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Investigation into the Reactivity of the Metal–Metal Triple Bond in $[\text{Cp}'(\text{CO})_2\text{M}]_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$; $\text{M} = \text{Mo}, \text{W}$) vs. Elemental Sulfur. Formation of Different $\text{Cp}'_2\text{M}_2\text{S}_4$ Isomers and Crystal Structures of $\text{Cp}'_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})_2$ and $\text{Cp}'_2(\text{CO})_2\text{W}_2(\mu\text{-S})_2\text{S}$

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The reaction of $[\text{Cp}'(\text{CO})_2\text{M}]_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$; $\text{M} = \text{Mo}, \text{W}$) with elemental sulfur results in the formation of three different isomers of $\text{Cp}'_2\text{M}_2\text{S}_4$ as well as a carbonyl-containing complex, $\text{Cp}'_2(\text{CO})_2\text{W}_2\text{S}_3$. Distribution of the reaction products depends on the reaction conditions. The structures of $\text{Cp}'_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})_2$ and $\text{Cp}'_2(\text{CO})_2\text{W}_2\text{S}_3$ have been established by X-ray crystallography. $\text{Cp}'_2\text{Mo}_2(\mu\text{-S}_2)(\mu\text{-S})_2$ contains three bridging sulfur ligands, one of which representing a $\mu\text{-S}_2$ group. $\text{Cp}'_2(\text{CO})_2\text{W}_2\text{S}_3$ consists of a planar $\text{W}_2(\mu\text{-S})_2$ core. The Cp' groups are in an antiparallel orientation with two terminal CO groups coordinated to one W atom and only one terminal sulfur ligand coordinated to the other. Both CO groups can be replaced by one sulfur ligand, giving two isomers of $\text{Cp}'_2\text{W}_2\text{S}_4$.

Introduction

The binuclear metal carbonyl derivatives $[\eta^5\text{-C}_5\text{R}_5\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{R} = \text{H}, \text{CH}_3$)¹ are models for unsaturated metal cluster compounds. The high reactivity of the metal–metal triple bond has been already demonstrated in a variety of addition² and substitution³ reactions toward both electrophilic and nucleophilic reagents. In order to continue our studies on the reactivity of the metal–metal triple bond vs. ligands containing heteroatoms,³ we selected elemental sulfur because of its versatile ligand behavior and its tendency to form cluster compounds.⁴ Whereas the chemistry of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2$ has been studied preferentially, little is known on comparative studies in the Cr, Mo, and W triad,^{5,6} especially of the pentamethylcyclopentadienyl derivatives.⁶

In a preliminary paper we described the reaction of $[\text{C}_5\text{Me}_5(\text{CO})_2\text{Cr}]_2$ and elemental sulfur, which gives as the

only isolable product a complex of composition $(\text{C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$.⁷ The presence of three different types of sulfur ligands has been established by X-ray crystallography, including a novel end-on coordinated $(\mu\text{-S},\text{S})$ disulfur bridge. We wish to report here the extension of this reaction to the Mo and W analogues I and II which results in the formation of a variety of dicyclopentadienyldimetal sulfides of the general formula $(\text{C}_5\text{Me}_5)_2\text{M}_2\text{S}_4$ ($\text{M} = \text{Mo}, \text{W}$) and $(\text{C}_5\text{Me}_5)_2(\text{CO})_2\text{W}_2\text{S}_3$.

Experimental Section

General Data. Infrared spectra were obtained with a Beckman 4240 spectrophotometer. NMR spectra were recorded at 60 MHz on a Varian T-60 spectrometer. Mass spectra were obtained with a Varian 311A instrument. Elemental analyses were performed by the Mikroanalytisches Laboratorium, Universität Regensburg, and by the Analytische Laboratorien Malissa & Reuter, D-5250 Engelskirchen, Germany (O, S, W). They are shown together with physical properties in Table I.

All procedures were carried out under nitrogen with solvents freshly distilled under nitrogen from appropriate drying agents. Pentamethylcyclopentadiene⁸ as well as $[\text{C}_5\text{Me}_5(\text{CO})_2\text{M}]_2$ ($\text{M} = \text{Mo}, \text{W}$)⁶ was prepared according to published procedures.

