27.97; H, 0.64. Found: C, 26.20; H, 0.56.

Crystal Structure Determinations. Details of data collection procedures, structure solution, and refinement are given in Table VII. Data were collected on an Enraf-Nonius CAD4F automated diffractometer, with graphite-monochromated X-radiation (λ = 0.71069 Å). Unit cell parameters were determined by refinement of the setting angles ($\theta \geqslant 12°$) of 25 reflections. Standards were measured every 2 h during data collection, and a linear correction was applied for complex **3a**. Lorentz, polarization, and absorption corrections were applied to both data sets, by Gaussian quatrature[59] for **3a** and by the method of Stuart and Walker[60] for **4**. Structures were solved by direct methods (MITHRIL[61]) and subsequent electron density difference syntheses. Hydrogen atoms were included in calculated positions for **4** (Cp C–H = 1.084 Å; Me C–H = 1.079 Å) and held fixed with fixed (0.05 Å^3) isotropic thermal parameters. Hydrogen atoms for **3a** were included at observed positions and thermal and positional parameters freely refined. Refinement was by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with the weighting function $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. All non-hydrogen atoms were allowed anisotropic thermal motion. Scattering factors were taken from ref 62 with corrections applied for anomalous dispersion. All calculations were carried out on a Gould-SEL 32/27 mini computer, using the GX suite of programs.[63]

Extended Hückel Calculations. Extended Hückel calculations[64,65] were carried out by using the programs ICON8 and FMO.[66] Orbital exponents and H_{ii}'s for Fe and Co were obtained from previous work.[36] Geometries were taken from the crystal structures and idealized to C_{3v} for "$Co_3(CO)_9$" and C_s for "$Fe_3(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)$" and "$Fe_3(\mu\text{-}H)(CO)_{10}$". Bond distances (Å) used were as follows: **3**: Co–Co = 2.478, Co–C_{alk} = 1.9, Co–C_{CO} = 1.8, C–O(carbonyl) = 1.15 Å. **4**: Fe–Fe = 2.56, Fe–C_{alk} = 1.936, Fe–C_{CO}(term) = 1.80, Fe–C_{CO}(bridge) = 1.80, 2.10, C–O(carbonyl) = 1.15 Å. **1**: Fe–Fe = 2.667, Fe–C_{alk} = 1.85, Fe–C_{CO}(term) = 1.75, C–O(carbonyl) = 1.15 Å. The same geometries were used for the alkylidyne groups throughout: CH, C–H = 1.1 Å; $COCH_3$, C–O = 1.32, O–C_{CH_3} = 1.43, C–H = 1.073 Å, and ∠C–O–C = 120°; CCH_3, C–C = 1.54 and C–H = 1.085 Å. All calculations were carried out on an ICL 2988. Orbital contour plots (at intervals of 0.05, 0.1, 0.2, 0.5, and 0.8 au^{-3}) were drawn by using the program PSI77.[67]

Registry No. **1a**, 55992-19-3; **1b**, 87698-64-4; **3a**, 41362-64-5; **4**, 101224-56-0; $Co_2(CO)_8$, 10210-68-1; $Co_3(\mu_3\text{-}CH)(CO)_9$, 15664-75-2; $Co_3(\mu_3\text{-}CCH_3)(CO)_9$, 13682-04-7; Co, 7440-48-4; Fe, 7439-89-6.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and calculated hydrogen atom positional parameters and complete listings of bond lengths and angles for **3a** and **4** (6 pages); listings of calculated and observed structure factors for **3a** and **4** (30 pages). Ordering information is given on any current masthead page.

---

(59) Coppens, P. *Crystallographic Computing*; Munksgaard: Copenhagen, 1970.

(60) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(61) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(62) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

(63) Mallinson, P. R.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 51.

(64) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(65) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179.

(66) Howell, J.; Rossi, A.; Wallace, D.; Haraki, K.; Hoffmann, R. *QCPE* **1977**, *10*, 344.

(67) Jorgensen, W. L. "PSI77", *QCPE* **1977**, *10*, 340.

Molybdenum–Molybdenum and Phosphorus–Phosphorus or Sulfur–Sulfur Bond Cleavage Reactions of Organic Substrates with Compounds Containing a Metal–Metal Triple Bond

Howard Alper,*[†1a] Frederick W. B. Einstein,*[1b] Frederick W. Hartstock,[1a] and Richard H. Jones[1b]

Departments of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4, and Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Received July 29, 1986

Reaction of the metal–metal triple-bonded complexes $(RC_5H_4)_2Mo_2(CO)_4$ (R = H, CH_3) with tetraalkyldiphosphine disulfides $[R_2'P(S)P(S)R_2']$ affords the mononuclear complexes $(R_2'PS)Mo(CO)_2(C_5H_5\text{-}\eta^5)$ in which the $R_2'PS$ unit acts as a three-electron ligand. A single-crystal X-ray analysis of one such complex (R = R′ = CH_3) revealed that the phosphorus–sulfur bond distance [2.003 (2) Å] was in between that of a typical PS single and double bond. Crystals of this complex are orthorhombic with a = 6.643 (2) Å, b = 13.643 (5) Å, c = 13.902 (3) Å, Z = 4, and space group $P2_12_12_1$. The structure was refined by full-matrix least-squares techniques to R_F = 0.026 and R_{wF} = 0.030 for 1355 reflections with $I > 3\sigma(I)$. Dithiocarbamate complexes were obtained when thiuram disulfides were used as the substrates. The structure of one such complex, $(\eta^5\text{-}C_5H_5)Mo(CO)_2[S_2CN(CH(CH_3)_2)_2]$, was confirmed by X-ray analysis. Crystals of the dithiocarbamate are triclinic with a = 7.800 (1) Å, b = 10.186 (3) Å, c = 10.250 (3) Å, α = 79.10 (3)°, β = 85.26 (2), γ = 83.63 (2)°, Z = 2, and space group $P\bar{1}$. The structure was refined by full-matrix least-squares techniques to R_F = 0.038 and R_{wF} = 0.051 for 2356 reflections with $I > 3\sigma(I)$.

