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# Synthesis and Structural Characterization of Molybdenum Dimers Bridged by the Dithiolene Ligand $S_2C_2(CF_3)_2$

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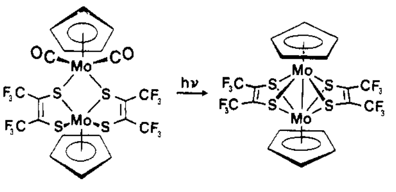
The complex $[CpMo(CO)_3]_2$ ($Cp = C_5H_5$) reacts with $S_2C_2(CF_3)_2$ in refluxing methylcyclohexane solution to give $Cp(CO)_2Mo[\mu\text{-}S_2C_2(CF_3)_2]_2MoCp$ (1). Complex 1 loses its CO ligands on photolysis in solution to give $[CpMo(\mu\text{-}S_2C_2(CF_3)_2)]_2$ (2). Complexes 1 and 2 were characterized by $^1H$ and $^{19}F$ NMR spectroscopy, elemental analysis, mass spectrometry, and X-ray diffraction techniques. Electrochemical properties of both compounds were also studied. Crystals of 1 are monoclinic of space group $P2_1/m$ with $a = 7.153$ (1) Å, $b = 13.404$ (9) Å, $c = 13.690$ (4) Å, $\beta = 98.54$ (2)°, and $Z = 2$. The structure was solved and refined to $R = 0.043$ and $R_w = 0.053$ by using 1895 independent reflections. The complex contains two asymmetrically bridging $S_2C_2(CF_3)_2$ ligands, and both CO ligands are attached to the same Mo atom. The Mo–Mo distance of 3.256 (1) Å suggests minimal Mo–Mo bonding. Crystals of 2 are monoclinic of space group $P2_1/a$ with $a = 13.030$ (1) Å, $b = 17.336$ (2) Å, $c = 10.741$ (7) Å, $\beta = 93.29$ (4)°, and $Z = 4$. The structure was solved and refined to $R = 0.044$ and $R_w = 0.057$ by using 2848 independent reflections. Complex 2 contains two symmetrically bridging $S_2C_2(CF_3)_2$ ligands and has an Mo–Mo bond of 2.584 (1) Å.

## Introduction

Recently there has been growing interest in the chemistry of dimeric molybdenum complexes with dithio chelating ligands. Examples of reactions of these complexes that have been reported include the replacement of hydrocarbon linkages in substituted 1,2-alkanedithiolate bridging ligands by unsaturated groups;[2,3] hydrogenation of bridging sulfido ligands to form hydrosulfido bridges;[4] reactions of bridging sulfido ligands with carbon disulfide and hydrogen to form thioformaldehyde bridges;[5] and reactions of complexes containing bridging 1,1-dithiolate ligands with nucleophiles and electrophiles.[6] A dimolybdenum complex bridged by an $S_2CH_2$ ligand has recently been reported to serve as a homogeneous catalyst for reduction of a variety of nitrogen-containing substrates at mild temperatures and pressures.[7] Since dimolybdenum complexes bridged by dithiolene ligands exhibit intense charge-transfer spectra,[8] we have begun to study the photochemistry of these compounds, with the hope of gaining a better understanding of the bonding in such compounds and of the types of reactions which they may be able to undergo.

In this connection, we have been investigating photochemical reactions of molybdenum complexes containing the dithiolene ligand $S_2C_2(CF_3)_2$ [1,2-bis(trifluoromethyl)ethenedithiolate]. Complexes of this ligand with molybdenum have proven more thermally stable and, hence, easier to work with, than analogous complexes of other dithiolene ligands; the $S_2C_2(CF_3)_2$ is also conveniently detected by $^{19}F$ NMR. In the course of these studies we have isolated and characterized two complexes, $Cp(CO)_2Mo[\mu\text{-}S_2C_2(CF_3)_2]_2MoCp$ (1) and $[CpMo(\mu\text{-}S_2C_2(CF_3)_2)]_2$ (2). Complex 1 readily photolyzes to yield 2 in tetrahydrofuran solution. We have also obtained X-ray crystal structures of both 1 and 2.



1 2

Complexes of molybdenum with the $S_2C_2(CF_3)_2$ ligand have been known since the early 1960s.[9,10] In 1963 King reported that $[CpMo(CO)_3]_2$ reacted with $S_2C_2(CF_3)_2$ in methylcyclohexane solution to give a purple-brown compound identified as $[CpMo(S_2C_2(CF_3)_2)]_2$.[11] We have repeated this procedure and have found the reaction to be more complex. The major product after reflux in methylcyclohexane is the purple carbonyl-containing complex 1. On exposure to light in solution 1 loses both carbonyl groups to form the yellow complex 2. Compound 2 is also light-sensitive in solution. In this paper we present the synthesis and characterization of 1 and 2. Further studies on the photoreactions of 2 and other molybdenum dithiolene complexes will be the subject of a future paper.

## Results and Discussion

**Characterization of Dimers.** When a methylcyclohexane solution of $[CpMo(CO)_3]_2$ and $S_2C_2(CF_3)_2$ is heated to reflux, the initially dark red solution rapidly becomes deep purple. Removal of solvent under vacuum gives a dark purple residue containing a variety of brightly colored compounds; if the reaction is continued for 2 h or longer, the purple compound 1 can be isolated chromatographically in ca. 50% yield. This compound exhibits very strong

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[1] Camille and Henry Dreyfus Teacher-Scholar, 1981–1986.

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

[3] Miller, D. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1980**, *102*, 4925.

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

[5] Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 3710.

[6] Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.

[7] Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W, K.; Rakowski DuBois, M. *Organometallics* **1986**, *5*, 951.

[8] McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49.

[9] King, R. B. *Inorg. Chem.* **1963**, *2*, 641.