Solution of the Structure. Rotating crystal and Weissenberg photographs ($\text{Cu K}\alpha$) showed the crystals to be triclinic (III) and

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Table I. Selected Properties of Compounds III-VIII

compd	color	yield, %	mol. wt. ^a		anal. calcd (found)			
			calcd	found	C	H	S	O
(C ₅ Me ₅) ₂ Mo ₂ (μ-S ₂)(μ-S) ₂ , III	dark blue prisms	18	590.6	582	40.67 (40.65)	5.12 (4.88)	21.72 (21.32)	
(C ₅ Me ₅) ₂ Mo ₂ (μ-S ₂)S ₂ , IV	brown-green needles	10	590.6	582	40.67 (40.69)	5.12 (4.25)	21.72 (21.69)	
(C ₅ Me ₅) ₂ Mo ₂ (μ-S ₂)S ₂ , V	brown prisms	10	590.6	582	40.67 (40.68)	5.12 (4.88)	21.72 (21.44)	
(C ₅ Me ₅) ₂ W ₂ (CO) ₂ (μ-S) ₂ S, VI	green spears	45	790.3	790	33.43 (32.62)	3.83 (3.66)	12.17 (11.91)	4.05 (4.03)
(C ₅ Me ₅) ₂ W ₂ (μ-S ₂)S ₂ , VII	green needles	8	766.4	766	31.34 (30.67)	3.95 (4.11)		
(C ₅ Me ₅) ₂ W ₂ (μ-S) ₂ S ₂ , VIII	red-brown prisms	54 ^b	766.4	766	31.34 (31.30)	3.95 (3.85)	16.73 (16.60)	

^a Determination by field desorption mass spectroscopy (from toluene solution, related to ⁹²Mo and ¹⁸⁴W, respectively).

^b From the reaction of VI with S₈ in boiling toluene.

Table II. Crystallographic Data

	C ₂₀ H ₃₀ Mo ₂ S ₄ (III)	C ₂₂ H ₃₀ O ₂ S ₃ W ₂ (VI)
color	dark blue	green
cryst type	triclinic	monoclinic
a, Å	8.169 (2)	14.632 (25)
b, Å	10.592 (5)	19.203 (43)
c, Å	14.251 (7)	9.000 (15)
α, deg	90.08 (4)	90
β, deg	95.41 (3)	96.8 (1)
γ, deg	107.51 (3)	90
V, Å ³	1170.2	2510.9
Z	2	4
radiation used in intensity measurement λ(Mo Kα), cm ⁻¹	0.7107 (graphite monochromator)	0.7107 (Ni filter)
temp	room	room
space group	P $\bar{1}$ -C _i ¹	C _{2h} ^s -P2 ₁ /n
cryst size, mm ⁻¹	0.2 × 0.15 × 0.15	0.1 × 0.05 × 0.05
μ(Mo Kα), cm ⁻¹	13.9	95.1
method of correcting for absorp ⁿ diffractometer	ψ scans, empirical (7 reflns) Syntex R3	none AED-Siemens
diffractometer	Syntex R3	AED-Siemens
diffractometer geometry	four circle	three circle
coll reflns	θ-2θ	θ-2θ
no of reflns	2298	2348
independent intens	2081 (I > 2.5σ(I))	1844 (I > 3σ(I))
agreement between equivalent refl ⁿ s, R _{merge}	4.71%	5.3%
2θ _{max} , 2θ _{min}	2° < 2θ < 50°	2° < 2θ < 60°
systematic absences		0k0, k = 2n + 1, h0l, h + l = 2n + 1
R _{iso}	7.5	10.6
R _{anis}	5.9	8.8
R _w	5.4	6.1

monoclinic (VI) and provided rough lattice constants. Exact lattice parameters for VI were calculated by least squares⁹ from diffractometrically determined θ values of 58 selected reflections (AED-Siemens, Mo Kα, θ-2θ scans, five-value method); the corresponding parameters of III were derived from the setting angles of 25 machine-centered reflections (Syntex R3, Mo Kα, θ-2θ scans, three-value method). Data collection was carried out on AED-Siemens (VI) and Syntex R3 (III) diffractometers, respectively. The intensities for III and VI were corrected for Lorentz and polarization factors, for the former an empirical (ψ scans) absorption correction including seven reflections was applied. The program package for the calculations was SHELXTL,¹⁰ which were carried out on a NOVA 3 computer; plots were drawn on a Tektronix plotter. Final refinements were performed by a cascade-matrix procedure. The hydrogen atoms (III) were located with the program HFIX (SHELXTL), only the temperature factors being refined (U = ¹/₃traceŪ; Ū = orthogonalized U tensor). The anisotropic temperature factor exponent takes the form -2π²(h²a*²U₁₁ + k²b*²U₂₂ + ... 2hka*b*U₁₂ + ...). Scattering factors were those of Hanson, Herman, Lea, and Skillman.¹¹ The

crystal data of III and VI are listed in Table II.