A wide variety of interesting reactions have been observed by using cyclopentadienylmolybdenum dicarbonyl dimer **1**, R = H, a compound containing a metal–metal triple bond, and organic substrates.[2,3] Use of organosulfur and organophosphorus compounds as reactants usually results in addition to the organometallic complex. For example, cyclic sulfides such as tetrahydrothiopyran undergo nucleophilic addition to **1**, R = H, affording **2** where the heterocyclic functions as a bridging ligand.[4] Com-

---

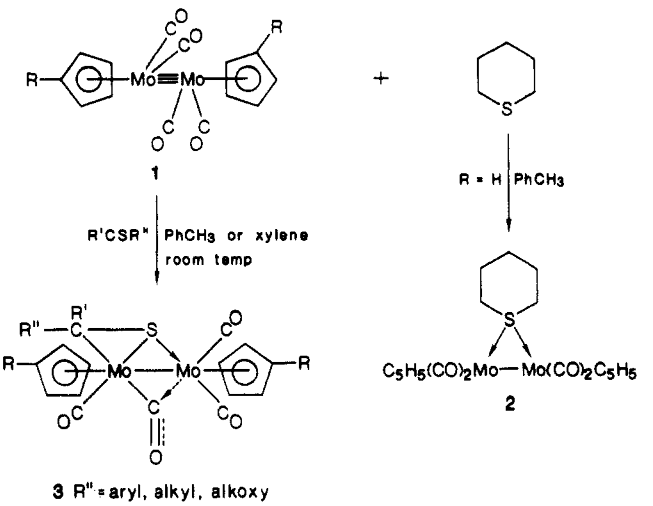
[†] John Simon Guggenheim Fellow, 1985–1986. Killam Research Fellow, 1986–1988.

(1) (a) University of Ottawa. (b) Simon Fraser University.

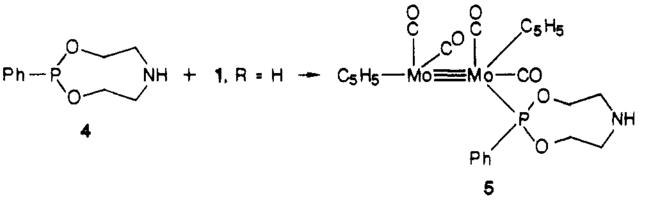
(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley; New York, 1982.

(3) Curtis, M. D.; Messerle, L.; Fontinos, N. A. In *Reactivity of Metal-Metal* Bonds; ACS Symposium Series No. 155; American Chemical Society: Washington, DC, 1981; pp 221–257 and references cited therein.

0276-7333/87/2306-0829$01.50/0 © 1987 American Chemical Society

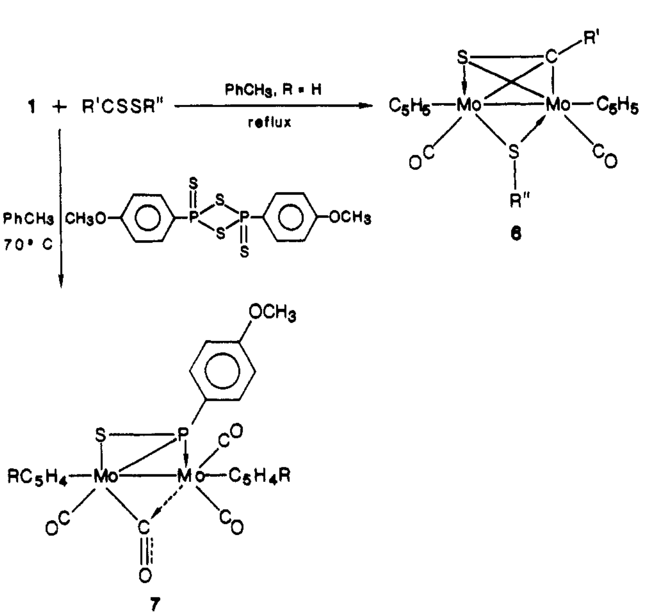


plexes of structural type **3**, in which the thione function is bonded to one molybdenum atom and the sulfur is donor bound to the other metal atom, result by exposure of **1** to a thioketone[5] or thio ester.[6] Triphenylphosphine sulfide undergoes unusual 1,1 addition to **1**.[7] Ligand substitution, with a retained metal–metal triple bond, has been observed in the reaction of **1** with the bicyclic aminophosphorane **4** affording **5** as the major product.[8]



