Reactions of Sulfido-Bridged Molybdenum Dimers with Diynes as a Route to Multinuclear Dithiolene Complexes

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The bridging sulfido ligands in dunuclear molybdenum complexes of the formula $(Me_nCpMo\mu\text{-}S)_2S_2CH_2$, where $n = 0$ or 1, react with alkynes to form alkenedithiolate complexes. These reactions have been extended to a series of diynes, including 2,4-hexadiyne, 1,4-diphenyl-1,3-butadiyne, 1,3-diethynylbenzene, and 1,4-bis(trimethylsilylethynyl)benzene, to form bis(alkenedithiolate) complexes. The corresponding mono-adducts have also been synthesized by the reaction of the molybdenum dimer with the diyne in a 1:1 molar ratio. The new alkyne adducts have been characterized by spectroscopic techniques and cyclic voltammetry, and both the 1:1 and 2:1 adducts of 1,4-diphenyl-1,3-butadiyne have been identified by X-ray structural determinations. Synthetic routes to a hexanuclear complex and higher molecular weight oligomers linked by alkenedithiolate ligands are also described. Tetranuclear complexes linked by the 1,3-dialkynes show two closely spaced oxidation waves in the cyclic voltammogram, suggesting a small degree of electronic communication between the dimers.

Introduction

Recent work in the area of metal dithiolene chemistry has been extensively reviewed.[1] Mononuclear metal complexes with alkenedithiolate ligands have been studied for many years because of the charge-delocalizing properties of the ligands and the various applications that extend from this property.[2-8] In addition, the pterin molecule containing the enedithiolate unit is known to occur in the molybdenum oxotransferase and hydroxylase enzymes,[8,9] and mononuclear enedithiolate complexes of molybdenum and tungsten have been the subject of renewed interest as potential models for the enzymes.[10,11] In this paper we explore the syntheses of new polynuclear alkenedithiolate complexes of molybdenum. In our early studies of dinuclear molybdenum complexes, we found that complexes containing $\mu\text{-}\eta^2\text{-}$

alkenedithiolate ligands undergo an unusual range of reactions. For example, we reported that complexes of the formula $(CpMo)_2(S_2CH_2)(SCR\text{=}CRS)$, **1**, react with protic acids to form an isomeric mixture of cationic derivatives, as shown in eq 1.[12] Studies of the protonated
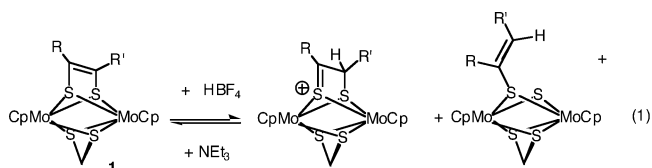
phenylacetylene adduct established that the addition of base, such as triethylamine, regenerated the original alkenedithiolate complex. In addition the isomeric cation mixture reacted with molecular hydrogen to give the 1,1-dithiolate-bridged complex and with nonbasic nucleophiles to give α- or β-substituted styrenes, e.g., Scheme 1.

The fact that these alkenedithiolate complexes are prepared from the reactions of unactivated alkynes with the $Cp_2Mo_2S_4$ core provides an exceptionally flexible synthetic route to more complex multimetallic structures that may show a similar range of unusual reactivities. Very few metal complexes that are connected by linked alkenedithiolate ligands as shown in Scheme 2 have been reported previously. The reaction of 1,4-diphenyl-1,3-butadiyne with $[ReS_4]^-$ and ethanedithiol resulted in the dinuclear rhenium complex I in Scheme 2.[13] Electrophilic attack of the C–H bond in CpCo-(1-Ph-ethenedithiolate) resulted in the linked structure II,[14] but this product was formed in very low (2%) yield. The homonuclear Pt_2 and mixed metal Ni–Pt deriva-

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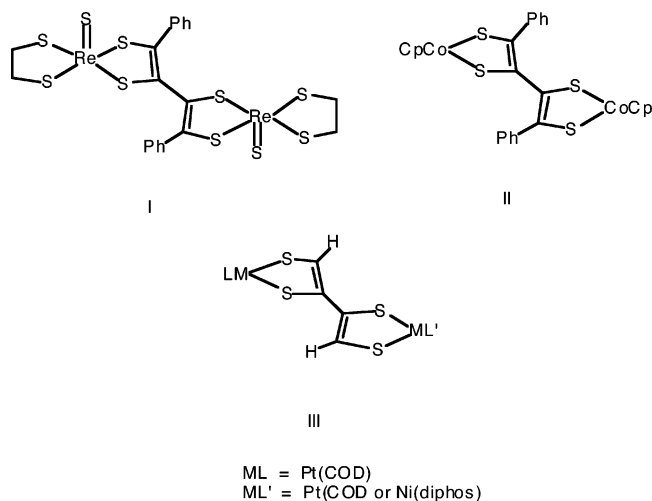
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Scheme 1

Scheme 2

ML = Pt(COD)
ML' = Pt(COD or Ni(diphos)
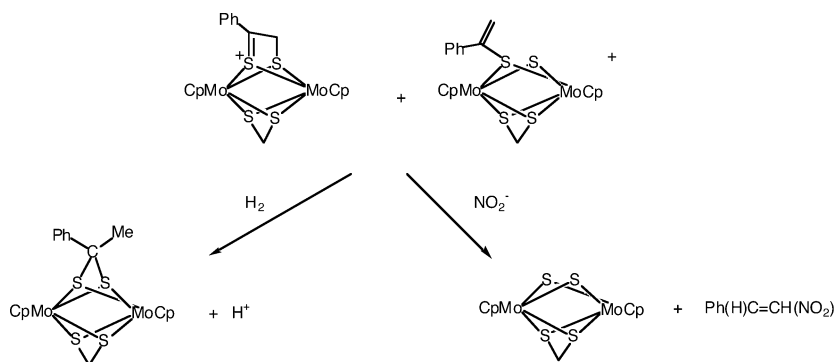
tives of structure III have been synthesized by metal ion addition to 1,2,3,4-butadienetetrathiolate generated in situ.[15] None of the products in Scheme 2 has been structurally characterized, and electrochemical studies that explore the electronic linking properties of the bis-alkenedithiolate ligand have not been reported. In this paper we report our initial synthetic investigations of the use of diynes to form multimetallic complexes that result from linked alkenedithiolate complexes of dinuclear molybdenum derivatives.

Results and Discussion

Syntheses of Tetranuclear Alkenedithiolate Complexes. The reactions of 2 equiv of $(MeCpMo\mu\text{-}S)_2\text{-}S_2CH_2$ with the conjugated dialkynes shown in eq 2 (Cp′ = MeCp) were carried out. The reactions led to the
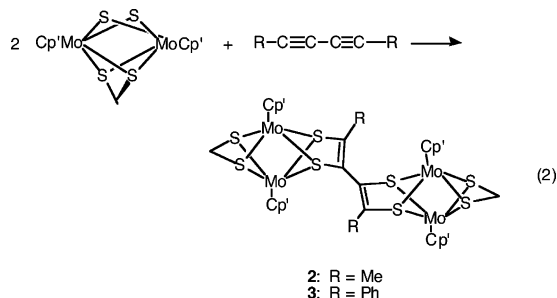
formation of bis-adducts **2** and **3**, which were isolated and characterized by spectroscopic techniques. The formulations of the products were confirmed by ^{1}H NMR

spectroscopy, electrospray mass spectral data, and elemental analyses. The NMR spectra were consistent with a structure with equivalent dimers, and a parent ion for each expected product was observed in the ESI mass spectra. Mono-adducts of the same dialkyne ligands were also prepared for comparative purposes, eq 3. These products, **4** and **5**, were also isolated and characterized by elemental analyses, mass spectra, and NMR data, as described in the Experimental Section.
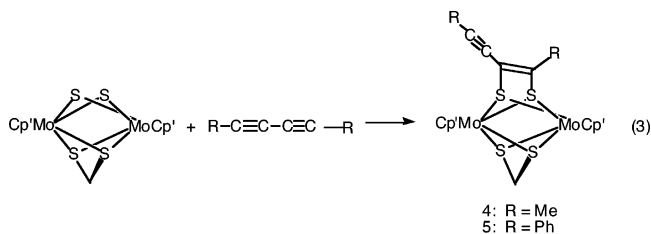

X-ray Diffraction Studies. The 1:1 and 2:1 adducts of the molybdenum dimers with 1,4 diphenyl-1,3-butadiyne were further compared by X-ray diffraction studies. A perspective drawing of the 1:1 adduct, **5**, is shown in Figure 1a, and selected bond distances and angles are given in Table 1. The structure of **5** is very similar to those observed for other alkyne adducts of the $Cp_2Mo_2S_4$ unit,[16] and the structural parameters of the molybdenum−sulfur bonds and angles as well as those of the bridging dithiolene ligand are within expected ranges. The dithiolene C−C distance (C7−C8) is 1.34(1) Å, while the distance for C9−C10 of the free alkyne is 1.20(1) Å. The uncoordinated alkyne has a near linear C9−C10−C(phenyl) angle of 177.0°, but the angle of the alkyne with the dithiolate ligand, C10−C9−C8, is distorted slightly, with a value of 167.6 (11)°.

