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# Sequential Construction of One, Two, or Three Dithiolene Ligands from Alkynes and Sulfur in Dinuclear Cyclopentadienyl Molybdenum Complexes

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This paper describes the sequential assembly of up to three dithiolene ligands from alkynes and elemental sulfur at a dimetal center. The dimolybdenum $\mu$-alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2]$ (**1a**−**c**; Cp = $\eta$-$C_5H_5$, $R^1$ = $R^2$ = H, $CO_2Me$; $R^1$ = H, $R^2$ = $CO_2Me$) undergo oxidative decarbonylation on reaction with elemental sulfur in refluxing toluene to give good to excellent yields of the terminal dithiolene complexes $[Mo_2(S)(\mu\text{-}S)_2(SCR^1{=}CR^2S)Cp_2]$ (**2a**−**c**). Further reaction of these complexes with 1 equiv of an alkyne $R^3C{\equiv}CR^4$ ($R^3$ = $R^4$ = H, $CO_2Me$; $R^3$ = H, $R^4$ = $CO_2Me$) followed by oxidation with elemental sulfur produces the bis(dithiolene) complexes $[Mo_2(\mu\text{-}S)_2(SCR^1{=}CR^2S)(SCR^3{=}CR^4S)Cp_2]$ (**4a**−**d**). Two examples, $[Mo_2(\mu\text{-}S)_2(S_2C_2H_2)_2Cp_2]$ and $[Mo_2(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}_2Cp_2]$, have been structurally characterized. Reaction of **2** with an excess of an activated alkyne $R^5C{\equiv}CR^6$ ($R^5$ = $R^6$ = $CO_2Me$) and sulfur, or of **4** with the alkyne alone, affords good yields of the tris(dithiolene) complexes $[Mo_2(SCR^1{=}CR^2S)(SCR^3{=}CR^4S)(SCR^5{=}CR^6S)Cp_2]$ (**6a**−**e**). The degree of control over the substituents in these complexes is demonstrated by the synthesis of $[Mo_2(S_2C_2H_2)\{\mu\text{-}S_2C_2(CO_2Me)_2\}\{\mu\text{-}S_2C_2(CO_2Et)_2\}Cp_2]$ (**6e**), which contains three different dithiolene ligands, as a single isomer.

## Introduction

Complexes containing dithiolene (1,2-enedithiolate) ligands rose to prominence in the 1960s and continue to be intensely studied today owing to their unique electronic and structural properties, which enable them to be used in applications such as tunable near-IR dyes and conducting materials.[1−3] In addition to the familiar homoleptic bis- and tris-dithiolene complexes, heteroleptic species containing cyclopentadienyl ligands have also been widely explored.[4] The involvement of dithiolene ligands in the active sites of molybdenum- and tungsten-containing oxotransferase enzymes has provided additional impetus for the investigation of complexes of these metals as possible model systems.[5]

One of the ways in which dithiolene ligands may be synthesized is through the combination of alkynes with sulfur;[6] indeed Schrauzer's first low yield synthesis of $[Ni(S_2C_2Ph_2)_2]$ involved heating nickel sulfide with diphenylacetylene.[7] More often, however, dithiolenes have been produced by the reaction of discrete metal sulfide (or polysulfide) complexes with activated alkynes such as dimethyl acetylenedicarboxylate (DMAD).[8] In some cases heating or photolysis of suitable precursor complexes with a mixture of sulfur and a large excess of the alkyne accomplishes a similar result.[9,10] Depending on the reactivity of the metal sulfide complex, reactions with less activated alkynes such as phenylacetylene and diphenylacetylene can also occur,[11] though reactions with acetylene itself are limited to only relatively few examples such as $[ReS_4]^-$ and $[Ru_2(\mu\text{-}S)_2(\mu\text{-}S_2)Cp^*{}_2]$.[12] The addition of acetylene itself to sulfur atoms to produce bridging

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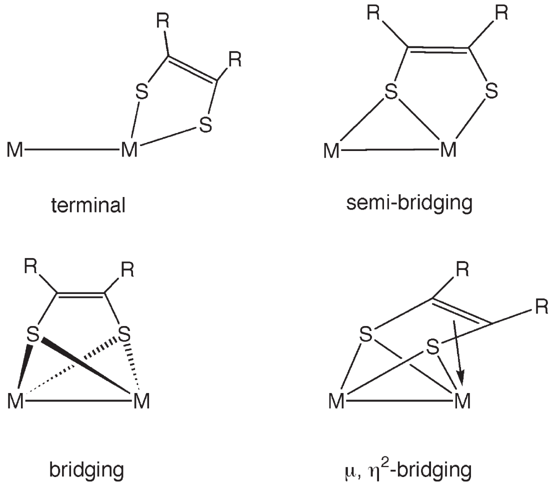
**Chart 1.** Bonding Modes Available to the Dithiolene Ligand in Dinuclear Complexes

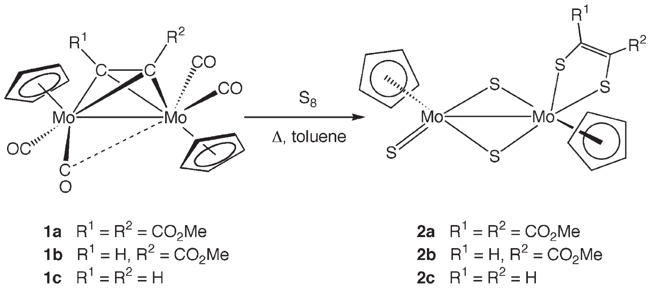


dithiolene ligands in dimolybdenum complexes is also well documented in the extensive work of Rakowski Dubois and co-workers.[13]

In this paper we describe how dinuclear molybdenum cyclopentadienyl complexes containing bridging alkyne ligands can be converted sequentially into mono-, bis-, and tris(dithiolene) species with an excellent degree of control over the substituents present and the regiochemistry, as shown by the successful synthesis of a compound containing three different dithiolene ligands. Dinuclear Mo(III) complexes with bridging dithiolene ligands such as $[Mo_2(\mu\text{-}SCR^1{=}CR^2S)_2Cp_2]$ have been known for many years, but this work represents the first general synthesis of those containing the terminal and semibridging modes of coordination (see Chart 1).

## Results and Discussion

**Scheme 1.** Synthesis of the Mono(dithiolene) Complexes **2**



As reported briefly in our preliminary communication,[14] the reaction of the dimolybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2]$ (**1a**, $R^1 = R^2 = CO_2Me$; **1b**, $R^1 = H$, $R^2 = CO_2Me$; **1c**, $R^1 = R^2 = H$; $Cp = \eta\text{-}C_5H_5$) with an excess of elemental sulfur in refluxing toluene results in the loss of all the carbonyl groups and affords excellent yields of the Mo(V) dithiolene complexes $[Mo_2(S)(\mu\text{-}S)_2(SCR^1{=}CR^2S)Cp_2]$ (**2a**−**c**) as green crystalline solids which can be readily isolated by column chromatography (Scheme 1). Surprisingly this reaction appears to represent the first example of the formation of dithiolene ligands by the insertion of sulfur into preformed metal-alkyne bonds.[15] The dithiolene ligand occupies a terminal position, as demonstrated by the presence of two inequivalent Cp resonances and the low field position of the dithiolene protons ($\delta$ 8.37 in **2c** and $\delta$ 9.41 in **2b**) in their $^1$H NMR spectra. Dimolybdenum complexes in which the dithiolene ligands occupy bridging positions usually display proton shifts at somewhat higher fields, for example, $\delta$ 6.43 for $[Mo_2(\mu\text{-}S_2C_2H_2)_2Cp_2]$[13] and $\delta$ 7.78/7.80 for the two isomers of $[Mo_2\{\mu\text{-}SCH{=}C(CO_2Me)S\}_2Cp_2]$.[16] The new complexes gave high intensity molecular ions in their mass spectra provided these were recorded in electron impact mode; unusually though, complete fragmentation occurred when fast atom bombardment mode was used.

Only two previous examples of a complex of this type have been reported. Rakowski Dubois and co-workers isolated $[Mo_2(O)(\mu\text{-}S)_2(SCH{=}CPhS)Cp_2]$ in 20% yield by exposure of $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2Cp_2]$ to air in the presence of phenylacetylene, and subsequent reaction of this compound with $S(SiMe_3)_2$ at 70 °C over a period of 4 weeks succeeded in replacing the terminal oxo ligand with a terminal sulfide to give $[Mo_2(S)(\mu\text{-}S)_2(SCH{=}CPhS)Cp_2]$; alternatively (and intriguingly) the same transformation was achieved by stirring with EtSH in $CH_2Cl_2$ at room temperature for 2 days. Since other alkynes did not react in the same way as phenylacetylene, no other complexes of this type with different dithiolene ligands were prepared.[17] The product was described as being rather air-sensitive, reverting rapidly to the oxo complex in solution. It should be noted that in contrast to this report, we find that complexes of type **2** are generally air-stable even in solution, though small amounts of green minor products which are the corresponding oxo complexes $[Mo_2(O)(\mu\text{-}S)_2(SCR^1{=}CR^2S)Cp_2]$ **3** were isolated from some syntheses (see Chart 2).[18] The tungsten analogue of **2c**, $[W_2(S)(\mu\text{-}S)_2(S_2C_2H_2)Cp_2]$, has also been prepared as a low yield product

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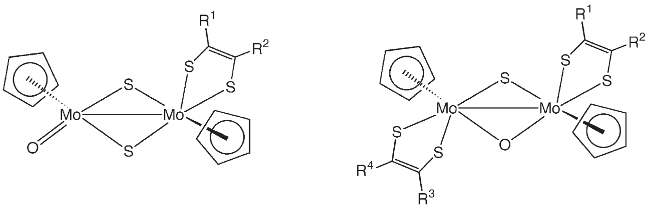
(18) Although we only discuss three dithiolene complexes **2a-c** in detail here, the reaction is successful for all alkyne complexes **1**, and in the synthesis of $[Mo_2(S)(\mu\text{-}S)_2(SCH{=}CPhS)Cp_2]$ by the same method, the spectroscopic data of the minor product match those of the oxo complex $[Mo_2(O)(\mu\text{-}S)_2(SCH{=}CPhS)Cp_2]$ given in ref 17.