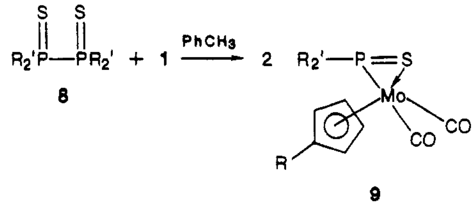
Cleavage of the organosulfur or -phosphorus ligand has been reported for several reactions involving **1**. Dimethyl or diphenyl disulfide adds to **1**, with rupture of the S–S bond, to give the metal–metal single-bond complexes $(C_5H_5)_2Mo_2(CO)_4(SR)_2$ (R = CH_3, Ph).[9] Dithio esters undergo carbon–sulfur bond cleavage on reaction with **1** to form a novel class of complexes (**6**) having a symmetrically bridging thioacyl function.[10] Such a cleavage reaction results in ring opening of dihydro-2-(3*H*)-thiophenethione.[11] Binuclear phosphinothioylidene complexes **7**, isolated by treatment of **1** with the dimer of (*p*-methoxyphenyl)thionophosphine sulfide (Lawesson's reagent), arise from a phosphorus–sulfur bond cleavage reaction.[12]

It seemed likely that appropriate organic substrates containing a weak phosphorus–phosphorus or sulfur–sulfur bond could experience cleavage of such bonds, and of the metal–metal bond, on reaction with **1**. Tetraalkyldiphosphine disulfides and tetraalkylthiuram disulfides appeared to be suitable candidates for this type of reaction, since they contain the noted type of bonds as well as P=S and C=S moieties capable of interacting with the metal. We now report that these two classes of compounds indeed do undergo cleavage reactions on treatment with **1**, affording mononuclear complexes.



Results and Discussion

(a) Tetraalkyldiphosphine Disulfides. When a mixture of tetramethyldiphosphine disulfide (**8**, R′ = CH_3) and **1**, R = CH_3, was refluxed in toluene for 15 h, complex **9**, R = R′ = CH_3, was isolated in 20% yield. The structure of **9**, R = R′ = CH_3 was determined on the basis of analytical and spectral data, as well as by an X-ray analysis. Two terminal carbonyl stretching absorptions were observed in the infrared spectrum (Nujol) at 1960 and 1875 cm^{-1}, in accord with data [1858, 1873 cm^{-1} (CH_2Cl_2)] reported for $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}SPPh_2)$, the latter being formed by the reaction of diphenylphosphine sulfide $[Ph_2(H)PS]$ with cyclopentadienylmolybdenum tricarbonyl chloride.[13] A molecular ion peak was observed in the mass spectrum (*m*/*e* 324) followed by successive loss of two carbon monoxide ligands. The proton magnetic resonance spectrum gave, in addition to the multiplet for the protons of the methyl-substituted cyclopentadienyl ring (centered at δ 5.17), signals at δ 1.73, 1.87, and 1.92 for the three methyl groups in **9**, R = R′ = CH_3. One carbonyl carbon signal appeared at δ 267.9 in the ^{13}C NMR indicative of the occurrence of a fluxional process in solution. The diethylphosphine sulfide complex **9**, R = H and R′ = C_2H_5, was also prepared by treatment of **8**, R′ = C_2H_5, with cyclopentadienylmolybdenum dicarbonyl dimer.



An X-ray determination of **9**, R = R′ = CH_3, was made in order to unequivocally establish the structure of the complex. Pertinent crystallographic and experimental parameters are listed in Table I, fractional coordinates in Table II, and selected interatomic distances and angles in

---

[4] Blechschmitt, K.; Guggolz, E.; Ziegler, M. L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 85.

[5] Alper, H.; Silavwe, N. D.; Birnbaum, G. I.; Ahmed, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 6582.

[6] Alper, H.; Einstein, F. W. B.; Nagai, R.; Petrignani, J. F.; Willis, A. C. *Organometallics* **1983**, *2*, 1291.

[7] Alper, H.; Hartgerink, J. *J. Organomet. Chem.* **1980**, *190*, C25.

[8] Wachter, J.; Riess, J. G.; Mitschler, A. *Organometallics* **1984**, *3*, 714.

[9] Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23.

[10] Alper, H.; Einstein, F. W. B.: Hartstock, F. W.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 173.

[11] Alper, H.; Einstein, F. W. B.; Hartstock, F. W.; Willis, A. C. *Organometallics* **1986**, *5*, 9.

[12] Alper, H.; Einstein, F. W. B.; Petrignani, J. F.; Willis, A. C. *Organometallics* **1983**, *2*, 1422.

[13] Ambrosius, H. P. M. M.; Noordik, J. H.; Ariaans, G. J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 832.

Table I. Crystal Data and Experimental Parameters

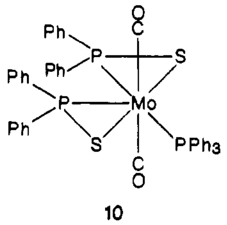
	9	15
formula	$C_{10}H_{13}MoO_2PS$	$C_{14}H_{19}MoNO_2S_2$
mol wt	324.18	393.37
space group	$P2_12_12_1$	$P\bar{1}$
a, Å	6.643 (2)	7.800 (1)
b, Å	13.643 (5)	10.186 (3)
c, Å	13.902 (3)	10.250 (3)
α, deg	90.0	79.10 (3)
β, deg	90.0	85.26 (2)
γ, deg	90.0	83.63 (2)
V, Å^3	1260.0	793.1
Z	4	2
d_{calcd}, g/mL	1.709	1.647
cryst dimens, mm	0.33 × 0.26 × 0.33	0.55 × 0.38 × 0.08
radiatn	Mo Kα	Mo Kα
μ(Mo Kα), cm^{-1}	12.80	10.60
transmiss factors	0.670–0.844	0.782–0.913
scan mode	$\omega/2\theta$	$\omega/2\theta$
scan width, deg in ω	1.20	1.10
scan speed, deg in ω	1.10–5.49	0.87–4.12
total no. of reflns	1683	2777
no. of obsd reflns	1355	2356
no. of variables	141	241
R_F	0.026	0.038
R_{wF}	0.030	0.051
GOF	1.13	1.03