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

[11] King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1587.

0276-7333/87/2306-0480$01.50/0

infrared bands at 1994 and 1950 cm$^{-1}$. The presence of two $^1H$ NMR resonances of equal area at $\delta$ 5.03 and 5.85 suggests nonequivalent cyclopentadienyl groups, while $^{19}F$ NMR quartets of equal area at −51.8 and −53.0 ppm (relative to internal $CFCl_3$) suggest one or more asymmetrically coordinating $S_2C_2(CF_3)_2$ ligands. The molecule does not give a parent ion in the mass spectrum but does show a weak envelope with the characteristic dimolybdenum pattern at *m/e* 774, corresponding to $[C_5H_5Mo(S_2C_2(CF_3)_2)]_2^+$. Elemental analysis and X-ray structure determination support the formulation $Cp(CO)_2Mo[\mu\text{-}S_2C_2(CF_3)_2]_2MoCp$.

When solutions of 1 are exposed to ultraviolet light in tetrahydrofuran solution, a steady color change from purple to yellow occurs. On removal of solvent a yellow product, 2, can be recovered in 90% yield. The product has no infrared bands between 1600 and 2200 cm$^{-1}$. Proton and $^{19}F$ NMR show single resonances at $\delta$ 6.27 and −60.7, respectively, suggesting equivalent $C_5H_5$ groups and symmetrically coordinating $S_2C_2(CF_3)_2$. The mass spectrum is essentially identical with that of 1, showing a dimolybdenum pattern at *m/e* 774 as the cluster of greatest mass. Elemental analysis and X-ray structural characterization support the formulation $[CpMo(\mu\text{-}S_2C_2(CF_3)_2)]_2$.

As mentioned above, King reported the synthesis of a purple-brown compound by reacting $[CpMo(CO)_3]_2$ with $S_2C_2(CF_3)_2$; he identified the product as having formula $[C_5H_5Mo(S_2C_2(CF_3)_2)]_2$ and suggested a structure slightly different from that shown for 2 above.[11] Supporting evidence included mass spectral and $^{19}F$ NMR data as well as a partial crystal structure.[12] However, our work has shown that the mass spectra of 1 and 2 are essentially identical (since 1 apparently loses its carbonyls very readily in the mass spectrometer). Furthermore, the $^{19}F$ NMR reported by King for his purple-brown compound matches the spectrum we obtained for the yellow compound 2 rather than the purple 1. We suggest that in the course of King's work some of the purple compound 1 photolyzed in room light, yielding samples of 2 that were used in subsequent characterizations. In our work we have obtained small amounts of 2 (<1%) as a byproduct of the synthesis of 1, and we have observed slow conversion of 1 into 2 in solution under fluorescent laboratory lighting. No 2 is formed when a solution of 1 is refluxed in methylcyclohexane or tetrahydrofuran for 8 h in the dark.

There have been two additional reports of complexes of formula $M_2(CO)_2(C_5H_5)_2(\text{dithiolene})_2$. $C_5H_5W(CO)_3H$ has been reported to react with $S_2C_2(CF_3)_2$ after prolonged reflux in hexane to give as one product $[C_5H_5W(CO)(S_2C_2(CF_3)_2)]_2$.[10] A structure containing asymmetrically bridging dithiolene ligands and having a single, nonbridging carbonyl attached to each tungsten has been proposed; however, no structural determination has been reported, and the infrared spectrum reported (three bands in the carbonyl region) is difficult to reconcile with the proposed structure. More recently, it has been reported that $[CpMo(CO)_3]_2$ reacts with 3,4-dimercaptotoluene under reflux in methylcyclohexane to give as the major product a purple compound of formula $[C_5H_5Mo(CO)S_2C_6H_3(CH_3)]_2$.[13] For this compound two carbonyl bands are observed in the infrared spectrum, at 1980 and 1930 cm$^{-1}$, and two singlets attributable to the cyclopentadienyl ligands occur in the $^1H$ NMR spectrum, at chemical shifts of 4.66 and 5.50 ppm. Visible and mass spectral data are also very similar to equivalent data for 1. We propose that this 3,4-dimercaptotoluene complex may very well be isostructural with 1. The 3,4-dimercaptotoluene complex also has been reported to lose its carbonyl groups photochemically to give $[CpMoS_2C_6H_3(CH_3)]_2$, which is isostructural with 2.

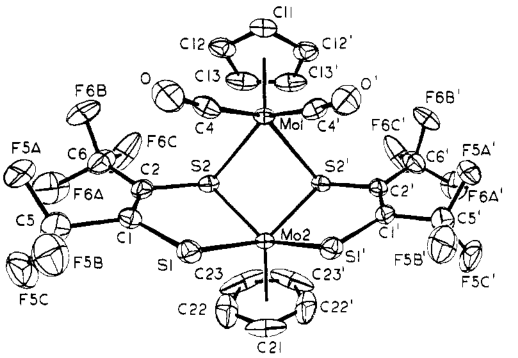

**Figure 1.** ORTEP drawing of $Cp(CO)_2Mo[\mu\text{-}S_2C_2(CF_3)_2]_2MoCp$ (1) showing labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