Preparations. Reaction of [C₅Me₅(CO)₂Mo]₂, I, with S₈. A mixture of 0.57 g (1 mmol) of I with 0.13 g (0.5 mmol) of S₈ and 100 mL of toluene was stirred at 45 °C for 22 h. After concentration of the solvent to 10 mL, the solution was filtered and transferred to a column (30 × 3 cm, SiO₂). With toluene first an orange red band was eluted containing a mixture of unreacted starting material along with [C₅Me₅(CO)₃Mo]₂. (C₅Me₅)₂Mo₂(μ-S₂)S₂, IV, and (C₅Me₅)₂Mo₂(μ-S₂)(μ-S)₂, III, were eluted with toluene and toluene/ether (4:1) as brown and dark blue bands, respectively. Both complexes as well as the following complexes were recrystallized from toluene/pentane mixtures at -35 °C. After a reaction period of 3 days the chromatographic workup gave the following products: with toluene [C₅Me₅(CO)₃Mo]₂ was eluted as an orange band followed by a dark brown band of V and a second brown band containing IV.

Conversion of (C₅Me₅)₂Mo₂(μ-S₂)(μ-S)₂, III, into (C₅Me₅)₂Mo₂(μ-S₂)S₂, IV. A dark blue solution of 105 mg (0.18 mmol) of III in 100 mL of toluene was stirred at 45 °C for 3 days. The color changes to brown-green. The concentrated solution was chromatographed on SiO₂ (column 20 × 2 cm). Complex IV was eluted with toluene as a brown band (yield 40 mg, 38%) and

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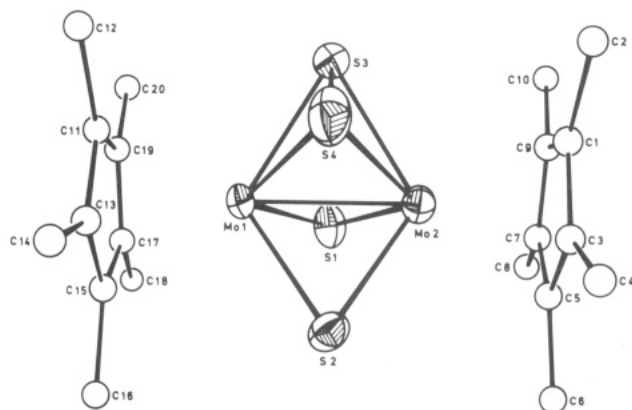


Figure 1. ORTEP drawing of the molecular structure of $(C_5Me_5)_2Mo_2(\mu-S_2)(\mu-S)_2$, III.

state of both Mo atoms seems thus to be preserved, for opening of the S_2^{2-} bridge would require a change in the oxidation state. Mo complexes such as V or its syn isomer are not formed in this reaction. As a byproduct, probably caused by traces of oxygen or water impurities in the reaction mixture, a complex of composition $(C_5Me_5)_2Mo_2OS_3$ can be isolated, in which one terminal sulfur is replaced by a terminal oxygen as indicated by IR absorptions at 903 and 484 cm^{-1} , respectively. Correspondingly, two CH_3 resonances are found in the 1H NMR spectrum at 1.98 and 1.92 ppm. The color of $(C_5Me_5)_2Mo_2OS_3$ is green in contrast to the red color of compound $(C_5Me_5)_2Mo_2(\mu-S)_2O_2$, a color which is characteristic for other complexes with two sulfide bridges.^{14,15} This interconversion of bridging sulfur into terminal sulfur to our knowledge is unique for Mo-S cluster compounds. The reverse step has been demonstrated by the reaction of $[C_5Me_5Mo(\mu-S)]_2$ with H_2 , C_2H_4 , and C_2H_2 and is combined with a change of the metal oxidation state.^{16,17}