Table II. Atomic Coordinates (×10^4) with Esd's in Parentheses and U_{eq} (×10^4) for the Non-Hydrogen Atoms of Compound 9

atom	x/a	y/b	z/c	U_{eq}, Å^2
Mo(1)	1911.4 (7)	659.8 (3)	810.1 (3)	237
P(1)	2976 (2)	−990.1 (9)	590.8 (8)	254
S(1)	190 (2)	−846 (1)	57 (1)	331
O(1)	6004 (8)	1156 (4)	−145 (4)	540
O(2)	623 (8)	1608 (3)	−1130 (3)	483
C(1)	4469 (9)	974 (4)	215 (4)	354
C(2)	1057 (9)	1253 (4)	−418 (4)	324
C(3)	−301 (9)	605 (5)	2184 (4)	362
C(4)	−413 (10)	1524 (4)	1723 (4)	366
C(5)	1496 (10)	1989 (5)	1787 (4)	402
C(6)	2818 (12)	1357 (5)	2258 (4)	429
C(7)	1714 (10)	490 (4)	2497 (4)	379
C(8)	−2001 (12)	−93 (6)	2344 (5)	529
C(9)	4803 (9)	−1405 (4)	−268 (4)	378
C(10)	3171 (13)	−1870 (4)	1563 (4)	387

Table III. A thermal ellipsoid plot of **9**, R = R′ = CH_3, is given in Figure 1.

The only other η^2-$R_2'PS$ complex for which an X-ray analysis has been made is (η^2-$Ph_2PS)_2Mo(CO)_2(PPh_3)$ (**10**), which has a pentagonal-bipyramidal configuration around the metal atom. The dimensions of the MoPS fragment in **9** are similar to those in **10** except that the Mo–S bond is significantly shorter [2.574 (1) Å] than those previously found [2.613 (2) and 2.630 (2) Å][13]. Consistent with this, the P–S bond is lengthened from that found in a typical P═S double bond (range of 1.926 (1)[14]–1.966 (2) Å[15]) but is shorter than that found for a P—S single bond [2.122 (1) Å[14]]. The bond angles of the η^2-$R_2'PSMo$ moiety are similar to those of one of two such units in **10**. Note that the nature of the R′ group in η^2-$R_2'PS$ probably influences the magnitude of the bond distances and angles in the η^2-$R_2'PSMo$ portion of the complex.



10

Table III. Selected Interatomic Distances (Å) and Angles (deg) for 9, R = R′ = CH_3

Bond Distances			
Mo(1)–P(1)	2.379 (1)	P(1)–C(9)	1.794 (6)
Mo(1)–S(1)	2.574 (1)	P(1)–C(10)	1.812 (5)
Mo(1)–C(1)	1.937 (6)	O(1)–C(1)	1.163 (7)
Mo(1)–C(2)	1.973 (6)	O(2)–C(2)	1.139 (7)
Mo(1)–C(3)	2.411 (5)	C(3)–C(4)	1.409 (9)
Mo(1)–C(4)	2.321 (6)	C(3)–C(7)	1.416 (9)
Mo(1)–C(5)	2.283 (6)	C(3)–C(8)	1.494 (9)
Mo(1)–C(6)	2.306 (6)	C(4)–C(5)	1.421 (9)
Mo(1)–C(7)	2.360 (5)	C(5)–C(6)	1.394 (9)
P(1)–S(1)	2.003 (2)	C(6)–C(7)	1.431 (9)

Bond Angles			
S(1)–Mo(1)–P(1)	47.5 (1)	C(10)–P(1)–C(9)	103.8 (3)
C(1)–Mo(1)–P(1)	83.9 (2)	P(1)–S(1)–Mo(1)	61.1 (1)
C(1)–Mo(1)–S(1)	113.1 (2)	O(1)–C(1)–Mo(1)	179.5 (5)
C(2)–Mo(1)–P(1)	111.3 (2)	O(2)–C(2)–Mo(1)	177.9 (6)
C(2)–Mo(1)–S(1)	81.3 (2)	C(7)–C(3)–C(4)	106.7 (6)
C(2)–Mo(1)–C(1)	78.0 (3)	C(8)–C(3)–C(4)	126.5 (6)
S(1)–P(1)–Mo(1)	71.4 (1)	C(8)–C(3)–C(7)	126.7 (6)
C(9)–P(1)–Mo(1)	125.8 (2)	C(5)–C(4)–C(3)	108.8 (6)
C(9)–P(1)–S(1)	114.2 (2)	C(6)–C(5)–C(4)	108.4 (6)
C(10)–P(1)–Mo(1)	123.5 (2)	C(7)–C(6)–C(5)	107.3 (6)
C(10)–P(1)–S(1)	114.0 (3)	C(6)–C(7)–C(3)	108.8 (6)