**Table I. Selected Distances and Angles in $Cp(CO)_2Mo[\mu\text{-}S_2C_2(CF_3)_2]_2MoCp$ (1)**

| | | | |
|---|---|---|---|
| | Distances, Å | | |
| Mol–Mo2 | 3.256 (1) | C1–C2 | 1.333 (6) |
| Mo1–S2 | 2.523 (1) | Mo1–C11 | 2.267 (6) |
| Mo2–S1 | 2.397 (1) | Mo1–C12 | 2.299 (5) |
| Mo2–S2 | 2.375 (1) | Mo1–C13 | 2.366 (4) |
| S1–S2 | 3.152 (1) | Mo2–C21 | 2.269 (7) |
| S1–S1′ | 3.210 (2) | Mo2–C22 | 2.293 (6) |
| S2–S2′ | 3.103 (2) | Mo2–C23 | 2.292 (5) |
| Mo1–C4 | 2.011 (5) | | |
| C4–O | 1.103 (5) | C–C$_{av}$(Mol)$^a$ | 1.40 (1) |
| S1–C1 | 1.721 (5) | C–C$_{av}$(Mo2)$^a$ | 1.31 (1) |
| S2–C2 | 1.786 (5) | | |
| | Angles, deg | | |
| Mo1–S2–Mo2 | 83.27 (4) | Mo2–S1–C1 | 106.13 (16) |
| Mo1–S2–C2 | 110.93 (14) | S1–C1–C2 | 122.92 (37) |
| Mo2–S2–C2 | 106.18 (15) | S2–C2–C1 | 119.57 (36) |
| S1–Mo2–S2 | 82.66 (4) | C2–C1–C5 | 112.30 (44) |
| S1–Mo2–S2′ | 138.31 (4) | C1–C2–C6 | 127.66 (47) |
| S1–Mo2–S1′ | 84.05 (6) | S1–C1–C5 | 113.72 (35) |
| C4–Mo1–C4′ | 76.05 (26) | S2–C2–C6 | 112.76 (38) |
| S2–Mo1–C4 | 85.10 (12) | | |

$^a$ C–C$_{av}$ is the average distance between adjacent carbon atoms within each cyclopentadienyl ring.

Complex 2 also shows photoreactivity. In tetrahydrofuran and chloroform solutions from which $O_2$ has been rigorously excluded, photolysis of 2 is slow, and an orange product is observed. However, in solutions containing dissolved oxygen 2 photolyzes more rapidly to give a blue product; we have found that other dithiolene-bridged dimers of structure similar to 2 also photolyze readily in the presence of dissolved oxygen. We are presently investigating the photochemical reactions of 2 and other dithiolene-bridged molybdenum dimers to determine the nature of the brightly colored products that are formed.

It should also be mentioned that solutions of 2 do not react with carbon monoxide in the dark at a pressure of 1 atm; even after vigorous stirring of a solution saturated with carbon monoxide (tetrahydrofuran solvent) for 24 h, no measurable change was observed.

**Description of Structures.** A perspective view of 1 is shown in Figure 1, and its structural parameters and selected bond distances and angles are given in Tables I and II, respectively. The molecule is formally of $C_s$ sym-

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(12) Baird, H. W., private communication. A partial X-ray structure determination (Cox, J. W. M.A. Thesis, Wake Forest College, 1965) indicated the presence of two molybdenum atoms bridged by four sulfur atoms. However, the unit cell parameters suggest that the crystal used was actually of compound 2 rather than 1.

(13) Miller, W. K.; Haltiwanger, R. C.; VanDerveer, M. C.; Rakowski DuBois, M. *Inorg. Chem.* **1983**, *22*, 2974.

**Table II. Atomic Positional Parameters for $Cp(CO)_2Mo[\mu\text{-}S_2C_2(CF_3)_2]_2MoCp$ (1)**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo1 | 0.28413 (9) | 0.2500 | 0.38290 (5) |
| Mo2 | 0.18568 (9) | 0.2500 | 0.14289 (5) |
| S1 | 0.4308 (2) | 0.3697 (1) | 0.1322 (1) |
| S2 | 0.0980 (2) | 0.3657 (1) | 0.2594 (1) |
| O | 0.6267 (6) | 0.3913 (4) | 0.3750 (4) |
| C1 | 0.3669 (8) | 0.4757 (5) | 0.1900 (4) |
| C2 | 0.2279 (8) | 0.4772 (5) | 0.2450 (4) |
| C4 | 0.5022 (8) | 0.3424 (5) | 0.3733 (4) |
| C5 | 0.4911 (11) | 0.5671 (6) | 0.1762 (6) |
| C6 | 0.1634 (11) | 0.5645 (6) | 0.3016 (6) |
| C11 | 0.3507 (14) | 0.2500 | 0.5500 (7) |
| C12 | 0.2441 (10) | 0.3346 (6) | 0.5244 (4) |
| C13 | 0.0619 (9) | 0.3027 (7) | 0.4841 (5) |
| C21 | 0.1160 (15) | 0.2500 | −0.0243 (7) |
| C22 | 0.0391 (12) | 0.3299 (6) | 0.0043 (7) |
| C23 | −0.0921 (9) | 0.3027 (8) | 0.0523 (5) |
| F5A | 0.5645 (7) | 0.6089 (4) | 0.2587 (4) |
| F5B | 0.6516 (8) | 0.5376 (5) | 0.1387 (4) |
| F5C | 0.4136 (9) | 0.6283 (4) | 0.1108 (4) |
| F6A | 0.1655 (15) | 0.6500 (5) | 0.2507 (6) |
| F6B | 0.2797 (8) | 0.5804 (5) | 0.3848 (4) |
| F6C | −0.0001 (8) | 0.5485 (5) | 0.3308 (5) |

metry as imposed crystallographically, possessing two asymmetrically bridging $S_2C_2(CF_3)_2$ ligands and, interestingly, having both carbonyl groups attached to Mo1.