The same reaction starting from $[C_5Me_5(CO)_2W]_2$, II, gives after 17 h in 45% yield a green product, VI, of composition $(C_5Me_5)_2(CO)_2W_2S_3$ (IR $\nu_{C=O}$ 1933 and 1852 cm^{-1}). A strong IR vibration at 481 cm^{-1} indicates a terminal $W=S$ ligand, and the 1H NMR spectrum exhibits two inequivalent sets of methyl groups (δ ($CDCl_3$) 2.14, 2.07). These data as well as additional IR frequencies at 573, 518, 510, and 402 cm^{-1} are consistent with the structure established by an X-ray examination (vide infra). As a byproduct the green complex VII is formed in 8% yield.

VI reacts with an excess of sulfur in boiling toluene (15 h) with formation of two $(C_5Me_5)_2W_2S_4$ isomers. The green product VII is obtained in 18% yield (ν_{W-S} 486 cm^{-1} ; δ_{CH_3} ($CDCl_3$) 2.19) and the brown complex VIII in 54% yield (ν_{W-S} 481 cm^{-1} ; δ_{CH_3} ($CDCl_3$) 2.23). Substitution of both CO groups in *anti*- $(C_5Me_5)_2(CO)_2W_2S_3$, VI, leads to the formation of *anti*- $(C_5Me_5)_2W_2(\mu-S)_2S_2$. An anti structure with two S^{2-} bridges is also assumed for VIII on the basis of a color comparison with V.

It is not clear whether one S_2^{2-} bridge or two S^{2-} bridges are present in complex VII. The former seems to be more likely because of the similarity of the W compound VII with its Mo analogue IV: the green color as well as a shoulder at 473 cm^{-1} in the IR spectrum, absent in all the other compounds, is common for both complexes. Furthermore, the CH_3 resonances in the 1H NMR spectrum for both IV and VII are slightly shifted to a higher field when compared to those for V and VIII, respectively. In any case, synthesis of VII and VIII via VI starting from $[C_5Me_5(CO)_2W]_2$ represents a stepwise oxidation of the W atoms. However, the formation of VII from VI must be accompanied by an intramolecular redox process if a disulfide bridge is assumed in VII.

X-ray Diffraction Studies of $(C_5Me_5)_2Mo_2(\mu-S_2)(\mu-S)_2$, III, and $(C_5Me_5)_2(CO)_2W_2(\mu-S)_2S$, VI. ORTEP drawings of the molecular structure of III and VI are shown in Figures 1 and 3,

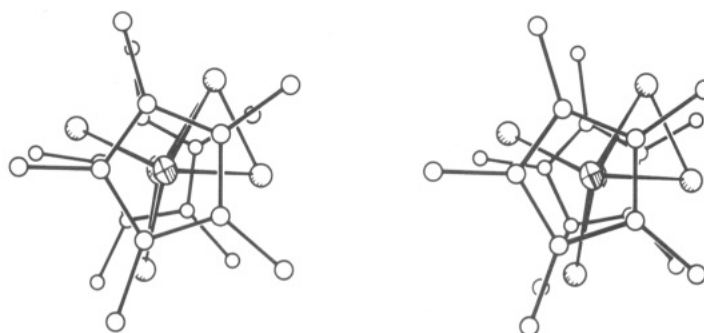


Figure 2. Stereoview of $(C_5Me_5)_2Mo_2(\mu-S_2)(\mu-S)_2$ viewed down along the metal axis.

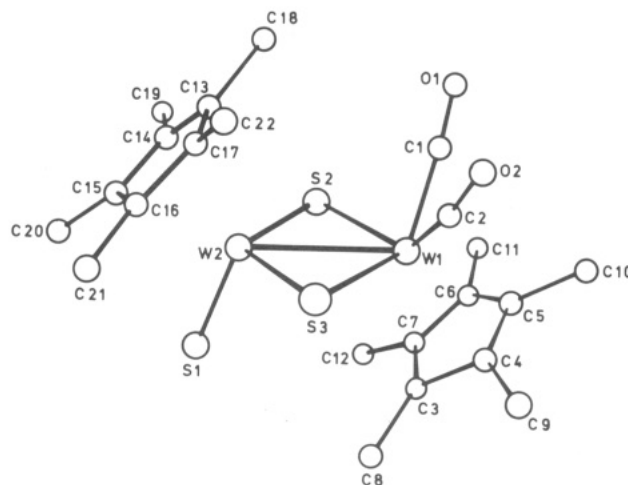


Figure 3. ORTEP drawing of the molecular structure of $(C_5Me_5)_2(CO)_2W_2(\mu-S)_2S$, VI.

respectively. Positional parameters and selected bond distances and angles for both structures are listed in Tables IV-VII.