The structure of the 2:1 adduct, **3**, confirms that each of the alkynes has formed an adduct with the sulfido bridges of a molybdenum dimer. A perspective drawing is shown in Figure 1b, and selected bond distances and angles are given in Table 2. The 1,3-diene portion of the bridging ligand is in an s-trans configuration with the C(7)−C(8)−C(9) and C(8)−C(9)−C(10) angles of the diene equal to 131.1(5)° and 127.8(4)°, respectively. The C(7)−C(8)−C(9)−C(10) torsion angle is 121.2 (6)°. The

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a)

b)
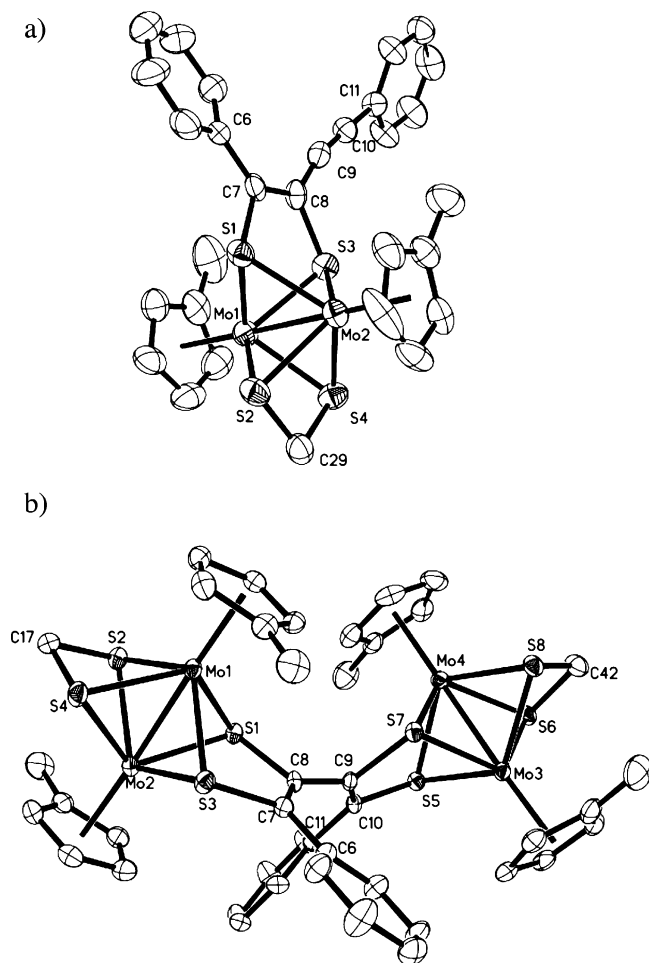
Figure 1. Perspective drawing and numbering scheme for (a) mono-adduct of $(MeCpMo\mu-S)_2S_2CH_2$ and 1,4-diphenylbutadiyne (**5**) and (b) bis-adduct of $(MeCpMo)_2(\mu-S)_2S_2CH_2$ and 1,4-diphenylbutadiyne (**3**). Thermal ellipsoids are shown at the 50% probability level.

**Table 1. Bond Distances and Selected Bond Angles for 1:1 Adduct, 5**

| Bond Distances (Å)			
Mo(1)−S(1)	2.435(3)	S(3)−C(8)	1.809(10)
Mo(1)−S(2)	2.450(3)	S(2)−C(29)	1.811(11)
Mo(1)−S(3)	2.453(3)	S(4)−C(29)	1.814(10)
Mo(1)−S(4)	2.443(3)	C(6)−C(7)	1.484(14)
Mo(2)−S(1)	2.442(3)	C(7)−C(8)	1.342(12)
Mo(2)−S(2)	2.462(3)	C(8)−C(9)	1.428(13)
Mo(2)−S(3)	2.431(2)	C(9)−C(10)	1.200(12)
Mo(2)−S(4)	2.440(3)	C(10)−C(11)	1.437(12)
S(1)−C(7)	1.808(9)	Mo(1)−Mo(2)	2.6009(12)
Bond Angles (deg)			
Mo(1)−S(1)−Mo(2)	64.45(7)	S(1)−C(7)−C(8)	115.8(8)
Mo(1)−S(3)−Mo(2)	64.36(6)	S(3)−C(8)−C(7)	116.8(7)
Mo(1)−S(2)−Mo(2)	63.93(7)	S(1)−C(7)−C(6)	115.1(7)
Mo(1)−S(4)−Mo(2)	64.36(7)	S(3)−C(8)−C(9)	112.9(7)
S(2)−C(29)−S(4)	96.6(5)	C(7)−C(8)−C(9)	130.3(10)
C(6)−C(7)−C(8)	129.1(9)	C(8)−C(9)−C(10)	167.6(11)

bond distances and angles of the dithiolate ligands are similar to those of previous structures of alkenedithiolate-bridged molybdenum dimers. The carbon−carbon linkage between the two dimers, C(8)−C(9), has a bond distance of 1.465 Å, characteristic of a single bond, while the C=C distances of the dithiolene linkages are almost identical, with a distance of 1.34 Å.

Other Alkenedithiolate Linking Ligands. The reactions of $(CpMo\mu-S)_2(S_2CH_2)$ with other diynes have

been carried out to introduce different linkers between the dinuclear units. For example, the reaction of 2 equiv of the molybdenum reagent with 1,3-diethynylbenzene led to the formation of the bis-adduct **6**, and the bis-adduct of 1,4-bis(trimethylsilylethynyl)benzene, **7**, was also prepared, as shown in eq 4.
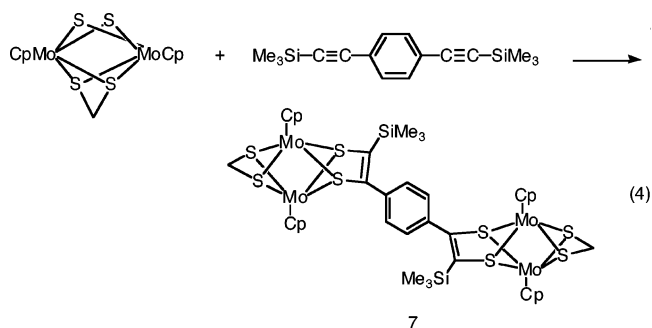
The formulations of the products were confirmed by electrospray mass spectral data and by elemental analyses. As expected the ^{1}H NMR data for these complexes were consistent with equivalent alkenedithiolate-bridged dimers within the structures. In each case one singlet was observed for the four Cp ligands and resonances for the linking unit were consistent with a symmetrical structure. The mono-adducts of the dialkynylbenzene ligands were also prepared for comparative purposes, eq 5. These products, **8** and **9**, were also
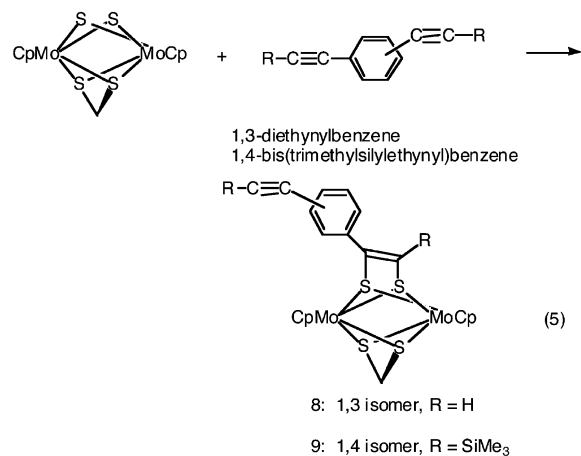
isolated and characterized by elemental analyses, mass spectra, and NMR data. For example in the NMR spectrum of the mono-adduct of 1,3-diethynylbenzene, **8**, a singlet for the proton of the free alkyne is observed at 3 ppm, while the proton of the coordinated alkenedithiolate ligand occurs downfield at 6.2 ppm. Four multiplets are observed for inequivalent phenyl protons.