The metal–metal distance, 3.256 (1) Å, is considerably greater than the sum of the van der Waals radii[14] and is indicative of minimal direct Mo–Mo interactions. The two bridging sulfur atoms are significantly closer to Mo2 (2.375 (1) Å) than to Mo1 (2.523 (1) Å); for the nonbridging sulfur atoms, the Mo2–S1 distance is intermediate (2.397 (1) Å) and somewhat shorter than the molybdenum–sulfur distances reported for dimeric molybdenum complexes containing symmetrically bridging dithiolene ligands.[13]

Within the $S_2C_2(CF_3)_2$ ligand itself, the carbon–carbon distance, 1.333 (6) Å, is shorter than the comparable distance, 1.400 (30) Å, reported in a vapor-phase electron diffraction study on the free ligand,[15] but is similar to the carbon–carbon distance in ethylene[16] and therefore is consistent with a double bond. The configuration of each dithiolene ring is essentially planar, with the asymmetrically bridging mode apparently having little effect on the planarity of the ligand system. The atoms S1, S2, C1, C2, C5, and C6 are all within 0.02 Å of the least-squares plane defined by those atoms. However, the S1–C1 distance, 1.721 (5) Å, is significantly shorter than the S2–C2 distance, 1.786 (5) Å, suggesting a greater degree of sulfur–carbon π interaction at the nonbridging sulfurs. The S1–C1 distance is comparable to the sulfur–carbon distance of 1.729 (10) Å reported for the free ligand, which has been estimated to have a bond order of approximately 1.25.[15]

The cyclopentadienyl ring attached to Mo1 is tilted slightly away from the bridging sulfur atoms of the dithiolene ligands. The Mo1–C13 distance (C13 is the position on the ring nearest the bridging sulfurs) of 2.366 (4) Å is significantly greater than the distances, Mo1–C12 (2.299 (5) Å) and Mo1–C11 (2.267 (6) Å). However, the cyclopentadienyl ring remains planar; the least-squares plane defined by the carbon atoms within the ring is within 0.011 Å of each of the atoms. The carbon atoms of the cyclopentadienyl ring attached to Mo2 are at similar distances from the metal, with Mo–C distances in the range 2.269–2.293 Å. The dihedral angle between the two planes defined by the Cp ligands is 56.8°.

**Table III. Selected Distances and Angles in $[CpMo(\mu\text{-}S_2C_2(CF_3)_2)]_2$ (2)**

| | | | | | |
|---|---|---|---|---|---|
| | | Distances, Å | | | |
| Mo1–Mo2 | 2.584 (1) | S1–S2 | 2.984 (2) | C11–C12 | 1.305 (9) |
| Mo1–S1 | 2.447 (2) | S3–S4 | 2.988 (2) | C15–C16 | 1.309 (9) |
| Mo1–S2 | 2.458 (2) | S1–S4 | 2.921 (2) | C11–C13 | 1.47 (1) |
| Mo1–S3 | 2.459 (2) | S2–S3 | 2.905 (2) | C12–C14 | 1.49 (1) |
| Mo1–S4 | 2.451 (2) | S1–C11 | 1.813 (7) | C15–C17 | 1.50 (1) |
| Mo2–S1 | 2.451 (2) | S2–C12 | 1.815 (6) | C16–C18 | 1.49 (1) |
| Mo2–S2 | 2.453 (2) | S3–C15 | 1.807 (6) | Mo–C(av)[a] | 2.28 (1) |
| Mo2–S3 | 2.458 (2) | S4–C16 | 1.804 (6) | C–C(av)[b] | 1.38 (2) |
| Mo2–S4 | 2.450 (2) | | | | |
| | | Angles, deg | | | |
| Mo1–S1–Mo2 | 63.67 (4) | S3–C15–C16 | 118.8 (5) | | |
| Mo1–S2–Mo2 | 63.59 (4) | S4–C16–C15 | 116.6 (5) | | |
| Mo1–S3–Mo2 | 63.41 (4) | Mo1–S1–C11 | 104.3 (1) | | |
| Mo1–S4–Mo2 | 63.52 (4) | Mo1–S2–C12 | 104.5 (2) | | |
| S1–Mo1–S2 | 75.07 (5) | Mo1–S3–C15 | 102.6 (2) | | |
| S3–Mo1–S4 | 74.84 (5) | Mo1–S4–C16 | 103.8 (2) | | |
| S1–Mo2–S2 | 74.96 (5) | C12–C11–C13 | 128.0 (7) | | |
| S3–Mo2–S4 | 74.98 (5) | C11–C12–C14 | 128.4 (7) | | |
| S1–C11–C12 | 117.0 (5) | C16–C15–C17 | 128.5 (6) | | |
| S2–C12–C11 | 118.0 (5) | C15–C16–C18 | 127.9 (6) | | |

[a] Average distance to carbon atoms in cyclopentadienyl rings. [b] Average distance between adjacent carbon atoms in cyclopentadienyl rings.