$(C_5Me_5)_2Mo_2(\mu-S_2)(\mu-S)_2$ crystallizes from a mixture of toluene/pentane (2:1) in space group $P\bar{1}-C_1^1$ with molecular symmetry D_h . The dominating feature of the structure is the nearly square-planar arrangement of the four sulfur atoms, perpendicular to the metal-metal bond and parallel to the two $(\eta^5-C_5Me_5)$ planes. Two types of sulfur ligands are found: (i) a $\mu-\eta^2-S_2$ ligand, S-(3)-S(4), (ii) two $\mu-S^{2-}$ ligands, S(1) and S(2). The disulfide bridge is symmetric with an average metal-sulfur bond length of 2.446 Å and an M-S-M angle of 64.1°, which is in contrast to the asymmetric coordination of the disulfide bridges in the known examples of Mo cluster sulfides.¹⁸ The observed S-S bond length of 2.095 (7) Å is close to that in other S_2 complexes.¹⁹ The Mo-S bond lengths of S(1) and S(2) are only slightly longer than those in corresponding Mo(V) complexes (see Table VIII), but there is a remarkable reduction of the angle of the S^{2-} bridge from values about 76 to 66.8° in III. The same observation was made for the $\mu-S^{2-}$ group in $(CH_3C_5H_4)_2Mo_2(\mu-S)_2(\mu-SCH_3)_2$.¹⁶ Concomitantly a contraction of the metal-metal bond to 2.599 (2) Å is found.

This short distance is within the range typical for Mo=Mo bonds, like in a binuclear alkoxy-bridged Mo(IV) complex (d (Mo-Mo) = 2.523 (1) Å).²⁰ Another example of a Mo=Mo bond in a Mo(IV) complex has been proposed in bis((μ -sulfido)(thiocarboxamido)(di-*n*-propylthiocarbamate)molybdenum) with a distance of 2.705 (2) Å.²¹ Formation of a formal metal-metal double bond is further supported by electron bookkeeping in order to explain the diamagnetism of III. As can be concluded from Table VIII, the metal-metal interaction seems to be affected by

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Table V. Positional and Thermal Parameters of $(C_3Me_3)_2(CO)_2W_2(\mu-S)_2S$ and Their Estimated Standard Deviations

