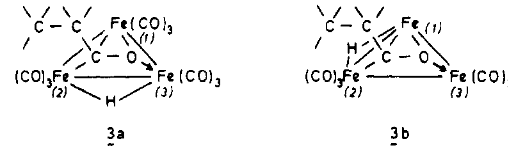

Figure 3. Proposed structures for 3.

spectrum shows an ethyl resonance that is slightly changed compared to 1 (Table III). In the high-field region, a hydride signal is observed at -24.70 ppm.

The same pattern as seen in 1 is observed in the ^{13}C NMR spectrum of 3. Especially in the CO region, the same type of spectrum is observed. Resonances at 247.5, 207.4, and 207.0 ppm compare well with those of 1, and the chemical shift is only slightly changed by protonation. Furthermore, the compound analyzes ae $HFe_3(CO)_9CO$-C_2H_5. From these observations, we can conclude that the core of the cluster is not affected by protonation and, in particular, that the μ_3 mode of bonding of the acyl group is preserved.

The spectroscopic data are consistent with the two structures presented in Figure 3. From the value of the chemical shift of the hydride, this ligand is clearly seen to bridge an iron-iron bond[17,18] and the two structures **3a** and **3b** are consistent with our data. However it is difficult to chose between these two forms. Nevertheless, the occurrence of the bonding of Fe(3) to the oxygen atom could favor structure **3a**.

Acknowledgment. This work has been supported by the CNRS (ATP Chimie Fine). We thank Renêe Enjalbert for assistance in X-ray preliminary studies and Dr. Jean Galy for helpful comments.

Note Added in Proof. Our hypothesis has been confirmed by an X-ray structure determination of $HFe_3(CO)_9COCH_3$ which appeared when this paper was submitted for publication. Wong, W. K.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M. A.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 842.

Registry No. 1, 86508-04-5; 2, 86508-05-6; 3, 86508-06-7; $[HFe_3(CO)_{11}]^-$, 55188-22-2.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table IIS.A), phenyl atomic parameters (Table IIS.B), and structure factors (22 pages). Ordering information is given on any current masthead page.

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Binuclear Phosphinothioylidene Complexes

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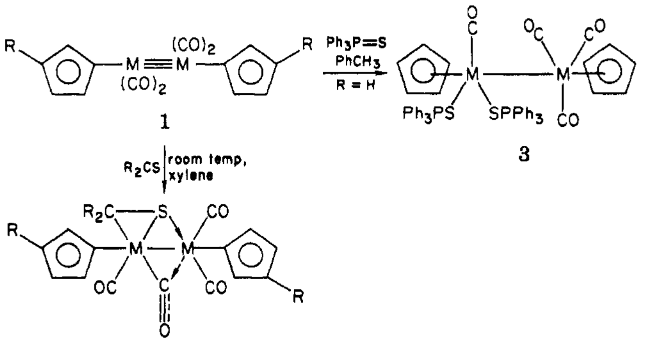
Lawesson's reagent (the dimer of (*p*-methoxyphenyl)thionophosphine sulfide) reacts with dicyclopentadienyltetracarbonyldimolybdenum or -ditungsten to give binuclear complexes containing a phosphinothioylidene ligand. These complexes were characterized on the basis of analytical and spectral data and a single-crystal X-ray analysis of the molybdenum complex. Crystal data of $[(C_5H_5)_2Mo_2(CO)_4(SPC_6H_4OCH_3)]$ are as follows: $a = 9.471$ (4) Å, $b = 9.119$ (3) Å, $c = 16.145$ (2) Å, $\alpha = 90.75$ (2)°, $\beta = 97.37$ (2)°, $\gamma = 126.89$ (3)°, $V = 1098.8$ Å^3 $Z = 2$, triclinic, space group $P\bar{1}$. Intensity data were collected by counter methods, Mo $K\alpha_1$ radiation. The structure was refined on 3541 reflections with $I > 2.30\sigma(I)$ to $R_F = 0.020$ and $R_{wF} = 0.028$. The P atom is σ bonded to Mo(1) and P=S π bonded to Mo(2): Mo—Mo = 3.245 (1) Å, Mo(1)—P = 2.326 (1) Å, Mo(2)—P = 2.451 (1) Å, Mo(2)—S = 2.567(1) Å, P=S = 2.022 (1) Å, Mo(1)-P-Mo(2) = 85.53 (3)°. One carbonyl attached to Mo(2) is semibridging: Mo(2)—C(21) = 1.968 (3) Å, Mo(1)···C(21) = 2.864 (3) Å, Mo(2)-C(21)-O(21) = 166.0 (2)°.

The reaction of metal-metal triple-bond complexes 1 with organosulfur compounds has been the subject of several investigations. Treatment of thioketones with 1 in xylene or toluene at room temperature gave a novel class of thione complexes 2 containing a semibridging carbonyl group.[2] These complexes undergo interesting ligand substitution and alkylation reactions on exposure to phosphites and alkoxyphosphines.[3]

A formal 1,1 addition to 1 occurs on reaction with triphenylphosphine sulfide to give 3.[4] In searching for other



types of suitable substrates capable of undergoing analogous transformations, we examined the reaction of 1 with

