

an unstable CpMo(CO)(η^4 -2-haloallyl) intermediate and are continuing our investigation of these processes.

As found with CpMo(CO)₂(2-methallyl),¹⁴ two conformers of CpMo(CO)(PPh₃)L are in rapid equilibrium at room temperature. In the dicarbonyl case, a strong steric interaction of the methyl with the Cp ring produces a substantial preference of endo to exo conformer. The expected tilting of the allyl¹⁵ so that it aligns with the Mo-P bond

relieves this interaction and produces more nearly equal concentrations of conformers.

Acknowledgment. We wish to thank the National Science Foundation for support of this work.

Registry No. 1, 103751-81-1; 1', 103751-88-8; 2, 103751-82-2; 2', 103751-89-9; 3, 103751-83-3; 4, 103751-85-5; 5, 103776-04-1; 6, 103751-87-7; 7, 103776-05-2; CpMo(CO)₂(η^3 -2-chloroallyl), 35208-92-5; CpMo(CO)₂(η^3 -2-bromoallyl), 35208-93-6; CpMo(CO)₂(η^3 -2-methylallyl), 12307-49-2.

Supplementary Material Available: Tables of complete data collection parameters, the values of the fractional coordinates, bond lengths and angles, and anisotropic thermal parameters (5 pages); a listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Reactions of Bimetallic Group VI (6⁺) Complexes. 3.¹ Synthesis, Characterization, and Reactivity of Dimeric Molybdenum(III) and Tungsten(III) Compounds with Bridging Thiolate Ligands. A Molybdenum-95 NMR Study on Dinuclear Molybdenum Complexes. Crystal Structure of [Mo^{III}₂(η^5 -C₅H₅)₂(SMe)₃(CO)₂]Br·H₂O

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Received November 12, 1985

Cationic tris(thiolato)-bridged dimolybdenum(III) and ditungsten(III) complexes [M₂(CO)₂(μ -SMe)₃(η^5 -C₅H₅)₂]X (1, M = Mo, 2, M = W; X = Cl, Br) are formed by treating [(η^5 -C₅H₅)(CO)₂M(μ -SMe)₂M(CO)₂(η^5 -C₅H₅)] with dimethyl disulfide in the presence of allyl halides. The corresponding BF₄⁻ and PF₆⁻ salts have been prepared by metathetical reactions. The bromide salt of 1, [Mo₂(CO)₂(μ -SMe)₃(η^5 -C₅H₅)₂]Br·H₂O, has been characterized by an X-ray diffraction study. Crystals are triclinic of space group P1̄ with two molecules in a unit cell of dimensions $a = 9.209$ (2) Å, $b = 10.203$ (2) Å, $c = 11.706$ (2) Å, $\alpha = 106.73$ (2)°, $\beta = 101.31$ (2)°, and $\gamma = 93.58$ (2)°. The structure has been solved by direct methods and refined by least squares to $R = 0.070$ for 1472 independent diffractometer-measured reflection intensities. The structure shows that 1 contains three μ -SMe ligands. The Mo-Mo bond length is 2.785 (2) Å, and two unusually short nonbonded contacts (3.00 (1) and 2.80 (1) Å) between the bridging sulfur atoms are observed. An ⁹⁵Mo NMR study suggests that the positive charge is located on one sulfur atom in 1. The reactivity of the new dimers toward nucleophiles has been studied, yielding dimeric compounds [(η^5 -C₅H₅)(CO)M(μ -SMe)₂M(CO)(η^5 -C₅H₅)] (M = Mo). Thermal treatment of 1 gives neutral products [(η^5 -C₅H₅)M(μ -SMe)₃(μ -X)M(η^5 -C₅H₅)] (M = Mo; X = Cl, Br). On photolysis in CH₂X₂ (X = Cl, Br) complexes 1 or 2 are transformed into dimeric species [(η^5 -C₅H₅)X(CO)M(μ -SMe)₂MX(CO)(η^5 -C₅H₅)] (M = Mo, W; X = Cl, Br). The reactivity of the sulfur donor ligands in dimolybdenum compounds resulting from 1 has also been examined. Molybdenum-95 spectra have been recorded for a series of dinuclear molybdenum complexes, and a new chemical shift range for molybdenum(III) and molybdenum(IV) is given.

Introduction

Thiolate-molybdenum or -tungsten complexes are of current interest, both because of their biological³ and

catalytic⁴ implications and also because thiols and thiolate anions undergo a variety of reactions with metal species. As a result, a wide range of binuclear molybdenum or

¹In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The *d*-transition elements comprise groups 3 through 12, and the *p*-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Table I. Spectroscopic Data (Room Temperature)

compd	IR $\nu(\text{CO})$, ^a cm ⁻¹	¹ H NMR δ	solv	¹³ C{ ¹ H} NMR δ	solv
1a	2010 (s), 1980 (w, sh)	5.87, 5.85, 2.59, 2.55, 2.41, 1.71, 1.69, 1.67	c	232.9 (s, ^d CO), 94.2 (s, Cp), 27.9 (s, CH ₃), 27.3 (s, CH ₃), 9.26 (s, CH ₃)	c
1c ₁	1995 (s), 1970 (w, sh)	5.74 (s, ^d 10 H), 2.56 (s, 3 H), 2.51 (s, 3 H), 1.57 (s, 3 H)	c	232.6 (s, CO), 94.2 (s, Cp), 28.05 (s, CH ₃), 27.35 (s, CH ₃), 9.30 (s, CH ₃)	c
1c ₂	1995 (s), 1970 (w, sh)	6.00 (s, 10 H), 2.67 (s, 3 H), 2.64 (s, 3 H), 1.75 (s, 3 H)	b	232.8 (s, CO), 94.3 (s, Cp), 28.0 (s, CH ₃), 27.3 (s, CH ₃), 9.26 (s, CH ₃)	c
1d	1995 (s), 1975 (w, sh)	5.79 (s, 10 H), 2.60 (s, 3 H), 2.56 (s, 3 H), 1.62 (s, 3 H)	c	94.2 (s, Cp), 27.95 (s, CH ₃), 27.25 (s, CH ₃), 9.15 (s, CH ₃)	c
1e	2005 (s), 1980 (w, sh)	5.80 (s, 10 H), 2.61 (s, CH ₃), 2.56 (s, CH ₃), 1.62 (s, CH ₃)	c	232.8 (s, CO), 94.25 (s, Cp), 27.95 (s, CH ₃), 27.25 (s, CH ₃), 9.15 (s, CH ₃)	c
2a	1985 (s), 1950 (w, sh)	5.95 (s, 10 H), 2.86 (s, 3 H), 2.80 (s, 3 H), 1.83 (s, 3 H)	b	222.4 (s, CO), 90.27 (s, Cp), 89.86 (s, Cp), 31.4 (s, CH ₃), 29.9 (s, CH ₃), 9.52 (s, CH ₃)	b
2b	1995 (s)	5.96 (s, 10 H), 2.83 (s, 3 H), 2.80 (s, 3 H), 1.83 (s, 3 H)	b		
5a	2000 (s), 1990 (m)	5.33 (s, 10 H), 2.43 (s, 6 H)	b	229.4 (s, CO), 95.25 (s, Cp), 21.04 (s, CH ₃)	b
5b	1990 (s), 1960 (m)	5.17 (s, 10 H), 2.49 (s, 6 H)	b	229.4 (s, CO), 94.70 (s, Cp), 23.37 (s, CH ₃)	b
5c		5.39 (s, 10 H), 2.59 (s, 6 H)	b	95.18 (s, Cp), 20.60 (s, CH ₃)	b
6a	1995 (s), 1965 (m)	5.38 (s, 10 H), 2.38 (s, 6 H)	b	223.5 (s, CO), 92.4 (s, Cp), 22.6 (s, CH ₃)	b
6b	1990 (s), 1965 (m)	5.42 (s, 10 H), 2.63 (s, 6 H)	b	222.2 (s, CO), 92.1 (s, Cp), 25.46 (s, CH ₃)	b
7a		5.35 (s, 10 H), 1.66 (s, 3 H), 1.50 (s, 3 H), 1.45 (s, 3 H)	b	93.19 (s, Cp), 93.07 (s, Cp), 29.7 (s, CH ₃), 14.5 (s, CH ₃), 12.6 (s, CH ₃)	b
7b		5.38 (s, 10 H), 1.72 (s, 3 H), 1.57 (s, 3 H), 1.50 (s, 3 H)	b	92.95 (s, Cp), 92.59 (s, Cp)	b

^aCH₂Cl₂. ^bCDCl₃. ^cCD₃CN. ^dSinglet.

tungsten compounds with sulfur ligands have been prepared, and among them the doubly⁵ and quadruply⁶ bridged complexes are well-known. In contrast, fewer triply bridged species have been studied. Of these there are relatively few structural studies of molybdenum or tungsten compounds in which the metal atoms are bridged exclusively by sulfur atoms. Recently the crystal and molecular structures of such complexes of molybdenum- or tungsten(V),⁷ molybdenum or tungsten(IV),⁸ or mixed oxidation states (III/I)⁹ and (IV/III)¹⁰ have been reported.

As part of our continuing interest in developing a novel molybdenum or tungsten thiolato chemistry, we have undertaken a study on the oxidation reactions of group VI (6) derivatives. Oxidative-addition reactions have been extensively studied as models for the homogeneous metal-assisted catalytic transformation of organic substrates. We have found that the hydride or halide complexes [CpMo(CO)₃X] (X = H, Br) (Cp = η^5 -C₅H₅) or the dimeric compounds [Cp(CO)₂M(μ -SR)₂M(CO)₂Cp] (M = Mo, W) react with alkyl or aryl disulfides, R-S-S-R, in the presence of an allyl halide to yield oxidized species 1 (M = Mo) or 2 (M = W), originally formulated, from spectroscopic studies, as derivatives containing a bridging halide.¹¹ We have now carried out an X-ray crystallographic structural determination on one of the compounds (1), previously described as [Cp(CO)(SR)Mo(μ -SR)(μ -Br)Mo(SR)(CO)-Cp], and find that instead of being a dibridged structure, it is in fact a triply bridged molybdenum(III) compound. Complexes 1 and 2 should therefore be formulated as [Cp(CO)M(μ -SR)₃M(CO)Cp]⁺X⁻. To our knowledge these

are the first examples of two [(C₅H₅)M^{III}] (M = Mo, W) units bridged by three sulfur atoms.

The synthesis of novel molybdenum complexes provided an opportunity to use ⁹⁵Mo NMR to gain important structural information. Applications of molybdenum-95 NMR, well-known for a few compounds of high symmetry,¹² have now been demonstrated for a variety of less symmetric mononuclear Mo(0),¹³ Mo(II),^{14a,b} Mo(IV),^{15,16} and Mo(VI)¹⁷ compounds, but until recently very little has been reported^{14,16} on ⁹⁵Mo NMR of di- or polynuclear molybdenum complexes. This is also, to our knowledge, the first study of molybdenum(III) systems by ⁹⁵Mo NMR.

A brief communication of a part of this work has already appeared.¹⁸

Results and Discussion

Oxidation Reactions of Dimeric Molybdenum(II) and Tungsten(II) Compounds. Syntheses and Characterization of Triply Bridged Molybdenum(III) and Tungsten(III) Complexes. Thermal treatment of the complexes [Cp(CO)₂M(μ -SMe)₂M(CO)₂Cp] (M = Mo, W) in tetrahydrofuran with an excess of dimethyl disulfide and an allyl halide led to the ready formation, in good yields, of the novel cationic species 1 or 2 which could be isolated as the halide salts (reaction 1). The materials behave as 1:1 electrolytes in nitromethane. These compounds were characterized by IR and NMR spectra (Table I) and elemental analyses (Experimental Section) and an X-ray

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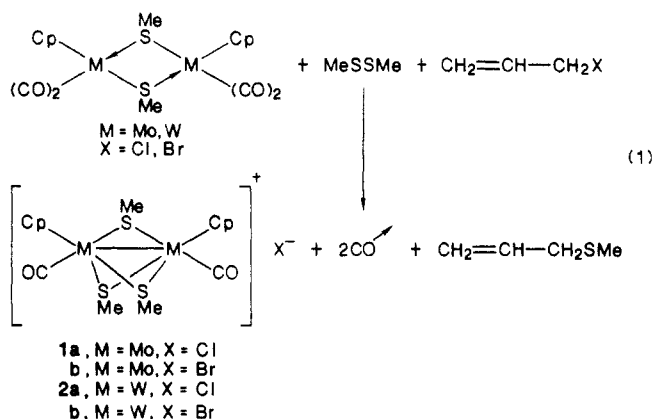
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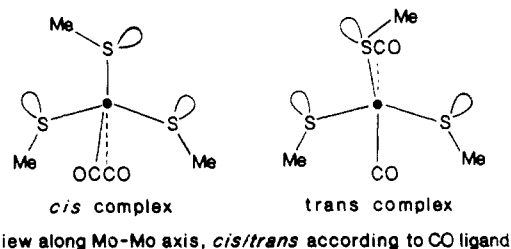
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diffraction study was performed on **1b**. The products of these oxidation reactions are quite insoluble in tetrahydrofuran but are readily soluble in dichloromethane, acetonitrile, or nitromethane.