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U, A^2
W(1)	0.2841 (1)	-0.1871 (1)	0.4902 (2)	0.053 (1)	0.0327 (9)	0.036 (1)	-0.001 (1)	0.0041 (9)	-0.0030 (9)	0.0406 (6)
W(2)	0.2361 (1)	-0.0331 (1)	0.5033 (2)	0.044 (1)	0.0312 (8)	0.043 (1)	0.001 (1)	0.0079 (9)	0.0003 (8)	0.0394 (6)
S(1)	0.2084 (8)	-0.0013 (5)	0.7207 (13)	0.13 (1)	0.050 (7)	0.055 (8)	-0.004 (6)	0.038 (8)	0.015 (6)	0.077 (5)
S(2)	0.1392 (6)	-0.1243 (4)	0.4467 (13)	0.046 (6)	0.032 (5)	0.063 (8)	0.010 (6)	0.002 (6)	-0.002 (4)	0.048 (4)
S(3)	0.3791 (6)	-0.0825 (5)	0.5361 (14)	0.054 (7)	0.045 (6)	0.08 (1)	0.014 (7)	0.010 (7)	-0.006 (5)	0.061 (5)
atom	x	y	z	U_{11}	atom	x	y	z	U_{11}	
C(1)	0.240 (2)	-0.219 (2)	0.302 (4)	0.07 (1)	C(11)	0.475 (2)	-0.252 (2)	0.691 (5)	0.09 (1)	
O(1)	0.204 (2)	-0.237 (2)	0.187 (4)	0.12 (2)	C(12)	0.359 (2)	-0.157 (2)	0.870 (4)	0.06 (1)	
C(2)	0.370 (3)	-0.197 (3)	0.386 (6)	0.13 (2)	C(13)	0.288 (2)	0.068 (2)	0.403 (4)	0.06 (1)	
O(2)	0.433 (2)	-0.201 (2)	0.289 (4)	0.13 (1)	C(14)	0.191 (2)	0.080 (2)	0.414 (4)	0.04 (1)	
C(3)	0.227 (2)	-0.225 (2)	0.716 (4)	0.05 (1)	C(15)	0.140 (2)	0.031 (2)	0.321 (4)	0.05 (1)	
C(4)	0.218 (2)	-0.279 (2)	0.616 (4)	0.06 (1)	C(16)	0.205 (2)	-0.001 (2)	0.246 (5)	0.06 (1)	
C(5)	0.308 (2)	-0.294 (2)	0.587 (4)	0.06 (1)	C(17)	0.291 (2)	0.020 (2)	0.292 (4)	0.05 (1)	
C(6)	0.373 (2)	-0.253 (2)	0.668 (4)	0.037 (9)	C(18)	0.360 (2)	0.111 (2)	0.485 (5)	0.08 (1)	
C(7)	0.314 (2)	-0.206 (2)	0.759 (4)	0.04 (1)	C(19)	0.147 (3)	0.131 (2)	0.505 (5)	0.09 (1)	
C(8)	0.147 (2)	-0.193 (2)	0.787 (4)	0.042 (9)	C(20)	0.035 (2)	0.029 (2)	0.299 (5)	0.09 (1)	
C(9)	0.128 (2)	-0.313 (2)	0.552 (5)	0.11 (2)	C(21)	0.175 (5)	-0.052 (2)	0.122 (5)	0.12 (2)	
C(10)	0.342 (3)	-0.354 (2)	0.504 (6)	0.13 (2)	C(22)	0.379 (2)	0.008 (2)	0.229 (6)	0.10 (2)	
atom	x	y	z	atom	x	y	z			
H(8A) ^a	0.087 (2)	-0.211 (2)	0.749 (4)	H(18A)	0.391 (2)	0.070 (2)	0.521 (5)			
H(8B)	0.139 (2)	-0.149 (2)	0.834 (4)	H(18B)	0.354 (2)	0.143 (2)	0.566 (5)			
H(8C)	0.177 (2)	-0.225 (2)	0.860 (4)	H(18C)	0.393 (2)	0.133 (2)	0.413 (5)			
H(9A)	0.135 (2)	-0.332 (2)	0.456 (5)	H(19A)	0.204 (3)	0.156 (2)	0.514 (5)			
H(9B)	0.070 (2)	-0.288 (2)	0.546 (5)	H(19B)	0.134 (3)	0.116 (2)	0.602 (5)			
H(9C)	0.127 (2)	-0.350 (2)	0.624 (5)	H(19C)	0.098 (3)	0.162 (2)	0.463 (5)			
H(10A)	0.396 (3)	-0.343 (2)	0.457 (6)	H(20A)	0.003 (2)	0.073 (2)	0.289 (5)			
H(10B)	0.290 (3)	-0.358 (2)	0.429 (6)	H(20B)	-0.001 (2)	-0.005 (2)	0.343 (5)			
H(10C)	0.352 (3)	-0.397 (2)	0.556 (6)	H(20C)	0.047 (2)	0.014 (2)	0.201 (5)			
H(11A)	0.511 (2)	-0.211 (2)	0.694 (5)	H(21A)	0.208 (3)	-0.041 (2)	0.040 (5)			
H(11B)	0.592 (2)	-0.283 (2)	0.614 (5)	H(21B)	0.110 (3)	-0.056 (2)	0.086 (5)			
H(11C)	0.485 (2)	-0.276 (2)	0.786 (5)	H(21C)	0.196 (3)	-0.095 (2)	0.166 (5)			
H(12A)	0.408 (2)	-0.126 (2)	0.850 (4)	H(22A)	0.371 (2)	-0.042 (2)	0.222 (6)			
H(12B)	0.385 (2)	-0.194 (2)	0.932 (4)	H(22B)	0.415 (2)	0.019 (2)	0.320 (6)			
H(12C)	0.316 (2)	-0.132 (2)	0.920 (4)	H(22C)	0.409 (2)	0.023 (2)	0.146 (6)			

^a $U_{11} = 0.40 (2)$.