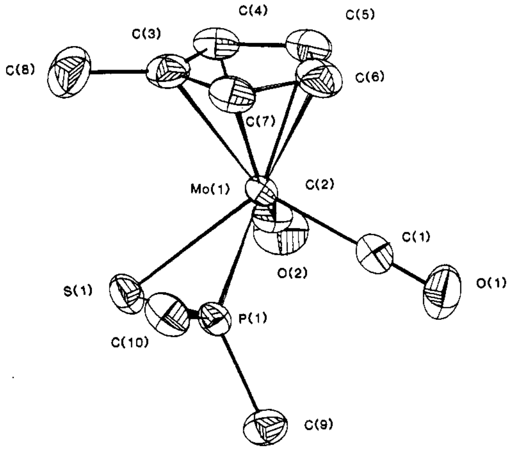
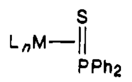
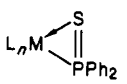


Figure 1. A view of the $MoC_{10}H_{13}O_2PS$ molecule showing the atom labeling scheme. Thermal ellipsoids show 50% probability levels, and hydrogen atoms have been deleted, here and in Figure 2.

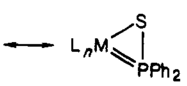
Rhodium and iridium complexes containing η^2-Ph_2PS ligands have been described as having structure **11**.[16] A more appropriate structural representation is **12**, with **13** possibly being a significant contributor to the resonance hybrid. Irrespective of which, if either, of the two structures (**12** or **13**) is the major contributor, the $SPPh_2$ acts as a formal three-election ligand to the metal, with either phosphorus or sulfur functioning as a one-electron ligand. This situation is analogous to that found for η^2-acyl complexes of molybdenum (and other metals).[17]



11



12



13

---

[14] Fluck, E.; Gongalez, G.; Peters, K.; von Schnerring, H. G. *Z. Anorg. Allg. chem.* **1980**, *473*, 25.

[15] Kerr, K. A.; Boorman, P. M.; Misener, B. S.; vanRoode, G. A. *Can. J. Chem.* **1977**, *55*, 3081.

[16] Thewissen, D. H. M. W. *J. Organometal. Chem.* **1980**, *192*, 115.

[17] Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550 and references cited therein.

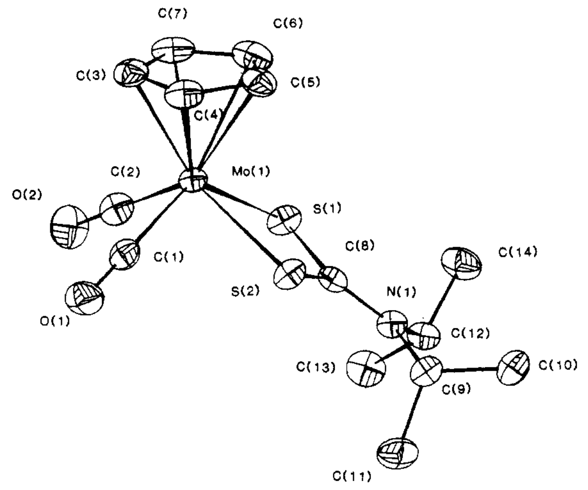
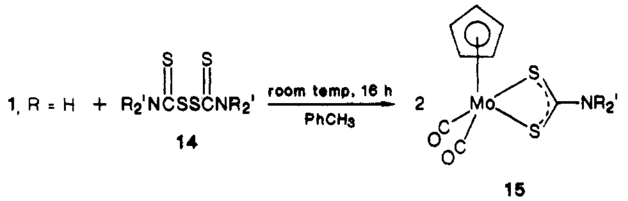


Figure 2. A view of the $MoC_{14}H_{19}NO_2S_2$ molecule.

Table IV. Atomic Coordinates (×10⁴) with Esd's in Parentheses and U_{eq} (×10⁴) for the Non-Hydrogen Atoms of Compound 15

atom	x/a	y/b	z/c	U_{eq}, Å^2
Mo(1)	1203.8 (5)	2539.9 (4)	2518.2 (4)	201
S(1)	1376 (2)	1524 (1)	466 (1)	255
S(2)	3449 (2)	3490 (1)	843 (1)	244
O(1)	4335 (5)	2140 (5)	4288 (4)	405
O(2)	1639 (6)	-446 (4)	3944 (4)	433
N(1)	3810 (5)	2501 (4)	-1434 (4)	225
C(1)	3181 (7)	2298 (5)	3633 (5)	278
C(2)	1448 (7)	647 (5)	3383 (5)	305
C(3)	-805 (7)	3275 (5)	4037 (5)	302
C(4)	-45 (7)	4415 (5)	3322 (5)	292
C(5)	-561 (7)	4643 (5)	1998 (6)	312
C(6)	-1569 (7)	3648 (6)	1877 (6)	361
C(7)	-1737 (7)	2781 (6)	3140 (6)	342
C(8)	2984 (6)	2501 (4)	-253 (5)	214
C(9)	5176 (6)	3430 (5)	-1881 (5)	263
C(10)	5024 (8)	4168 (6)	-3309 (6)	366
C(11)	6960 (7)	2675 (6)	-1658 (7)	390
C(12)	3561 (6)	1530 (5)	-2319 (5)	233
C(13)	3994 (8)	66 (5)	+1679 (6)	333
C(14)	1772 (7)	1772 (6)	-2862 (6)	367

(b) Tetraalkylthiuram Disulfides. Mononuclear dithiocarbamate complexes **15** are formed in good yield by simply stirring a thiuram disulfide [**14**, R′ = CH_3, C_2H_5, $CH(CH_3)_2$] with **1**, R = H, in toluene at room temperature.