The pattern of $\nu(\text{CO})$ absorptions for **1** and **2** is, as expected for cationic species, shifted to higher frequencies relative to values for the neutral starting compounds. These IR spectra, recorded in dichloromethane solutions, invariably show a strong carbonyl-stretching band accompanied by a shoulder (Table I). Clearly, this feature must be due to the presence at room temperature of more than one isomer of each complex. Two sets of isomers are possible: cis and trans configurations and isomers due to the relative orientations of the Me groups and lone pairs on bridging sulfur. ^1H NMR spectra of **1** and **2** at room



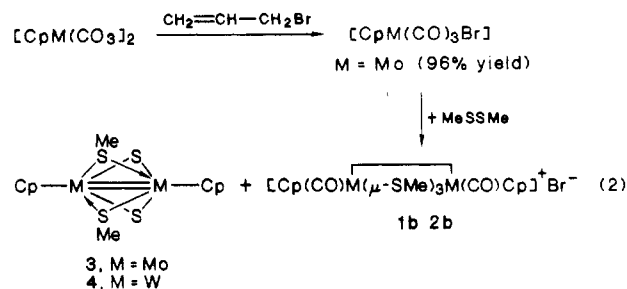
temperature confirm the existence of two isomers, A and B, in acetonitrile- d_3 solution. At low temperature, between -40 and 5°C , only one isomer, A, is present. The ^1H NMR spectrum of **1a** at $+5$ and $+76^\circ\text{C}$ is presented in Figure 1. At 5°C there are three methyl group signals of equal intensity; this pattern is similar to those observed previously for tris(thiolato)-bridged dimolybdenum complexes^{9b,11} confirming such a geometry for compounds **1** and **2**. When the NMR sample is warmed to 76°C , isomer A converts irreversibly into isomer B. At room temperature, the NMR spectrum of complex **1a** exhibits two sets of signals at δ 5.87 (Cp), 2.59, 2.55, and 1.67 (SMe) which correspond to isomer A and at δ 5.85 (Cp), 2.41, 1.71, and 1.69 (SMe) corresponding to isomer B. From their relative intensities, the ratio of A to B at room temperature is 5:1, and it declines to 2.5:1 at 76°C . This isomerization is not fast on the NMR time scale between -40 and $+76^\circ\text{C}$. The interconversion of isomers differing in the orientations of the methyl groups and lone pairs on bridging sulfur are usually rapid on the NMR time scale. Thus, these features suggest that the interconversion of A and B is due to cis-trans isomerization of the carbonyl groups. Since the crystals of **1b** for X-ray determination were obtained at low temperature (-30°C) and the carbonyls were found to adopt a cis orientation, we assign the cis configuration to isomer A.

An alternative preparative route to the tris(thiolato)-bridged dimolybdenum(III) or tungsten(III) complexes utilizes the reaction between bromide complexes $[\text{CpM}(\text{CO})_3\text{Br}]$ (M = Mo, W) and dimethyl disulfide (reaction 2). This route gives lower yields than that described in



Figure 1. ^1H NMR spectra of **1a** at $+5$ and $+76^\circ\text{C}$ (in CD_3CN).

$(\text{CO})_3\text{Br}]$ (M = Mo, W) and dimethyl disulfide (reaction 2). This route gives lower yields than that described in

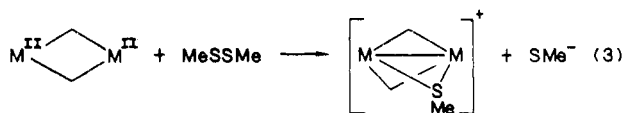


reaction 1, except for **2b** for which higher yields (15–20%)

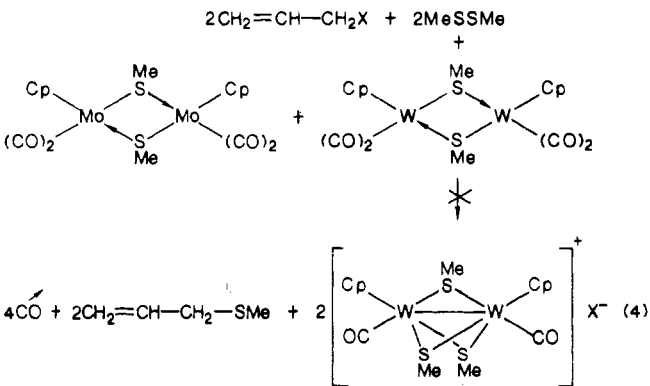
are obtained according to reaction 2 (see experimental Section). When $[\text{CpM}(\text{CO})_3\text{Br}]$ is reacted with dimethyl disulfide, quadruply bridged compounds 3 ($M = \text{Mo}$) and 4 ($M = \text{W}$) are also formed, and, if the gaseous products of the reactions are removed periodically, they become the major products (65–80% yield). The molybdenum species 3 has already been described,¹⁹ but to our knowledge 4 ($M = \text{W}$) is new. 4 has been identified by comparison of its spectral data with those of the molybdenum complex $[\text{CpMo}(\mu\text{-S})_2(\mu\text{-SMe})_2\text{MoCp}]$; the NMR data provide evidence of two isomers in solution in the ratio of 1:3.

In reaction 2, both 1 and 2 are most likely produced by initial formation of $[\text{Cp}(\text{CO})_2\text{M}(\mu\text{-SMe})_2\text{M}(\text{CO})_2\text{Cp}]$ followed by oxidative addition of MeSSMe according to reaction 1. This pathway is supported by the fact that higher yields are obtained when the reactants are the dimeric complexes $[\text{Cp}(\text{CO})_2\text{M}(\mu\text{-SMe})_2\text{M}(\text{CO})_2\text{Cp}]$ rather than $[\text{CpM}(\text{CO})_3\text{X}]$ ($X = \text{H}$ or Br). In other respects, it is obvious that the oxidizing agent in reactions 1 and 2 is dimethyl disulfide, since the reaction of $[\text{Cp}(\text{CO})_2\text{M}(\mu\text{-SMe})_2\text{M}(\text{CO})_2\text{Cp}]$ ($M = \text{Mo}$) with $\text{CH}_2=\text{CHCH}_2\text{X}$ in refluxing tetrahydrofuran yields a compound with IR and NMR spectra quite different to those of 1. Therefore, it is clear that allyl halide is acting only as a halide source in reaction 1.

Presumably addition of dimethyl disulfide to the M^{II} dimer results in metal–metal bond formation as represented by eq 3, i.e., with a unit increase in the formal



oxidation number of each metal center. Formation of a metal–metal bond in this way represents a classical response²⁰ of a binuclear metal complex to oxidative addition, the opposite of that demonstrated by multiply bonded analogues for which identical chemistry occurs with a reduction in bond order.²¹ Attempts to synthesize the heterodinuclear complexes $[\text{Cp}(\text{CO})\text{Mo}(\mu\text{-SMe})_3\text{W}(\text{CO})\text{Cp}]^+\text{X}^-$ by reacting a mixture (1:1) of $[\text{Cp}(\text{CO})_2\text{Mo}(\mu\text{-SMe})_2\text{Mo}(\text{CO})_2\text{Cp}]$ and $[\text{Cp}(\text{CO})_2\text{W}(\mu\text{-SMe})_2\text{W}(\text{CO})_2\text{Cp}]$ with dimethyl disulfide and allyl halide failed (eq 4). This result excludes a mechanism for the formation of 1 or 2 involving mononuclear intermediates arising from the cleavage of two metal–sulfur bonds.



X-ray Diffraction Study of $[\text{Cp}(\text{CO})\text{Mo}(\mu\text{-SMe})_3\text{Mo}(\text{CO})\text{Cp}]^+\text{Br}^- \cdot \text{H}_2\text{O}$ (1b)

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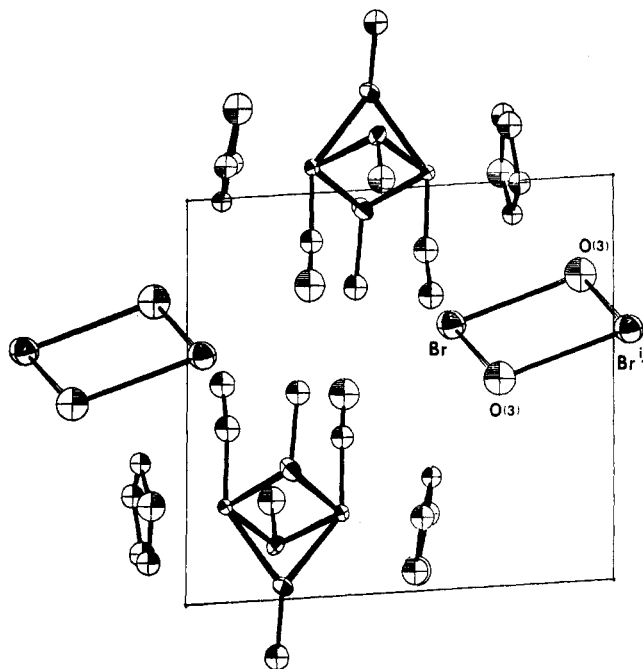


Figure 2. Orthogonal projection of the structure of the (001) plane. Two equivalences by an inversion center bimetallic cations are located; aggregates $\text{Br}_2(\text{OH})_2$ are represented by their hydrogen bonds around a center of inversion.

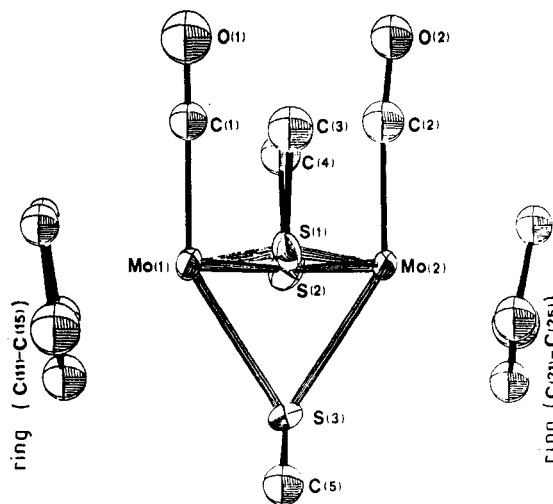


Figure 3. ORTEP view of the bimetallic species. The atoms are described enclosing 30% probability ellipsoids or spheres.

$[\text{Cp}(\text{CO})\text{Mo}(\mu\text{-SMe})_3\text{Mo}(\text{CO})\text{Cp}]^+\text{Br}^- \cdot \text{H}_2\text{O}$ (1b). The complex crystallizes in space group $P\bar{1}$ with two molecules per unit cell. The crystal structure of 1b consists of the binuclear cation tris(μ -methanethiolato)bis[carbonyl(η^5 -cyclopentadienyl)molybdenum(III)] and of uncoordinated bromide ion which is linked to two water molecules [O(3)] of crystallization. The packing of these ions is displayed on the orthogonal projection on the (001) plane (Figure 2). The bimetallic group is described along with the atom numbering in the ORTEP view (Figure 3). Positional and thermal parameters and selected bond distances and angles are listed in Tables II and III, respectively.

The core of the cationic fragment is defined by three sulfur atoms which bridge the two molybdenum atoms, each sulfur atom being linked to a methyl group. The remaining coordination positions of each molybdenum atom are filled by one carbonyl group and one cyclopentadienyl ligand. The nearly planar cyclopentadienyl rings lie outside of the sandwiched bimetallic core. This structure type could be regarded as two strongly distorted pyramids

Table II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2, \times 10^4$) with Estimated Standard Deviations^{a,b}

atom	x	y	z	U_{eq}
Mo1	8518 (2)	4378 (2)	2177 (2)	313 (11)
Mo2	8245 (2)	1715 (2)	2355 (2)	317 (11)
Br	5612 (4)	2616 (4)	6547 (4)	971 (25)
S1	8791 (6)	2294 (6)	572 (6)	428 (35)
S2	7858 (6)	3780 (6)	3899 (6)	462 (37)
S3	10557 (6)	3363 (6)	3165 (6)	422 (34)
C1	6431 (26)	4119 (23)	1351 (22)	447 (59)
O1	5198 (23)	3979 (20)	802 (18)	766 (59)
C2	6126 (24)	1495 (21)	1600 (20)	446 (53)
O2	4850 (20)	1218 (18)	1105 (16)	616 (50)
C3	7250 (30)	1719 (27)	-785 (25)	572 (70)
C4	5941 (31)	3966 (29)	3963 (26)	664 (78)
C5	12029 (33)	2952 (30)	2316 (27)	701 (83)
C11	7836 (27)	6553 (25)	2385 (24)	525 (69)
C12	8402 (27)	6097 (25)	1282 (24)	561 (69)
C13	9932 (32)	5986 (29)	1662 (27)	545 (75)
C14	10286 (26)	6351 (23)	2848 (22)	506 (58)
C15	9090 (31)	6701 (27)	3420 (27)	675 (76)
C21	7221 (27)	-139 (23)	2819 (23)	566 (61)
C22	7668 (23)	-650 (21)	1712 (20)	438 (52)
C23	9164 (30)	-382 (27)	1834 (25)	623 (70)
C24	9753 (30)	213 (27)	3076 (26)	642 (73)
C25	8529 (27)	467 (27)	3763 (25)	601 (70)
O3	3426 (27)	561 (25)	3864 (22)	1090 (76)

^a For Mo, Br, and S atoms, the thermal factor was of the form $T = \exp[-2(U_{11}h^2a^* + \dots + 2U_{12}hka^*b^* + \dots)]$ and $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$. ^b For other atoms, $U_{eq} = U_{isotropic}$.

connected via three sulfur bridges.