**Chart 2.** Structures of the Mono- and Bis(dithiolene) Oxo Complexes



**3** **5**

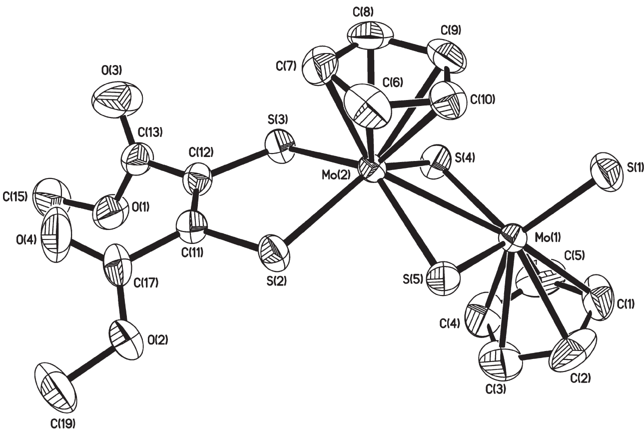
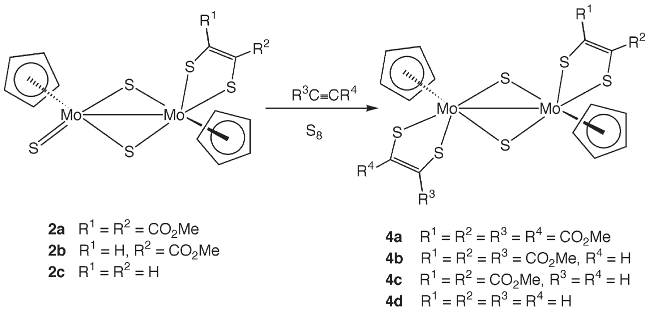


**Figure 1.** Molecular structure of complex **2a** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2(S)(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}Cp_2]$ (**2a**)

| | | | |
|---|---|---|---|
| Mo(1)−S(1) | 2.1464(16) | Mo(1)−S(5) | 2.265(2) |
| Mo(1)−S(4) | 2.2770(18) | Mo(1)−Mo(2) | 2.9948(8) |
| Mo(2)−S(4) | 2.3824(19) | Mo(2)−S(2) | 2.3865(17) |
| Mo(2)−S(3) | 2.3900(17) | Mo(2)−S(5) | 2.4046(17) |
| S(2)−C(11) | 1.744(6) | S(3)−C(12) | 1.729(6) |
| C(11)−C(12) | 1.329(10) | | |
| Mo(1)−S(4)−Mo(2) | 79.96(6) | Mo(1)−S(5)−Mo(2) | 79.73(6) |

**Scheme 2.** Synthesis of the Bis(dithiolene) Complexes **4**



of the treatment of bis(ethanedithiolate) complex $[W_2(\mu\text{-}SCH_2CH_2S)_2Cp_2]$ with acetylene.[19]

The X-ray crystal structure of the unsubstituted complex **2c** was reported in our previous communication;[14] we have also now determined that of **2a**, which is shown in Figure 1, with selected bond lengths and angles collected in Table 1. The Mo−Mo distance is 2.9948(8) Å, and Mo(1) has a pseudotetrahedral coordination (if the Cp ligand is regarded as occupying one site) whereas Mo(2) is in a square-based pyramidal environment; the coordination geometry is thus very similar to that in $[Mo_2O(\mu\text{-}S)_2(SCH{=}CPhS)Cp_2]$.[17] The bond lengths from Mo(1) to the bridging sulfur atoms S(4) and S(5) are significantly shorter than those from Mo(2). In the dithiolene ligand the S(2)−C(11) and S(3)−C(12) bonds [1.744(6) and 1.729(6) Å respectively] and the C(11)−C(12) distance [1.329(10) Å] are comparable to those in $[Cp^*Mo\{S_2C_2(CO_2Me)_2\}_2]$ and $[CpMo(S_2C_2Ph_2)_2]$, for example.[10,20] The central $Mo_2(\mu\text{-}S)_2$ portion of the molecule is not planar; the dihedral angle between the two intersecting $Mo_2S$ planes is 161.0°. The dithiolene ligand is also not planar: there is a fold angle of 16.4° between the SCCS and SMoS planes.[21]

**Bis(dithiolene) Complexes.** Treatment of green **2a** with 1 equiv. of DMAD in tetrahydrofuran (THF) at −78 °C afforded an air sensitive brown solution. Attempts to characterize or crystallize this compound were unsuccessful, but we suggest that it contains a second dithiolene ligand formed by addition of the alkyne to two of the sulfur atoms. Realizing that this requires an internal redox reaction ($2\ S^{2-} \rightarrow {}^{-}SCR{=}CRS^{-}$), we reasoned that oxidation of the intermediate might be necessary to afford a stable complex by reoccupying the second bridging position. This can be done simply by redissolving it in $CH_2Cl_2$ and exposing the solution to air, in which case roughly equal yields of two green bis(dithiolene) complexes $[Mo_2(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}_2Cp_2]$ (**4a**, 40%) and $[Mo_2(\mu\text{-}S)(\mu\text{-}O)\{S_2C_2(CO_2Me)_2\}_2Cp_2]$ (**5**, 32%; see Chart 2) can be isolated by column chromatography, together with several minor products. However a cleaner, more synthetically useful reaction is obtained by dissolution of the brown intermediate in toluene, addition of an excess of sulfur, and heating to reflux for 1 h, affording **4a** as the major product in 80% yield (Scheme 2). Its highly symmetrical structure could be inferred from the presence of just two singlets in an intensity ratio of 10:12 in its $^1H$ NMR spectrum; mass spectral and analytical data also indicated the formula shown. The lower symmetry of **5** caused by the presence of one bridging oxo and one bridging sulfido ligand results in the observation of one Cp resonance but two methyl resonances in the $^1H$ NMR spectrum.

In a similar way, the unsymmetrical complex $[Mo_2(\mu\text{-}S)_2\{SCH{=}C(CO_2Me)S\}\{S_2C_2(CO_2Me)_2\}Cp_2]$ (**4b**) containing two different dithiolene ligands was prepared in 70% yield by addition of methyl propiolate and sulfur to **2a**, or alternatively in 40% yield by treatment of **2b** with DMAD and sulfur. The $^1H$ NMR spectrum of **4b** showed a peak at $\delta$ 9.10, again typical of a proton attached to a terminal dithiolene ligand.

As mentioned above, formation of dithiolene ligands by addition of unactivated alkynes to coordinated sulfur are rather rare. However, treatment of **2a** with acetylene at room temperature also gave a brown solution from which $[Mo_2(\mu\text{-}S)_2(S_2C_2H_2)\{S_2C_2(CO_2Me)_2\}Cp_2]$ **4c** could be isolated in 60% yield after addition of sulfur. The order in which the dithiolene

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(21) The corresponding values for **2c** were as follows: Mo(1)−Mo(2) 2.984(1), S(4)−C(11) 1.708(5), S(5)−C(12) 1.705(4), C(11)−C(12) 1.348(7) Å. The $Mo_2S_2$ fold angle was 161.3°, and the dithiolene fold angle was 20.9°.

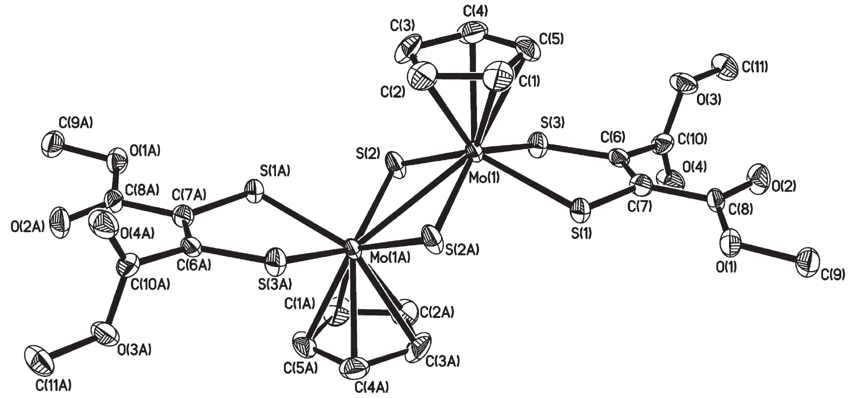

**Figure 2.** Molecular structure of $[Mo_2(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}_2Cp_2].C_7H_8$ **4a** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms and the toluene molecule of crystallization have been omitted for clarity.