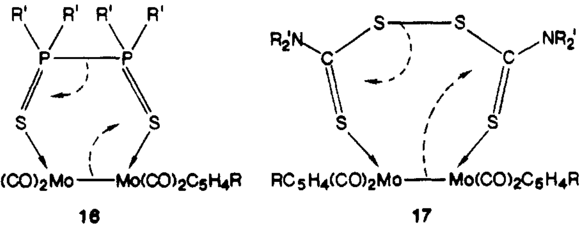
The analytical and spectral data [e.g. ν_{CO} 1942, 1852 cm^{-1} (Nujol) for **15**, R′ = $CH(CH_3)_2$] support the assigned structure. The two terminal carbonyl ligands of **15**, R′ = $CH(CH_3)_2$, gave a single carbon resonance at δ 257.1 (as for **9**), and the resonance for the carbon of the dithiocarbamate moiety (δ 207.6) is similar to that for other dithiocarbamate complexes.[18] An X-ray analysis of **15**, R′ = $CH(CH_3)_2$ (see Figure 2 for the thermal ellipsoid diagram and Tables I, IV, and V for relevant data), indicates that the gross features of **9** and **15** are similar although there are differences in detail [e.g., the C(1)-Mo(1)C(2) bond angle is less in **15** than in **9** while the S(2)Mo(1)C(1) and S(1)Mo(1)C(2) angles of **15** and the C(2)Mo(1)S(1) angle of **9** are similar]. The Mo–S distances (average 2.497 Å) agree with data reported for other Mo thiocarbamate complexes.[19] The plane of the cyclopentadienyl ring is tilted (6.9°) with respect to the plane defined by C(1), C(2), S(1), and S(2) in order to maximize the separation of those atoms from the cyclopentadienyl ring (which are pseudotrans to the carbonyl groups). While molybdenum (and tungsten) complexes of type **15** have been known for over 20 years,[20-22] an X-ray analysis has apparently not been reported for this class of complexes.

Table V. Selected Interatomic Distances (Å) and Angles (deg) for 15, R′ = $CH(CH_3)_2$

	Bond Distances		
Mo(1)-S(1)	2.502 (1)	N(1)-C(12)	1.500 (6)
Mo(1)-S(2)	2.491 (1)	O(1)-C(1)	1.146 (7)
Mo(1)-C(1)	1.961 (5)	O(2)-C(2)	1.152 (7)
Mo(1)-C(2)	1.959 (5)	C(3)-C(4)	1.412 (8)
Mo(1)-C(3)	2.284 (5)	C(3)-C(7)	1.411 (8)
Mo(1)-C(4)	2.308 (5)	C(4)-C(5)	1.417 (8)
Mo(1)-C(5)	2.409 (5)	C(5)-C(6)	1.379 (8)
Mo(1)-C(6)	2.408 (5)	C(6)-C(7)	1.428 (9)
Mo(1)-C(7)	2.328 (5)	C(9)-C(10)	1.521 (7)
S(1)-C(8)	1.719 (5)	C(9)-C(11)	1.526 (7)
S(2)-C(8)	1.728 (5)	C(12)-C(13)	1.524 (7)
N(1)-C(8)	1.324 (6)	C(12)-C(14)	1.523 (7)
N(1)-C(9)	1.489 (6)		
	Bond Angles		
S(2)-Mo(1)-S(1)	68.49 (4)	C(5)-C(4)-C(3)	107.9 (5)
C(1)-Mo(1)-S(1)	120.7 (1)	C(6)-C(5)-C(4)	108.5 (5)
C(1)-Mo(1)-S(2)	79.9 (1)	C(7)-C(6)-C(5)	108.3 (5)
C(2)-Mo(1)-S(1)	82.1 (1)	C(6)-C(7)-C(3)	107.6 (5)
C(2)-Mo(1)-S(2)	121.1 (2)	S(2)-C(8)-S(1)	109.2 (3)
C(2)-Mo(1)-C(1)	73.1 (2)	N(1)-C(8)-S(1)	127.3 (4)
C(8)-S(1)-Mo(1)	91.1 (2)	N(1)-C(8)-S(2)	123.5 (4)
C(8)-S(2)-Mo(1)	91.2 (2)	C(10)-C(9)-N(1)	112.9 (4)
C(9)-N(1)-C(8)	119.2 (4)	C(11)-C(9)-N(1)	110.1 (4)
C(12)-N(1)-C(8)	123.7 (4)	C(11)-C(9)-C(10)	112.2 (4)
C(12)-N(1)-C(9)	117.0 (4)	C(13)-C(12)-N(1)	113.4 (4)
O(1)-C(1)-Mo(1)	179.1 (5)	C(14)-C(12)-N(1)	112.0 (4)
O(2)-C(2)-Mo(1)	176.3 (5)	C(14)-C(12)-C(13)	112.0 (5)
C(7)-C(3)-C(4)	107.6 (5)		

It should be pointed out that one of the methods described for the synthesis of **15** involves reaction of the thiuram disulfide with cyclopentadienylmolybdenum tricarbonyl dimer in refluxing methylcyclohexane (bp 101 °C).[20] Since **1** and related complexes containing a triple bond are generated by thermal decarbonylation of metal–metal single-bonded compounds,[9] it is quite likely that **1** was generated in the thiuram–$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ reaction.