The nonbonded distances within the cationic fragment are, in general, in agreement with accepted van der Waals limits with two outstanding exceptions; viz., the sulfur atoms S(1) and S(3) and S(2) and S(3) are within 3.00 and 2.80 Å of each other, respectively. A similar feature has been noted previously between two bromine atoms by McCarley co-workers²² in the complexes $[(SC_4H_8)Br_2M(\mu-Br)_2(\mu-SC_4H_8)MBr_2(SC_4H_8)]$ ($M = Nb, Ta$) and between two pairs of sulfur atoms by Knox and co-workers^{9b}

in $\{(\eta^7-C_7H_7)Mo(\mu-S-t-Bu)_3Mo(CO)_2[P(OMe)_3]\}$. It seems likely that the distortion from equal separations of the bridging atoms is mainly a function of the lowering in symmetry from a pure square-pyramidal geometry. Consistent with this are the $\sim 88^\circ$ angles S(1)-Mo-CO and S(2)-Mo-CO and the $\sim 145^\circ$ angle S(3)-Mo-CO which are smaller than expected for a pure pyramid. The compression of the S(2)⋯S(3) distance is large and comparable to the sulfur-sulfur interaction found by Stiefel et al.²³ in $\{MoO_2[SC(CH_3)_2CH_2NH(CH_3)]_2\}$. Nevertheless the 2.80-Å separation is at least 0.5 Å too long to allow us to entertain the idea of a bond between those sulfur atoms; the S-S bond length in a dialkyl disulfide complex is about 2.1 Å.²⁴

The sulfur ligands bridge symmetrically, the molybdenum-sulfur distances falling within the range 2.439 (6)-2.470 (5) Å, which correspond to values typically found for sulfur atoms bridging two molybdenum atoms.²⁵ The CH_3 groups have a syn configuration on S(1) and S(2), and the Mo(1), S(1), S(2), and Mo(2) atoms are coplanar. The

carbonyl groups are in a cis configuration with respect to the Mo(1)-S(1)-S(2)-Mo(2) plane and are perpendicular to that plane; their Mo-C and C-O distances are in the range 1.93-1.94 and 1.17-1.18 Å, respectively, and compare well with those found in related molybdenum complexes.^{1,25a} The C(3) and C(4) atoms and the carbonyl groups lie above the Mo(1)-S(1)-S(2)-Mo(2) plane, whereas S(3) lies beneath it. The Mo(1)⋯Mo(2) vector is nearly perpendicular to the bisector mirror of the two cyclopentadienyl rings. One feature of this structure is near linearity of the Cp-Mo-Mo-Cp axis, such a linearity was also observed in the metal-metal triple-bond compound $[Cp_2Mo_2(CO)_4]$.²⁶

The Mo-Mo separation, 2.785 Å, is consistent with a Mo-Mo single bond.²⁷ This can be compared with 3.940 Å in $[Cp(CO)_2Mo(\mu-SPh)_2Mo(CO)_2Cp]$,^{25a} in which no metal-metal bond is required. The Mo-S-Mo angles subtended at the μ -S atoms (Table III) are acute ($\sim 69^\circ$) and are comparable to those required for a structure in which metal-metal attraction exists (see Table IV). These are complemented by the obtuse angle S(1)-Mo-S(2) ($\sim 110.7^\circ$). The anomalous angles are those involving S(2)-Mo-S(3) ($\sim 70^\circ$) and S(3)-Mo-S(1) ($\sim 75^\circ$) which are much lower than the expected values for a bimetallic-pyramidal structure.

Compound **1b** is the first example of a triply bridged binuclear structure in which the two molybdenum(III) are bridged by three SR groups. Table IV compares known molybdenum and tungsten dimers involving quadruple, triple, double, or single bridges. It appears that the longest Mo⋯Mo distance for metal-metal bonded compounds occurs in low-valent and doubly bridged species and the shortest Mo⋯Mo distance occurs in high-valent and quadruply bridged products.

The locations of the bromide ions and water molecules suggest that hydrogen bonds stabilize the **1b** species (Figure 2). The Br⋯O distances are in the range 3.34-3.39 Å, and in comparison to the average value of 3.28 Å,³⁷ the distances suggest hydrogen bonds in **1b**. The shortest interatomic distance, 3.6-3.8 Å, between the bimetallic species and the bromide ions involve C(3), C(4), C(11), C(14), and C(21) atoms (Table III). These features imply weak hydrogen bonds through C-H groups and Br⁻. The Mo⋯Br distances (>5 Å) exclude an interaction between these atoms.

Reactivity Studies of $[Cp(CO)M(\mu-SMe)_3M(CO)-Cp]^+X^-$ ($M = Mo, W$). Reactions with Oxidizing Agents. Complexes **1** do not form observable dications or other oxidized species with oxidizing agents such as I_2 , AgX , or $NOPF_6$. Attempts to isolate oxidized products were unsuccessful; for example, treatment of **1a** or **1b** with

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Table III. Interatomic Distances (Å), Angles (deg), and Dihedral Angles (deg) with Estimated Standard Deviations^a

Bond Distances					
Mo(1)-S(1)	2.463 (6)	Mo(1)-Mo(2)	2.785 (2)	Mo(1)-S(3)	2.453 (5)
Mo(2)-S(1)	2.459 (6)	Mo(1)-S(2)	2.439 (6)	Mo(2)-S(3)	2.470 (5)
S(1)-C(3)	1.832 (27)	Mo(2)-S(2)	2.446 (6)	S(3)-C(5)	1.833 (29)
Mo(1)-C(1)	1.939 (23)	S(2)-C(4)	1.801 (27)	Mo(1)...O(1)	3.104 (20)
Mo(2)-C(2)	1.948 (21)	C(1)-O(1)	1.166 (25)	Mo(2)...O(2)	3.123 (17)
Mo(1)-C(11)	2.302 (23)	C(2)-O(2)	1.180 (23)	Mo(2)-C(21)	2.309 (22)
Mo(1)-C(12)	2.285 (23)			Mo(2)-C(22)	2.304 (19)
Mo(1)-C(13)	2.314 (27)			Mo(2)-C(23)	2.312 (25)
Mo(1)-C(14)	2.344 (22)			Mo(2)-C(24)	2.354 (25)
Mo(1)-C(15)	2.360 (27)			Mo(2)-C(25)	2.342 (25)
mean	2.321			mean	2.324
Mo(1)-G(1)	1.990			Mo(2)-G(2)	1.988
C(11)-C(12)	1.45 (3)			C(21)-C(22)	1.40 (3)
C(12)-C(13)	1.41 (3)			C(22)-C(23)	1.36 (3)
C(13)-C(14)	1.30 (3)			C(23)-C(24)	1.38 (3)
C(14)-C(15)	1.41 (3)			C(24)-C(25)	1.50 (3)
C(15)-C(11)	1.46 (3)			C(25)-C(21)	1.43 (3)
mean	1.41			mean	1.41
Bond Angles					
S(1)-Mo(1)-S(2)	110.8 (0.2)	S(2)-Mo(1)-S(3)	69.9 (0.2)	S(3)-Mo(1)-S(1)	75.2 (0.2)
S(1)-Mo(2)-S(2)	110.7 (0.2)	S(2)-Mo(2)-S(3)	69.5 (0.2)	S(3)-Mo(2)-S(1)	74.9 (0.2)
S(1)-Mo(1)-C(1)	87.0 (0.7)	S(2)-Mo(1)-C(1)	90.9 (0.7)	S(3)-Mo(1)-C(1)	146.2 (0.7)
S(1)-Mo(2)-C(2)	88.6 (0.6)	S(2)-Mo(2)-C(2)	88.1 (0.6)	S(3)-Mo(2)-C(2)	144.4 (0.6)
Mo(1)-S(1)-Mo(2)	68.9 (0.2)	Mo(1)-S(2)-Mo(2)	69.5 (0.2)	Mo(1)-S(3)-Mo(2)	68.9 (0.1)
Mo(1)-S(1)-C(3)	115.8 (0.8)	Mo(1)-S(2)-C(4)	112.2 (0.9)	Mo(1)-S(3)-C(5)	114.5 (0.9)
Mo(2)-S(1)-C(3)	113.8 (0.9)	Mo(2)-S(2)-C(4)	115.4 (0.9)	Mo(2)-S(3)-C(5)	115.0 (0.9)
Mo(1)-C(1)-O(1)	176.5 (2.3)			Mo(2)-C(2)-O(2)	173.1 (1.8)
Nonbonding Distances					
S(1)...S(2)	4.03 (1)	S(1)...S(3)	3.00 (1)	S(2)...S(3)	2.80 (1)
Br...O(3)	3.39 (3)	Br...O(3)i	3.34 (3)	Br...Bri	6.87 (3)
Br...O(3)...Bri 107 (1)					
Br...C(3)	3.58 (3)	Br...C(4)	3.72 (3)	O(3)...O(3)i	4.03 (4)
C(1)...C(3)	3.20 (4)	C(1)...C(4)	3.22 (4)	Br...C(14)	3.73 (3)
		Br...C(11)	3.70 (3)	C(2)...C(3)	3.22 (4)
		C(1)...C(2)	2.78 (4)	Br...C(21)	3.84 (3)
C(1)-S(1)	3.05 (3)	C(1)...S(2)	3.14 (3)	C(2)...C(4)	3.20 (4)
C(2)...S(1)	3.10 (3)	C(2)...S(2)	3.08 (3)	C(1)...S(3)	4.21 (3)
O(1)...C(2)	3.06 (4)	O(1)...C(3)	3.43 (4)	C(2)...S(3)	4.21 (3)
O(2)...C(1)	3.12 (4)	O(2)...C(3)	3.53 (4)	O(1)...C(4)	3.63 (4)
				O(2)...C(4)	3.60 (4)
				O(2)...C(5)	3.53 (4)
G(1)-Mo(1)-Mo(2) 168.5 (0.5); G(2)-Mo(2)-Mo(1) 168.9 (0.5)					
Least-Squares Best Planes					
plane 1		C(11)-C(12)-C(13)-C(14)-C(15)		plane within 0.02 Å	
plane 2		C(21)-C(22)-C(23)-C(24)-C(25)		0.04 Å	
plane 3		Mo(1)-S(1)-Mo(2)-S(2)		0.03 Å	
plane 4		Mo(1)-S(3)-Mo(2)		0.00 Å	
Dihedral angles: 1-2, 20 (1); 1-3, 81 (1); 1-4, 87 (1); 2-3, 80 (1); 2-4, 90 (1); 3-4, 93 (1)					

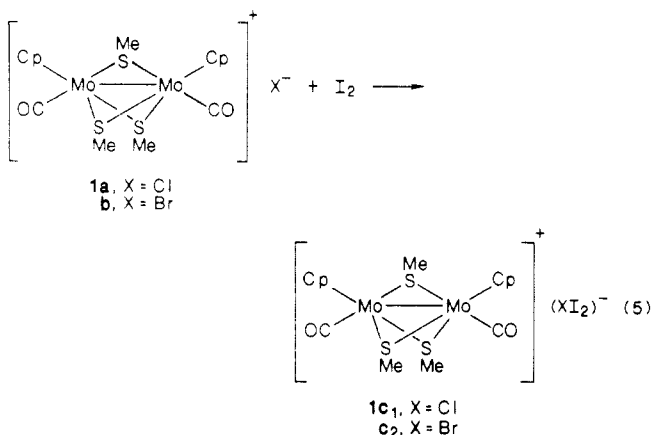
^aG(1) and G(2) correspond to the centers of gravity of the cyclopentadienyl rings 1 and 2, respectively.