ligands are introduced is important in this case as the reaction of the acetylene-derived dithiolene complex **2c** with DMAD and sulfur produced the tris(dithiolene) complex **6c** instead (vide infra). Pleasingly however, addition of acetylene to **2c** in the same way provided a route to the parent compound $[Mo_2(\mu\text{-}S)_2(S_2C_2H_2)_2Cp_2]$ **4d** in 38% yield. Bis(dithiolene) complexes of type **4** are previously unknown for molybdenum, though two examples containing tungsten exist: the tungsten analogue of **4d**, $[W_2(\mu\text{-}S)_2(S_2C_2H_2)_2Cp_2]$ was another low yield product of the treatment of $[W_2(\mu\text{-}SCH_2CH_2S)_2Cp_2]$ with acetylene[19] and $[W_2(\mu\text{-}S)_2(S_2C_2Ph_2)_2Cp^*{}_2]$ was prepared by oxidative dimerization of $[Cp^*W(S)(S_2C_2Ph_2)]^-$.[22]

Compounds of type **4**, like **2**, are formally Mo(V) dimers. As such it seemed possible that oxidation of the corresponding Mo(III) bridging dithiolene complex $[Mo_2\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Cp_2]$[9,16] with elemental sulfur might induce the dithiolene ligands to adopt terminal coordination and thus form a viable alternative route to **4a**. In practice, however, this proved rather disappointing: heating a toluene solution with an excess of sulfur for a week produced only an 11% yield of **4a**. Changing the solvent to xylene, or changing the sulfurizing agent to ethylene sulfide or $P_2S_5$ fared little better; in the latter case, no **4a** was formed and the only identifiable products were monodithiolene complex **2a** and the heterocycle 5-carbomethoxy-1,2-dithiole-3-thione.[23]

Crystals of **4a** and **4d** were both subjected to X-ray diffraction analysis; the resulting structures are shown in Figures 2 and 3 with selected bond lengths and angles listed in Tables 2 and 3. Complex **4d** is isostructural with its tungsten analogue,[19] in that the unit cell contains two independent molecules, one of which is centrosymmetric by virtue of lying on an inversion center, whereas the other is not. In the first case the central $Mo_2(\mu\text{-}S)_2$ portion of the molecule is constrained to be planar, whereas in the second it is slightly puckered; there is an angle of 161.1° between the Mo(1)−Mo(2)−S(1) plane and the Mo(1)−Mo(2)−S(2) plane, virtually the same as in **2c**. Each molybdenum atom is in a square based pyramidal environment, with the Cp ligands occupying a *trans* orientation across the metal−metal bond. The Mo−Mo bond lengths in the two molecules [3.0771(5) and 3.0473(7) Å respectively] are longer than that in **2c**, as are in general the Mo−S and C−S bonds of the dithiolene ligands, though the C=C bonds show little change. As expected the bonds between the molybdenum atoms and the bridging sulfide ligands are intermediate between the two different values in **2c**, reflecting replacement of the terminal sulfido ligand by the second dithiolene. The dithiolene ligands are again not fully planar, with fold angles of 23.4° and 22.3° for the noncentrosymmetric molecule and 18.8° for the centrosymmetric one. The structure of **4a**, which crystallized as a toluene solvate, is purely centrosymmetric and is very similar to the second molecule of **4d**; the degree of dithiolene folding here is 21.1°.

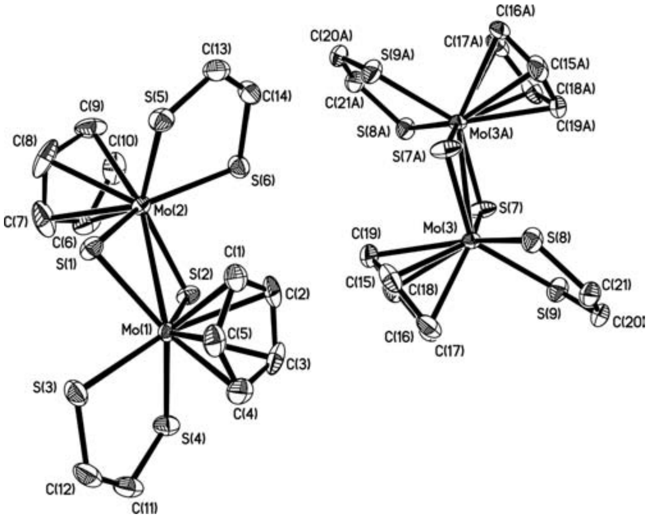

**Figure 3.** Molecular structure of $[Mo_2(\mu\text{-}S)_2(S_2C_2H_2)_2Cp_2]$ **4d** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}_2Cp_2].C_7H_8$ (**4a**)[a]

| | | | |
|---|---|---|---|
| Mo(1)−S(2)#1 | 2.3385(15) | Mo(1)−S(2) | 2.3440(15) |
| Mo(1)−S(1) | 2.4081(14) | Mo(1)−S(3) | 2.4256(14) |
| Mo(1)−Mo(1)#1 | 3.0720(9) | S(1)−C(7) | 1.741(5) |
| S(3)−C(6) | 1.702(6) | C(6)−C(7) | 1.359(8) |
| S(1)−Mo(1)−S(3) | 78.97(5) | Mo(1)#1−S(2)−Mo(1) | 82.00(5) |

[a] Symmetry transformations used to generate equivalent atoms: #1 − $x$, $-y + 1$, $-z + 1$; #2 $-x + 1$, $-y + 2$, $-z + 1$.

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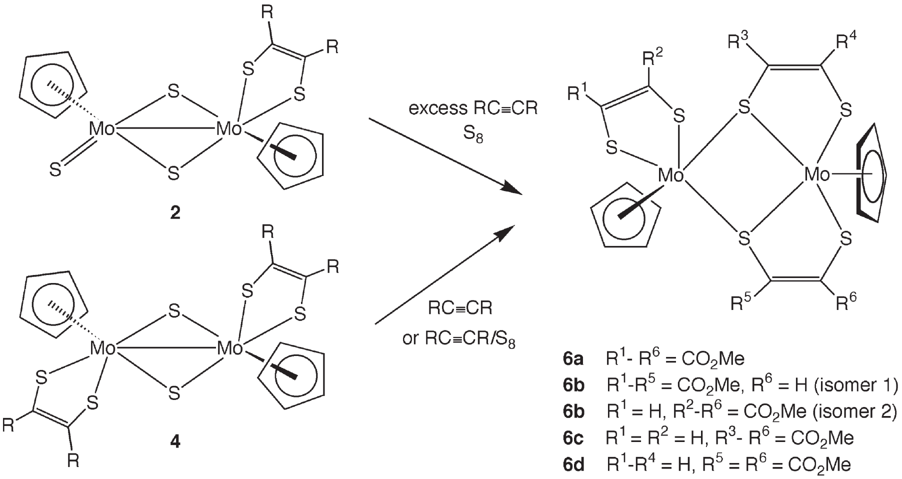
(22) d'Arbeloff, S. E.; Hitchcock, P. B.; Nixon, J. F.; Nagasawa, T.; Kawaguchi, H.; Tatsumi, K. *J. Organomet. Chem.* **1998**, *564*, 189.

(23) Stachel, H. D.; Zoukas, T. *Archiv. der Pharmazie* **1991**, *324*, 131.

**Scheme 3.** Synthesis of the Tris(dithiolene) Complexes **6**



**6a** $R^1$- $R^6 = CO_2Me$
**6b** $R^1$-$R^5 = CO_2Me$, $R^6$ = H (isomer 1)
**6b** $R^1$ = H, $R^2$-$R^6 = CO_2Me$ (isomer 2)
**6c** $R^1 = R^2$ = H, $R^3$- $R^6 = CO_2Me$
**6d** $R^1$-$R^4$ = H, $R^5 = R^6 = CO_2Me$
**6e** $R^1 = R^2$ = H, $R^3 = R^4 = CO_2Et$, $R^5 = R^6 = CO_2Me$

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2(\mu\text{-}S)_2(S_2C_2H_2)_2Cp_2]$ (**4d**)[a]

| | | | |
|---|---|---|---|
| Mo(1)−S(2) | 2.3603(11) | Mo(1)−S(1) | 2.3628(11) |
| Mo(1)−S(4) | 2.3977(11) | Mo(1)−S(3) | 2.4078(11) |
| Mo(1)−Mo(2) | 3.0771(5) | Mo(2)−S(1) | 2.3406(10) |
| Mo(2)−S(2) | 2.3409(11) | Mo(2)−S(5) | 2.4202(11) |
| Mo(2)−S(6) | 2.4347(11) | Mo(3)−S(7) | 2.3424(11) |
| Mo(3)−S(7)#1 | 2.3494(11) | Mo(3)−S(8) | 2.3899(12) |
| Mo(3)−S(9) | 2.4154(12) | Mo(3)−Mo(3)#1 | 3.0473(7) |
| S(3)−C(12) | 1.724(5) | S(4)−C(11) | 1.722(5) |
| S(5)−C(13) | 1.728(5) | S(6)−C(14) | 1.730(5) |
| S(8)−C(21) | 1.714(5) | S(9)−C(20) | 1.722(5) |
| C(11)−C(12) | 1.349(7) | C(13)−C(14) | 1.337(7) |
| C(20)−C(21) | 1.336(7) | | |
| S(4)−Mo(1)−S(3) | 79.54(4) | S(5)−Mo(2)−S(6) | 77.89(4) |
| S(8)−Mo(3)−S(9) | 78.72(4) | Mo(2)−S(1)−Mo(1) | 81.72(3) |
| Mo(2)−S(2)−Mo(1) | 81.77(3) | Mo(3)−S(7)−Mo(3)#1 | 81.01(4) |

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y + 1, -z + 1$.