**Table IV. Atomic Positional Parameters for $[CpMo(\mu\text{-}S_2C_2(CF_3)_2)]_2$ (2)**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo1 | 0.05585 (5) | 0.31544 (3) | −0.17730 (5) |
| Mo2 | 0.08474 (4) | 0.18777 (3) | −0.29439 (5) |
| S1 | 0.1873 (1) | 0.3034 (1) | −0.3299 (2) |
| S2 | −0.0395 (1) | 0.2846 (1) | −0.3744 (2) |
| S3 | −0.0479 (1) | 0.1999 (1) | −0.1418 (2) |
| S4 | 0.1792 (1) | 0.2178 (1) | −0.0965 (2) |
| C1 | −0.0010 (9) | 0.3787 (6) | −0.0071 (9) |
| C2 | 0.0976 (8) | 0.3957 (6) | −0.0119 (10) |
| C3 | 0.1111 (8) | 0.4362 (6) | −0.1215 (12) |
| C4 | 0.0120 (11) | 0.4413 (5) | −0.1787 (10) |
| C5 | −0.0570 (8) | 0.4010 (6) | −0.1092 (10) |
| C6 | 0.1352 (8) | 0.0625 (5) | −0.2915 (9) |
| C7 | 0.1986 (7) | 0.1039 (5) | −0.3627 (9) |
| C8 | 0.1401 (8) | 0.1281 (5) | −0.4683 (8) |
| C9 | 0.0381 (8) | 0.1048 (5) | −0.4582 (9) |
| C10 | 0.0364 (8) | 0.0626 (5) | −0.3466 (10) |
| C11 | 0.1283 (6) | 0.3452 (4) | −0.4713 (7) |
| C12 | 0.1296 (6) | 0.3346 (4) | −0.4922 (7) |
| C13 | 0.1993 (7) | 0.3859 (6) | −0.5498 (9) |
| C14 | −0.0367 (7) | 0.3579 (6) | −0.6032 (8) |
| C15 | 0.0116 (6) | 0.1616 (4) | 0.0012 (7) |
| C16 | 0.1113 (6) | 0.1680 (4) | 0.0212 (7) |
| C17 | −0.0645 (7) | 0.1260 (5) | 0.0833 (8) |
| C18 | 0.1764 (7) | 0.1400 (5) | 0.1312 (7) |
| F1 | 0.1599 (6) | 0.4396 (4) | −0.6180 (7) |
| F2 | 0.2703 (5) | 0.4212 (5) | −0.4837 (7) |
| F3 | 0.2489 (6) | 0.3447 (5) | −0.6169 (7) |
| F4 | 0.0031 (5) | 0.3618 (6) | −0.7036 (5) |
| F5 | −0.1169 (6) | 0.3173 (6) | −0.6192 (7) |
| F6 | −0.0770 (7) | 0.4233 (5) | −0.5924 (8) |
| F7 | −0.0983 (6) | 0.0631 (5) | 0.0467 (7) |
| F8 | −0.1471 (5) | 0.1631 (5) | 0.0895 (7) |
| F9 | −0.0363 (5) | 0.1216 (5) | 0.1996 (6) |
| F10 | 0.1533 (7) | 0.0745 (4) | 0.1718 (7) |
| F11 | 0.1665 (7) | 0.1801 (6) | 0.2282 (6) |
| F12 | 0.2696 (5) | 0.1364 (6) | 0.1135 (6) |

Complex **2** is isostructural with the previously reported molybdenum (III) dimers of the ethenedithiolate and 3,4-toluenedithiolate ligands.[13] A perspective view is shown in Figure 2, and its structural parameters and selected bond distances and angles are given in Tables III and IV,

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[14] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.

[15] Hencher, J. L.; Shen, Q.; Tuck, D. G. *J. Am. Chem. Soc.*, **1976**, *98*, 899.

[16] Bartell, L. S.; Roth, E. A.; Hollowell, C. D.; Kuchitsu, K.; Young, J. E. *J. Chem. Phys.* **1965**, *42*, 2683.

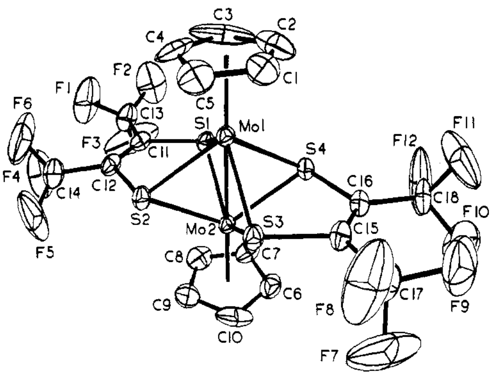
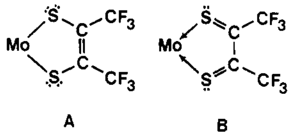


**Figure 2.** ORTEP drawing of $[CpMo(\mu\text{-}S_2C_2(CF_3)_2)]_2$ (2) showing labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

respectively. The four bridging sulfur atoms are in a plane which bisects the molybdenum–molybedenum bond vector; the idealized symmetry is $C_{2h}$. The metal–metal distance of 2.584 (1) Å is slightly greater than those of the previously reported dithiolene-bridged molybdenum dimers (2.576 (1) Å for $[CpMo(S_2C_2H_2)]_2$; 2.580 (1) Å for $[CpMoS_2C_6H_3(CH_3)]_2$[13]) but remains consistent with a single bond.[17] Within the bridging ligands the carbon–carbon distance, 1.305 (9) Å, is similar to the value of 1.310 (6) Å, reported for $[CpMo(S_2C_2H_2)]_2$; both are shorter than the carbon–carbon distance in ethylene. The dithiolene ligand can be described by the following limiting resonance forms:



The short carbon–carbon distance within this ligand, together with the rather long sulfur–carbon distance of 1.810 (6) Å, suggests that form A provides the more accurate description of the dithiolene ligand in this case. Other bond distances and angles are very similar to those reported for similar dimers; for example, the Mo–S–Mo angle in 2, 63.55 (4)°, is essentially identical with that of $[CpMo(S_2C_2H_2)]_2$.

As mentioned above, compound 1 loses its carbonyls readily on photolysis. One can rationalize that Mol satisfies its new electron requirements in several ways. Sulfur atoms S1 and S1′ contribute additional electron density to Mol by assuming a bridging function such that the dithiolene ligands become symmetrically bridging. In addition, the Mo–Mo distance is shortened by more than 0.77 Å in the process of formation of a metal–metal bond. In this connection it is interesting that $^{95}$Mo NMR data for 1 suggest it to be a mixed Mo(II)–Mo(IV) dimer, whereas 2 appears to be an essentially "normal" dimer of Mo(III).[18] Consequently, one may describe this reaction as formally involving an intramolecular electron transfer from Mol to Mo2. These suggested oxidation states of molybdenum are also consistent with the predominance of form A of the ligand; that is, the dithiolene may be treated as having a formal charge of approximately −2.