Table IV. Comparison of Selected Structural Features of Bridged Binuclear Molybdenum or Tungsten Complexes

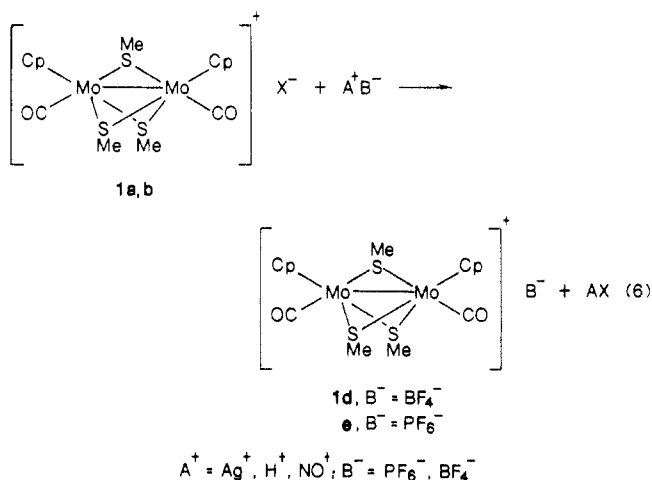
complex	ref	M-M, Å	M-S-M, deg	M-X-M, ^a deg	ox. states	bridge no.	M-M bond multiplicity
[{Mo}(μ-SMe) ₄ {Mo}] ²⁺	28	2.614 (1)	64.3		Mo ^{III} -Mo ^{III}	4	1
[{Mo}(μ-SMe) ₄ {Mo}]	29	2.603 (2)	64		Mo ^{III} -Mo ^{III}	4	1
[{Mo}(μ-SMe) ₂ (μ-S) ₂ {Mo}]	19	2.582 (2)	64		Mo ^{IV} -Mo ^{IV}	4	1
[{Mo}(μ-S-t-Bu) ₃ {Mo}]	9b	2.946 (1)	72		Mo ^{III} -Mo ^I	3	1
[{Mo}(μ-Cl) ₃ {Mo}]	30	3.051 (1)		76	Mo ^{III} -Mo ^{III}	3	1
[{Mo}(μ-Br)(μ-OH) ₂ {Mo}] ⁺	31	2.882 (2)		66(Br), 88(OH)	Mo ^{III} -Mo ^{III}	3	1
[{Mo}(μ-SMe) ₃ {Mo}] ⁺	this work	2.785 (2)	69		Mo ^{III} -Mo ^{III}	3	1
[{Mo}(μ-SMe) ₂ (μ-OH){Mo}]	25b	2.726 (1)	66.6	89.2	Mo ^{IV} -Mo ^{IV}	3	1
[{Mo}(μ-SMe) ₃ {Mo}]	25b	2.852 (2)	74		Mo ^{IV} -Mo ^{IV}	3	1
[{W}(μ-SEt) ₂ (μ-S){W}]	8	2.524 (1)	63.5		W ^{IV} -W ^{IV}	3	2
[{Mo}(μ-SPh) ₂ (μ-O){Mo}]	32	2.683 (2)	62.2	80	Mo ^V -Mo ^V	3	1
[{Mo}(μ-S)(μ-O) ₂ {Mo}]	33	2.628 (2)	63.9	80	Mo ^V -Mo ^V	3	1
[{W}(μ-SMe)(μ-I){W}]	1	2.936 (1)	73.2	62.1	W ^{II} -W ^{II}	2	1
[{Mo}(μ-SEt) ₂ {Mo}]	34	2.682 (1)	67.9		Mo ^{III} -Mo ^{III}	2	2
[{Mo}(μ-S-t-Bu) ₂ {Mo}]	25a	2.616 (2)	65.5		Mo ^{IV} -Mo ^{IV}	2	2
[{W}(μ-S) ₂ {W}]	35	2.791 (1)	73.2		Mo ^V -Mo ^V	2	1
[{Mo}(μ-(SCH ₂) ₆){Mo}]	36	3.211 (2)	86.2		Mo ^I -Mo ^I	1	1

^aX = Cl, Br, I, or O.

iodine at room temperature affords solids **1c** (eq 5). Their

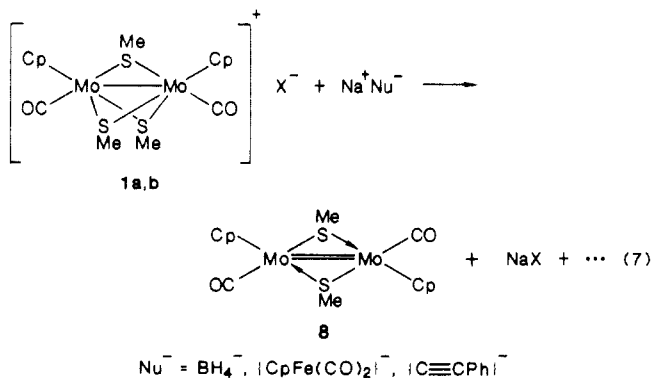


formulation as 1:1 electrolytes was confirmed by their molar conductance in nitromethane (see Experimental Section). The corresponding BF₄⁻ and PF₆⁻ salts **1d** and **1e** have been isolated by the metathetical reactions indicated in eq 6. The three complexes **1c–e** and **1b** have very similar IR and NMR spectra, implying that they are isostructural (Table I).



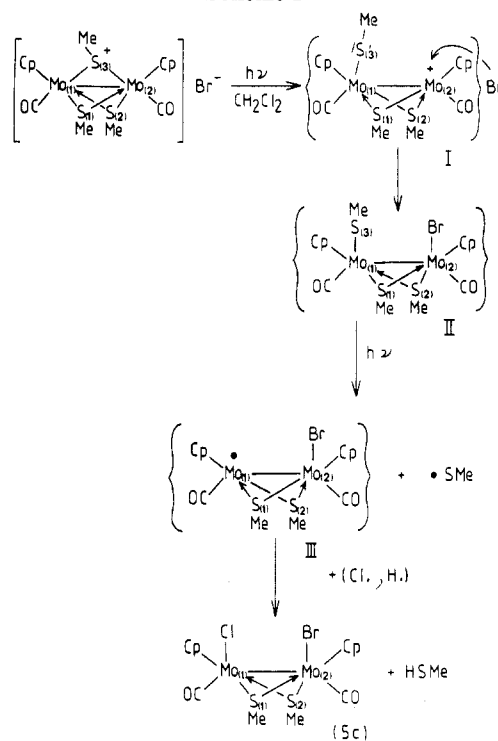
Reactions with Nucleophiles and Reducing Agents.

Complexes **1** are reactive toward nucleophilic reagents, for example, **1a** or **1b** and sodium borohydride, when mixed at 40 °C, afford mixtures of bimetallic syn-trans and anti-trans compounds **8** (~65% yield) (eq 7), which have been described previously.^{25a,38} Use of Na⁺[CpFe(CO)₂]⁻ or NaC≡CPh as the reactants with **1** also gives **8** in good yields.



A better route to complex **8** uses zinc as the reducing agent which reacts with **1a** in dichloromethane at room

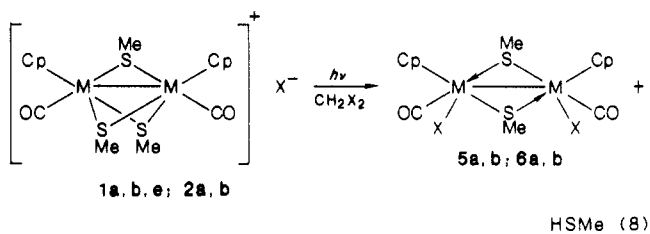
Scheme I



temperature to give stereospecifically the syn-trans complex **8** in ca. 95% yield.

Soft nucleophiles, e.g., phosphines and phosphites, do not react with the dinuclear complexes **1** not even to displace a carbonyl group.

Photolytic Behavior of Complexes 1 and 2: Synthesis and Reactions of [Cp(CO)ClM(μ-SMe)₂MCl(CO)Cp] (5 or 6). Photolysis of complex **1a** or **1e** in dichloromethane gives product **5a** of stoichiometry [Mo₂(C₅H₅)₂Cl₂(SMe)₂(CO)₂], in good yield (~80%) (eq 8). Similarly, photolysis of **1b** in dibromomethane affords



compound **5b** of stoichiometry [Mo₂(C₅H₅)₂Br₂(SMe)₂(CO)₂]; when dichloromethane is used as the solvent, however, a mixed complex **5c**, [Mo₂(C₅H₅)₂BrCl(SMe)₂(CO)₂] is formed. Similar complexes **6a,b** are obtained in very low yields (~12%) from the tungsten species **2a,b**.

These novel compounds are formulated as shown on the basis of spectroscopic studies and elemental analyses. The ions of highest mass in the mass spectra show that they are dinuclear species (see Experimental Section), and their formulation as molecular complexes was confirmed by their molar conductance in nitromethane. Although thiolato dinuclear complexes containing a bridging chloride have been described,³⁹ it appears logical that the two bridging ligands in **5** and **6** are SR groups rather than halide groups. This is indeed consistent with the well-known tendency for terminal thiolate groups to convert to bridging.⁴⁰ To

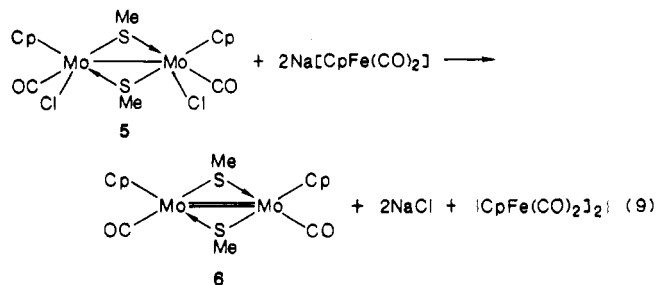
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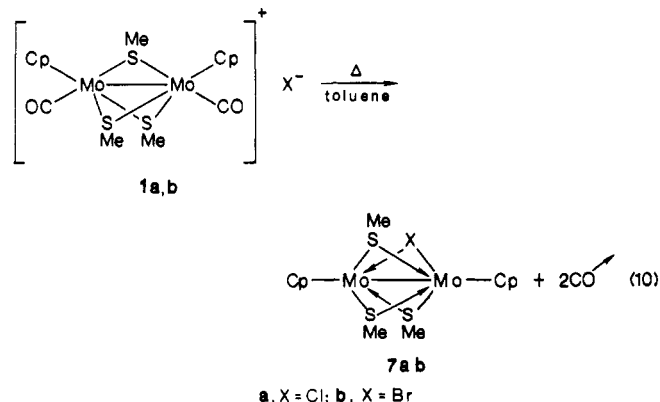
complete the molecular structure of these products, the 18-electron rule implies a single metal-metal bond. At room temperature, only one isomer of these doubly thiolato-bridged complexes is observed.

In Scheme I we present the proposed mechanism for the formation of **5** or **6** by photolysis of **1** or **2** in CH_2X_2 . The assumption of such a mechanism is supported: (i) by the location of the positive charge of the compounds **1** on one sulfur atom (see " ^{95}Mo NMR study" section); (ii) by the production of mixed-halide derivatives when the bromide species **1b** was photolyzed in dichloromethane (example selected in Scheme I), and (iii) by the characterization of DSMe formed in the NMR tube when CD_2Cl_2 as solvent. The first step would be the opening of the S(3)Me bridge by creating a vacant site on the molybdenum (2) atom. One can imagine then an ionic process with a nucleophilic attack of Br^- on the metal (2) center giving the intermediate II. We consider further an homolytic cleavage of the Mo(1)-S(3)Me bond with formation of Mo \cdot and SMe \cdot radicals which then react respectively with Cl \cdot and H \cdot , which are formed in the solution by photolytic cleavage of CH_2Cl_2 , leading to the final products. It can be pointed out that when the photolysis in CD_2Cl_2 was monitored by ^1H NMR, only three types of well-defined peaks were noticed in the spectra: those corresponding respectively to the starting material **1**, to DSMe, and to the final adduct **5**. No intermediates were detected, nor was broadening of the signals observed during the course of the photolytic reaction. These features are consistent with a slow first step and with very fast subsequent steps. Furthermore, there is no loss of CO in the reaction.

The molybdenum complexes **5** react with $\text{Na}[\text{CpFe}(\text{CO})_2]$ to form the dinuclear derivatives **8** as shown in eq 9. Complex **5** does not react with hexafluorobutylene.