**Tris(dithiolene) Complexes.** In the synthesis of bis(dithiolene) complex **4a**, a small purple band was noted on the chromatography column. Its identification as the tris(dithiolene) complex $[Mo_2\{S_2C_2(CO_2Me)_2\}_3Cp_2]$ (**6a**) prompted us to investigate the reaction of the bis(dithiolene) complexes with additional alkynes. In fact it transpires that the tris(dithiolene) species can be produced either by reaction of monodithiolene complex **2a** with an excess of DMAD in THF at −78 °C followed by addition of sulfur in refluxing toluene, or by heating **4a** with DMAD. Although no additional sulfur is required by the stoichiometry of the latter reaction, the same outcome is accomplished more rapidly in the presence of both DMAD and sulfur (Scheme 3). This enabled the isolation of **6a** in yields of up to 88%. Its $^1$H NMR spectrum contained two Cp resonances and three peaks due to methyl groups in an overall ratio of 10:18. These data agreed with those in the literature: **6a** is a known compound, having been previously made by Sugiyama et al. by the thermal or photochemical reaction of $[Mo_2(CO)_6Cp_2]$ with DMAD and sulfur,[9] though the existence of a tris(dithiolene) complex of this type was first suggested by King as long ago as 1967 based on the mass spectrum of $[Mo_2(NO)_2\{S_2C_2(CF_3)_2\}_2Cp_2]$.[24] As in the formation of the bis(dithiolene) complexes, an internal redox reaction has occurred with the production of the formally dianionic dithiolene ligand from two $S^{2-}$ ligands, but in this case there is no reoxidation of the metal centers, which remain as Mo(IV).

Since no structural information was reported for **6a**, we performed a crystal structure determination of the methanol solvate. A view of the molecule is shown in Figure 4, with significant bond lengths and angles given in Table 4. As expected, one of the dithiolene ligands occupies a terminal position on Mo(2) whereas the other two adopt what we term the semibridging mode of coordination, in which one sulfur atom bridges between the two metals and the other is bound only to Mo(1). This type of bonding is well established in a number of cases, especially in dimolybdenum chemistry.[9,10,20,24−26] Each molybdenum thus attains a square-based pyramidal Cp-$MoS_4$ coordination sphere. The structure is thus very similar to that of one isomer of the related dicarbonyl $[Mo_2(CO)_2\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Cp_2]$[9] but with the two CO ligands replaced by a third dithiolene. The metal−metal distance in **6a** is 3.573 Å, which precludes any direct Mo−Mo bonding. The Mo(2)−S distances to the sulfur atoms of the terminal dithiolene ligand are rather short (av. 2.341 Å) whereas those to the bridging dithiolene sulfurs are quite long (av. 2.488 Å). The terminal dithiolene ligand, like those in the mono- and bis(dithiolene) complexes, displays a fold angle of 22.4°. The elongation of some of the thermal ellipsoids in the Cp rings of this complex (and of **6d** below) may indicate the presence of a rotational or librational motion in the solid state.

We realized that the stepwise nature of our route to the tris-dithiolene complexes would afford us the versatility to incorporate two or even three different dithiolene ligands into the final product. Although bis- and tris(dithiolene) complexes are common, compounds which

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[24] King, R. B.; Bisnette, M. *Inorg. Chem.* **1967**, *6*, 469.

[25] Adams, H.; Morris, M. J.; Morris, S. A.; Motley, J. C. *J. Organomet. Chem.* **2004**, *689*, 522.

[26] (a) Miki, Y.; Takagi, H.; Ichimura, A.; Akashi, H.; Shibahara, T. *Chem. Lett.* **2002**, 482. (b) Roesselet, K.; Doan, K. E.; Johnson, S. D.; Nicholls, P.; Miessler, G. L.; Kroeker, R.; Wheeler, S. H. *Organometallics* **1987**, *6*, 480.

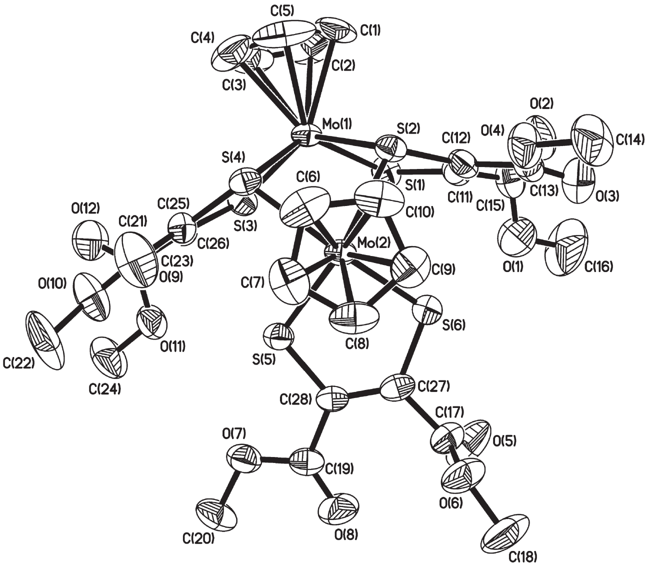

**Figure 4.** Molecular structure of $[Mo_2\{S_2C_2(CO_2Me)_2\}_3Cp_2]\cdot MeOH$ **6a** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms and the methanol of crystallization have been omitted for clarity.

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2\{S_2C_2(CO_2Me)_2\}_3Cp_2]\cdot MeOH$ (**6a**)

| | | | |
|---|---|---|---|
| Mo(1)−S(4) | 2.3808(11) | Mo(1)−S(1) | 2.3840(12) |
| Mo(1)−S(3) | 2.3856(11) | Mo(1)−S(2) | 2.3942(12) |
| Mo(2)−S(5) | 2.3264(11) | Mo(2)−S(6) | 2.3555(12) |
| Mo(2)−S(2) | 2.4861(11) | Mo(2)−S(4) | 2.4900(12) |
| S(1)−C(11) | 1.726(5) | S(2)−C(12) | 1.776(5) |
| S(3)−C(26) | 1.736(5) | S(4)−C(25) | 1.778(5) |
| S(5)−C(28) | 1.728(4) | S(6)−C(27) | 1.727(4) |
| C(11)−C(12) | 1.337(6) | C(25)−C(26) | 1.332(6) |
| C(27)−C(28) | 1.351(6) | | |
| S(4)−Mo(1)−S(3) | 82.26(4) | S(1)−Mo(1)−S(3) | 84.72(4) |
| S(4)−Mo(1)−S(2) | 78.16(4) | S(1)−Mo(1)−S(2) | 81.59(4) |
| S(5)−Mo(2)−S(6) | 81.66(4) | S(6)−Mo(2)−S(2) | 87.51(4) |
| S(5)−Mo(2)−S(4) | 83.38(4) | S(2)−Mo(2)−S(4) | 74.45(4) |
| Mo(1)−S(2)−Mo(2) | 94.12(4) | Mo(1)−S(4)−Mo(2) | 94.35(4) |

contain two or three *different* dithiolene ligands are extremely rare.[27] Hence the reaction of **4a** with methyl propiolate and sulfur was examined, and found to produce two inseparable isomers of $[Mo_2\{SCH{=}C(CO_2Me)S\}\{S_2C_2(CO_2Me)_2\}_2Cp_2]$ **6b**, as shown by the presence of two signals in the $^1H$ NMR spectrum at $\delta$ 9.66 and 9.35 in a 4:1 ratio. The same two isomers were formed in a combined yield of over 90% on the addition of an excess of DMAD and sulfur to $[Mo_2(S)(\mu\text{-}S)_2\{SCH{=}C(CO_2Me)S\}Cp_2]$ (**2b**).

The $^{13}C$ NMR spectrum of this complex deserves some comment. Comparison of the $^1H$-coupled and $^1H$ decoupled spectra allowed the complete assignment of the spectrum, as in the coupled spectrum the ester carbons of the $CO_2Me$ groups appear as quartets, and the two dithiolene carbons of the $SCH{=}C(CO_2Me)S$ ligand appear as doublets with large (175 Hz, CH) and small (6 Hz, $CCO_2Me$) couplings, respectively. This leaves the dithiolene carbons of the DMAD-derived dithiolenes as the only signals which remain as singlets. Eleven signals are expected for the dithiolene ligands of each isomer, but only 21 are observed *in toto* (evidently two of the quartets overlap). In this way we can identify the two doublets for the major isomer at $\delta$ 170.2 (CH) and 137.9 ($CCO_2Me$), and the corresponding doublets at $\delta$ 165.5 (CH) and 156.6 ($CCO_2Me$) for the minor isomer. In the complex $[NiMo(\mu\text{-}S_2C_2Ph_2)_2Cp_2]$, which contains the same semibridging bonding mode, the two dithiolene carbons appear at 170.2 and 135.1 ppm.[20] It is therefore clear that in the major isomer of **6b**, the methyl propiolate occupies a semibridging position, with the SCH terminally bonded and the $SCCO_2Me$ bridging, whereas in the minor isomer it seems likely that this ligand occupies the terminal position, as shown in the structural diagrams. This also agrees with the high chemical shift of the CH protons of both isomers in the $^1H$ NMR spectra.

One limitation of the synthesis however is that the bis(dithiolene) complexes did not react with unactivated alkynes; hence to prepare a tris(dithiolene) complex containing the unsubstituted SCH=CHS ligand, it must be present in the starting material. Reaction of $[Mo_2(S)(\mu\text{-}S)_2(S_2C_2H_2)Cp_2]$ (**2c**) with an excess of DMAD and sulfur duly afforded a moderate yield (28%) of $[Mo_2(S_2C_2H_2)\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Cp_2]$ (**6c**). In this case only one isomer is present, and the observation of only one CH resonance (at $\delta$ 8.54) and two methyl peaks in the $^1H$ NMR spectrum indicates that the $S_2C_2H_2$ ligand occupies the terminal position exclusively. However it was noted that when the same compound was prepared by refluxing the bis(dithiolene) complex **4c** with an excess of DMAD, a small amount of a second isomer was also formed in which the SCH=CHS ligand occupies the semibridging position.