**Electrochemical Studies.** The electrochemistry of compounds 1 and 2 was studied in methylene chloride solution. Potentials from cyclic voltammetry are summarized in Table V. Both compounds display reversible or quasi-reversible one electron oxidation waves. However, when controlled potential electrolysis is carried out ($E$ = +1.3 V for 1 and $E$ = +1.1 V for 2), both compounds decompose to a mixture of products. The reversible nature of the oxidation waves suggests that one-electron oxidation products are at least somewhat stable and may be isolable at lower temperatures. Both compounds can be irreversibly reduced. Although compound 1 appears from $^{95}$Mo NMR data (vide supra) to contain molybdenum in both the 2+ and the 4+ oxidation states while compound 2 appears to contain only $Mo^{3+}$, the potentials of their electrode reactions are quite similar, with the potentials of 1 about 0.1 V more positive than for 2. These similarities do not, however, extend to be the kinetics of the electrode reactions. Compound 1 displays $\Delta E_p$ values for oxidation that are independent of scan rate and equal to the values expected for an electrochemically reversible system (52 mV at 0 °C) while compound 2 displays $\Delta E_p$ values that only approach the reversible limit at slow scan speeds. This suggests that the wave shape in 2 is kinetically controlled and that electron transfer is therefore slower in compound 2 than in compound 1.

**Table V. Electrochemical Data for Molybdenum Dithiolene Complexes**[a]

| complex | ox. | | | red. |
|---|---|---|---|---|
| | $E_{1/2}$,[b] V | $\Delta E_p$, mV | $\Delta E_p$,[c] mV | $E_{p,c}$,[d] V |
| $Cp(CO)_2Mo[\mu\text{-}S_2C_2(CF_3)_2]_2MoCp$ | 1.02 | 53 | 52 | −1.24 |
| $[CpMo(\mu\text{-}S_2C_2(CF_3)_2)]_2$ | 0.88 | 65 | 79 | −1.37 |

[a] Measured at 0 °C in 0.1 M tetra-*n*-butylammonium hexafluorophosphate in $CH_2Cl_2$ at a glassy carbon electrode relative to SCE using a scan rate of 20 mV/s. [b] Average of cathodic and anodic peak potentials in cyclic voltammograms. [c] Measured at scan rate of 90 mV/s. [d] $E_{p,c}$ is the cathodic peak potential for the irreversible reduction waves.

Rakowski DuBois et al. have reported the presence of reversible or quasi-reversible oxidation waves for a number of sulfur-bridged cyclopentadieny molybdenum dimers in acetonitrile.[6] Most of the complexes reported easily underwent single electron oxidations with potentials in the range of 0.0–0.3 V vs. SCE. Of particular interest is $[CpMo(S_2C_2H_2)]_2$ that differs from our compound 2 only by having H instead of $CF_3$ on the dithiolene ligands and that oxidizes at +0.15 V. We have studied the electrochemistry of $[CpMo(S_2C_2H_2)]_2$ in $CH_2Cl_2$ and obtained a potential of +0.23 V vs. SCE. The presence the $CF_3$ groups in compound 2 causes a substantial anodic shift of the oxidation potential. The direction in the shift is to be expected because of the electron-withdrawing nature of the $-CF_3$ group as compared with −H. The magnitude of the shift is large (>0.6 V), suggesting that the substituents on the dithiolene ligands should play a major role in determining the reactions which these compounds can undergo. We have, in fact, found some interesting differences between the photochemical behavior of compound 2 and $[CpMo(S_2C_2H_2)]_2$. This chemistry will be the subject of a future paper. Also included will be a more complete description of the electrochemistry of $[CpMo(S_2C_2H_2)]_2$ in $CH_2Cl_2$.

## Experimental Section

Bis(trifluoromethyl)-1,2-dithietene was synthesized according to the method of Krespan[19] and stored under a nitrogen atmo-

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(17) Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7470.

(18) Young, C. G.; Minelli, M.; Enemark, J. H.; Miessler, G.; Janietz, N.; Kauermann, H.; Wachter, J. *Polyhedron* **1986**, *5*, 407. Compound 1 exhibits a single $^{95}$Mo resonance at −789 ppm (relative to $Mo(CO)_6$); this is comparable to the values for a number of Mo(II) compounds. No signal corresponding to Mo(IV) is observed. Compound 2 gives a single resonance at +2301 ppm characteristic of Mo(III).

(19) Krespan, C. G.; McKusick, B. C. *J. Am. Chem. Soc.* **1961**, *83*, 3434.

sphere at 0 °C. $[CpMo(CO)_3]_2$ was prepared according to the published procedures.[20,21] Chloroform and methylene chloride were passed down a basic alumina column immediately before use. Tetrahydrofuran was distilled from lithium aluminum hydride under a purified nitrogen atmosphere immediately prior to use. For the electrochemical measurements high-purity methylene chloride supplied by Burdick and Jackson Laboratories and electrometric grade tetrabutylammonium hexafluorophosphate from Southwestern Analytical Chemicals were used. All other solvents were reagent grade and used without further purification.

**Physical Measurements.** $^1H$ and $^{19}F$ NMR spectra were obtained by using a Varian Associates EM-360L 60-MHz spectrometer. The $^{19}F$ spectra were referenced to internal standard $CFCl_3$ with positive shifts downfield. Infrared spectra were recorded on an IBM Instruments IR/32 instrument. A Cary 210 spectrophotometer was used to record visible–UV spectra. Electrochemical measurements were carried out with a locally produced potentiostat and potential wave-form generator. A three electrode system was used with a glassy carbon indicator electrode, a platinum-coil counter electrode, and a saturated calomel (SCE) reference electrode. A platinum coil was used as the working electrode during electrolysis experiments. To compensate for solution resistance, positive-feedback IR compensation was employed.