Thermal Study of Complexes 1. When being refluxed in toluene, compound **1a** or **1b** lose CO and are converted into products of stoichiometry $[\text{Mo}_2(\text{C}_5\text{H}_5)_2(\text{SMe})_3(\text{X})]$ ($\text{X} = \text{Cl}, \text{Br}$) (eq 10). These compounds are formulated on

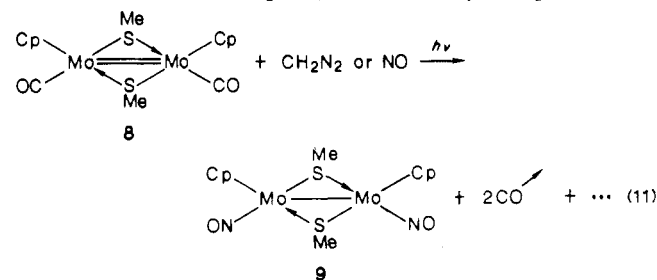


the basis of their mass spectra, molecular ions being ob-

served at m/e 498 and 542 for **7a** and **7b**, respectively. The NMR and IR spectra are consistent with this formulation. The ^1H NMR spectra of complexes **7** exhibit two types of signals: a singlet, ca 5.3 ppm, corresponding to the cyclopentadienyl groups and three singlets, ca. 1.5 ppm, corresponding to SMe groups (relative intensities 10:3:3:3). The ^{13}C NMR spectra show similar pattern to the ^1H NMR spectra; however, for complex **7b** the methyl signals are not resolved.

To our knowledge, these mixed quadruply bridged molybdenum(III) complexes are novel and are very similar to $[\text{CpMo}(\mu\text{-SMe})_4\text{MoCp}]$ described by Connelly and Dahl.²⁹

Reactions of $[\text{Cp}(\text{CO})\text{Mo}(\mu\text{-SMe})_2\text{Mo}(\text{CO})\text{Cp}]$. The multiple metal-metal bonded complexes usually have a remarkable reactivity.^{22b,41,42} However, Knox et al.^{25a} observed that the double-bonded complex $[\text{Cp}(\text{CO})\text{Mo}(\mu\text{-SR})_2\text{Mo}(\text{CO})\text{Cp}]$ appears much less reactive than the triple-bonded complex $[\text{Cp}(\text{CO})_2\text{Mo}\equiv\text{Mo}(\text{CO})_2\text{Cp}]$. On photolysis, complex **8** reacts with diazomethane or with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide to give the known derivative **9** (eq 11), identified by comparison of



its spectral data with those of an authentic sample.⁴³ Curiously, **9** is obtained in higher yields when the diazomethane is used as reactant and no μ -methylene complex is observed.

The reactivity of **8** with unsaturated molecules such as alkynes has also been investigated. No reaction with hexafluorobutylene was observed.

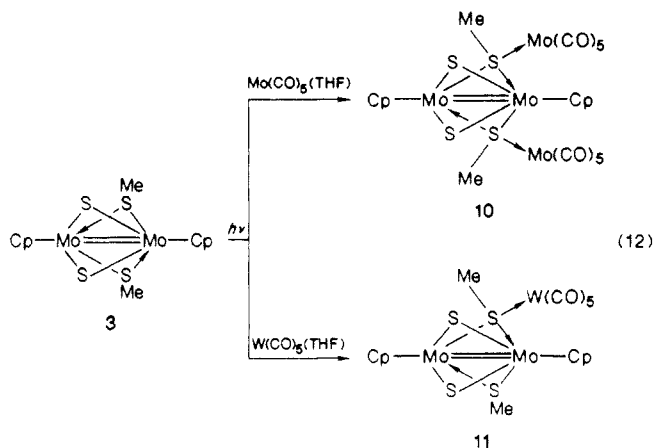
Reactions of $[\text{CpMo}(\mu\text{-S})_2(\mu\text{-SMe})_2\text{MoCp}]$ (3**).** Complexes **3**, obtained in reaction 2, have four sulfur atoms which might be expected to react with electrophiles. Photolysis of a 1:1 mixture of **3** and $\text{M}(\text{CO})_5(\text{THF})$ ($\text{M} = \text{Mo}, \text{W}$) led to the isolation of two new compounds of stoichiometry $[\text{Mo}_4(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{10}(\text{S})_2(\text{SMe})_2]$ ($\text{M} = \text{Mo}$, **10**) and $[\text{Mo}_2\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_5(\text{S})_2(\text{SMe})_2]$ ($\text{M} = \text{W}$, **11**), respectively (eq 12). Complexes **10** and **11** are diamagnetic and are formulated from spectroscopic studies and elemental analyses. The ^1H and ^{13}C spectra (Table V) give evidence of only one isomer in solution at room temperature. Complexation of **3** with the $\text{Mo}(\text{CO})_5$ moieties causes both the methanethiolate signals to be shifted downfield. The coordination of **3** with $\text{W}(\text{CO})_5$ results in a splitting of the methanethiolate signals, one is shifted downfield whereas the second remains unchanged relative to the reactant one. These features suggest a coordination of the $\text{M}(\text{CO})_5$ entity with methanethiolate ligands in **10** and **11** rather than with sulfide ligand. However, in the absence of an X-ray structure determination, one cannot conclusively rule out coordination to the sulfide. Typical CO

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signals are detected (ca. 220 ppm downfield of Me₄Si) in the ¹³C NMR spectrum of 10.

Insertion of alkynes into metal-sulfur bonds have been observed, and some products have been structurally characterized.⁴⁴ However, no reaction of 3 with hexafluorobutylene was observed.

Dealkylation reactions of 3 with [CpFe(CO)₂]₂ or [CpV(CO)₄] in refluxing toluene failed. Furthermore, no reaction was observed between 3 and CO under atmospheric pressure.

Molybdenum-95 NMR Study on Dinuclear Molybdenum Complexes. The chemical shift range for molybdenum species is very large and covers more than 7000 ppm, indicating that minor electronic or structural changes can be easily detected. The chemical shift ranges found for mononuclear complexes^{13,17} to date are as follows: Mo(0), -770 to -2200 ppm; Mo(II), -100 to -2100 ppm; Mo(IV), -300 to -3000 ppm; Mo(VI), +3200 to -200 ppm. The known chemical shifts for polynuclear species fall outside these ranges and vary with oxidation state in the following way: Mo(II), +4030 to -220 ppm;^{14a,b,16} Mo(IV), +1160 to +990 ppm;¹⁶ Mo(V), +980 to +250 ppm.^{14c,16} For both, mononuclear and polynuclear species, the ranges for several oxidation states overlap and the chemical shift is not therefore an independent indicator of oxidation state.

Chemical shift and line width data are listed in Table VI for various binuclear molybdenum species. Resonances for binuclear Mo(III), Mo(II), and Mo(IV) containing respectively formal single and double metal-metal bonds have been observed for the first time.

The compounds studied all have relatively high electric field gradients at the molybdenum nucleus, and the large line widths observed (see Table VI) suggest that the quadrupolar contribution to the line width is important in these species.

Heavy-metal shieldings are dominated by the paramagnetic term of Ramsey's treatment⁴⁵ which is given by eq 13, where Δ*E* is the mean electronic energy, between

$$\sigma_{\text{para}} = -K \frac{1}{\Delta E} (\langle r^{-3} \rangle_{\text{np}} P_i + \langle r^{-3} \rangle_{\text{nd}} D_i) \quad (13)$$

HOMOs and LUMOs, $\langle r^{-3} \rangle_{\text{np}}$ and $\langle r^{-3} \rangle_{\text{nd}}$ are radial expansion terms representing the average inverse cubes of the distances of the relevant p and d electrons from the nucleus, and *P_i* and *D_i* are measures of the degree of electronic imbalance in the relevant p and d orbitals, respectively. Evidence that the (Δ*E*)⁻¹ term is important for

Table V. NMR Data of Sulfido-Bridged Complexes^a

compd	¹ H δ	¹³ C δ
3 (isomer I)	6.47 (s, ^b 10H), 1.06 (s, 6 H)	98.19 (Cp), 18.39 (CH ₃)
3 (isomer II)	6.45 (s, 10 H), 1.18 (s, 6 H)	98.19 (Cp), 21.74 (CH ₃)
4 (isomer I)	6.48 (s, 10 H), 1.35 (s, 6 H)	95.19 (Cp), 19.61 (CH ₃)
4 (isomer II)	6.43 (s, 10 H), 1.55 (s, 6 H)	
10	5.35 (s, 5 H), 5.30 (s, 5 H), 2.0 (s, 3 H), 1.95 (s, 3 H)	226.7 (CO), 221.49 (CO), 217.80 (CO), 94.30 (Cp), 94.11 (Cp), 30.48 (CH ₃)
11	6.55 (s, 10 H), 1.36 (s, 3 H), 1.06 (s, 3 H)	99.35 (Cp), 26.63 (CH ₃), 19.41 (CH ₃)

^a CHCl₃ solvent. ^b Singlet.

the shielding of molybdenum nuclei is provided by the temperature dependences of its chemical shift. Here the temperature dependences were measured for the two complexes 1d and 3 (see Table VI). These are higher than those obtained for other molybdenum compounds.^{13a} An increase in temperature results in a downfield shift which is consistent with a decrease of Δ*E*, i.e., an easier accessibility of the electronic excited states.

The width of the observed range (1800 ppm) is significant. It indicates that the ⁹⁵Mo nucleus is in a different molecular and electronic environment in most of the binuclear species examined here. The resonances are singlets and found downfield of the Na₂(MoO₄) reference for complexes with formal multiple metal-metal bonds and upfield of the reference for every compound having a single metal-metal bond or no metal-metal bond.

This series (Table VI) shows that the chemical shift depends on the following factors: (i) the oxidation state of the metal; (ii) the σ donor/π acceptor ability of ligands; (iii) the geometry around the metal; (iv) the number of bridged sulfur atoms; (v) the presence of multiple metal-metal bonds.

Comparison of the ⁹⁵Mo NMR spectra of [(η⁵-C₅H₅)(CO)Mo(μ-SMe)₂Mo(CO)(η⁵-C₅H₅)] (8) with that of the parent species [(η⁵-C₅H₅)(CO)₂Mo(μ-SMe)₂Mo(CO)₂(η⁵-C₅H₅)] (13) reveals major changes in the chemical shifts (Δδ = 700 ppm). The magnitude of the Δδ(⁹⁵Mo) for the molybdenum(II) compounds cannot readily be attributed to the difference in the number of carbonyl ligands since a decrease of one unit of the CO ligands usually contributes to a deshielding of only 100–250 ppm.^{13d} Therefore it seems more likely that differences in the number of metal-metal bonds which will put constraints upon the interbond angles at the metal atoms may play an important part here. Further the deshielded metals in the multiple Mo-Mo bond complexes may be also considered to be in accord with an important bimetallic character of the HOMO. Indeed an increase of the metal-metal bond number results in successive deshielding of the metal nucleus mainly via a decrease of Δ*E*.

The spectrum of complex 10 exhibits three singlets; the position of one of them (-1403 ppm) is close to those reported earlier for [Mo(CO)₅L],^{13d} and therefore we attribute this resonance to the molybdenum(0). Comparison of the shielding data for [(CpMo)₂(μ-S)₂(μ-SMe)₂] (3)

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Table VI. ^{95}Mo NMR Data for Dinuclear Molybdenum Complexes

compd	ref	δ		$\nu_{1/2}$, Hz
		room temp	50 °C	
[Cp(CO)Mo(μ -SMe) $_3$ Mo(CO)Cp]Br (1b)	this work	-590 ^a		...
[Cp(CO)Mo(μ -SMe) $_3$ Mo(CO)Cp]I $_2$ Cl (1c)	this work	-588 ^a		170
[Cp(CO)Mo(μ -SMe) $_3$ Mo(CO)Cp]BF $_4$ (1d)	this work	-591 ^a	-575	215
[Cp(CO)Mo(μ -SMe) $_3$ Mo(CO)Cp]PF $_6$ (1e)	this work	-594 ^a		110
<i>syn-trans</i> -[Cp(CO)Mo(μ -SMe) $_2$ Mo(CO)Cp] (8a)	this work	+555 ^b		114
<i>anti-trans</i> -[Cp(CO)Mo(μ -SMe) $_2$ Mo(CO)Cp] (8b)	this work	+512, ^b +500		80
[Cp(Mo(μ -S) $_2$ (μ -SMe) $_2$ MoCp] (isomer I) (3)	this work	+445 ^b	+466	86
[CpMo(μ -S) $_2$ [SMeMo(CO) $_5$]MoCp] (10)	this work	+328, ^b +174, -1403		100
[Cp(NO)Mo(μ -SMe) $_2$ Mo(NO)Cp] (9)	this work	-1019 ^b		230
[Cp(CO) $_2$ Mo(μ -SMe) $_2$ Mo(CO) $_2$ Cp] (13)	14a	-158, -213		
[Cp(CO)Mo(μ -SMe) $_3$ Mo(CO) $_3$] (14)	14a	-560, -870		
[(O $_2$ C- <i>n</i> -Pr) $_2$ Mo \equiv Mo(O $_2$ C- <i>n</i> -Pr) $_2$] (16)	16	+3730		
[(O $_2$ CCF $_3$) $_2$ Mo \equiv Mo(O $_2$ CCF $_3$) $_2$] (16)	16	+4026		
[(CNCMe $_3$) $_4$ (bpy)Mo(μ -CN)Mo(bpy)(CNCMe $_3$)] (14b)	14b	+69, -61		

^aTaken in CD $_3$ CN. ^bTaken in CDCl $_3$.

