphenyl (0.007 g, 0.04 mmol) were mixed together in 0.3 mL of $CDCl_3$; the solution was degassed and sealed under 1 atm of hydrogen at −196 °C in an NMR tube. The solution turned from green to a muddy blue color over a period of 45 h at room temperature. The products in solution were identified by ^1H NMR: $(CpMo\mu\text{-}S)_2S_2CH_2$, 19%; $(CpMo)_2(S_2CH_2)(SCH_2CH(Ph)S)$, **6**, 8%; and $(CpMo)_2(S_2CH_2)(S_2C(Ph)CH_3)$, **4**, 53%.

The presence of the styrene adduct, **6**, was confirmed by an independent synthesis of the compound. Styrene (10 μL, 0.09 mmol) was added to a $CDCl_3$ solution of $(CpMo\mu\text{-}S)_2S_2CH_2$ (0.027 g, 0.06 mmol) in an NMR tube and sealed under nitrogen. An NMR spectrum showed the appearance of resonances characteristic of an alkene adduct along with those of free styrene and $(CpMo\mu\text{-}S)_2S_2CH_2$: ^1H NMR ($CDCl_3$) δ 7.3 (m, 5, Ph), 6.10 (s, 2, S_2CH_2), 5.50 (s, 5, Cp), 5.47 (s, 5, Cp), 1.76 (m, 1, CH), 1.45 ppm (br s, 2, SCH_2).

The reaction of **1** with hydrogen was repeated as described above with the addition of 0.1 equiv of trifluoroacetic acid. The only product observed by NMR was $(CpMo)_2(S_2CH_2)(S_2C(Ph)CH_3)$, **4**, yield 78%.

Reaction of $[(MeCpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)]I$ with Hydrogen. The title complex (0.10 g, 0.16 mmol) was dissolved in 5 mL of chloroform, and pyridine (26 μL, 0.32 mmol) was added. The solution was degassed and 1 atm of H_2 was added at −196 °C. As the solution was stirred for 2–3 days, the color changed from purple to brown. The solution was filtered under nitrogen to collect a white powder, which was identified by NMR and IR spectra as a pyridinium salt. The filtrate was evaporated to dryness, and the resulting brown solid was dissolved in THF-d_8 under nitrogen. The ^1H NMR spectrum confirmed the presence of $(MeCpMo)_2(S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SCH_3)$.[10] The same molybdenum product formed when the reaction was carried out with triethylamine and hydrogen in THF-d_8 in a sealed NMR tube.

Reactions of the Protonated Phenylacetylene Adduct 2 with Nucleophiles. A. CH_3OH. A purple solution of **2** (BF_4^- salt, 0.10 g, 30 mmol) in acetonitrile (8 mL) was treated with wet methanol (3–4 mL). The solution was stirred at room temperature for $^1/_2$ h, during which time the color changed to blue-purple. GC/MS analyses of the reaction mixture at this time showed the presence of α-methoxystyrene and acetophenone (2:1 ratio). A trace of styrene was also detected. After 1 h a blue precipitate had appeared in the reaction vessel. GC/MS spectral analysis showed acetophenone as the only organic product. Proton NMR in $CDCl_3$ showed the blue precipitate to be the complex $(CpMo\mu\text{-}S)_2S_2CH_2$, yield 70%.

B. $(PPN)NO_2$. Equimolar amounts of **2** (BF_4^- salt) and $(PPN)NO_2$ were dissolved in dry CD_3CN in an NMR tube. The blue-purple solution was immediately frozen and degassed in vacuo via 3 freeze–pump–thaw cycles, and the NMR tube was then sealed under vacuum. As soon as the solution was allowed to thaw, a blue precipitate began to appear, and the solution turned a blue color. After 1 min NMR spectroscopy indicated that the reaction was complete. The reaction mixture was exposed to air, and the solution was filtered. The blue precipitate was identified by NMR as $(CpMo\mu\text{-}S)_2S_2CH_2$. Analysis of the filtrate by GC/MS revealed a trace of acetophenone, but the major organic product was β-nitrostyrene, identified by comparison with a standard sample.

C. (PPN)Cl. A procedure similar to that described in B was followed. The reaction proceeded over a period of 60 min. At this time, an NMR spectrum showed that none of the original molybdenum cation remained. After 3 h, the solution was filtered to isolate $(CpMoS)_2(S_2CH_2)$ in ~50% yield. Analysis of the solution by GC showed it to contain acetophenone as the major organic product with a small amount of β-chlorostyrene.

D. Pyridine. Complex **2** (BF_4^- salt, 0.010 g, 0.014 mmol) and pyridine (2 μL, 0.014 mmol) were stirred in acetone (5 mL) at room temperature in a sealed flask. After about 30 min the solution was pale blue, and a blue precipitate was present. After having stirred for an additional 20 min, the solvent was removed in vacuo. An NMR spectrum of the remaining solid indicated that $(CpMo\mu\text{-}S)_2S_2CH_2$ was the only molybdenum complex present. No pyridinium salt could be identified. When the reaction was repeated in a sealed NMR tube, the ^1H NMR spectrum of the products indicated that a pyridinium salt was present. However, after filtration the only organic product to be identified in the solution by GC/MS analysis was styrene.

Reaction of 3A + B with Methanol. The protonated 2-butyne adduct (Br^- salt, 0.016 g, 0.03 mmol) was dissolved in 0.5 mL of $CDCl_3$ with reagent grade methanol (1.3 μL, 0.03 mmol) in an NMR tube. The solution was degassed and sealed under nitrogen. The reaction proceeded at room temperature over a period of 4 days to form primarily $(CpMo\mu\text{-}S)_2S_2CH_2$ and 2-butanone. An unidentified cationic molybdenum dimer (Cp, 7.2 ppm) was also formed in ~20% yield.

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Supplementary Material Available: Anisotropic temperature factors (1 page); calculated and observed structure factors for the crystal structure of **2A** (34 pages). Ordering information can be found on any current masthead page.