Mass spectra were obtained by the mass spectrometry service laboratory at the University of Minnesota, and microanalyses were determined by Galbraith Laboratories.

**Preparation of Compounds. $Cp(CO)_2Mo[\mu\text{-}S_2C_2(CF_3)_2]_2MoCp$ (1).** $[CpMo(CO)_3]_2$ (0.49 g, 1.0 mmol) and $S_2C_2(CF_3)_2$ (0.56 g, 2.5 mmol) were dissolved in 20 mL of methylcyclohexane and refluxed under a slow flow of nitrogen for 2 h, during which time the originally purple-red solution became black. The solvent was removed under vacuum. The black residue was then dissolved in 75:25 hexane/ethyl acetate (v/v) and chromatographed on an alumina column, eluting with additional hexane/ethyl acetate. The major bright purple band was separated on the column from a number of smaller, brightly colored bands. Removal of solvent under vacuum left a dark purple residue; the product was recrystallized in the dark from $CH_2Cl_2$/heptane to give dark purple crystals, yield 0.41 g (49%). $^1H$ NMR ($CDCl_3$): $\delta$ 5.03 (s, 5 H), 5.85 (s, 5 H). $^{19}F$ NMR ($CDCl_3$): $\delta$ −51.8 (quartet, 6 F, $J$ = 12 Hz), −53.0 (quartet, 6 F). Mass spectrum [$m/e$ (relative abundance), assignment]: 774 (8), $Cp_2Mo_2[S_2C_2(CF_3)_2]_2^+$, 450 (100), $Cp_2Mo_2S_4^+$; 386 (55), $Cp_2Mo_2S_2^+$; 354 (21), $Cp_2Mo_2S^+$; 322 (18), $Cp_2Mo_2^+$; 226 (64), $S_2C_2(CF_3)_2^+$. IR ($CH_2Cl_2$): 1994, 1950 $cm^{-1}$ (C=O). Electronic absorption spectrum in tetrahydrofuran at 30 °C ($\lambda_{max}$, nm ($\epsilon$)): 553 (5800), 472 (4900), 389 (12 300), 349 (7100). Anal. Calcd for $Mo_2C_{20}H_{10}F_{12}O_2S_4$: C, 28.93; H, 1.21; S, 15.44. Found: C, 28.83; H, 1.17; S, 15.53.

**$[CpMo(\mu\text{-}S_2C_2(CF_3)_2)]_2$ (2).** Complex 1 (100 mg, 0.12 mmol) was dissolved in 40 mL of freshly distilled tetrahydrofuran in a quartz flask. The purple solution was placed under a purified nitrogen atmosphere and photolyzed for 2 h, yielding a yellow solution. The solvent was removed by vacuum to give a yellow-brown residue. This material was recrystallized from $CH_2Cl_2$/heptane to yield yellow crystals, yield 85 mg (91%). $^1H$ NMR ($CDCl_3$): $\delta$ 6.27 (s). $^{19}F$ NMR ($CDCl_3$): $\delta$ −60.7 (s). Mass spectrum [$m/e$ (relative abundance), assignment]: 774 (22), $Cp_2Mo_2[S_2C_2(CF_3)_2]_2^+$; 612 (6), $Cp_2Mo_2S_2[S_2C_2(CF_3)_2]^+$; 450 (100), $Cp_2Mo_2S_4^+$; 386 (43), $Cp_2Mo_2S_2^+$. Electronic absorption spectrum in tetrahydrofuran at 30 °C ($\lambda_{max}$, nm ($\epsilon$)): 457 (1500), 339 (3500). Anal. Calcd for $Mo_2C_{18}H_{10}F_{12}S_4$: C, 27.92; H, 1.30; S, 16.56. Found: C, 27.80; H, 1.32; S, 16.74.

**Photochemical Techniques.** Photolyses were performed in quartz vessels using a 450-W Ace/Hanovia Hg-vapor lamp. Corning filter 7058 having UV cutoff at 238 nm was used to minimize high-energy radiation and possible solvent photolysis. Photolyses were performed under a purified nitrogen atmosphere except where noted otherwise.

**Collection and Reduction of X-ray Data.** Crystals of both 1 and 2 were obtained by slow evaporation of $CH_2Cl_2$/heptane solutions in the dark. In each case the cell constants were determined by least-squares refinement of the angular settings of 25 Mo K$\alpha$ ($\lambda$ = 0.71069 Å) reflections centered on a CAD 4 diffractometer using the Enraf-Nonius automatic peak searching and centering program.[22] Data collection was carried out on the diffractometer using graphite-monochromatized Mo K$\alpha$ radiation and employing a variable-rate $\omega$–$2\theta$ scan technique. A summary of the crystal data and intensity measurement parameters appears in Table VI. No decrease in the intensities of periodically remeasured reflections was noted. Data were corrected for Lorenz, polarization, background, and absorption effects.