The initial step in both the phosphorus–phosphorus and sulfur–sulfur bond cleavage reactions may involve addition of the organic ligands to **1** affording **16** and **17**, respectively.



Molybdenum–molybdenum and either P–P or S–S bond

---

[18] Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745.

[19] Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Neaves, B. D.; Dahlstrom, P.; Hyde, J.; Zubieta, J. *J. Organomet. Chem.* **1981**, *213*, 109.

[20] Cotton, F. A.; McCleverty, J. A. *Inorg. Chem.* **1964**, *3*, 1398.

[21] Glass, W. K.; Shiels, A. *J. Organomet. Chem.* **1974**, *67*, 401.

[22] Abrahamson, H. B.; Freeman, M. L. *Organometallics* **1983**, *2*, 679.

[23] Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 209.

rupture would then afford the observed products. Thus, we believe that the presence of a weak P–P or S–S bond is, as anticipated, critical for the concurrent cleavage of the metal–metal bond in the dimolybdenum system.

Experimental Section

General Data. See ref 11 for information on melting point and spectral determinations and on elemental analyses. The tetraalkyldiphosphine disulfides, tetraalkylthiuram disulfides, and cyclopentadienylmolybdenum tricarbonyl dimer were commercial products and were used as received. Bis(methylcyclopentadienyl)dimolybdenum hexacarbonyl was synthesized following literature procedures.

Schlenk and vacuum line techniques were used, and all reactions were run under a dry nitrogen atmosphere.

Reaction of 1, R = CH_3, with Tetramethyldiphosphine Disulfide (8, R′ = CH_3). A toluene (20 mL) solution of bis(methylcyclopentadienyl)dimolybdenum hexacarbonyl (1.00 g, 1.93 mmol) was refluxed overnight. Analysis by infrared spectroscopy revealed that 1, R = CH_3, was generated, and then **8**, R′ = CH_3 (0.372 g, 2.00 mmol), was added, and the resulting reaction mixture was refluxed for 15 h. The contents of the Schlenk tube were evaporated to dryness, and silica gel column chromatography (1:1 hexane–methylene chloride as eluant) afforded **9**, R = R′ = CH_3 as an orange-brown solid in 20% yield: mp 56–58 °C; IR (Nujol) ν_{CO} 1960, 1875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73, 1.87, 1.92 (s, 9 H, CH_3 groups), 5.17 (m, 4 H, C_5H_4); ^{13}C NMR ($CDCl_3$) δ_{CO} 267.9; mass spectrum, *m/e* 324 [m]$^+$, 296 [M - CO]$^+$, 268 [M - 2CO]$^+$. Anal. Calcd for $C_{10}H_{13}MoO_2PS$: C, 37.05; H, 4.04; S, 9.89. Found: C, 37.26; H, 3.89; S, 10.11.

Reaction of 1, R = H, with Tetraethyldiphosphine Disulfide (8, R′ = C_2H_5). Application of the previous procedure to 1, R = H, and **8**, R′ = C_2H_5, afforded **9**, R = H and R′ = C_2H_5, as an orange-brown complex in 59% yield: mp 88–90 °C; IR (Nujol) ν_{CO} 1960, 1880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H, CH_3), 1.25 (t, 3 H, CH_3), 2.00 (q, 2 H, CH_2), 2.10 (q, 2 H, CH_2), 5.30 (s, 5 H, C_5H_5); mass spectrum, *m/e* 338 [M]$^+$, 310 [M - CO]$^+$, 282 [M - 2CO]$^+$.

Reaction of 1, R = H, with Tetraisopropylthiuram Disulfide [14, R′ = $CH(CH_3)_2$]. The molybdenum–molybdenum triple-bond complex 1, R = H, was generated by refluxing a toluene solution (20 mL) of bis(cyclopentadienyl)dimolybdenum hexacarbonyl (1.00 g, 2.04 mmol) for 18–24 h. After the solution was cooled to room temperature, 0.71 g (2.00 mmol) of the thiuram disulfide 14, R′ = $CH(CH_3)_2$, was added, and the reaction mixture was stirred overnight at room temperature. Evaporation of the reaction mixture afforded the crude product, which was purified by silica gel column chromatography using methylene chloride as the eluant. The yield of bright orange **15**, R′ = $CH(CH_3)_2$, was 0.90 g (57%): mp 200–203 °C; IR, (Nujol) ν_{CO} 1942, 1852 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 [d, 12 H, $CH(CH_3)_2$] 4.20 [m, 2 H, $CH(CH_3)_2$], 5.33 (s, 5 H, C_5H_5); ^{13}C NMR ($CDCl_3$) δ 19.9 (methyl carbons), 49.3 (CH), 94.3 (C_5H_5), 207.6 (S_2CN), 257.1 (CO). Anal. Calcd for $C_{14}H_{19}MoNO_2S_2$: C, 42.74; H, 4.87; N, 3.56. Found: C, 42.36; H, 5.13; N, 3.51.

Reaction of 1, R = H, with Tetraethylthiuram Disulfide (14, R′ = C_2H_5). The procedure described for tetraisopropylthiuram disulfide was applied to 14, R′ = C_2H_5, and gave the red complex 15, R′ = C_2H_5, in 83% yield: mp 123–125 °C; IR (Nujol) ν_{CO} 1930, 1860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, 6 H, CH_3), 3.62 (q, 4 H, CH_2), 5.44 (s, 5 H, C_5kH_5); mass spectrum, *m/e* 365 [M]$^+$.