Table VI. Selected Bond Lengths (*d*, Å) and Bond Angles (ω , Deg) for (η -C₅Me₅)₂Mo₂(μ -S₂)(μ -S)₂

Bond Lengths (<i>d</i>)					
Mo(1)-Mo(2)	2.599 (2)	Mo(1)-S(4)	2.449 (5)	Mo(1)-C(5)	2.34 (1)
Mo(1)-S(1)	2.361 (4)	Mo(1)-C(1)	2.31 (1)	Mo(1)-C(7)	2.38 (2)
Mo(1)-S(2)	2.353 (4)	Mo(1)-C(3)	2.33 (1)	Mo(1)-C(9)	2.36 (2)
Mo(1)-S(3)	2.446 (4)				
Mo(2)-S(1)	2.362 (5)	Mo(2)-S(4)	2.443 (4)	Mo(2)-C(15)	2.37 (2)
Mo(2)-S(2)	2.362 (4)	Mo(2)-C(11)	2.29 (2)	Mo(2)-C(17)	2.34 (1)
Mo(2)-S(3)	2.448 (5)	Mo(2)-C(13)	2.33 (2)	Mo(2)-C(19)	2.33 (1)
S(3)-S(4)	2.095 (7)	S(1)-S(3) ^a	3.054	S(2)-S(4) ^a	3.039
S(1)-S(2) ^a	3.098				
Bond Angles (ω)					
Mo(1)-Mo(2)-S(1)	56.6 (1)	Mo(1)-Mo(2)-S(4)	58.0 (1)	Mo(2)-Mo(1)-S(3)	58.0 (1)
Mo(1)-Mo(2)-S(2)	56.4 (1)	Mo(2)-Mo(1)-S(1)	56.6 (1)	Mo(2)-Mo(1)-S(4)	57.8 (1)
Mo(1)-Mo(2)-S(3)	57.9 (1)	Mo(2)-Mo(1)-S(2)	56.7 (1)		
Mo(1)-S(1)-Mo(2)	66.8 (1)	Mo(1)-S(3)-Mo(2)	64.1 (1)	Mo(1)-S(3)-S(4)	64.7 (2)
Mo(1)-S(2)-Mo(2)	66.9 (1)	Mo(1)-S(4)-Mo(2)	64.2 (1)	Mo(2)-S(3)-S(4)	64.5 (2)
S(1)-Mo(1)-S(2)	82.2 (1)	S(1)-Mo(2)-S(3)	78.8 (2)	S(2)-Mo(2)-S(3)	111.2 (1)
S(1)-Mo(1)-S(3)	78.9 (1)	S(1)-Mo(2)-S(4)	111.6 (2)	S(2)-Mo(2)-S(4)	78.4 (1)
S(1)-Mo(1)-S(4)	111.4 (2)	S(2)-Mo(1)-S(3)	111.6 (2)	S(3)-Mo(1)-S(4)	50.7 (2)
S(1)-Mo(2)-S(2)	82.0 (1)	S(2)-Mo(1)-S(4)	78.5 (2)	S(3)-Mo(2)-S(4)	50.7 (2)

^a Nonbonded distances.Table VII. Selected Bond Lengths (*d*, Å) and Bond Angles (ω , Deg) for (η -C₅Me₅)₂W₂(CO)₂(μ -S)₂S