**Table VI. Summary of Crystal Data and Intensity Collection**

| | 1 | 2 |
|---|---|---|
| | Crystal Parameters | |
| formula | $C_{20}H_{10}F_{12}Mo_2O_2S_4$ | $C_{18}H_{10}F_{12}Mo_2S_4$ |
| fw, amu | 830.42 | 774.40 |
| cryst system | monoclinic | monoclinic |
| space group | $P2_1/m$ | $P2_1/a$ |
| cell parameters | | |
| $a$, Å | 7.153 (1) | 13.030 (1) |
| $b$, Å | 13.404 (9) | 17.336 (2) |
| $c$, Å | 13.690 (4) | 10.741 (7) |
| $\bar{\beta}$, deg | 98.54 | 93.29 |
| $V$, Å$^3$ | 1298 | 2422 |
| $Z$ | 2 | 4 |
| $d$(calcd), g/cm$^3$ | 2.135 | 2.123 |
| temp, °C | 23 | 23 |
| linear abs coeff, cm$^{-1}$ | 13.74 | 14.54 |
| | Measurement of Intensity Data | |
| radiatn | Mo K$\bar{\alpha}$ ($\lambda$ = 0.71069 Å, graphite monochromatized) | Mo K$\bar{\alpha}$ ($\lambda$ = 0.71069 Å, graphite monochromatized) |
| scan range, $2\theta$, deg | 0–50 | 0–50 |
| max, min transmissn factors | $a$ | 1.00, 0.88 |
| unique data collected | 2393 | 4248 |
| final no. of variables | 187 | 326 |
| unique data used | 1895 ($F_o^2 \geq 1.0\sigma(F_o^2)$) | 2848 ($F_o^2 \geq 1.0\sigma(F_o^2)$) |
| $R^b$ | 0.043 | 0.044 |
| $R_w{}^b$ | 0.053 | 0.057 |
| GOF | 2.16 | 1.59 |

[a] Absorption correction not necessary, since the minimum transmission factor was greater than 0.90. [b] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as follows: $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|))^2/(\sum w|F_o|)^2]^{1/2}$. The GOF is $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO and NV are the number of observations and the number of variables, respectively.

**Solution and Refinement of Structures.** Conventional heavy-atom techniques were used to solve the structures.[23] For 1, the systematic extinctions ($0h0$, $h$ odd) indicated the space group to be $P2_1$ or $P2_1/m$. With $Z$ = 2, $P2_1$ was regarded as more likely. However, the Patterson map suggested that $P2_1/m$ was possible, and successive Fourier maps confirmed this. All of the non-hydrogen atoms were found, and least-squares refinement in $P2_1/m$ converged at $R$ = 0.070 with all atoms anisotropic. A difference Fourier map at this point indicated that the $CF_3$ groups were disordered significantly but that the $C_5$ rings were not. Each $CF_3$ group occurred at a major position (F5A-C and F6A-C in the final

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(20) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99.

(21) Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 116.

(22) All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius CAD 4-SDP-PLUS programs. This crystallographic computing package is described by: Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1968; pp 64–71. *Structure Determination Package and SDP-PLUS User's Guide*; B.A. Frenz & Associates, Inc.: College Station, TX, 1982.

(23) Values of the atomic scattering factors used in the calculations were taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Vol. IV.

list) and a minor position (F5D-F and F6D-F). The extent to which the two positions were occupied was estimated by least-squares refinement of the occupancy factors for each of the 12 F atoms while all other parameters were held constant. This refinement indicated that the major and minor positions were filled in roughly a 0.75/0.25 ratio with uncertainties in these values of approximately 0.05. These groups were treated independently, but F5A-C all had the same occupancy factor (0.82) and F5D-F had the complementary factor (0.18). F6A-F were treated similarly with occupancies of 0.73 for F6A-C and 0.27 for F6D-F. Five of the six independent H atoms could also be seen in the difference Fourier map. All six were included at idealized positions based on the ring carbon positions. After further least-squares refinements the occupancy factors were readjusted in the same fashion as previously. For the final cycles of refinement the H atoms were given fixed $B$'s of 10.0 and the minor F atoms were put in at idealized positions, staggered with respect to the major positions, and with fixed $B$'s of 10.0. The final refinement converged at $R = 0.043$. A difference Fourier map at this point showed no significant features.

The space group $P2_1/m$ was originally regarded as unlikely because it required molecules to pack on opposite sides of a mirror plane—a situation that does not allow a favorable fit. The disorder found in the $CF_3$ groups alleviates this problem, at least in part. There are two arguments, besides the low $R$ value for $P2_1/m$, against $P2_1$ being the correct space group (with only approximate $P2_1/m$ symmetry). First, the $C_5H_5$ rings do not show disorder, and there is no obvious reason why they should not be rotated with respect to the mirror plane. Second, the disorder in the $CF_3$ groups is not 50/50; if $P2_1$ were correct, with an ordered molecule, the $P2_1$ refinement would be expected to show a 50/50 disorder.

For molecule **2**, a trial structure was obtained from a combination of direct methods and Patterson and Fourier maps.

Originally the trial structure appeared to involve disordered molecules (one Mo and two half Mo atoms per molecule) in $P2_1/a$. It was then recognized that this could be transformed to two ordered molecules in the asymmetric unit in $P_a$. This model readily gave all the light atom positions and refined to $R = 0.074$ with essentially the same results as finally obtained. However, convergence was slow, and, while correlation was high, the matrix never became singular. It was then realized that a change of origin could convert this model to a model with one molecule in the asymmetric unit in $P2_1/a$. At this point the Patterson map was calculated and found to give this last model directly. The MULTAN solutions were inspected further, and a solution with a lower figure of merit was also found. We mention this because the solution in the wrong space group ($P_a$) might have been mistaken for the correct solution if we had not looked at the correlation coefficients.

Difference Fourier maps at the later stages of the refinement showed the $CF_3$ groups to be rotationally disordered. However, an occupancy refinement showed that the major orientation for each $CF_3$ group was approximately 95% occupied and the minor component (staggered 60° with respect to the major component) was approximately 5% occupied. Since the disorder was small, it was decided to ignore it. There was no indication of disorder in the cyclopentadienyl groups, and H atoms were included at their idealized positions in the final stages of refinement.

One final comment: the molecule is very close to having a center of symmetry and should probably be considered as one more member of a very small set of centric molecules that do not lie on inversion centers in the crystal structure.

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**Supplementary Material Available:** Listings of anisotropic thermal parameters and least-squares planes (8 pages); listings of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.