Electrochemical Studies. The cyclic voltammograms for a series of dinuclear alkenedithiolate complexes $(Me_nCpMo)_2(S_2CH_2)(S(R)C=C(R)S)$ have been studied previously.[16a,17] The CVs for selected examples of these complexes have now been obtained using a glassy carbon electrode in benzonitrile/0.3 M Bu$_4$NBF$_4$ solutions relative to the internal standard ferrocene so that direct comparisons can be made with the new complexes reported here. The complexes typically show

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Table 2. Bond Distances, Selected Bond Angles, and Selected Torsion Angles for 2:1 Adduct, 3

Bond Distances (Å)			
Mo(1)−S(1)	2.4466(12)	S(3)−C(7)	1.828(5)
Mo(1)−S(2)	2.4640(14)	S(2)−C(17)	1.817(5)
Mo(1)−S(3)	2.4495(13)	S(4)−C(17)	1.848(6)
Mo(1)−S(4)	2.4425(13)	C(6)−C(7)	1.469(7)
Mo(2)−S(1)	2.4450(12)	C(7)−C(8)	1.338(7)
Mo(2)−S(2)	2.4610(13)	C(8)−C(9)	1.465(6)
Mo(2)−S(3)	2.4407(14)	C(9)−C(10)	1.345(7)
Mo(2)−S(4)	2.4521(13)	C(10)−C(11)	1.486(6)
S(1)−C(8)	1.816(5)	Mo(1)−Mo(2)	2.6044(6)

Selected Bond Angles (deg)			
Mo(1)−S(1)−Mo(2)	64.34(3)	S(1)−C(8)−C(7)	117.4(4)
Mo(1)−S(3)−Mo(2)	64.36(3)	S(3)−C(7)−C(8)	115.1(4)
Mo(1)−S(2)−Mo(2)	63.85(3)	S(1)−C(8)−C(9)	111.2(3)
Mo(1)−S(4)−Mo(2)	64.30(3)	S(3)−C(7)−C(6)	116.8(3)
S(2)−C(17)−S(4)	96.1(3)	C(7)−C(8)−C(9)	131.1(5)
C(6)−C(7)−C(8)	128.2(4)	C(8)−C(9)−C(10)	127.8(4)
C(9)−C(10)−C(11)	126.0(4)		

Selected Torsion Angles (deg)			
S(3)−C(7)−C(8)−C(9)	169.3(4)	C(7)−C(8)−C(9)−C(10)	121.2(6)
S(5)−C(10)−C(9)−C(8)	165.9(4)		

a quasi-reversible one-electron oxidation wave attributed to the MoIII−III→MoIII−IV couple near −0.2 to −0.3 V, as shown in Table 3. One or two irreversible oxidations are observed at more positive potentials. The potentials show a small variation that correlates with the electron-donating abilities of the alkyne and Cp substituents. Although the mixed valence Mo(III)/IV alkenedithiolate adducts have not been isolated, closely related mixed valence cations with 1,2-alkanedithiolate ligands, e.g., $[(CpMoSC_3H_6S)_2]^+$, have been prepared and characterized as class III (completely delocalized) structures.[18]

The cyclic voltammograms of the new 1:1 diyne adducts, **4**, **5**, **8**, and **9**, were recorded in benzonitrile under the conditions reported above, and potentials are included in Table 3. Each of the complexes shows a quasi-reversible oxidation wave near −0.2 to −0.3 V vs ferrocene for the MoIII−III→MoIII−IV couple, and in most cases an irreversible wave near +0.4 V is observed. The potentials are consistent with the nature of the substituents on the alkeneditiolate ligands; for example, the hexadiyne adduct is more readily oxidized than the diphenylbutadiyne adduct by ca. 80 mV, as expected for the more electron-donating substituents provided by the former ligand.

The cyclic voltammograms of the tetranuclear complexes linked by the dialkynylbenzene ligands, **6** and **7**, were almost identical to those observed for the corresponding mono-adducts. For example, for the adducts of 1,4-bis(trimethylsilylethynyl)benzene, the mono-adduct, **9**, showed an oxidation at −0.23 V vs Fc with a $\Delta E_P = 96$ mV and $i_a/i_c = 1$, while the CV of the bis-adduct, **7**, displayed an oxidation at −0.23 V, $\Delta E_p = 87$ mV and $i_a/i_c = 1$. The data indicate that in the oxidized, monocationic bis-adducts **6** and **7**, no electronic communication through the phenyl-bridged alkenedithiolate ligands is evident, and each dinuclear molybdenum unit is independent of the other.

However, the cyclic voltammograms and differential pulse voltammograms of the 2:1 adducts of the 1,3- and 2,4-diynes, **2** and **3**, show sets of two closely spaced

oxidation waves; for example, the CV data for **3** together with the differential pulse voltammogram for the two reversible waves are shown in Figure 2. The first and second oxidation waves for **2** are observed at $E_{1/2} = -0.321$ ($\Delta E_P = 63$ mV) and -0.185 V ($\Delta E_P = 61$ mV) vs Fc and for **3** at -0.261 ($\Delta E_P = 83$ mV) and -0.112 V ($\Delta E_p = 80$ mV) vs Fc. These waves are assigned to the following couples in the tetranuclear species: $Mo^{3+}-Mo^{3+}/Mo^{3+}-Mo^{3+}$ to $Mo^{3+}-Mo^{4+}/Mo^{3+}-Mo^{3+}$ and $Mo^{3+}-Mo^{4+}/Mo^{3+}-Mo^{3+}$ to $Mo^{3+}-Mo^{4+}/Mo^{3+}-Mo^{4+}$. The second pair of oxidation waves for **3** is irreversible, and the anodic peak potentials are given in Table 3. The splitting of the Mo(III)/(IV) oxidation waves indicates that there is electronic communication between the two dimers in **2** and **3**. Although the relatively small splitting of the waves, 130 mV for **2** and 150 mV for **3**, shows that the coupling is quite weak, to our knowledge, this is the first example of such communication associated with a bis-dithiolene ligand.

A number of dinuclear complexes have been linked by unsaturated ligands in previous studies. For example, extensive studies of quadruply bonded Mo and W dimers linked through the backbone of bridging dicarboxylate and diamidate ligands have been reported.[19−22] These dimers have also been linked by metal alkoxide units.[23] The degree of electronic communcation has been shown to vary from completely localized to completely delocalized, depending on the nature and geometry of the bridging ligand. Studies of singly bonded ruthenium dimers linked by polyalkynes coordinated in axial positions trans to the M−M bond have also been reported.[24] The splitting of the oxidation waves is generally significantly larger for these systems than the differences in $E_{1/2}$ values observed here.

The coupling between the dimers in **2** and **3** may occur through space as a result of electrostatic interactions, and/or the coupling may result from electron delocalization mediated by the unsaturated bis-dithiolene ligand. We attempted to prepare an analogue of **3** containing a saturated bis-alkanedithiolate ligand so that the electrochemical properties of the dithiolene and dithiolate derivatives could be compared. Although the sulfido ligands of $(MeCpMo\mu-S)_2(S_2CH_2)$ react reversibly with mono-alkenes to form alkanedithiolate ligands, no reactions were observed when this dimer was reacted with conjugated dienes, such as *trans,trans*-1,4-diphenyl-1,3-butadiene or *trans-trans*-2,4-hexadien-1-ol, in stoichiometric or excess ratios. Steric hindrance that would

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Table 3. Electrochemical Data for Alkyne Adducts[a]

complex	$E_{1/2}$, V vs Fc, MoIII→MoIV (ΔE_p, mV)	$E_{1/2}$ or E_p, other oxidations
(CpMo)$_2$(S$_2$CH$_2$)(SC(Et)=C(Et)S)	−0.299 (130)	0.134 (274)
(CpMo)$_2$(S$_2$CH$_2$)(SC(H)=C(CO$_2$Et)S)	−0.186 (133)	0.315 (irr), 0.819 (irr)
(MeCpMo)$_2$(S$_2$CH$_2$)(SC(Ph)=C(Ph)S)	−0.246 (91)	0.400 (182)
(MeCpMo)$_2$(S$_2$CH$_2$)(SC(CO$_2$Me)=C(CO$_2$Me)S)	−0.092 (185)	0.724 (irr)
4 (1:1 add, 2,4-hexadiyne)	−0.278 (129)	0.296 (irr), 0.691 (irr)
5 (1:1 add, 1,4-Ph$_2$-1,3-butadiyne)	−0.196 (75)	0.380 (irr), 0.732 (irr)
8 (1:1 add. 1,3-diethynylbenzene)[b]	−0.205 (124)	0.41 (irr)
9 (1:1 add, 1,4-dialkynylbenzene)[b]	−0.228 (94)	not det.
6 (2:1 add, 1,3-diethynylbenzene)[b]	−0.227 (75)	∼0.42 (irr)
7 (2:1 add, 1,4-dialkynylbenzene)[b]	−0.234 (87)	∼0.42 (irr)
2 (2:1 add, 2,4-hexadiyne)	−0.321 (63)	0.403 (irr), 0.715 (irr)
	−0.185 (61)	
3 (2:1 add, 1,4-Ph$_2$-1,3-butadiyne)	−0.261 (83)	0.622 (irr), 0.771 (irr)
	−0.112 (80)	