Reaction of 1, R = H, with Tetramethylthiuram Disulfide (14, R′ = CH_3). The procedure described for 14, R′ = $CH(CH_3)_2$, was applied to 14, R′ = CH_3, affording the red complex 15, R′ = CH_3, in 37% yield: mp 225–227 °C; IR (Nujol) ν_{CO} 1930, 1845 cm^{-1}; ^1H NMR ($CDCl_3$) δ (s, 6 H, CH_3), 5.35 (s, 5 H, C_5H_5); mass spectrum , *m/e* 337 [M]$^+$.

X-ray Structure Determinations for 9, R = R′ = CH_3, and 15, R′ = $CH(CH_3)_2$. Data were collected on an Enraf-Nonius CAD4-F diffractometer equipped with a graphite monochromator and were corrected for Lorentz polarization and absorption effects.[24] The crystals were cooled, using a locally developed apparatus based on a commercial Enraf-Nonius system, to 215 K (**9**) or 228 K (**15**). The unit cell parameters and an orientation matrix were obtained from the accurate setting angles of 25 reflections [$32 \geq 2\theta \geq 43°$ (**9**); $25 \geq 2\theta \geq 34°$ (**15**)]. A total of 1683 reflections were collected for **9** of which 1355 were considered to be observed ($I > 3\sigma(I)$) and used in subsequent calculations. For **15**, 2777 reflections were collected of which 2356 were considered to be observed. The data collection was carried out at different temperatures so as to minimize icing of the gononiometer head due to the different atmospheric humidities at the time of the data collection.

The structures were solved by conventional heavy-atom methods and refined by full-matrix least squares. The positions of the majority of the hydrogen atoms were located in difference Fourier syntheses and were refined with restraints being applied to C–H bonds.[25,26] All non-hydrogen atoms were refined anisotropically, and common isotropic temperature factors were assigned to structurally similar hydrogen atoms. The refinement was considered complete when the ratio of calculated shifts to estimated standard deviations was less than 0.1.

The final residuals were $R_F = 0.026$ and $R_{wF} = 0.030$ for **9** and $R_F = 0.038$ and $R_{wF} = 0.051$ for **15**, and the goodness of fit was 1.13 for **9** and 1.03 for **15**. During the final cycles of refinement the weighting scheme employed a three-term Chebyshev series: $w = [46.9t(x) + 64.5t_1(x) + 25.2t_2(x)]^{-1}$ for **9** and $w = [50.6t(x) + 67.3t_1(x) + 23.8t_2(x)]^{-1}$ for **15**, where $x = F_o/F_{max}$ and t_n is the polynomial function.[27] The largest peak in the final difference map was of height 0.47 e A^{-3} and was situated 1.487 Å from the Mo atom for **9**, while those for **15** were symmetrically 0.935 Å from the Mo atom (1.7 e A^{-3}). Complex neutral atom scattering factors were taken from ref 28. Computer programs were run on an in house VAX 11-750.[29,30] In addition to the tables cited above, data for **9** and **15** on anisotropic thermal parameters, hydrogen atom coordinates, and mean plane calculations and tables of calculated and observed structure factors are available as supplementary material. A thermal ellipsoid plot of **9**, R = R′ = CH_3, is given in Figure 1 and that for **15**, R′ = $CH(CH_3)_2$, is illustrated in Figure 2.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this research.

Registry No. 1 (R = CH_3), 69140-73-4; 1 (R = H), 56200-27-2; **8** (R′ = CH_3), 3676-97-9; **8** (R′ = C_2H_5), 3790-23-6; **9** (R = R′ = CH_3), 106799-99-9; **9** (R = H, R′ = C_2H_5), 106800-00-4; **14** (C′ = $CH(CH_3)_2$), 4136-91-8; **14** (R′ = C_2H_5), 97-77-8; **14** (R′ = CH_3), 137-26-8; **15** (R′ = $CH(CH_3)_2$), 106800-01-5; **15** (R′ = C_2H_5), 32984-93-3; **15** (R′ = CH_3), 52201-61-3; Mo, 7439-98-7; bis(methylcyclopentadienyl)dimolybdenum hexacarbonyl, 33056-03-0; bis(cyclopentadienyl)dimolybdenum hexacarbonyl, 12091-64-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, and mean plane calculations for **9**, R = R′ = CH_3, and **15**, R′ = $CH(CH_3)_2$ (8 pages); listings of structure factor amplitudes for **9** and **15** (35 pages). Order information is given on any current masthead page.

---

(24) Alcock, N. W. *Crystallographic Computing*; Ahmed, F. R., Ed. Munksgaard: Copenhagen, 1969; p 271.

(25) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091.

(26) Rollet, J. S. *Crystallographic Computing*; Ahmed, F. R., ed. Munksgaard: Copenhagen, 1969; p 169.

(27) Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.., Sect. A: Cryst. Phys., Diffr., Theor. Gem. Crystallogr.* **1979**, *A35*, 698.

(28) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(29) Gabe, E. J.; Larson, A. C.; Lee, F. L.; Le Page, Y., *The NRC Crystal Structure System*; National Research Council of Canada: Ottawa, 1984.

(30) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W., *Crystals User Guide*; Chemical Crystallography Laboratory: University of Oxford, Oxford, 1985.

(31) Davies, E. K. *SNOOPI Plot Program*; Chemical Crystallography Laboratory: University of Oxford, Oxford, 1984.