{(CpMo) $_2$ (μ -S) $_2$ [(μ -SMeMo(CO) $_5$] $_2$] (10) shows a high-field shift (\sim 200 ppm) of the metal resonance on introduction of a Mo(CO) $_5$ ligand into the coordination sphere of the SMe groups which indicates a substantial π -interaction between molybdenum and sulfur atoms. This effect may be a function of the ability of the two entering molybdenum atoms to donate π -electron density into the empty sulfur d orbitals and then to compete with the primary molybdenum atoms by reducing their back-donation of electron density from their d orbitals into the sulfur orbitals and therefore increasing the electron density at the primary molybdenum atoms. This may be accounted for in terms of influences dominated by (r^{-3}).

Of additional interest was the possibility of using ^{95}Mo NMR spectroscopy of differentiate two chemically distinct molybdenum environments in dinuclear compounds. The dimolybdenum(III,I) complex [(η^5 -C $_5$ H $_5$)(CO)Mo(μ -SMe) $_3$ Mo(CO) $_3$] (14) shows two distinct ^{95}Mo NMR signals separated by 310 ppm.^{14a} A comparison of these signals with the corresponding data for [(η^5 -C $_5$ H $_5$)(CO)Mo(μ -SMe) $_3$ Mo(CO)(η^5 -C $_5$ H $_5$)]⁺X⁻ (X = Br, I $_2$ Cl, BF $_4$, PF $_6$) (1) leads to the assignment of the more deshielded signal to the cyclopentadiene C-bound molybdenum(III) and the more shielded signal to the molybdenum(I) atom bound to the three carbonyl groups.

For complexes 1 chemical shifts are high field relative to those of the neutral parent species [Cp(CO) $_2$ Mo(μ -SMe) $_2$ Mo(CO) $_2$ Cp] (13). This important feature suggests a location of the positive charge on one sulfur atom in 1. Indeed if the positive charge was located on one molybdenum atom (or even delocalized over both metals), this would give rise to a downfield shift of the Mo signal of 1 relative to that of 13. Furthermore the presence of only one signal on the spectra of 1 is also in accordance with this conclusion.

The formally molybdenum(III) complex [Cp(NO)Mo(μ -SMe) $_2$ Mo(NO)Cp] (9) is to be compared to the ionic compounds 1. The metal atoms are more shielded in the nitrosyl molecular complex 9 than in the ionic derivatives 1. This effect is somewhat unexpected since a substitution of CO by a less powerful π -acceptor NO⁴⁶ usually results in deshielding of the metal nucleus mainly via a decrease of ΔE . Moreover a decrease of one polarizable sulfur ligand into the coordination sphere in 9 would normally produce a more positive chemical shift. This demonstrates that the

^{95}Mo chemical shift is extremely sensitive to various factors, and here the observed shift could be due to a geometrical effect.

A good correlation is observed between the chemical shift of the ^{95}Mo resonances and the infrared frequency of carbonyl groups in complexes 1 (see Table I), 8 (1885 and 1850 cm $^{-1}$), and 13 (1980, 1950, and 1870 cm $^{-1}$), indeed the more deshielded molybdenum corresponds with the more low-frequency shifted CO (see Table VI).

The ^{95}Mo nuclei in the dinuclear species examined in the present work are less deshielded than those reported until now.^{14b,16} The chemical range for dinuclear Mo(IV) is now +1160 to +174 ppm and for Mo(III) -560 to -1200 ppm. However as for mononuclear species, the ^{95}Mo chemical shift cannot be used to distinguish clearly among dinuclear species of Mo(II) and Mo(IV).¹⁶ The striking feature of the results discussed here is the deshielding of the multiple metal-metal bonds complexes compared to compounds having simple or no metal-metal bonds.

Experimental Section

Preparations were carried out under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods and degassed before use. The thiolates [M(CO) $_3$ (SMe)(η^5 -C $_5$ H $_5$)] and [Mo(CO) $_4$ (μ -SMe) $_2$ (η^5 -C $_5$ H $_5$) $_2$] (M = Mo, W) and the bromide [M(CO) $_3$ Br(η^5 -C $_5$ H $_5$)] (M = Mo, W) were prepared according to the literature methods.^{20,47}

Measurements. Infrared spectra of dichloromethane solutions were obtained with a Pye-Unicam SP 2000 spectrophotometer. Mass spectra were recorded on a Varian Mat 311 in the "Mesures Physiques" laboratory, University of Rennes, and NMR spectra, in CDCl $_3$ or CD $_3$ CN solution, were measured on a JEOL FX100 spectrometer (^1H , ^{13}C , ^{19}F) and were referenced to Me $_4$ Si or CFCl $_3$. ^{95}Mo NMR spectra were recorded at 6.44 MHz using the pulsed FT NMR technique on a JEOL FX100 spectrometer; the field homogeneity was adjusted by shimming on the ^2H resonance of $^2\text{H}_2\text{O}$ in a solution of Na $_2$ MoO $_4$ (2 M) of apparent pH 11.0. Chemical shifts were referenced externally by using the sample replacement method to the above solution for which $\mathcal{L} = 6517$ MHz at 20 °C. Spectral data were collected at room temperature unless stated otherwise. The 90° pulse was found to be 82 μs . Chemical shifts were calculated in parts per million with positive values in the low-field direction relative to the reference.

Chemical analyses were performed by the "Centre de Micro-analyse du CNRS de Lyon". Molar conductivities (Ω^{-1} cm 2 mol $^{-1}$) were determined at room temperature in nitromethane ($c = 10^{-3}$ M).

X-ray Crystallography. Slightly air-sensitive brown crystals of 1b were obtained by recrystallization from a CH $_2$ Cl $_2$ -hexane mixture and examined by X-ray crystallography. [Mo $_2$ (η^5 -C $_5$ H $_5$) $_2$ (SMe) $_3$ (CO) $_2$]Br·H $_2$ O (1b): M_r 617, triclinic, $a = 9.209$ (2) Å, $b = 10.203$ (2) Å, $c = 11.706$ (2) Å; $\alpha = 106.73$ (2)°, $\beta = 101.31$

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(2)°, $\gamma = 93.58$ (2)°; $V = 1024.6 \text{ \AA}^3$; $Z = 2$, $D(\text{calcd}) = 2.00 \text{ g cm}^{-3}$; Mo $K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$; $\mu(\text{Mo } K\alpha) = 3.3 \text{ mm}^{-1}$; space group $P\bar{1}$. A small crystal ($0.13 \times 0.10 \times 0.05 \text{ mm}$) was sealed in a Lindeman tube and used for data collection on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (Centre de Diffusion Atomique de Lyon I). The cell dimensions given above were obtained by least squares from setting angles of 25 reflections ($15 < \theta < 25^\circ$) by using Mo $K\alpha$ radiation with a graphite monochromator; intensities of 3387 independent reflections with $2\theta \leq 50^\circ$ were collected by using the ω - 2θ scan method ($-10 \leq h \leq 10$; $-12 \leq k \leq 12$; $0 \leq l < 13$). One standard reflection, scanned every 100 reflections, was used to place the intensity data on a common scale; systematic variations in this standard were not observed. L_p corrections were applied, but no correction for absorption was made (the transmission factors ranged from 0.72 to 0.88). A total of 1472 reflections with $F > 5\sigma(F)$ were considered as observed and used in the structure refinement. The structure was solved by using direct methods (Subprogram EES from SHELX 76⁴⁸). After refinement of the molybdenum and sulfur coordinates, all the non-hydrogen atoms were located in subsequent electron density maps. The function minimized in the F refinement was $[\sum w^{1/2}(|F_o| - |F_c|)] / [\sum w^{1/2}|F_o|]$ with a weighting scheme $w = 1.06 / [\sum \sigma^2|F_o| + 0.005 F_o^2]$. Full-matrix refinement by SHELX 76⁴⁸ and with anisotropic Mo, Br, and S atoms and isotropic C and O atoms led to a final $R_w = 0.074$ and $R = 0.070$ with 127 independent refined parameters; two hydrogen atoms were clearly evident in final difference Fourier synthesis, the highest residual electron density being 1.2 e \AA^{-3} and $F(000) = 592$. The scattering of neutral Mo, S, Br, O, and C atoms were taken from Cromer and Mann,⁴⁹ anomalous dispersion term included.⁵⁰

Final positional and thermal parameters are listed in Table II. Interatomic distances and angles with estimated standard deviations are given in Table III.

Syntheses of Complexes $[\text{M}_2(\text{CO})_2(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]^+\text{X}^-$.

(a) $[\text{M}_2(\text{CO})_2(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]^+\text{Cl}^-$ ($\text{M} = \text{Mo}$ (1), W (2)). The dimeric complex $[\text{M}_2(\text{CO})_4(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]$ ($\text{M} = \text{Mo}$, $\sim 0.4 \times 10^{-2} \text{ mol}$; $\text{M} = \text{W}$, $2 \times 10^{-3} \text{ mol}$) and an excess of allyl chloride and dimethyl disulfide were heated in tetrahydrofuran at reflux for 48 h. The gaseous products of the reaction were removed periodically. Compounds **1a** and **2a** are insoluble in THF and were obtained by filtration, washed with THF, and dried [yields: 70% ($\text{M} = \text{Mo}$) and 75% ($\text{M} = \text{W}$)]. Compound **1a** was separated from $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu\text{-SMe})_2\text{Mo}(\eta^5\text{-C}_5\text{H}_5)]$ (yield ca. 7%).

1a is a yellow-brown solid which is soluble in dichloromethane, acetonitrile, or acetone. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{ClMo}_2\text{O}_2\text{S}_3$: C, 32.4; H, 3.5; Cl, 6.4. Found: C, 31.9; H, 3.6; Cl, 6.4. Molar conductivity: 76.

2a is a red compound which is soluble in dichloromethane and acetonitrile. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{ClO}_2\text{S}_3\text{W}_2$: Cl, 4.8; H, 2.6. Found: Cl, 4.8; H, 2.4. Complex **2a** decomposed in the mass spectrometer, giving $[(\text{C}_5\text{H}_5)(\text{CO})\text{W}(\text{SMe})_2(\text{S})\text{W}(\text{CO})(\text{C}_5\text{H}_5)]^+$ and CH_3Cl ; the mass spectrum showed subsequent ions corresponding to $[(\text{C}_5\text{H}_5)(\text{CO})\text{W}(\text{SMe})_2(\text{S})\text{W}(\text{CO})(\text{C}_5\text{H}_5)]^+$, m/e 680, $[(\text{C}_5\text{H}_5)(\text{CO})\text{W}(\text{SMe})_2\text{W}(\text{CO})(\text{C}_5\text{H}_5)]^+$, m/e 648, $[(\text{C}_5\text{H}_5)\text{W}(\text{SMe})_2\text{W}(\text{C}_5\text{H}_5)]^+$, m/e 609, $[(\text{C}_5\text{H}_5)\text{WS}_2\text{W}(\text{C}_5\text{H}_5)]^+$, m/e 549, and $[\text{CH}_3\text{Cl}]^+$, m/e 50. Molar conductivity: 73.

(b) $[\text{M}_2(\text{CO})_2(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]^+\text{Br}^-$ ($\text{M} = \text{Mo}$ (1b), W (2b)). The preparation of **1b** has already been described previously.¹¹ However, it could also be obtained according to two new procedures.

Method A. Using $[\text{M}_2(\text{CO})_4(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]$ ($\text{M} = \text{Mo}$, W). The reactions were carried out as described above for **1a** and **2a**. **1b** was obtained with a good yield (ca. 60%) and was separated from $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu\text{-S})_2(\mu\text{-SMe})_2\text{Mo}(\eta^5\text{-C}_5\text{H}_5)]$ (**3**) (yield ca. 7%). **2b** was obtained in a very low yield. Its mass spectrum is similar to this of **2a**. Molar conductivity: 72.

Method B. Using $[\text{M}(\text{CO})_3\text{Br}(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$, W). Refluxing a mixture of 1.6 g of $[\text{M}(\text{CO})_3\text{Br}(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$, 0.1 mol; $\text{M} = \text{W}$, $3 \times 10^{-3} \text{ mol}$) and a large excess of dimethyl

disulfide in THF for 4–5 days gave compounds **1b** or **2b** which are insoluble in THF. **1b** and **2b** were separated by filtration (yields: ca. 35%, $\text{M} = \text{Mo}$; ca. 10%, $\text{M} = \text{W}$). The filtrates were evaporated, and the residues were redissolved in a minimum of dichloromethane and the solutions chromatographed on Florisil. Elution with CH_2Cl_2 served to remove the violet ($\text{M} = \text{Mo}$) or the green ($\text{M} = \text{W}$) bands which were evaporated to yield product **3** ($\text{M} = \text{Mo}$) or **4** ($\text{M} = \text{W}$).

If the gaseous products of the reactions are removed periodically, the yields of **3** and **4** increase to ca. 80% and 67%, respectively.