[a] Recorded in benzonitrile/0.3 M n-Bu$_4$NBF$_4$ at a glassy carbon electrode. Scan rates are 200 mV/s unless otherwise indicated. [b] Scan rate = 50 mV/s.
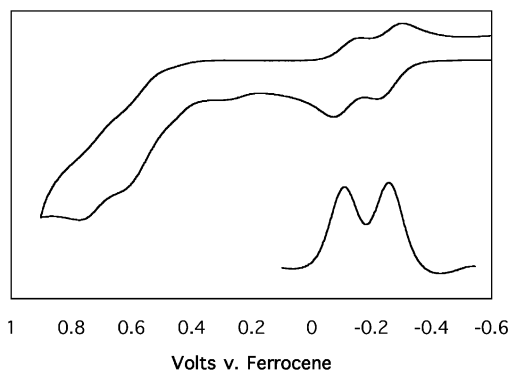
Figure 2. Cyclic voltammogram and differential pulse voltammogram of **3** recorded in benzonitrile/0.3 M Bu$_4$NBF$_4$ at a scan rate of 200 mV/s.

occur at the sp³-hybridized carbons of the resulting alkanedithiolate ligands may account for the lack of reactivity in these cases.

Reactions of the Tetranuclear Complex 3 with Acid. The reaction of **3** with protic acid was studied. If the reaction proceeded in a manner analogous to the dinuclear protonation (see eq 1), this proton addition would provide a means of reversibly changing the nature of the bridging ligand beween the dimers. However the addition of 2 equiv of HBF$_4$ or HSO$_3$CF$_3$ to **3** did not result in a reversible protonation; instead, we observed the oxidation of the complex and the formation of hydrogen, which was detected in the NMR spectrum when the protonation was carried out in a sealed NMR tube. The dicationic oxidized product, [**3**]$^{2+}$ was paramagnetic and did not give a sharp NMR spectrum. The complex was characterized by mass spectroscopy and cyclic voltammetry. The envelope observed at m/z 1336 in the mass spectrum is consistent with an intact tetranuclear dication with a single triflate anion (P − OTf). The CV of the oxidized product shows waves at the same potentials as observed for **3**. The product is proposed to contain two mixed valence MoIII/IV dithiolene-bridged dimers linked by the butadiene fragment.

The electronic spectrum of the 1,4-diphenyl-1,3-buatadiene adduct [**3**]$^{2+}$ has been compared with that of the neutral starting complex **3**. A band in the visible region shifts from 610 nm for **3** to 700 nm for [**3**]$^{2+}$, and a new absorption is observed for the dication in the

near-IR region at 990 nm (ϵ = 1500 M^{-1} cm^{-1}). The latter band is associated with transitions in the individual delocalized dimers in [**3**]$^{2+}$. The band occurs at wavelengths similar to those observed for previously studied mixed valence dimolybdenum complexes with dithiolate ligands.[18] Although we were unable to isolate the monocation of **3**, the electronic spectrum of [**3**]$^+$ was obtained by mixing equimolar solutions of **3** in THF and [**3**]$^{2+}$ in CH$_3$CN. A very broad, unresolved absorption was observed in the visible region (see Experimental Section), and an intervalence transfer band between dimers was not resolved or identified. Such a band may not be observed because of the small difference in potentials observed between the [**3**]$^+$ and [**3**]$^{2+}$ waves and the assignment of weak coupling and largely localized electron density between the dimers.

The reactions of protic acid were also studied with the analogue of **3** with unsubstituted Cp ligands, as these derivatives were expected to be slightly less prone to oxidation. However once again the NMR spectra indicated that a paramagnetic product had formed, suggesting an irreversible oxidation had occurred.

X-ray Diffraction Study of [3]$^{2+}$. A single crystal of the oxidized tetranuclear complex derived from adduct formation with 1,4-diphenyl-1,3-butadiyne was isolated, and an X-ray diffraction study was carried out.[25] A perspective drawing of the dication is shown in Figure 3, and selected distances and angles are given in Table 4. Almost all the bond distances in the structure of the dication are very similar to those of the neutral analogue discussed above, but a small, but significant change in bond distances is observed for the Mo−Mo bonds. The average value of the two M−M bonds decreases from 2.6047(6) Å in the neutral complex to 2.5896(10) Å in the dication. The molecular orbital descriptions of a simplified neutral MoIII−III dimer [CpMo(SH)$_2$]$_2$ indicated that the HOMO of the complex includes a δ bonding overlap of two metal d orbitals and an antibonding contribution from the sulfur p orbitals.[26] In the tetranuclear dication, an electron has been removed from the HOMO of each dimer. The

(25) Structural comparisons of three redox states of complexes showing strong electronic coupling between dimolybdenum units have been reported.[21a]

(26) DuBois, D. L.; Miller, W. K.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1981**, *103*, 3429. (b) Bursten, B. C.; Cayton, R. H. *Inorg. Chem.* **1989**, *28*, 2846.
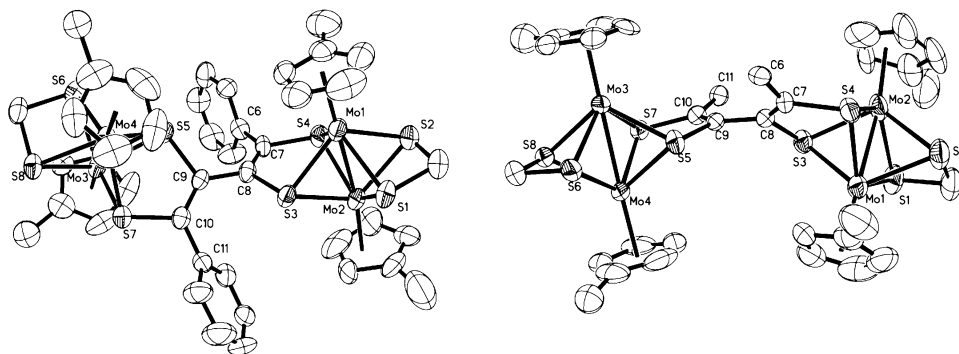
Figure 3. Two perspective views and numbering scheme for the dication [**3**]$^{2+}$. The view on the left shows the orientation of the linking 1,4-diphenylbis(ethenedithiolate) ligand. The view on the right better shows the relative orientations of the two molybdenum dimers. Phenyl rings are omitted from this ORTEP for clarity.

observed M−M bond shortening upon oxidation of **3** to [**3**]$^{2+}$ suggests that the antibonding contribution to the orbital has been diminished and that the sulfur antibonding interaction is a more important contributor than the metal−metal interaction in the HOMO of this system.

A comparison of Figures 1b and 3 shows that the relative orientations of the two molybdenum dimers are significantly different for **3** and [**3**]$^{2+}$. This arises from the much larger C7−C8−C9−C10 torsion angle for [**3**]$^{2+}$ (146°) compared to that of **3** (121°).

Syntheses of Complexes of Higher Nuclearity. In our early work, the hydrosulfido-bridged dimer [CpMo(μ-S)(μ-SH)]$_2$ was found to react with alkynes to form the bis-alkyne adduct with the elimination of H$_2$.[27] A similar type of reaction of the hydrosulfido complex can be carried out with 2 equiv of **5** to form the hexanuclear complex, **10**, eq 6. The reaction proceeds

(6)

10
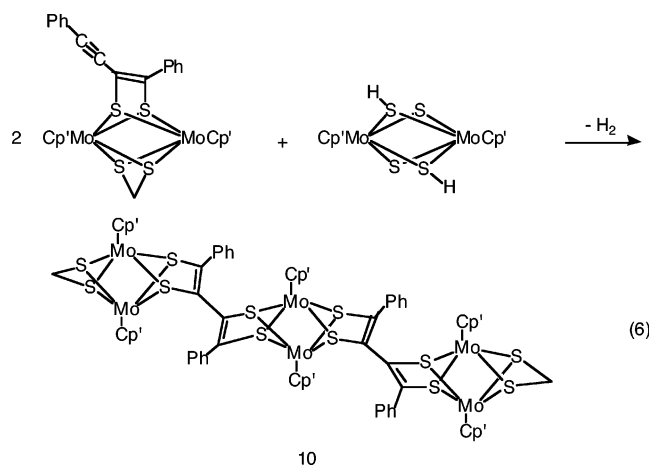
at room temperature overnight to form a brown product, which was purified by column chromatography. The mass spectrum of the product shows a parent ion peak at 1868, consistent with the proposed trimer of dimers. The ^{1}H NMR spectrum of the product suggests that a mixture of isomers is present. Isomers are likely to result from syn or anti orientations of the two methanedithiolate complexes about the central dimer. (Only the anti isomer is shown in eq 6.) For example, NMR resonances assigned to the methanedithiolate protons