Bond Lengths (<i>d</i>)					
W(1)-W(2)	3.045 (2)	W(1)-C(2)	1.66 (6)	W(2)-S(2)	2.272 (9)
W(1)-S(2)	2.430 (9)	W(1)-Cp'(cent)	2.02 (4)	W(2)-S(3)	2.285 (9)
W(1)-S(3)	2.450 (10)	W(2)-S(1)	2.13 (1)	W(2)-Cp'(cent)	2.06 (4)
W(1)-C(1)	1.85 (4)				
Bond Angles (ω)					
W(1)-W(2)-S(1)	112.6 (3)	W(2)-W(1)-S(2)	47.4 (2)	W(2)-W(1)-Cp'(cent)	128.2 (8)
W(1)-W(2)-S(2)	51.9 (2)	W(2)-S(1)-S(3)	47.6 (2)	W(1)-S(2)-W(2)	80.7 (3)
W(1)-W(2)-S(3)	52.4 (2)	W(2)-W(1)-C(1)	108 (1)	W(1)-S(3)-W(2)	80.0 (3)
W(1)-W(2)-Cp'(cent)	131.0 (8)	W(2)-W(1)-C(2)	109 (2)		
S(2)-W(1)-S(3)	95.0 (3)	S(1)-W(2)-S(2)	104.2 (4)	S(2)-W(2)-S(3)	104.3 (3)
C(1)-W(1)-C(2)	70 (2)	S(1)-W(2)-S(3)	105.8 (4)		

Table VIII. Relevant Structural Parameters of Selected Sulfido-Bridged Molybdenum Complexes

complex ^a	M-M, Å	M-S(bridge), Å	M-S-M, deg	ref
Cp ₂ Mo ₂ (μ -S) ₂ S ₂	2.905 (1)	2.297 (2)	78.38 (6)	14
<i>syn</i> -[Mo ₂ (μ -S) ₂ S ₂ (S ₂ C ₂ H ₄) ₂] ²⁻	2.863 (2)	2.320 (3)	76.22 (9)	22
<i>anti</i> -[Mo ₂ (μ -S) ₂ S ₂ (S ₂ C ₂ H ₄) ₂] ²⁻	2.878 (2)	2.321 (2)	76.72 (7)	22
Mo ₂ (μ -S) ₂ (η^2 -SCNR ₂) ₂ (S ₂ CNR ₂) ₂ (R = n-C ₃ H ₇)	2.705 (2)	2.242 (2), 2.340 (2)	72.3 (1)	21
(CH ₃ C ₃ H ₄) ₂ Mo ₂ (μ -S) ₂ (μ -SCH ₃) ₂	2.582 (1)	2.352 (2)	66.58 (6)	16
Cp ₂ Mo ₂ (μ -S ₂)(μ -S) ₂	2.599 (2)	2.357 (4)	66.8 (1)	this work

^a Cp' = η^5 -C₅Me₅.

the formal oxidation state of the metal, as well as by the nature of the sulfur bridges. The incorporation of one disulfide and two sulfide bridges in molecule III, which consequently leads to the formation of a relative short metal-metal bond, is quite unusual in the chemistry of group 6B metal sulfides. In this way the unfavorable Mo(V) configuration with four sulfide bridges has been avoided.¹⁷ An analogous principle was recently found in (C₅Me₅)₂Cr₂S₅ with the only exception that one μ -S²⁻ ligand is replaced by an η^1 (μ -S,S) ligand.⁷

(C₅Me₅)₂(CO)₂W₂(μ -S)₂S crystallizes from a mixture of toluene/pentane (1:1) as dark green spears in space group C_{2h}⁵-P2₁/n. The characteristic feature of the structure is the anti arrangement of all nonbridging ligands around the W₂(μ -S)₂ plane, leaving both tungsten atoms in different coordination states. The originally bridging carbonyls are converted into terminal functions on one side (W(1)) of the molecule, whereas on the other side (W(2)) there is only one terminal sulfur ligand. If a direct W-W bond is postulated, although the found distance of 3.045 (2) Å is very long compared to known values of S²⁻-bridged W(IV) complexes,²³ the

two tungsten atoms achieve d¹⁶ and d¹⁸ electron configuration, respectively. This mixed-valence state is balanced by the sulfide bridges: S(2) and S(3) are bonded more closely to the "electron-deficient" center W(2) (mean 2.278 Å) than to W(1) (mean 2.440 Å). The W-S-W angle (average 80.3°) still seems indicative of a direct bond between the metal atoms.

Registry No. I, 12132-04-6; II, 70634-77-4; III, 82167-40-6; IV, 82167-39-3; V, 78085-81-1; VI, 82167-38-2; VII, 82167-37-1; VIII, 82167-36-0; S, 7704-34-9; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Tables of observed and calculated structure factors and bond distances and angles for compounds III and VI (29 pages). Ordering information is given on any current masthead page.