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{S}_4\text{W}_2$ (**4**): C, 22.0; H, 2.5; S, 19.5; W, 56.0. Found: C, 22.9; H, 2.7; S, 18.4; W, 55.0. (Good analyses of **4** are unavailable, the samples being contaminated by a variable amount of solvents). Molar conductivity: 3.7.

(c) $[\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]^+(\text{XI}_2)^-$ (**1c**). A mixture of **1a** or **1b** ($1.5 \times 10^{-3} \text{ mol}$) and iodine ($3 \times 10^{-3} \text{ mol}$) was stirred in dichloromethane for 24 h, after which time the color changed from red to brown. The solution was filtered to remove insoluble material. The filtrate was evaporated to yield the crude product which was recrystallized from a CH_2Cl_2 -hexane mixture; brown crystals of **1c** were recovered: yields 88% ($\text{X} = \text{Cl}$) and 51% ($\text{X} = \text{Br}$). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{ClI}_2\text{Mo}_2\text{O}_2\text{S}_3$ (**1c**): C, 22.2; H, 2.3; I, 31.4; S, 11.8. Found: C, 22.2; H, 2.2; I, 31.7; S, 11.2. Molar conductivity: 80. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{BrI}_2\text{Mo}_2\text{O}_2\text{S}_3$ (**1c**): C, 21.1; H, 2.2; I, 29.8; Mo, 22.5. Found: C, 21.8; H, 2.0; I, 29.2; Mo, 22.5. Molar conductivity: 81.

(d) $[\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]^+(\text{BF}_4)^-$ (**1d**). A mixture of **1a** ($0.6 \times 10^{-3} \text{ mol}$) and silver tetrafluoroborate ($0.6 \times 10^{-3} \text{ mol}$) were stirred in the dark for 24 h in dichloromethane. The solution was filtered to remove silver chloride and intractable products.

Evaporation of the solvent produced a red compound, yield 68%. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{BF}_4\text{Mo}_2\text{O}_2\text{S}_3$: C, 29.7; H, 3.1; F, 12.7; Mo, 31.6. Found: C, 29.7; H, 3.1; F, 12.7; Mo, 31.2. Molar conductivity: 92.

(e) $[\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]^+(\text{PF}_6)^-$ (**1e**). **Method A. Using $\text{Ag}(\text{PF}_6)$.** The procedure given for the synthesis of **1d** was followed. The red product **1e** was recrystallized from a CH_2Cl_2 /hexane mixture. Yield: 85% when the reactant is **1a** and 55% when the reactant is **1b**. Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{F}_6\text{Mo}_2\text{O}_2\text{PS}_3$: C, 27.1; H, 2.9; F, 16.9; S, 14.4. Found: C, 26.8; H, 2.9; F, 16.9; S, 14.3. Molar conductivity: 83.

Method B. Using HPF_6 . In a similar way **1e** is obtained from **1b** in a good yield (68%).

Photolytic Transformation of Complexes $[\text{M}_2(\text{CO})_2(\mu\text{-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]^+\text{X}^-$ to $[(\eta^5\text{-C}_5\text{H}_5)(\text{X})(\text{CO})\text{M}(\mu\text{-SMe})_2\text{M}(\text{CO})(\text{X})(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$, W).

(a) **Transformation of **1a** and **1e**.** A nitrogen gas purge was used to deoxygenate 50 mL of dichloromethane to which was added 1.5 g of **1a**. The solution was irradiated with an UV lamp from a distance of 5 cm, and the progress of the photoreaction was monitored by infrared spectra. After 2 days the color changed from red to yellow-brown and decomposition of **1a** was nearly complete. The solution was then evaporated to dryness, and the residue was redissolved in a minimum of dichloromethane and the solution chromatographed on Florisil. Elution with a CH_2Cl_2 /THF mixture (100/5) gave a green band from which black-green crystals of **5a** were isolated in about 80% yield.

Complex **5a** was also obtained on using **1e** in dichloromethane instead of **1a**; yield 75%. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{Mo}_2\text{O}_2\text{S}_3$: C, 31.0; H, 3.0; Mo, 35.3. Found: C, 31.6; H, 3.1; Mo, 34.6. The mass spectrum showed ions corresponding to $[(\text{C}_5\text{H}_5)\text{ClMo}(\text{SMe})_2\text{MoCl}(\text{C}_5\text{H}_5)]^+$, m/e 487, $[(\text{C}_5\text{H}_5)\text{ClMo}(\text{S})\text{MoCl}(\text{C}_5\text{H}_5)]^+$, m/e 472, $[(\text{C}_5\text{H}_5)\text{ClMo}(\text{S})_2\text{MoCl}(\text{C}_5\text{H}_5)]^+$, m/e 457, $[(\text{C}_5\text{H}_5)\text{ClMo}(\text{SMe})_2\text{MoCl}]^+$, m/e 422, and $[\text{Mo}_2(\text{C}_5\text{H}_5)_2]^+$, m/e 322. Molar conductivity: 8.

(b) **Decomposition of **1a** in CD_2Cl_2 .** A degassed solution of **1a** in CD_2Cl_2 was transferred into an NMR tube. The NMR tube was then sealed and irradiated at room temperature. After 6 h, new resonances in the spectrum could be assigned to **5a** and free DSME. Conversion was >95% after 2 days. No intermediate was detected.

(c) **Decomposition of **1b**.** The reaction was carried out as described above for compounds **1a** and **1e** by using dibromomethane. **1b** is photochemically unstable and is mainly converted

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to the dark brown compound **5b** (yield 35%). Anal. Calcd for $C_{14}H_{16}Br_2Mo_2O_2S_2$: C, 26.6; H, 2.5; Mo, 30.3; S, 10.3. Found: C, 26.5; H, 2.5; Mo, 29.9; S, 10.3. The mass spectrum showed ions corresponding to $[(C_5H_5)_2BrMo(SMe)_2MoBr(C_5H_5)]^+$, m/e 576, $[(C_5H_5)_2BrMo(S)(SMe)MoBr(C_5H_5)]^+$, m/e 561, $[(C_5H_5)_2BrMo(S)_2MoBr(C_5H_5)]^+$, m/e 546, and $[Mo_2(C_5H_5)_2]^+$, m/e 322. Molar conductivity: 5.

When the reaction described above was carried out by using dichloromethane as solvent instead of dibromomethane, a mixture of **5a**, **5b**, and **5c** was obtained and identified on the basis of spectral and mass data. The mass spectrum showed ions corresponding to $[(C_5H_5)_2BrMo(SMe)_2MoBr(C_5H_5)]^+$, m/e 576, $[(C_5H_5)_2BrMo(S)(SMe)MoBr(C_5H_5)]^+$, m/e 561, $[(C_5H_5)_2BrMo(S)_2MoBr(C_5H_5)]^+$, m/e 546, $[(C_5H_5)_2ClMo(SMe)_2MoBr(C_5H_5)]^+$, m/e 531.5, $[(C_5H_5)_2ClMo(S)(SMe)MoBr(C_5H_5)]^+$, m/e 516.5, $[(C_5H_5)_2ClMo(S)_2MoBr(C_5H_5)]^+$, m/e 501.5, $[(C_5H_5)_2ClMo(SMe)_2MoCl(C_5H_5)]^+$, m/e 487, $[(C_5H_5)_2ClMo(S)(SMe)MoCl(C_5H_5)]^+$, m/e 472, and $[(C_5H_5)_2ClMo(S)_2MoCl(C_5H_5)]^+$, m/e 457.

(d) **Decomposition of 2a and 2b.** Solutions of tungsten complexes **2a** (in dichloromethane) or **2b** (in dibromomethane) were irradiated for 3 days until the disappearance of the reactants. The products were purified by chromatography on Florisil; elution with CH_2Cl_2/THF (100/5) gave a greenish band from which yellow-green solids of **6a** or **6b** were isolated in ca. 12% yield. Anal. Calcd for $C_{14}H_{16}Cl_2O_2S_2W_2$ (**6a**): C, 23.4; S, 8.9. Found: C, 23.9; S, 8.0. The mass spectrum (^{184}W , ^{35}Cl) showed ions corresponding to $[M]^+$, m/e 718, $[(C_5H_5)_2ClW(SMe)_2W(CO)Cl(C_5H_5)]^+$, m/e 690, $[(C_5H_5)_2ClW(SMe)_2WCl(C_5H_5)]^+$, m/e 662, $[(C_5H_5)_2ClWS(SMe)WCl(C_5H_5)]^+$, m/e 647, $[(C_5H_5)_2ClWS_2WCl(C_5H_5)]^+$, m/e 632, $[(C_5H_5)_2WS(SMe)WCl(C_5H_5)]^+$, m/e 612, $[(C_5H_5)_2WS_2WCl(C_5H_5)]^+$, m/e 597, and $[CH_3Cl]^+$, m/e 50.

The mass spectrum (^{184}W , ^{79}Br , and ^{81}Br) of complex **6b** showed ions corresponding to $[M]^+$, m/e 808; $[(C_5H_5)_2BrW(SMe)_2W(CO)Br(C_5H_5)]^+$, m/e 780, $[(C_5H_5)_2BrW(SMe)_2WBr(C_5H_5)]^+$, m/e 752, $[(C_5H_5)_2BrW(SMe)SWBr(C_5H_5)]^+$, m/e 737, $[(C_5H_5)_2BrWS_2WBr(C_5H_5)]^+$, m/e 722, $[(C_5H_5)_2BrWWSBr(C_5H_5)]^+$, m/e 658, $[(C_5H_5)_2WS_2WBr(C_5H_5)]^+$, m/e 643, $[(C_5H_5)_2WS_2W(C_5H_5)]^+$, m/e 562, and $[CH_3Br]^+$, m/e 94 and 96. Molar conductivity: 4.7.

Thermal Transformation of Complexes $[Mo_2(CO)_2(\mu-SMe)_3(\eta^5-C_5H_5)_2]X^-$ (1) to $[(\eta^5-C_5H_5)Mo(\mu-SMe)_3(\mu-X)Mo(\eta^5-C_5H_5)]$ (7). Approximately 1 g of **1a** or **1b** was placed in a thick glass reaction vessel fitted with a Teflon stopcock. The vessel was evacuated, and under nitrogen toluene (~50 mL) was transferred into it. The solution was heated at reflux for 48 h, after which time the color changed from dark red to brown. The solution was filtered to remove the unreacted complex **1** and the filtrate was evaporated to yield the crude product which was recrystallized from hexane at $-40^\circ C$. Brown crystals were recovered.

Yields: ca 65% (**7a**, X = Cl) and 85% (**7b**, X = Br). Anal. Calcd for $C_{13}H_{19}ClMo_2S_3$ (**7a**): C, 31.3. Found: C, 32.2. The mass spectrum showed ions corresponding to $[M]^+$, m/e 498, $[(C_5H_5)Mo(Cl)(SMe)_2SMo(C_5H_5)]^+$, m/e 483, $[(C_5H_5)Mo(Cl)(SMe)(S)_2Mo(C_5H_5)]^+$, m/e 468, $[(C_5H_5)Mo(Cl)(S)_3Mo(C_5H_5)]^+$, m/e 453, $[(C_5H_5)Mo(S)_3Mo(C_5H_5)]^+$, m/e 418, $[(C_5H_5)Mo(Cl)(S)_3Mo]^+$, m/e 388, $[(C_5H_5)Mo(S)Mo(C_5H_5)]^+$, m/e 354, $[C_5H_5]^+$, m/e 65; $[HCl]^+$, m/e 36, and $[Cl]^+$, m/e 35. Molar conductivity: 5.5.

The mass spectrum of complex **7b** showed ions corresponding to $[M]^+$, m/e 542, $[(C_5H_5)Mo(Br)(SMe)_2(S)Mo(C_5H_5)]^+$, m/e 527, $[(C_5H_5)Mo(Br)(SMe)(S)_2Mo(C_5H_5)]^+$, m/e 512, $[(C_5H_5)Mo(Br)(S)_3Mo(C_5H_5)]^+$, m/e 497, $[(C_5H_5)Mo(Br)(S)_3Mo]^+$, m/e 433, $[(C_5H_5)Mo(S)_3Mo(C_5H_5)]^+$, m/e 418, $[(C_5H_5)Mo(S)Mo(C_5H_5)]^+$, m/e 354, $[HBr]^+$, m/e 81; $[Br]^+$, m/e 80, and $[C_5H_5]^+$, m/e 65. Molar conductivity: 19.