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

**Table 4. Bond Distances, Selected Bond Angles, and Selected Torsion Angles for Oxidized 2:1 Adduct, [3]$^{2+}$**

Bond Distances (Å)			
Mo(1)−S(3)	2.458(2)	S(4)−C(7)	1.793(8)
Mo(1)−S(4)	2.455(2)	S(1)−C(17)	1.826(10)
Mo(1)−S(1)	2.458(3)	S(2)−C(17)	1.824(11)
Mo(1)−S(2)	2.458(3)	C(6)−C(7)	1.455(12)
Mo(2)−S(3)	2.441(2)	C(7)−C(8)	1.354(11)
Mo(2)−S(4)	2.429(3)	C(8)−C(9)	1.477(10)
Mo(2)−S(1)	2.451(3)	C(9)−C(10)	1.351(10)
Mo(2)−S(2)	2.454(2)	C(10)−C(11)	1.479(12)
S(3)−C(8)	1.815(8)	Mo(1)−Mo(2)	2.5958(11)

Selected Bond Angles (deg)			
Mo(1)−S(3)−Mo(2)	63.99(6)	S(3)−C(8)−C(7)	118.3(6)
Mo(1)−S(4)−Mo(2)	64.21(7)	S(4)−C(7)−C(8)	116.5(7)
Mo(1)−S(1)−Mo(2)	63.84(7)	S(3)−C(8)−C(9)	115.6(6)
Mo(1)−S(2)−Mo(2)	64.80(6)	S(4)−C(7)−C(6)	115.9(6)
S(1)−C(17)−S(2)	96.3(5)	C(7)−C(8)−C(9)	125.8(8)
C(6)−C(7)−C(8)	127.5(7)	C(8)−C(9)−C(10)	127.1(7)
C(9)−C(10)−C(11)	126.5(7)		

Selected Torsion Angles (deg)			
S(4)−C(7)−C(8)−C(9)	170.9(6)	C(7)−C(8)−C(9)−C(10)	146.4(8)
S(7)−C(10)−C(9)−C(8)	169.9(6)		

are observed as two singlets of unequal intensity with a total integration value of four protons. Multiplets for the Me*Cp* protons are observed between 5.4 and 5.8 ppm, while two sets of phenyl multiplets are observed at 7.2 and 6.65 ppm. The integration ratio of the Me*Cp* to total phenyl protons agrees with the expected value of 24:20. The differential pulse voltammogram for the trimer, **10**, shows two reversible oxidation waves at −0.23 and 0.018 V vs Fc in a ratio of approximately 2:1. These are assigned to the Mo$^{III-III}$ to Mo^{III-IV} couples in the methanedithiolate-bridged dimers and the central bis-dithiolene complex, respectively. The assignment is consistent with the relative current amplitudes and also with the relative oxidation potentials of dinuclear complexes (CpMo)$_2$(S$_2$CH$_2$)(SC(R)=C(R)S) and [CpMo(SC(R)=C(R)S)]$_2$. For similar R groups, the former methanedithiolate-bridged derivatives generally are oxidized more easily than the bis(dithiolene) complexes.[17]

In the reaction described above, the methanedithiolate complex, which has only one set of reactive sulfido bridges, serves as a capping reagent. The reaction of [MeCpMo(S)(SH)]$_2$ with 1,4-diphenyl-1,3-butadiyne was carried out in a 1:1 ratio in THF at room temperature overnight to determine whether soluble polymeric or oligomeric products could be formed, as shown in eq 7. A coordination polymer that incorporates repeating

units of a dinuclear Cp-molybdenum complex has been reported previously.[28]
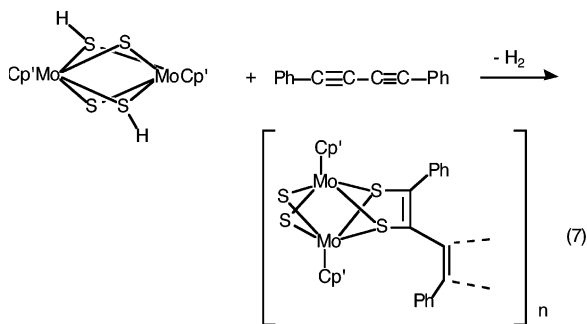
The reaction produced a red soluble material that was isolated in ca. 50% yield after filtration through alumina. The NMR spectrum of the product shows broadened, poorly resolved resonances with chemical shifts very similar to the sharper multiplets observed for the hexanuclear complex discussed above. The ESI$^+$ mass spectrum of the material shows envelopes at $m/z = 680$, 1360, 2040, 2720, 3400, and 4080 in decreasing intensities. The observed m/z values represent multiples of 680, corresponding to $[(MeCpMo)_2S_4 + PhC\equiv C-C\equiv CPh]_n$, and can be assigned to dimolybdenum–alkenedithiolate chains containing from 2 to 12 molybdenum ions ($n = 1-6$). For the more intense envelopes, the complex isotope patterns for the multiple molybdenum ions have been calculated and found to agree with the observed spectra. Several other m/z envelopes are also observed in the spectrum, and some of these are assigned in the Experimental Section. The cyclic voltammogram for this material was recorded in dichloromethane. Two closely spaced quasi-reversible oxidations of equal current amplitude are observed at -0.17 (110) and 0.048 (87) V vs Fc, suggesting a communication between dimers similar to that observed for the tetranuclear complexes. Similar observations of two oxidation waves have been reported for ferrocene-containing polymers.[29] Further work will be necessary to determine the extent of oligomerization/polymerization in this product.

Although our syntheses of polynuclear products have focused primarily on derivatives of 1,4-diphenyl-1,3-butadiyne, we have obtained evidence that the reactions are quite general and similar products are formed with the other diynes. For example, the reaction of the monoadduct **4** (2 equiv) with [MeCpMo(S)(SH)]$_2$ forms a hexanuclear product analogous to **10**, and the reaction of [MeCpMo(S)(SH)]$_2$ with 1 equiv of 1,4-bis(trimethylsilylethynyl)benzene forms a coordination polymer similar to that shown in eq 7. NMR and mass spectroscopic data for these products are included in the Experimental Section.

Summary. The cyclopentadienyl molybdenum dimers containing bridging sulfido ligands react readily with diynes to form polynuclear alkenedithiolate complexes. Reactions proceed with conjugated 1,3- and 2,4-diynes as well as with dialkynylarenes. No evidence for deactivation of the second alkyne of the diyne toward dithiolene formation has been observed after formation of the first dithiolene adduct. Products containing from one to three dinuclear units have been synthesized by appropriate synthetic routes, and isolated and characterized, and preliminary work indicates that larger molecular weight products can also be synthesized. The electrochemical properties of the products have been studied by cyclic voltammetry. The bis-adducts of the molybdenum dimers with the 1,3- and 2,4-diynes show evidence for weak electronic communication between discrete dimer units, whereas the bis-adducts of 1,3- and 1,4-dialkynylarenes do not. The new dinuclear, tetranuclear, and hexanuclear complexes reported here provide the framework for interesting further synthetic elaborations, and they will be the subject of further studies. In addition, these studies suggest that reactions of the molybdenum dimers with polyynes may give rise to new materials.

Experimental Section

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran was distilled from sodium/benzophenone and degassed with nitrogen prior to use. All other solvents were obtained from Fisher or Aldrich and used without further purification. 1,4-Diphenylbutadiyne, 2,4-hexadiyne, 1,4-bis(trimethylsilylethynyl)benzene, and trifluoromethanesulfonic acid were obtained from Aldrich and used without further purification. 1,3-Diethynylbenzene was purchased from Lancaster. (Me$_n$CpMoμ-S)$_2$S$_2$CH$_2$ and [Me$_n$CpMo(S)(SH)]$_2$ (where $n = 0$ or 1) were prepared according to literature methods.[30]

Instrumentation. ^{1}H NMR spectra were acquired with a Varian Inova 400- or 500-MHz instrument. Chemical shifts (δ) are reported relative to tetramethylsilane. Electrospray ionization (ESI) mass spectra were collected using an HP 59987A electrospray with an HP 5989B mass spectrometer. Electronic spectra were collected on an Agilent 8453 UV–visible spectrometer. Cyclic voltammograms and square wave voltammograms were obtained using a Cypress systems model CS-1200 computer-aided electrolysis system using a glassy carbon working electrode. The voltammograms were recorded under a nitrogen atmosphere on 0.3 M Bu$_4$NBF$_4$ benzonitrile solutions. The ferrocene/ferrocenium couple was used as internal reference. Permethylferrocene/permethylferrocenium or cobaltocene/cobaltocenium were used as secondary references when the ferrocene couple was obscured. All potentials are reported with respect to the ferrocene/ferrocenium couple. Elemental analyses were carried out by Desert Analytics Laboratory, Tucson, AZ.