In a similar way, heating symmetrical bis(dithiolene) complex **4d** with DMAD produced a 92% yield of $[Mo_2(S_2C_2H_2)(\mu\text{-}S_2C_2H_2)\{\mu\text{-}S_2C_2(CO_2Me)_2\}Cp_2]$ (**6d**) as a single isomer in which one of the acetylene-derived ligands occupies the terminal position and the other the semibridging location, as shown unambiguously by the presence of four CH peaks and two inequivalent methyls in the $^1H$ NMR spectrum. This was also confirmed by an X-ray structure determination, the result of which is summarized in Figure 5 and Table 5. The structure is very similar to that of **6a**, and it appears that the dithiolene substituents exert little influence over the geometry of the two different semibridging ligands. The fold angle of the terminal dithiolene in this case is 17.0°.

To construct a complex containing three different dithiolenes, we employed three different symmetrical alkynes (to minimize the number of possible isomers). Treatment of bis(dithiolene) complex **4c**, containing one ligand derived from acetylene and one derived from DMAD, with an excess of diethyl acetylenedicarboxylate in refluxing toluene afforded a 72% yield of $[Mo_2(S_2C_2H_2)\{\mu\text{-}S_2C_2(CO_2Me)_2\}\{\mu\text{-}S_2C_2(CO_2Et)_2\}Cp_2]$ (**6e**) as a single isomer in which the acetylene-derived ligand occupies the terminal position. Again comparison of $^1H$-coupled and $^1H$-decoupled spectra was used to assign the $^{13}C$ NMR spectrum unambiguously. It is not yet clear exactly which factors control the preferred position of each type of dithiolene ligand within the tris(dithiolene) complexes, and further experiments are planned to address this question.

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[27] (a) Argyropoulos, D.; Lyris, E.; Mitsopoulou, C.; Katakis, D. *J. Chem. Soc., Dalton Trans.* **1997**, 615. (b) Sugimori, A.; Tachiya, N.; Kajitani, M.; Akiyama, T. *Organometallics* **1996**, *15*, 5664.

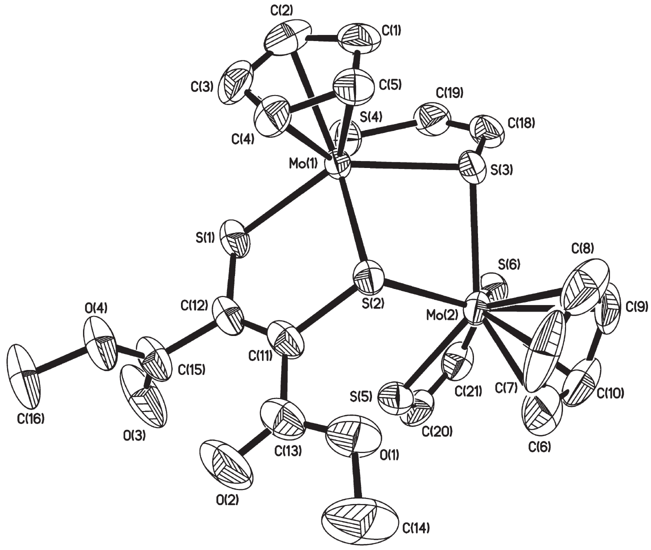

**Figure 5.** Molecular structure of $[Mo_2(S_2C_2H_2)(\mu\text{-}S_2C_2H_2)\{\mu\text{-}S_2C_2(CO_2Me)_2\}Cp_2]$ **6d** in the crystal (ORTEP plot, 50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2(S_2C_2H_2)(\mu\text{-}S_2C_2H_2)\{\mu\text{-}S_2C_2(CO_2Me)_2\}Cp_2]$ (**6d**)

| | | | |
|---|---|---|---|
| Mo(1)−S(4) | 2.3850(13) | Mo(1)−S(1) | 2.3896(11) |
| Mo(1)−S(2) | 2.3970(11) | Mo(1)−S(3) | 2.3990(11) |
| Mo(2)−S(5) | 2.3408(12) | Mo(2)−S(6) | 2.3429(12) |
| Mo(2)−S(2) | 2.4993(11) | Mo(2)−S(3) | 2.5012(12) |
| S(1)−C(12) | 1.728(5) | S(2)−C(11) | 1.769(5) |
| S(3)−C(18) | 1.758(5) | S(4)−C(19) | 1.738(5) |
| S(5)−C(20) | 1.720(5) | S(6)−C(21) | 1.713(5) |
| C(11)−C(12) | 1.346(7) | C(18)−C(19) | 1.317(8) |
| C(20)−C(21) | 1.347(7) | | |
| S(4)−Mo(1)−S(1) | 83.86(4) | S(1)−Mo(1)−S(2) | 82.40(4) |
| S(4)−Mo(1)−S(3) | 82.16(4) | S(2)−Mo(1)−S(3) | 79.01(4) |
| S(5)−Mo(2)−S(6) | 81.62(4) | S(5)−Mo(2)−S(2) | 83.88(4) |
| S(6)−Mo(2)−S(3) | 84.35(4) | S(2)−Mo(2)−S(3) | 75.20(4) |
| Mo(1)−S(2)−Mo(2) | 93.33(4) | Mo(1)−S(3)−Mo(2) | 93.24(4) |

Although good yields of most of the tris(dithiolene) complexes were obtained, there was some evidence that a certain degree of isomerization and alkyne scrambling were occurring during the reactions; hence in some reactions involving DMAD, small amounts of **6a** were isolated in addition to the major products. These side reactions also appeared more prevalent in cases where both alkyne and sulfur were present, and as a result the presence of sulfur, although speeding the reactions up, can lead to lower yields of the complexes containing different dithiolene ligands, such as **6d** and **6e**.

## Conclusions

In conclusion, we have shown that combination of alkynes with sulfur at a dimolybdenum center can lead selectively to good yields of complexes containing one, two, or three dithiolene ligands. In the case of the bis(dithiolene) complexes, the reaction is successful even in cases where neither the added alkyne nor the initial dithiolene ligand contains electron-withdrawing groups. In the case of the tris(dithiolene) complexes the only limitation is that the final stage must involve the addition of an activated alkyne. The versatile nature of the synthesis and the almost complete control over the substituents present will allow fine-tuning of the chemical and electrochemical properties of the complexes, which will be reported separately. Moreover the ready availability of functionalized dithiolene complexes of type **2** derived from 1,3-dithiole-2-thione heterocycles[14] should allow the retention of this functionality in **4** and ultimately **6**. In this way we intend to explore the chemistry of dimolybdenum complexes containing terminal dithiolenes to complement that already extensively developed for their bridging dithiolene counterparts.

## Experimental Section

General experimental techniques were as detailed in previous papers from this laboratory.[16,20] The $^1H$ and $^{13}C$ NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 Fourier transform machine with automated sample-changer or on Bruker AMX400 or DRX-500 spectrometers. Chemical shifts are given on the $\delta$ scale relative to $SiMe_4 = 0.0$ ppm. The $^{13}C\{^1H\}$ NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a Fisons/BG Prospec instrument operating either in electron impact mode (where stated) or fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix; the figures reported are the highest intensity peak of each isotope envelope. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.[28] Unless otherwise specified, light petroleum refers to the fraction boiling in the range 60−80 °C. The complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2]$ were prepared by a slight modification of the literature procedure.[29]

**Synthesis of $[Mo_2(S)(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}Cp_2]$ (2a).** A solution of $[Mo_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4Cp_2]$ (1.5 g, 2.60 mmol) and elemental sulfur (0.42 g, 1.64 mmol of $S_8$, that is, 5.05 equiv of S) in toluene (150 mL) was heated to reflux for 5 h, causing a color change from red to green. After addition of a small amount of silica, the solvent was removed by rotary evaporation and the solid loaded onto a chromatography column. The product was eluted with dichloromethane and triturated with light petroleum to give a dark green solid (1.22 g, 1.95 mmol, 75%). Crystals suitable for X-ray diffraction were grown by vapor diffusion of light petroleum (boiling range 40−60 °C) into a dichloromethane solution; somewhat disconcertingly the crystals appear red under the microscope.

**2a**: Mp > 250 °C. $^1H$ NMR: $\delta$ 6.00 (s, 5H, Cp), 5.50 (s, 5H, Cp), 3.87 (s, 6H, Me); $^{13}C$ NMR: $\delta$ 165.1 ($CO_2Me$), 154.7 ($CCO_2Me$), 103.8 (Cp), 100.9 (Cp), 53.0 (Me). Found: C, 31.00; H, 2.42; S, 25.60. Anal. Calcd for $C_{16}H_{16}Mo_2O_4S_5$: C, 30.77; H, 2.58; S, 25.67%. MS (EI): *m*/*z* 624 ($M^+$), 592 ($M-S^+$), 482, 450, 418, 386, 353, 323 ($Mo_2S_{5-n}Cp_2^+$, $n = 0-5$).