Reactions of $[Mo_2(CO)_2(\mu-SMe)_3(\eta^5-C_5H_5)_2]X^-$ (1) with Sodium Salts. (a) Reaction of **1a with Sodium Acetylide.** Sodium acetylide (0.43 g, 3.5×10^{-3} mol) dissolved in tetrahydrofuran (~30 mL) was added to complex **1a** (1.5 g, 2.7×10^{-3} mol) dissolved in dichloromethane (~80 mL) and stirred at room temperature for 12 h. The color of the solution changed from red to dark brown. The solution was filtered to remove sodium chloride. The filtrate was evaporated and the residue stirred with a hexane/ CH_2Cl_2 mixture (1/1). The unreacted compound **1a** (0.2 g) was filtered and the filtrate was chromatographed on

Florisil. Elution with hexane/ CH_2Cl_2 mixtures gave a greenish band which provided 0.42 g (33%) of syn-anti isomers of $trans-[(\eta^5-C_5H_5)(OC)Mo(\mu-SMe)_2Mo(CO)(\eta^5-C_5H_5)]$ (**8**).

(b) **Reaction of 1a with Sodium Borohydride.** A suspension of sodium borohydride in tetrahydrofuran (0.35 g, 1×10^{-2} mol) was added to complex **1a** (1 g, 1.8×10^{-3} mol) dissolved in dichloromethane (~80 mL) and heated at $40^\circ C$ for 3 or 4 days, after which time the color changed from red to brown. The solution was filtered to remove sodium chloride and unreacted sodium borohydride. The filtrate was evaporated and the residue dissolved in a minimum of dichloromethane and chromatographed on Florisil. Elution with hexane/ CH_2Cl_2 mixture (1/3) developed a yellow-brown band which provided 0.48 g (57%) of brown syn-trans complex **8** after recrystallization from the same solvent. Elution with CH_2Cl_2 gave 50 mg (6%) of greenish crystals anti-trans complex **8**.

(c) **Reaction of 1a with $Na[Fe(CO)_2(\eta^5-C_5H_5)]$.** A solution of $Na[Fe(CO)_2(\eta^5-C_5H_5)]$ (0.36 g, 1.8×10^{-3} mol) in tetrahydrofuran (~100 mL) was added to 1.0 g (1.8×10^{-3} mol) of **1a**. The mixture was stirred vigorously and heated at $40^\circ C$ for 40 h. The solution was then filtered to remove sodium chloride. The solvent was evaporated and the residue redissolved in a minimum of dichloromethane/hexane mixtures gave 0.62 g (73%) of syn- and anti-trans-**8** and 0.2 g of $[Fe(CO)_2(\eta^5-C_5H_5)]_2$.

Reaction of Complexes $[Mo_2(CO)_2(\mu-SMe)_3(\eta^5-C_5H_5)_2]X^-$ (1) with Zinc. **1a** (1.0 g, 1.8×10^{-3} mol) was stirred in CH_2Cl_2 with 1.2 g of zinc at room temperature for 3 days. The solution was filtered to remove 1.4 g of zinc dichloride. The filtrate was evaporated, giving 0.8 g (94%) of syn-trans complex **8** after recrystallization from a dichloromethane/hexane mixture.

Attempted Reaction of $[(\eta^5-C_5H_5)(Cl)(CO)Mo(\mu-SMe)_2Mo(CO)Cl(\eta^5-C_5H_5)]$ (5a) with Unsaturated Molecules. Degassed solution of **5a** (1.0 g, 1.8×10^{-3} mol) in THF was irradiated with an excess of hexafluorobutene (3.8×10^{-3} mol) for 5 days. The solution was then evaporated to dryness, and on the NMR spectrum of the residue only starting material was detected.

Reaction of $[(\eta^5-C_5H_5)(Cl)(CO)Mo(\mu-SMe)_2Mo(CO)Cl(\eta^5-C_5H_5)]$ (5a) with $Na[Fe(CO)_2(\eta^5-C_5H_5)]$. A THF solution of **5a** (1.0 g, 1.8×10^{-3} mol) was degassed and added to 0.75 g (3.6×10^{-3} mol) of $Na[Fe(CO)_2(\eta^5-C_5H_5)]$. The solution was warmed to $40^\circ C$ for 4 days. Removal of the solvent provided only syn- and anti-trans- $[(\eta^5-C_5H_5)(CO)Mo(\mu-SMe)_2Mo(CO)(\eta^5-C_5H_5)]$ (**8**) (yield 72%), and $[CpFe(CO)_2]_2$ with NaCl.

Reactions of $[(\eta^5-C_5H_5)(CO)Mo(\mu-SMe)_2Mo(CO)(\eta^5-C_5H_5)]$ (8) with Diazomethane and with Diazald. (a) **Reaction with CH_2N_2 .** An ethereal solution of diazomethane was added to 1.2 g (2.5×10^{-3} mol) of **8** dissolved in THF. The mixture was stirred at $-30^\circ C$ and irradiated for 24 h. The solution was then evaporated to dryness, the residue was redissolved in a minimum of CH_2Cl_2 , and the solution was chromatographed on Florisil. Elution with a CH_2Cl_2/THF mixture (100/5) gave a yellow-brown band from which yellow crystals of **9** were isolated in about 20–25% yield and a violet band giving 0.25 g a violet, unstable, unidentified product.

(ii) **Reaction with Diazald.** When in tetrahydrofuran a mixture of **8** (1.2 g) and diazald (1.1 g) is refluxed for 16 h, 0.5 g of complex **8** was recovered and only 0.15 g of **9** was formed (yield 13%).

Attempted Reaction of $[(\eta^5-C_5H_5)(CO)Mo(\mu-SMe)_2Mo(CO)(\eta^5-C_5H_5)]$ (8) with Unsaturated Molecules. The molybdenum complex **8** (0.7 g, 1.5×10^{-3} mol) and excess of hexafluorobutene (3.8×10^{-3} mol) were photolyzed in THF for 2 days. The solvent was removed and the starting complex was recovered and identified by IR and NMR spectra.

Reactivity of Complex $[(\eta^5-C_5H_5)Mo(\mu-SMe)_2(\mu-S)_2Mo(\eta^5-C_5H_5)]$ (3). (a) **Reactions of Complex 3 with Molybdenum or Tungsten Hexacarbonyl.** A tetrahydrofuran solution of the violet complex **3** (isomer I) (1.0 g, 2×10^{-3} mol) was added to 2.2×10^{-3} mol of $M(CO)_6$ ($M = Mo$ or W) dissolved in THF. The

mixture was stirred and irradiated for several days until the color changed from violet to brown. The solution was then evaporated to dryness, and the residue was extracted with CH_2Cl_2 . The solution was chromatographed over Florisil. Elution with hexane/ CH_2Cl_2 (2/1) gave a red-brown ($M = \text{Mo}$) or brown ($M = \text{W}$) band, from which the product 10 ($M = \text{Mo}$) or 11 ($M = \text{W}$) was isolated in about 23% ($M = \text{Mo}$) or 40% ($M = \text{W}$) yield. Further elution with CH_2Cl_2 gave the violet starting compound 3. Complexes 10 and 11 are soluble in common organic solvents and are recrystallized from a CH_2Cl_2 /hexane mixture.

Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{Mo}_4\text{O}_{10}\text{S}_4$ (10): C, 27.8; Mo, 40.3. Found: C, 27.8; Mo, 40.4. Complex 10 decomposed in the mass spectrometer giving the $[(\text{C}_5\text{H}_5)\text{Mo}(\text{SMe})_4\text{Mo}(\text{C}_5\text{H}_5)]$ species, suggesting that some recombination took place in the spectrometer. Molar conductivity: 1.5. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{Mo}_2\text{O}_5\text{S}_4\text{W}$ (11): C, 25.4; S, 15.9; Mo, 23.8; W, 22.8. Found: C, 24.8; S, 15.9; Mo, 21.2; W, 22.0. Molar conductivity: 1.1.

(b) **Attempted Dealkylation Reactions of (3).** (i) **With $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$** The molybdenum complex 3 (0.8 g, 1.6×10^{-3} mol) and excess of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (0.4 g) were refluxed in toluene for 24 h. Removal of the solvent in vacuo provided only ferrocene and starting complex.

(ii) **With $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4]$** Reaction of 3 (0.7 g) in THF with 1 equiv of $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4]$ at 40 °C for 4 days also resulted in no reaction.

(c) **Attempted Reaction of 3 with Unsaturated Molecules.** Complex 3 (0.8 g, 1.6×10^{-3} mol) in tetrahydrofuran was photolyzed or heated for 60 h with 2×10^{-3} mol of hexafluorobutyne.

After removal of the solvent, only starting complex was detected.

(d) **Attempted Reaction of 3 with CO.** 3 was dissolved in THF and 1 atm of CO was added. The solution was stirred at 60 °C for 24 h. The starting compound was recovered and identified by IR and NMR spectra.

Acknowledgment. We are grateful to Dr. D. Davies (University of Leicester) for his comments on this paper and to Mr. J. Y. Le Gall for assistance with the NMR. M.B.G-L is indebted to CNPq (Brasil) for a fellowship. We thank the CNRS for financial support.

Registry No. 1a, 103619-72-3; 1b, 103667-00-1; 1c (X = Cl), 103667-03-4; 1c (X = Br), 103750-97-6; 1d, 103667-04-5; 1e, 103667-05-6; 2a, 103619-73-4; 2b, 103667-01-2; 3, 103619-81-4; 5a, 103639-17-4; 5b, 103619-76-7; 5c, 103619-77-8; 6a, 103639-18-5; 6b, 103619-78-9; 7a, 103619-79-0; 7b, 103619-80-3; 8a, 81874-19-3; 8b, 81874-18-2; 9, 103728-97-8; 10, 103619-82-5; 11, 103619-83-6; $[\text{Mo}_2(\text{CO})_4(\text{M-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]$, 103619-74-5; $[\text{W}_2(\text{CO})_4(\text{M-SMe})_2(\eta^5\text{-C}_5\text{H}_5)_2]$, 103619-75-6; $[\text{Mo}(\text{CO})_3\text{Br}(\eta^5\text{-C}_5\text{H}_5)]$, 12079-79-7; $[\text{W}(\text{CO})_3\text{Br}(\eta^5\text{-C}_5\text{H}_5)]$, 37131-50-3; $\text{Na}[\text{Fe}(\text{CO})_2(\eta^3\text{-C}_5\text{H}_5)]$, 12152-20-4; $[\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$, 11117-09-2; $\text{Mo}(\text{CO})_6$, 13939-06-5; $\text{W}(\text{CO})_6$, 14040-11-0; MeSSMe, 624-92-0; sodium acetylide, 1066-26-8.

Supplementary Material Available: A table of anisotropic thermal parameters (1 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Synthesis, Phosphorus-31 Shift Correlated Two-Dimensional (COSY) Nuclear Magnetic Resonance Spectra, and Structure of the Tris(trimethyl phosphite)-Substituted Phosphido-Bridged Heteronuclear Dimer

$[(\text{MeO})_3\text{P}]_2(\text{CO})_2\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_2[\text{P}(\text{OMe})_3]$

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Received February 25, 1986

Trimethyl phosphite reacts with the phosphido-bridged heterobinuclear complex $(\text{CO})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (1), affording mono-, $[(\text{MeO})_3\text{P}](\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (2), di-, $[(\text{MeO})_3\text{P}]_2(\text{CO})_2\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (3a), and tri-, $[(\text{MeO})_3\text{P}]_2(\text{CO})_2\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_2[\text{P}(\text{OMe})_3]$ (4), substituted derivatives characterized by microanalysis and infrared and ^1H and ^{31}P NMR spectroscopy. Crystals of 4 are triclinic of space group $P\bar{1}$ with $a = 10.240$ (2) Å, $b = 11.555$ (3) Å, $c = 16.273$ (3) Å, $\alpha = 76.24$ (2)°, $\beta = 77.97$ (2)°, $\gamma = 71.86$ (2)°, and $Z = 2$. The crystal structure was solved and refined to R and R_w values of 0.039 and 0.048, respectively, by using 4380 observed ($I \geq 3\sigma(I)$) reflections measured on a Syntex $\text{P}2_1$ diffractometer. In the heterobimetallic complex, one trimethyl phosphite ligand is located on the cobalt atom approximately trans to the Ru-Co bond and the two remaining phosphites on the ruthenium, one trans to the Ru-Co bond and the other trans to the phosphido bridge ($\text{Ru-P}(1)\text{-Co} = 76.01$ (3)°). An analysis of the ^{31}P NMR spectrum of 4 using two-dimensional (2D) (COSY) techniques has revealed large trans $(\text{MeO})_3\text{P-PPh}_2$ ($^2J_{\text{PPh}_2\text{-P}(\text{OMe})_3} = 177.4$ Hz) and trans $(\text{MeO})_3\text{P-P}(\text{OMe})_3$ ($^3J_{\text{P}(\text{OMe})_3\text{-P}(\text{OMe})_3} = 80.6$ Hz) couplings and much smaller cis coupling constants.

Two fundamental aspects of the rapidly developing chemistry of heterobimetallic complexes¹⁻¹¹ are the selectivities of the two metal sites for various substrates and the degree to which one metal influences the reactivity patterns of the second center. For saturated 34-electron heterobinuclear carbonyls with strong metal-metal inter-

actions key questions concern the sites and mechanisms (associative or dissociative) of simple substitution reac-

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