Synthesis of Bis-adduct of (MeCpMoμ-S)$_2$S$_2$CH$_2$ with 2,4-Hexadiyne, 2. (MeCpMoμ-S)$_2$S$_2$CH$_2$ (0.200 g, 0.406 mmol) and 2,4-hexadiyne (0.0158 g, 0.203 mmol) were stirred for 2 h in tetrahydrofuran. As the reaction proceeded, the color of the solution changed from blue to green. The solvent was removed in vacuo, and the solid was recrystallized by layering hexane onto a methylene chloride solution to give green microcrystals. Yield: 0.143 g, 66%. ^{1}H NMR (CDCl$_3$, 500 MHz): 1.19 (s, 6 H, Me), 2.02 (s, 6 H, CpCH_3), 5.65 (m, 16 H, CH$_3$$Cp$), 6.25 (br s, 4 H, CH$_2$). ^{13}C NMR (CDCl$_3$, 400 MHz): δ 16.63 (CH$_3$Cp), 20.43 (S–C–CH$_3$) 89.46 (=C), 90.66 (=C), 93.50 (Cp), 94.62 (Cp), 95.81 (Cp), 112.379 (CH$_2$) Anal. Calcd for C$_{32}$H$_{38}$Mo$_4$S$_8$: C, 36.16; H, 3.60. Found: C, 35.84; H 3.53. MS, m/z (ESI positive ion): 1063 (P$^+$). Cyclic voltammetry, $E_{1/2}$, V (ΔE_P, mV): -0.321 (63) (Mo^{3+}Mo^{3+}/Mo^{3+}Mo$^{3+}\rightarrow$ Mo^{3+}Mo^{3+}/Mo^{3+}Mo^{4+}); -0.185 V (61) (Mo^{3+}Mo^{3+}/Mo^{3+}Mo$^{4+}\rightarrow$ Mo^{3+}Mo^{4+}/Mo^{3+}Mo^{4+}); E_{pa}, 0.403 (irrev); and E_{pa}, 0.715 V (irrev).

(28) Allshouse, J.; Haltiwanger R. C.; Allured, V.; Rakowski DuBois, M. *Inorg. Chem.* **1994**, *33*, 2505.

(29) (a) Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246. (b) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926.

(30) Cowans, B. A.; Rakowski DuBois, M. In *Organometallic Synthesis;* King, R. B., Eisch, J., Eds.; 1986; Vol. III, p 262.

Synthesis of Bis-adduct of (MeCpMoμ-S)$_2$S$_2$CH$_2$ with 1,4-Diphenylbutadiyne, 3. (MeCpMoμ-S)$_2$S$_2$CH$_2$ (0.128 g, 0.26 mmol) and 1,4-diphenylbutadiyne (0.026 g, 0.13 mmol) were stirred in 40 mL of tetrahydrofuran for 1 h. The solvent was removed in vacuo, and the solid was recrystallized by slow diffusion of diethyl ether into a methylene chloride solution. Yield: 0.100 g, 65%. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 2.05 (s, ~11 H, *CH$_3$*Cp), 5.67 (m, 16 H, CH$_3$*Cp*), 6.35 (br s, 4 H, CH$_2$), 6.73 (m, 4 H, Ph), 7.24 (2 m, 6 H, Ph). Anal. Calcd for C$_{42}$H$_{42}$Mo$_4$S$_8$: C, 42.50; H, 3.56. Found: C, 42.12; H 3.69. MS, *m/z* (ESI positive ion): 1187 (P$^+$); 694 (P − 1,4 diphenylbutadiyne$^+$). Cyclic voltammetry, $E_{1/2}$, V (ΔE_p, mV): −0.261 (83) (Mo^{3+}Mo^{3+}/Mo^{3+}Mo^{3+}→ Mo^{3+}Mo^{3+}/Mo^{3+}Mo^{4+}); −0.112 (80) (Mo^{3+}Mo^{3+}/Mo^{3+}Mo^{4+}→ Mo^{3+}Mo^{4+}/Mo^{3+}Mo^{4+}); E_{pa}, 0.622 (irrev); and E_{pa}, 0.771 (irrev). Visible spectrum in tetrahydrofuran, nm (M^{-1} cm^{-1}), 427 (4.41 × 10^3), 610 (6.30 × 10^2), 700 (sh).

Synthesis of Mono-adduct of (MeCpMoμ-S)$_2$S$_2$CH$_2$ with 2,4-Hexadiyne, 4. A solution of 2,4-hexadiyne (0.951 g, 12.2 mmol) in 15 mL of tetrahydrofuran was added to a solution of (MeCpMoμ-S)$_2$S$_2$CH$_2$ (0.300 g, 0.609 mmol) in 40 mL of tetrahydrofuran. The solution was stirred for 30 min, and the solvent was removed in vacuo. The green solid was recrystallized by adding 10 mL of acetonitrile to a solution in 3 mL of diethyl ether. Yield: 0.091 g, 26%. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.58 (s, 3 H, ≡C−CH$_3$), 1.97 (s, 3 H, S−C−CH$_3$), 2.08 (s, 6 H, *CH$_3$*Cp), 5.75 (2 m, 8 H CH$_3$*Cp*), 6.25 (s, 2 H, CH$_2$). MS, *m/z* (ESI positive ion): 570 (P$^+$). Cyclic voltammetry, $E_{1/2}$, V (ΔE_P, mV): −0.278 (129) (Mo^{3+}Mo^{3+} → Mo^{3+}Mo^{4+}); E_{pa}, 0.296 (irrev); and E_{pa}, 0.691 (irrev).

Synthesis of Mono-adduct of (MeCpMoμ-S)$_2$S$_2$CH$_2$ with 1,4-Diphenylbutadiyne, 5. (MeCpMoμ-S)$_2$S$_2$CH$_2$ (0.133 g, 0.27 mmol) and 1,4-diphenylbutadiyne (0.970 g, 4.06 mmol) were stirred in 50 mL of tetrahydrofuran for 30 min. The solvent was removed in vacuo, and the solid was placed on an alumina column and washed with 200 mL of hexane to remove excess 1,4-diphenylbutadiyne. The product was removed from the column with acetone, and water was layered on the acetone solution to yield green crystals. Yield: 0.016 g, 8.5%. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 2.11 (s, 6 H, *CH$_3$*Cp), 5.80 (2 m, 8 H, CH$_3$*Cp*), 6.33 (s, 2 H, CH$_2$), 7.25 (m, ~9 H, Ph), 7.57 (m, 2 H, Ph). Anal. Calcd for C$_{29}$H$_{26}$Mo$_2$S$_4$: C, 50.14; H, 3.77. Found: C, 50.26; H 3.60. MS, *m/z* (ESI positive ion): 694 (P$^+$); 492 (P − 1,4 diphenylbutadiyne$^+$). Cyclic voltammetry, $E_{1/2}$, V (ΔE_P, mV): −0.196 V (75) (Mo^{3+}Mo^{3+} → Mo^{3+}Mo^{4+}); E_{pa}, 0.380 (irrev); and E_{pa}, 0.732 (irrev).

Synthesis of Bis-adduct of (CpMoμ-S)$_2$S$_2$CH$_2$ with 1,3-Diethynylbenzene, 6. (CpMoμ-S)$_2$S$_2$CH$_2$ (0.157 g, 0.338 mmol) was dissolved in 20 mL of THF. 1,3-Diethynylbenzene (21 μL, 0.169 mmol) was syringed into the solution over the course of 5 min. The solution immediately turned green, and a green precipitate formed. The mixture was allowed to stir for 5 h, after which it was filtered and the green solid was collected (0.062 g, 0.059 mmol). The solvent from the green filtrate was removed, and the residue was redissolved in CH$_2$Cl$_2$ and then layered with hexanes and placed in the freezer overnight. A second crop of product (0.072 g, 0.068 mmol) was collected by filtration. Yield: 0.134 g, (75.1%). MS (MALDI$^+$): *m/z* 986 (P$^+$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.05 (s, 1 H, Ph), 7.047 (s, 2 H, Ph), 6.95 (t, 1 H, Ph), 6.62 (s, 2 H, ≡CH), 6.27 (s, 4 H, S$_2$CH$_2$), 5.86 (s, 20 H, Cp). CV, $E_{1/2}$ V vs Fc (ΔE_p mV): −0.227 (75). Anal. Calcd for C$_{32}$H$_{30}$Mo$_4$S$_8$: C, 36.44; H, 2.80. Found: C, 36.29; H, 3.08.