In some syntheses, low yields of a second green complex were obtained which was characterized as the corresponding oxo complex **3a**: Mp 270−274 °C. $^1H$ NMR: $\delta$ 6.22 (s, 5H, Cp), 5.85 (s, 5H, Cp), 3.90 (s, 6H, Me). $^{13}C$ NMR: $\delta$ 164.8 ($CO_2Me$), 154.9 ($CCO_2Me$), 105.6 (Cp), 100.8 (Cp), 52.6 (Me). Found: C, 31.64; H, 2.55; S, 21.18. Anal. Calcd for $C_{16}H_{16}Mo_2O_5S_4$: C, 31.59; H, 2.65; S, 21.08%. MS (EI): *m*/*z* 609 ($M+H^+$), 577 ($M+H-S^+$).

**Synthesis of $[Mo_2(S)(\mu\text{-}S)_2\{SCH{=}C(CO_2Me)S\}Cp_2]$ (2b).** In a similar manner to above, $[Mo_2(\mu\text{-}HC{\equiv}CCO_2Me)(CO)_4Cp_2]$

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[28] For the monodithiolene complexes, erratic analytical data, particularly for the determination of sulfur, were obtained in some cases, which we attribute to incomplete combustion and formation of side products such as molybdenum sulfide or carbide.

[29] (a) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (b) Adams, H.; Gill, L. J.; Morris, M. J. *Organometallics* **1996**, *15*, 4182.

(1.00 g, 1.93 mmol) and $S_8$ (316 mg, 1.23 mmol of $S_8$) reacted to give green **2b** (719 mg, 1.27 mmol, 66%).

**2b**: Mp > 250 °C. $^1$H NMR: $\delta$ 9.41 (s, 1H, CH), 6.00 (s, 5H, Cp), 5.45 (s, 5H, Cp), 3.90 (s, 3H, Me). $^{13}$C NMR: $\delta$ 162.9 ($CO_2Me$), 161.1 (CH), 148.7 ($CCO_2Me$), 103.7 (Cp), 100.6 (Cp), 52.5 (Me). Found: C, 30.11; H, 2.55; S, 26.79. Anal. Calcd for $C_{14}H_{14}Mo_2O_2S_5$: C, 29.68; H, 2.49; S, 28.30%. MS (EI) *m*/*z* 566 ($M^+$), 534 ($M-S^+$), 482, 450, 418, 386, 353, 322 ($Mo_2S_{5-n}Cp_2^+$, $n = 0-5$).

**Synthesis of [$Mo_2(S)(\mu$-$S)_2(S_2C_2H_2)Cp_2$] (2c).** Complex **2c** was prepared in a similar manner from [$Mo_2(\mu$-$C_2H_2)(CO)_4Cp_2$] (100 mg, 0.22 mmol) and sulfur (27 mg, 0.11 mmol of $S_8$). The product was eluted from the column as a dark green band with a 1:1 mixture of $CH_2Cl_2$ and light petroleum (69 mg, 0.14 mmol, 64%). On some occasions further elution with a 3:2 mixture of the same solvents produced an additional green band, tentatively identified as [$Mo_2(O)(\mu$-$S)_2(S_2C_2H_2)Cp_2$] (**3c**) [$^1$H NMR: $\delta$ 8.45 (s, 2H, CH), 6.20 (s, 5H, Cp), 5.20 (s, 5H, Cp). $^{13}$C NMR: $\delta$ 150.0 (CH), 105.7 (Cp), 100.3 Cp)]. MS (EI) *m*/*z* 492 ($M^+$)].

**2c**: Mp 196−198 °C. $^1$H NMR: $\delta$ 8.37 (s, 2H, CH), 6.00 (s, 5H, Cp), 5.38 (s, 5H, Cp). $^{13}$C NMR: $\delta$ 149.5 (CH), 103.7 (Cp), 100.1 (Cp). Found: C, 28.11; H, 2.27; S, 31.56. Anal. Calcd for $C_{12}H_{12}Mo_2S_5$: C, 28.35; H, 2.36; S, 31.50%. MS (EI): *m*/*z* 508 ($M^+$), 482 ($M - C_2H_2^+$), 482, 450, 418, 386, 353, 323 ($Mo_2S_{5-n}Cp_2^+$, $n = 0-5$).

**Synthesis of [$Mo_2(\mu$-$S)_2\{S_2C_2(CO_2Me)_2\}_2Cp_2$] (4a). Method 1 (Air Oxidation).** A solution of complex **2a** (424 mg, 0.679 mmol) in THF (30 mL) was cooled to −78 °C and treated with 1 equiv of DMAD (0.083 mL). The solution was allowed to warm to room temperature, and the solvent was removed *in vacuo*. The brown residue was redissolved in $CH_2Cl_2$ (30 mL) and stirred in air for 4 h, causing a color change to green. The solvent was removed and the products separated by column chromatography. After the elution of several minor products, elution with a 97:3 mixture of dichloromethane and acetone successfully separated [$Mo_2(\mu$-$S)_2\{S_2C_2(CO_2Me)_2\}_2Cp_2$] (**4a**; 215 mg, 0.269 mmol, 40%) and [$Mo_2(\mu$-$O)(\mu$-$S)\{S_2C_2(CO_2Me)_2\}_2Cp_2$] (**5a**; 172 mg, 0.219 mmol, 32%). Data for **5a**: $^1$H NMR: $\delta$ 6.33 (s, 10 H, Cp), 3.75, 3.67 (both s, 6 H, Me). Found: C, 33.41; H, 2.92; S, 20.33. Anal. Calcd for $C_{22}H_{22}Mo_2O_9S_5$: C, 33.76; H, 2.83; S, 20.48%.

**Method 2 (Sulfur Oxidation).** A solution of complex **2a** (389 mg, 0.623 mmol) in THF (30 mL) was cooled to −78 °C and treated with 1 equiv of DMAD (0.077 mL). The solution was allowed to warm to room temperature, and the solvent was removed *in vacuo*. The brown residue was dissolved in toluene (30 mL), and an excess of sulfur (0.5 g) was added. The solution was then heated to reflux for 1 h. Column chromatography as above produced a small band due to unchanged **2a** followed by a large green zone of **4a** (399 mg, 0.492 mmol, 80%). Crystals suitable for X-ray diffraction were grown by diffusion of light petroleum into a toluene solution.

**4a**: Mp 264−268 °C. $^1$H NMR: $\delta$ 5.58 (s, 10 H, Cp); 3.88 (s, 12H, Me). $^{13}$C NMR: $\delta$ 164.7 ($CO_2Me$), 150.3 ($CCO_2Me$), 104.7 (Cp), 53.0 (Me). Found: C, 33.00; H, 2.84; S, 24.05. Anal. Calcd for $C_{22}H_{22}Mo_2O_8S_6$: C, 33.09; H, 2.78; S, 24.09%. MS: *m*/*z* 798 ($M^+$).

**Synthesis of [$Mo_2(\mu$-$S)_2\{SCH{=}C(CO_2Me)S\}\{S_2C_2(CO_2Me)_2\}Cp_2$] (4b). Method 1 (from Complex 2a with Air Oxidation).** In the same manner as above, reaction of **2a** (528 mg, 0.846 mmol) with 1 equiv of methyl propiolate (0.071 mL) followed by oxidation in air gave a green solution from which complex **4b** (185 mg, 0.25 mmol, 29.5%) and a second green band tentatively identified as the oxo complex [$Mo_2(\mu$-$O)(\mu$-$S)\{SCH{=}C(CO_2Me)S\}\{S_2C_2(CO_2Me)_2\}Cp_2$] (**5b**; 21 mg, 0.03 mmol, 3.5%) [$^1$H NMR: $\delta$ 8.26 (s, 1H, CH), 6.28 (s, 5H, Cp), 6.27 (s, 5H, Cp), 3.76, 3.72, 3.70 (all s, 3H, Me)] were isolated by column chromatography. The yields of pure products are low because of the difficulty in separating these two complexes.

**Method 2 (from Complex 2a with Sulfur Oxidation).** In a similar manner to the above, a THF solution of **2a** (501 mg, 0.802 mmol) was treated with 1 equiv of methyl propiolate (0.07 mL) at −78 °C; the solution was then warmed to room temperature, evaporated to dryness, and dissolved in toluene. After addition of an excess of sulfur (0.6 g) the solution was heated to reflux for 1 h, producing a green solution. The solution was evaporated to dryness and absorbed onto silica. Subsequent chromatography, eluting with a 99:1 mixture of $CH_2Cl_2$ and acetone, afforded a green band of **4b** (416 mg, 0.561 mmol, 70%).

**Method 3 (from Complex 2b).** A solution of [$Mo_2(S)(\mu$-$S)_2\{SCH{=}C(CO_2Me)S\}Cp_2$] (222 mg, 0.392 mmol) in THF (30 mL) was treated with 1 equiv of DMAD (0.048 mL) at −78 °C. As above the solution was warmed to room temperature, evaporated, then redissolved in toluene. Sulfur (0.25 g) was added, and the solution heating to reflux for 1 h. Column chromatography as above produced several minor bands followed by a large green zone due to **4b** (116 mg, 0.156 mmol, 40%).

**4b**: Mp 242−246 °C. $^1$H NMR: $\delta$ 9.10 (s, 1H, CH), 5.57 (s, 5H, Cp), 5.52 (s, 5H, Cp), 3.84 (s, 6H, 2Me), 3.83 (s, 3H, Me). $^{13}$C NMR: $\delta$ 165.0, 164.8, 162.7 ($CO_2Me$), 157.6 (CH), 150.0, 149.6, 144.6 ($CCO_2Me$), 104.9, 104.1 (Cp), 53.0 (2Me), 52.6 (Me). Found: C, 31.74; H, 2.78; S, 24.04. Anal. Calcd for $C_{20}H_{20}Mo_2O_6S_6$: C, 32.44; H, 2.72; S, 25.97%. MS *m*/*z* 740 ($M^+$).

**Synthesis of [$Mo_2(\mu$-$S)_2(S_2C_2H_2)\{S_2C_2(CO_2Me)_2\}Cp_2$] 4c.** Acetylene gas was bubbled through a solution of complex **2a** (205 mg, 0.328 mmol) in THF (30 mL) at room temperature for 5 min. The vessel was sealed and stirred for a further 5 min, producing a brown solution. The solvent was removed, and the residue dissolved in toluene. Addition of sulfur (0.5 g) and refluxing for 1 h caused the solution to turn green. The solvent was removed, and the residue chromatographed as above. After the elution of several minor products, the major product **4c** was eluted with a 99:1 mixture of $CH_2Cl_2$ and acetone as a green band (135 mg, 0.198 mmol, 60%).

**4c**: Mp: 228−230 °C. $^1$H NMR: $\delta$ 8.20 (s, 2H, CH), 5.60 (s, 5H, Cp), 5.43 (s, 5H, Cp), 3.88 (s, 6H, Me). $^{13}$C NMR: $\delta$ 165.2 ($CO_2Me$), 148.6 ($CCO_2Me$), 146.8 (CH), 102.7 (Cp), 105.3 (Cp), 52.9 (Me). Found: C, 31.79; H, 2.42; S, 28.20. Anal. Calcd for $C_{18}H_{18}Mo_2O_4S_6$: C, 31.67; H, 2.66; S, 28.18%. MS *m*/*z* 682 ($M^+$).

**Synthesis of [$Mo_2(\mu$-$S)_2(S_2C_2H_2)_2Cp_2$] 4d.** Acetylene gas was bubbled through a solution of complex **2c** (262 mg, 0.515 mmol) in THF (30 mL) at room temperature. After 5 min the vessel was sealed and stirred for a further 5 min. The solvent was removed from the brown solution, and toluene (30 mL) and sulfur (0.5 g) were added. The solution was heated to reflux for 1 h. The green solution was then absorbed onto silica and chromatographed. Elution with a 3:1 mixture of light petroleum and $CH_2Cl_2$ produced a green band of **4d** (235 mg, 0.414 mmol, 80%).

When the reaction was carried out with aerobic oxidation, a 25% yield of **4d** was obtained, together with the monodithiolene oxo complex **3c** and the bis(dithiolene) oxo complex [$Mo_2(\mu$-$O)(\mu$-$S)(S_2C_2H_2)_2Cp_2$] (**5d**) [$^1$H NMR: $\delta$ 8.12 (d, 2H, $J$ = 6 Hz, CH), 7.86 (d, 2H, $J$ = 6 Hz, CH), 5.45 (s, 10H, Cp)].

**4d**: Mp 210−214 °C. $^1$H NMR: $\delta$ 7.93 (s, 4H, CH), 5.43 (s, 10H, Cp). $^{13}$C NMR: $\delta$ 144.7 (CH), 103.5 (Cp). Found C, 29.67; H, 2.37; S, 33.90. Anal. Calcd for $C_{14}H_{14}Mo_2S_6$: C, 29.68; H, 2.49; S, 33.96%. MS *m*/*z* 506 ($M^+$).

**Synthesis of [$Mo_2\{S_2C_2(CO_2Me)_2\}_3Cp_2$] (6a). Method 1 (from Complex 2a).** A solution of [$Mo_2S(\mu$-$S)_2\{S_2C_2(CO_2Me)_2\}Cp_2$] (**2a**) (209 mg, 0.335 mmol) in THF (30 mL) was cooled to −78 °C and treated with 3 equiv of DMAD (0.123 mL). The solution was allowed to warm to room temperature and evaporated to dryness. The brown residue was

**Table 6.** Summary of Crystallographic Data for Complexes **2a**, **4a**·$C_7H_8$, **4d**, **6a**·MeOH and **6d**

| | **2a** | **4a**·$C_7H_8$ | **4d** | **6a**·MeOH | **6d** |
|---|---|---|---|---|---|
| empirical formula | $C_{16}H_{16}Mo_2O_4S_5$ | $C_{30}H_{32}Mo_2O_8S_6$ | $C_{14}H_{14}Mo_2S_6$ | $C_{29}H_{32}Mo_2O_{13}S_6$ | $C_{20}H_{20}Mo_2O_4S_6$ |
| formula weight | 624.47 | 904.80 | 566.49 | 972.79 | 708.60 |
| $T$/K | 150(2) | 150(2) | 150(2) | 150(2) | 293(2) |
| crystal system | monoclinic | triclinic | monoclinic | monoclinic | triclinic |
| space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ |
| $a$/Å | 7.0717(12) | 7.3455(13) | 7.9933(9) | 13.8568(11) | 10.6901(9) |
| $b$/Å | 25.671(4) | 9.2760(17) | 23.340(3) | 12.6101(10) | 10.7485(9) |
| $c$/Å | 11.4625(18) | 12.838(2) | 14.4095(17) | 21.3874(18) | 11.1600(9) |
| α/deg | 90 | 75.422(4) | 90 | 90 | 96.789(2) |
| $\beta$/deg | 94.323(9) | 76.800(7) | 100.233(2) | 97.201(2) | 98.747(2) |
| $\gamma$/deg | 90 | 79.007(4) | 90 | 90 | 90.567(2) |
| $V$/Å$^3$ | 2075.0(6) | 816.0(3) | 2645.6(5) | 3707.7(5) | 1258.00(18) |
| $Z$ | 4 | 1 | 6 | 4 | 2 |
| density (calcd)/Mgm$^{-3}$ | 1.999 | 1.841 | 2.133 | 1.743 | 1.871 |
| $\mu$/mm$^{-1}$ | 1.732 | 1.203 | 2.123 | 1.075 | 1.521 |
| $F$(000) | 1232 | 456 | 1668 | 1960 | 704 |
| crystal size/mm$^3$ | 0.21 × 0.18 × 0.02 | 0.25 × 0.12 × 0.04 | 0.28 × 0.16 × 0.16 | 0.32 × 0.21 × 0.18 | 0.21 × 0.21 × 0.18 |
| $\theta$ range for data collection/deg | 2.97 to 27.68 | 2.29 to 28.33 | 2.26 to 28.28 | 1.66 to 28.31 | 1.91 to 28.33 |
| reflections collected | 17699 | 5001 | 15849 | 23078 | 7893 |
| independent reflections | 4855 [$R$(int) = 0.0739] | 3667 [$R$(int) = 0.0841] | 6365 [$R$(int) = 0.0729] | 8950 [$R$(int) = 0.0761] | 5661 [$R$(int) = 0.0568] |
| data/restraints/parameters | 4673/0/246 | 3667/3/188 | 6365/0/298 | 8950/0/451 | 5661/0/289 |
| Goodness-of-fit on F$^2$ | 1.018 | 1.090 | 1.041 | 0.912 | 1.159 |
| final R1, wR2 [$I > 2\sigma(I)$] | R1 = 0.0468, wR2 = 0.1140 | R1 = 0.0550, wR2 = 0.1680 | R1 = 0.0434, wR2 = 0.1006 | R1 = 0.0462, wR2 = 0.1113 | R1 = 0.0407, wR2 = 0.1264 |
| (all data) | R1 = 0.0726, wR2 = 0.1431 | R1 = 0.0760, wR2 = 0.2066 | R1 = 0.0548, wR2 = 0.1060 | R1 = 0.0778, wR2 = 0.1330 | R1 = 0.0551, wR2 = 0.1575 |
| largest diff. peak and hole/ e Å$^{-3}$ | 0.932 and −1.297 | 1.962 and −1.373 | 1.411 and −1.870 | 0.857 and −0.850 | 1.187 and −1.111 |

dissolved in toluene (30 mL), an excess of sulfur was added (0.4 g), and then the solution was refluxed for 1 h. Separation by column chromatography gave a purple band of **6a** (202 mg, 0.214 mmol, 64%) which was eluted with a 24:1 mixture of $CH_2Cl_2$ and acetone.

**Method 2 (from Complex 4a with DMAD).** A solution of $[Mo_2(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}_2Cp_2]$ (**4a**) (107 mg, 0.134 mmol) and 2 equiv of DMAD (0.032 mL) in toluene (30 mL) was heated to reflux for 2 h. The solvent was removed, and the residue chromatographed as above to yield 111 mg (0.117 mmol, 88%) of **6a**.

**Method 3 (from Complex 4a with DMAD and Sulfur).** A solution of complex **4a** (199 mg, 0.249 mmol), sulfur (0.25 g), and 2 equiv of DMAD (0.06 mL) in toluene (30 mL) was heated to reflux for 1 h. Purification as above gave 207 mg (0.220 mmol, 88%) of **6a**.

The spectroscopic data of **6a** matched those given in the literature.[9] Recrystallization from methanol and diethyl ether gave black blocks suitable for X-ray diffraction.

**Synthesis of $[Mo_2\{SCH{=}C(CO_2Me)S\}\{S_2C_2(CO_2Me)_2\}_2Cp_2]$ 6b. Method 1 (from Complex 4a).** A toluene (30 mL) solution of $[Mo_2(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}_2Cp_2]$ **4a** (200 mg, 0.250 mmol), sulfur (0.25 g), and 2 equiv of methyl propiolate (0.045 mL) was heated to reflux for 1 h. The purple solution was evaporated to dryness, and the products separated by chromatography. Elution with a 24:1 mixture of $CH_2Cl_2$ and acetone gave the two isomers of **6b** as a purple band (203 mg, 0.230 mmol, 92%). The isomer ratio in the product is 4:1 by this method.