Synthesis of Bis-adduct of (CpMoμ-S)$_2$S$_2$CH$_2$ with 1,4-Bis(trimehylsilylethynyl)benzene, 7. (CpMoμ-S)$_2$S$_2$CH$_2$ (0.204 g, 0.439 mmol) was dissolved in 20 mL of THF. 1,4-Bis[(trimethylsilyl)ethynyl]benzene (0.065 g, 0.240 mmol) was added to the solution slowly, under a flow of nitrogen. The solution immediately turned green, and a green precipitate formed. The mixture was allowed to stir at room temperature for 4 h, it was then filtered, and the green solid was collected

(0.165 g, 0.138 mmol). The solvent from the green filtrate was removed, and the residue was redissolved in approximately 2−3 mL of CH$_2$Cl$_2$ and hexanes were added. The mixture was placed in the freezer, and after 24 h another crop of the product (0.017 g, 0.014 mmol) was collected by filtration. Yield: 0.182 g (69.2%). MS (MALDI$+$): *m/z* 1200 (P$^+$); 737 (P$^+$ − ((CpMoμ-S)$_2$S$_2$CH$_2$)). ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.64 (s, 4 H, Ph bridge), 6.22 (s, 4 H, S$_2$CH$_2$), 5.84 (s, 20 H, Cp), −0.28 (s, 18 H, SiMe$_3$). CV, $E_{1/2}$ V vs Fc (ΔE_p mV): −0.234 (87). Anal. Calcd for C$_{38}$H$_{46}$Mo$_4$S$_8$Si$_2$: C, 38.06; H, 3.84. Found: C, 38.51; H, 3.67.

Synthesis of Mono-adduct of (CpMoμ-S)$_2$S$_2$CH$_2$ with 1,3-Diethynyl)benzene, 8. (CpMoμ-S)$_2$S$_2$CH$_2$ (0.101 g, 0.217 mmol) was dissolved in 5 mL of THF. 1,3-Diethynylbenzene (27 μL, 0.214 mmol) was syringed into the solution and the solution immediately turned green. The mixture was allowed to stir for 18 h, after which the solvent was removed in vacuo. The resulting green residue was washed with cold (−78 °C) petroleum ether and then chromatographed on a short CH$_2$Cl$_2$/neutral alumina column. One green band was eluted with 100% CH$_2$Cl$_2$, which contained the product. Yield: 0.054 g (42.1%). MS (ESI$^+$): *m/z* 591 (P$^+$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36, 7.25, 7.18, 7.12 (m, 4 H, Ph), 6.77 (s, 1 H, =CH), 6.28 (s, 2 H, S$_2$CH$_2$), 5.89 (s, 10 H, Cp), 2.99 (s, 1 H, C≡CH). CV, $E_{1/2}$ V vs Fc (ΔE_p, mV): −0.205 (129). Anal. Calcd for C$_{21}$H$_{18}$Mo$_2$S$_4$: C, 42.70; H, 3.05. Found: C, 42.48; H, 3.01.

Synthesis of Mono-adduct of (CpMoμ-S)$_2$S$_2$CH$_2$ with 1,4-Bis(trimethylsilylethynyl)benzene, 9. (CpMoμ-S)$_2$-S$_2$CH$_2$ (0.077 g, 0.166 mmol) was dissolved in 10 mL of THF. 1,4-Bis[(trimethylsilyl)ethynyl]benzene (0.045 g, 0.166 mmol) was added to the solution slowly, under a flow of nitrogen. The solution immediately turned green, and the mixture was allowed to stir at room temperature for 3 h. The solvent was removed in vacuo, and the green residue was washed with cold (−78 °C) petroleum ether. The residue was then eluted through a short neutral alumina column. One green band was eluted with 100% CH$_2$Cl$_2$, and it contained the product. Yield: 0.035 g (28.7%). MS (MALDI$^+$): *m/z* 735 (P$^+$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.12 (s, 2 H, Ph), 6.63, 6.60 (2s, 2 H, Ph), 6.08 (s, 2 H, S$_2$CH$_2$), 5.80 (s, 10 H, Cp), −0.26 (s, 18 H, SiMe$_3$). CV, $E_{1/2}$ V vs Fc (ΔE_p, mV): −0.228 (94). Anal. Calcd for C$_{27}$H$_{34}$Mo$_2$S$_4$Si$_2$: C, 44.13; H, 4.63. Found: C, 44.53; H, 4.61.

Synthesis of Hexanuclear Complex 10. Complex **5** (0.116 g, 0.168 mmol) and [MeCpMo(μ-S)(μ-SH)]$_2$ (0.040 g, 0.083 mmol) were stirred in THF under N$_2$ for 3 days. The solution was filtered in air, and the solvent was removed by rotary evaporation. The resulting solid was chromatographed on an alumina column with chloroform, and the main brown band was collected. The solvent was removed by rotary evaporation, and ether was layered on the resultant brown oil. After 1 h a brown powder formed that could be removed by filtration. Yield: 0.061 g, 39%. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 1.77 (2 s, ~5 H, *CH$_3$*Cp), 1.98 (s, ~5 H, *CH$_3$*Cp), 2.04 (s, ~5 H, *CH$_3$*Cp), 5.64 (m, 24 H, CH$_3$*Cp*), 6.22, 6.18 (2 s, 4 H, CH$_2$), 6.74 (3 m, 8 H, Ph), 7.22 (m, 13 H, Ph). MS, *m/z* (ESI positive ion): 1868 (P$^+$); 1173, (P − 694); 694 (MeCpMoμ-S)$_2$S$_2$CH$_2$ + diyne). Cyclic voltammetry, $E_{1/2}$, V (ΔE_P, mV): −0.225 V (86); 0.023 V (70); E_{pa}, 0.302 (irrev); and E_{pa}, 0.681 (irrev). Differential pulse voltammetry, E_p (|i|), −0.229 V (10.8 uA), 0.018 V (7.5 uA). Vis spectrum in THF (nm, (M^{-1} cm^{-1})): 432 (9.3 × 10^3); ~500 (sh); 624 (1.3 × 10^3); 700 (sh); ~800 (weak sh).

A similar procedure was followed with **4** to form an analogous hexanuclear complex. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.09 (overlapping singlets, 12 H, Me); 2.05, 1.99, 1.87 (3 s, 18 H, *CH$_3$*Cp), 5.52 (m, 16 H, CH$_3$*Cp*), 5.48, 5.43 (2 m, 8 H, CH$_3$*Cp*), 6.17 (overlapping singlets, 4 H, CH$_2$). MS, *m/z* (ESI positive ion): 1618 (P$^+$); 1128, (P − (MeCpMoμ-S)$_2$S$_2$CH$_2$)); 634 (P − 2(MeCpMoμ-S)$_2$S$_2$CH$_2$).

Reaction of [MeCpMo(μ-S)(μ-SH)]$_2$ with 1,4-Diphenyl-1,3-butadiyne. 1,4-Diphenylbutadiyne (0.262 g, 1.29 mmol) and [MeCpMo(S)SH]$_2$ (0.622 g, 1.29 mmol) were stirred at

Table 5. Crystal Data and Collection Parameters for the Bis-adduct of (MeCpMo)$_2$(μ-S)$_2$S$_2$CH$_2$ and 1,4-Diphenylbutadiyne (3), the Mono-adduct of (MeCpMo)$_2$(μ-S)$_2$S$_2$CH$_2$ and 1,4-Diphenylbutadiyne (5), and the Product of Reaction of 3 with Trifluoromethanesulfonic Acid [3]$^{2+}$

	3	5	3^{2+}
formula	C$_{42}$H$_{42}$Mo$_4$S$_8$	C$_{29}$H$_{26}$Mo$_2$S$_4$	(C$_{42}$H$_{42}$Mo$_4$S$_8$)(CF$_3$SO$_3$)$_2$(C$_3$H$_6$O)$_{0.9}$
fw (amu)	1187.00	694.62	1535.46
cryst syst	monoclinic	orthorhombic	triclinic
a (Å)	14.8754(6)	17.5179(13)	10.4965(5)
b (Å)	16.9565(7)	11.9804(9)	15.1664(6)
c (Å)	16.4576(6)	25.3939(19)	18.0759(8)
α (deg)	90	90	76.5010(10)
β (deg)	92.8870(10)	90	78.3560(10)
γ (deg)	90	90	80.0590(10)
volume (Å^3)	4145.9(3)	5329.5(7)	2716.6(2)
space group	$P2(1)/n$ (#14)	$Pbca$ (#61)	$P\bar{1}$ (#2)
Z	4	8	2
density, calc (g/cm^3)	1.902	1.731	1.877
λ(Mo Kα)	0.71073	0.71073	0.71073
temp (K)	138	158	155
scan type, deg	ω scans, 0.3	ω scans, 0.3	ω scans, 0.3
θ range (deg)	1.80 to 27.48	1.98 to 27.48	2.00 to 27.48
no. of indep reflns	9474 [R(int) = 0.0817]	6112 [R(int) = 0.2828]	12 454 [R(int) = 0.0893]
no. of reflns obsd	31 624	40 162	21 662
absorp coeff (mm^{-1})	1.618	1.273	1.356
R1 (for $F_o > 4\sigma F_o$)^a	0.0484 for 6826 data	0.0802 for 2840 data	0.0736 for 6227 data
R1, wR2 (all data)^b	0.0780, 0.130	0.1884, 0.1920	0.1603, 0.1934
GOF^c	0.997	0.951	0.950
largest peak, hole (e$^-$/Å^{-3})	1.51, −1.63	1.740, −1.063	1.408, −0.0866

^{a} $R = R_1 = \sum ||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. ^{c} GOF $= S = [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$ where M is the number of reflections and N is the number of parameters refined.

room temperature in 200 mL of THF under N$_2$ for 1−3 days. The solution was filtered in air (to remove a small amount of solid that NMR showed to be impure product), and solvent was removed from the filtrate by rotary evaporation. The resulting solid was filtered through alumina with chloroform, and the red-brown filtrate was collected. Layering ether on this solution resulted in precipitation of a red-brown powder. Yield: 0.464 g, 52%. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.81 (br, 6 H, *CH$_3$*Cp), 5.32 (br, 8 H, CH$_3$*Cp*), 6.72 (br, 4 H, Ph), 7.22 (br, ~7 H, Ph). MS (ESI positive ion), *m/z*, intensity, 1 unit = ([MeCpMoS$_2$]$_2$ + 1,4 diphenylbutadiyne): 680 (17) [(1 unit)]$^+$; 882 (48) [(1 unit) + 1,4 diphenylbutadiyne]$^+$; 1360 (32) [2 units]$^+$; 1562 (15) [(2 units) + 1,4 diphenylbutadiyne]$^+$; 2040 (26) [3 units]$^+$; 2242 (2.3) [(3 units) + 1,4 diphenylbutadiyne]$^+$; 2720 (5) [4 units]$^+$; 2922 (2.7) [(4 units) + 1,4 diphenyl-butadiyne]$^+$; 3400 (3.2) [5 units]$^+$; 3602 (2.3) [(5 units) + 1,4 diphenylbutadiyne]$^+$; 4080 (2.2) [6 units]$^+$. Cyclic voltammetry in CH$_2$Cl$_2$, $E_{1/2}$, V (ΔE_P, mV): −0.169 (110); 0.048 V (87); E_{pa}, 0.966 (irrev). Visible spectrum in tetrahydrofuran, (nm, M^{-1} cm^{-1} per unit), 481 (3.34 × 10^3), ~580 (sh); 677 (3.87 × 10^2), 809 (sh, ~1.43 × 10^2).

A similar procedure was followed with 1,4-bis(trimethylsilylethynyl)benzene to form a polymeric product. ^{1}H NMR (CDCl$_3$): δ −0.29 (18 H, Me$_3$Si), 2.0 (overlapping singlets, 6 H, *CH$_3$*Cp), 5.60 (m, 8 H, CH$_3$*Cp*), 6.65, 6.76 (2m, 4 H, Ph). MS (ESI positive ion), *m/z*, 1 unit = ([MeCpMoS$_2$]$_2$ + 1,4-bis-(trimethylsilylethynyl)benzene): 748 [(1 unit)]$^+$; 1498 [2 units]$^+$; 1768 [(2 units) + diyne]$^+$; 2244 [3 units]$^+$; 2518 [(3 units) + diyne]$^+$; 2996 [4 units]$^+$; 3265 [(4 units) + diyne]$^+$; 3744 [5 units]$^+$; 4017 [(5 units) + diyne]$^+$; 4764 [(6 units) + diyne]$^+$.

Synthesis of [3]$^{2+}$ Complex **3** (0.068 g, 0.0572 mmol) and trifluoromethanesulfonic acid (10.1 uL, 0.144 mmol) were stirred in 40 mL of methylene chloride under nitrogen for 3 days. The solution was filtered to obtain 0.050 g of a green solid. This solid could be recrystallized by dissolving in acetonitrile and letting diethyl ether slowly diffuse into the solution. Yield: 33%. No resonances for the product were observed by NMR, but when the reaction was performed in an NMR tube, a sharp resonance assigned to H$_2$ was observed at 4.63 ppm. MS, *m/z* (ESI positive ion): 1336 (P − CF$_3$SO$_3$)$^+$; 1186 (P − 2CF$_3$SO$_3$)$^+$; 694 ((MeCpMoμ-S)$_2$(S$_2$CH$_2$) + diyne). Cyclic voltammetry: potentials are identical to those reported

for **3**. Visible absorption spectrum in acetonitrile, nm (M^{-1} cm^{-1}): shoulder at ~433 (4.25 × 10^3), 699 (2.63 × 10^3), 989 (1.51 × 10^3).

Visible Absorption Spectrum of [3]$^+$. Complex **3** was dissolved in tetrahydrofuran, and [3]$^{2+}$ was dissolved in acetonitrile to make 0.45 mM solutions. Both of these solutions were degassed with nitrogen, then 1 mL of each solution was syringed into a 1 cm quartz cell that had been evacuated and filled with nitrogen. The visible absorption spectrum was obtained immediately after mixing. A very broad absorption band extending from ~500 to 1000 nm was observed with λ_{max} at 691 nm (1.71 × 10^3).

X-ray Crystallography. A crystal of appropriate size was mounted on a glass fiber using Paratone-N oil, transferred to a Siemens SMART diffractometer/CCD area detector, centered in the beam (Mo Kα; λ = 0.71073 Å; graphite monochromator), and cooled to −135 to −115 °C by a nitrogen low-temperature apparatus that had been previous calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A minimum of a hemisphere of data was collected using 0.3° ϖ scans at 30 s per frame. The raw data were integrated and the unit cell parameters refined using SAINT. Data analysis was performed using XPREP. Absorption correction was applied using SADABS. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Structure solutions and refinements were performed (SHELXTL-Plus V5.0) on F^2. Crystal data and collection parameters are given in Table 5. **Bis-adduct of (MeCpMoμ-S)$_2$S$_2$CH$_2$ with 1,4-Diphenyl-1,3-butadiyne (3).** Crystals suitable for X-ray diffraction studies were grown by letting ether diffuse into a solution of the compound in dichloromethane at room temperature. Preliminary data indicated a monoclinic cell with the $P(2_1)/n$ space group. All non-H atoms were refined anisotropically. All H-atoms were placed in idealized positions and were included in structure factor calculations but were not refined.

Mono-adduct of (MeCpMoμ-S)$_2$S$_2$CH$_2$ and 1,4-Diphenyl-1,3-butadiyne (5). Crystals suitable for X-ray diffraction studies were grown by letting ether diffuse into a solution of

the compound in dichloromethane at room temperature. Preliminary data indicated a monoclinic cell with the *Pbca* space group. All non-H atoms were refined anisotropically. All H atoms were placed in idealized positions and were included in structure factor calculations but were not refined.

[3](OTf)₂. Crystals suitable for X-ray diffraction studies were grown by letting ether diffuse into a solution of the compound in acetone at room temperature. Preliminary data indicated a triclinic cell with the *P*1̄ space group. A molecule of acetone cocrystallized and was found to be present 90% of the time. The disorder in one of the two triflate counterions was modeled by letting one of the sulfurs and one of the oxygens refine to two equivalent positions. The methylcyclo-pentadienyl ligands attached to Mo3 and Mo4 were also disordered, and the disorder was modeled by letting the methyl groups refine to two equivalent positions. All atoms other than hydrogen, the disordered sulfur and oxygen, and the disordered methyl groups were refined anisotropically. All H atoms were

placed in idealized positions and were included in structure factor calculations but were not refined.

Supporting Information Available: Tables of crystal and refinement data, positional and equivalent isotropic thermal parameters, bond distances and angles, and torsional angles for **3**, **[3]²⁺**, and **5**; ESI mass spectra for polymeric formulation. This material is available free of charge via the Internet at http://pubs.acs.org.

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