**Method 2 (from Complex 2b).** Two equivalents of DMAD (0.035 mL) and an excess of sulfur (0.25 g) were added to a solution of $[Mo_2S(\mu\text{-}S)_2\{SCH{=}C(CO_2Me)S\}Cp_2]$ **2b** (99 mg, 0.134 mmol) in toluene (30 mL), which was then refluxed for 1 h. Chromatography as above gave **6b** (116 mg, 0.131 mmol, 98%). The isomer ratio is 5:3 by this route.

**6b**: Mp 208−212 °C. $^1$H NMR (major isomer): $\delta$ 9.66 (s, 1H, CH), 5.18 (s, 5H, Cp), 4.90 (s, 5H, Cp), 3.99, 3.98, 3.88, 3.77. 3.76 (all s, 3H, Me). $^1$H NMR (minor isomer): $\delta$ 9.35 (s, 1H, CH), 5.07 (s, 5H, Cp), 4.95 (s, 5H, Cp), 3.99 (s, 6H, Me), 3.90, 3.89, 3.76 (all 3H, Me). $^{13}$C NMR: $\delta$ 173.8, 173.4, 173.2 (all $CCO_2Me$), 170.2 (CH of major isomer), 169.0 (2 $CO_2Me$), 169.0, 168.8, 165.6 (all $CO_2Me$), 165.5 (CH of minor isomer) 165.3, 163.8, 162.9, 162.8, 162.1 (all $CO_2Me$), 160.7, 160.6 (both $CCO_2Me$), 156.6 ($CCO_2Me$ of $SCH{=}C(CO_2Me)S$ ligand in minor isomer), 137.9 ($CCO_2Me$ of $SCH{=}C(CO_2Me)S$ ligand in major isomer), 136.9, 136.2, 136.1 (all $CCO_2Me$), 95.7 (Cp, major), 95.6, 95.3 (both Cp, minor), 95.1 (Cp, major), 53.2, 53.1, 53.0, 52.8, 52.7, 52.3 (all Me). Found: C, 35.08; H, 2.90; S, 21.59. Anal. Calcd for $C_{26}H_{26}Mo_2O_{10}S_6$: C, 35.38; H, 2.97; S, 21.79%. MS $m/z$ 882 (M$^+$).

**Synthesis of $[Mo_2(S_2C_2H_2)\{\mu\text{-}S_2C_2(CO_2Me)_2\}_2Cp_2]$ (6c). Method 1 (from Complex 2c).** Three equivalents of DMAD (0.200 mL) were added to a solution of $[Mo_2S(\mu\text{-}S)_2(S_2C_2H_2)Cp_2]$ (**2c**; 270 mg, 0.531 mmol) in THF (30 mL) at −78 °C. After warming to room temperature the solvent was removed. The brown residue was dissolved in toluene (30 mL) and treated with sulfur (0.4 g), then heated to reflux for 1 h. The purple solution was evaporated to dryness and chromatographed. Elution with a 49:1 mixture of $CH_2Cl_2$ and acetone gave a purple band of **6c** (121 mg, 0.147 mmol, 28%).

**Method 2 (from Complex 4c).** Two equivalents of DMAD (0.04 mL) were added to a solution of $[Mo_2(\mu\text{-}S)_2(S_2C_2H_2)\{S_2C_2(CO_2Me)_2\}Cp_2]$ (**4c**; 101 mg, 0.148 mmol) in toluene (30 mL), and the solution was refluxed for 1 h. Column chromatography as above gave 64 mg (0.077 mmol, 52%) of **6c**. Further elution with a 24:1 mixture of $CH_2Cl_2$ and acetone gave a second purple band (18 mg, 0.0221 mmol, 14%) which consisted of an isomer of **6c** [$^1$H NMR: $\delta$ 8.82 (d, $J$ = 5 Hz, 1H, CH), 8.00 (d, $J$ = 5 Hz, 1H, CH), 5.10 (s, 5H, Cp), 4.85 (s, 5H, Cp), 3.95 (s, 3H, Me), 3.86 (s, 3H, Me), 3.77 (s, 6H, 2Me)]. When carried out in the presence of an excess of sulfur, the yield of **6c** was 53%, and several additional minor products were observed including a small amount of **6a**.

**6c**: Mp 272−274 °C. $^1$H NMR: $\delta$ 8.54 (s, 2H, CH), 4.98, 4.92 (both s, 5H, Cp), 3.98, 3.90 (both s, 6H, Me). $^{13}$C NMR: $\delta$ 173.2 ($CCO_2Me$), 169.1 ($CO_2Me$), 163.2 ($CO_2Me$), 156.1 (CH), 137.2 ($CCO_2Me$), 95.6, 94.7 (Cp), 53.2, 53.1 (Me). Found: C, 35.05; H, 2.89; S, 23.57. Anal. Calcd for $C_{24}H_{24}Mo_2O_8S_6$: C, 34.95; H, 2.93; S, 23.33%. MS $m/z$ 824 (M$^+$).

**Synthesis of [$Mo_2(S_2C_2H_2)(\mu$-$S_2C_2H_2)\{\mu$-$S_2C_2(CO_2Me)_2\}$-$Cp_2$] (6d).** A solution of [$Mo_2(\mu$-$S)_2(S_2C_2H_2)_2Cp_2$] (**4d**; 109 mg, 0.192 mmol) in toluene (30 mL) was treated with 2 equiv of DMAD (0.05 mL) and heated to reflux for 1 h. The purple solution was evaporated and purified by chromatography, eluting with a 49:1 mixture of $CH_2Cl_2$ and acetone, to give 126 mg (0.178 mmol, 92%) of **6d**. When the same reaction was carried out in the presence of an excess of sulfur the yield of **6d** dropped to 29% and several additional byproduct, including **2c** and **6c**, were also observed.

**6d**: Mp 232−234 °C. $^1$H NMR: $\delta$ 8.72, 8.49, 8.35, 7.83 (all d, $J$ = 5 Hz, 1H, CH), 4.92, 4.82 (s, 5 H, Cp), 3.97, 3.90 (s, 3 H, Me). $^{13}$C NMR: $\delta$ 174.0 ($CCO_2Me$), 169.6 ($CO_2Me$), 163.5 ($CO_2Me$), 156.4, 155.2, 154.4, 137.6 (all CH), 133.2 ($CCO_2Me$), 94.6, 94.3 (Cp), 53.1, 52.8 (Me). Found: C, 34.08; H, 2.86; S, 26.84. Anal. Calcd for $C_{20}H_{20}Mo_2O_4S_6$: C, 33.90; H, 2.84; S, 27.15%. MS *m*/*z* 708 ($M^+$).

**Synthesis of [$Mo_2(S_2C_2H_2)\{\mu$-$S_2C_2(CO_2Me)_2\}\{\mu$-$S_2C_2(CO_2Et)_2\}Cp_2$] (6e).** A solution of [$Mo_2(\mu$-$S)_2(S_2C_2H_2)\{S_2C_2(CO_2Me)_2Cp_2$] (**4c**; 204 mg, 0.299 mmol) and 2 equiv of diethyl acetylenedicarboxylate (0.100 mL) in toluene (50 mL) was heated to reflux for 2 h. The solvent was removed, and the residue chromatographed. Elution with a 24:1 mixture of $CH_2Cl_2$ and acetone gave a purple band containing **6e** (184 mg, 0.215 mmol, 72%). When the same reaction was conducted in the presence of an excess of sulfur, the yield of **6e** was 63%.

**6e**: Mp 249−251 °C. $^1$H NMR: $\delta$ 8.52 (s, 2 H, CH), 5.02, 4.92 (s, 5H, Cp), 3.99, 3.89 (s, 3H, $CO_2Me$), 3.45, 3.36 (q, $J$ = 7 Hz, 2H, $CH_2$), 1.45, 1.35 (t, $J$ = 7 Hz, 3H, Me of $CO_2Et$). $^{13}$C NMR: $\delta$ 173.2, 173.2, ($CCO_2R$), 169.2 ($CO_2Me$), 168.7 ($CO_2Et$), 163.2 ($CO_2Me$), 162.7 ($CO_2Et$), 156.0, 155.9 (CH), 137.5, 136.8 ($CCO_2R$), 95.5, 94.6 (Cp), 62.2, 62.0 ($CH_2$), 53.1, 53.0 (Me of $CO_2Me$), 14.3, 14.2 (Me of $CO_2Et$). Found: C, 36.56; H, 3.34; S, 22.51. Anal. Calcd for $C_{26}H_{28}Mo_2O_8S_6$: C, 36.62; H, 3.31; S, 22.56%. MS *m*/*z* 851 ($M^+$).

**Crystal Structure Determinations.** The crystal data for the five structures are collected in Table 6. General procedures were as described in previous publications. A Bruker Smart CCD area detector with Oxford Cryosystems low temperature system was used for data collection at 150(2) K. Complex scattering factors were taken from the program package SHELXTL[30] as implemented on a Viglen Pentium computer. Hydrogen atoms were placed geometrically and refined in riding mode (including torsional freedom for methyl groups) with $U_{iso}$ constrained to be 1.2 times $U_{eq}$ of the carrier atom (1.5 for methyl groups).

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**Supporting Information Available:** Crystallographic information files for the five structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data* (*Revision 5.1*); Bruker AXS Ltd.: Madison, WI, 1997.