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

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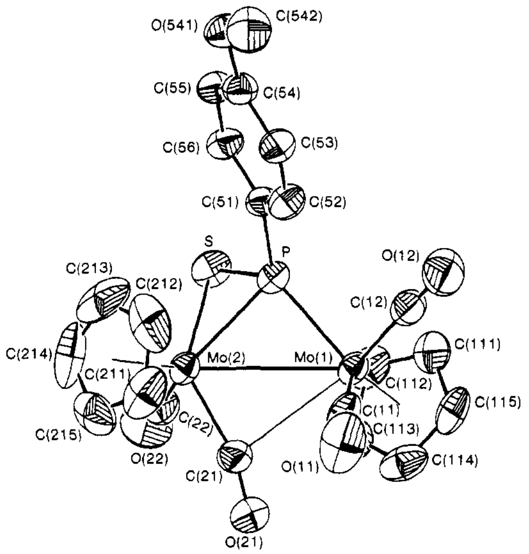
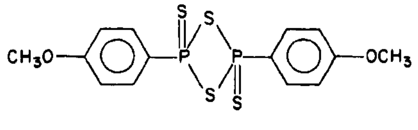


Figure 1. ORTEP diagram of $[(C_5H_5)_2Mo_2(CO)_4(SPC_6H_4OCH_3)]$ showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been deleted from the diagram.

the dimer of (*p*-methoxyphenyl)thionophosphine sulfide (4), also known as Lawesson's reagent. The latter is a



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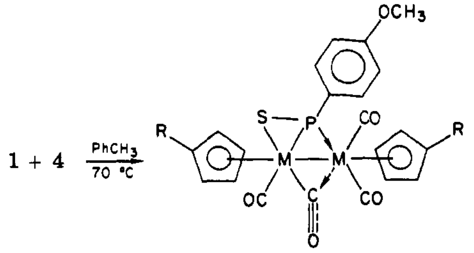
valuable commercial product used for the thiation of ketones, esters, amides, and thioesters.[5-11] We now describe the interesting class of complexes obtained from this investigation.

Results and Discussion

Reaction of dicyclopentadienyltetracarbonyldimolybdenum (1, R = H, M = Mo), generated in situ by heating $(C_5H_5)_2Mo_2(CO)_6$ is toluene,[12] with Lawesson's reagent (4) at 70°C afforded complex 5, R = H, M = Mo,



5

which contains a phosphinothioylidene moiety. This complex was identified on the basis of analytical and spectral data and an X-ray structure determination. The infrared spectrum (KBr) displayed terminal metal carbonyl stretching bands at 1961 (s), 1922 (vs), and 1866 (vs) cm^{-1} and an absorption at 1848 cm^{-1} assigned to the semibridging carbonyl group. These bands are at similar positions to those of the thioketone complexes 2,[2] except for the band of the semibridging carbonyl group which occurs at higher frequency in 5. The proton magnetic resonance spectrum of 5, R = H, M = Mo, gave singlets for the two different cyclopentadienyl rings (δ 4.86, 5.10) and the methoxy group (δ 3.83) and a complex multiplet (δ 6.9–7.9) for the four benzenoid protons that couple to phosphorus.

Table I. Crystal Data

$C_{21}H_{17}Mo_2O_5PS$
fw = 604.28
crystal system: triclinic
space group: $P\bar{1}$
a = 9.471 (4) Å
b = 9.119 (3) Å
c = 16.145 (2) Å
α = 90.75 (2)°
β = 97.37 (2)°
γ = 126.89 (3)°
V = 1098.8 Å^3
Z = 2
ρ_{calcd} = 1.826 g cm^{-3}
$\rho_{obsd}{}^a$ = 1.82 g cm^{-3}
μ = 13.15 cm^{-1}

[a] By flotation in CCl_4/CH_2I_2.

Table II. Fractional Atomic Coordinates

atom	*x*	*y*	*z*
Mo(1)	0.18169 (3)	0.50553 (3)	0.22777 (1)
Mo(2)	0.22727 (3)	0.19679 (3)	0.16834 (1)
S	0.12783 (8)	0.10038 (9)	0.31113 (4)
P	0.29856 (8)	0.37429 (8)	0.30280 (4)
C(51)	0.5085 (3)	0.4689 (3)	0.3714 (1)
C(52)	0.6593 (3)	0.6446 (3)	0.3647 (2)
C(53)	0.8231 (3)	0.7185 (3)	0.4138 (2)
C(54)	0.8388 (3)	0.6166 (3)	0.4713 (1)
C(55)	0.6881 (3)	0.4419 (4)	0.4797 (1)
C(56)	0.5259 (3)	0.3693 (3)	0.4308 (2)
O(541)	0.9947 (2)	0.6741 (2)	0.5215 (1)
C(542)	1.1525 (4)	0.8501 (4)	0.5140 (2)
C(11)	0.3470 (4)	0.6558 (4)	0.1497 (2)
O(11)	0.4439 (3)	0.7493 (3)	0.1052 (2)
C(12)	0.3668 (4)	0.7277 (4)	0.3023 (2)
O(12)	0.4696 (3)	0.8615 (3)	0.3467 (2)
C(21)	0.1271 (4)	0.2792 (4)	0.0839 (2)
O(21)	0.0669 (3)	0.3026 (3)	0.0232 (1)
C(22)	−0.0221 (3)	−0.0296 (4)	0.1407 (2)
O(22)	−0.1672 (3)	−0.1629 (3)	0.1261 (1)
C(111)	−0.0320 (4)	0.4797 (4)	0.2942 (2)
C(112)	−0.1064 (3)	0.3023 (4)	0.2616 (2)
C(113)	−0.1316 (3)	0.2918 (4)	0.1748 (2)
C(114)	−0.0688 (4)	0.4675 (5)	0.1528 (2)
C(115)	−0.0084 (4)	0.5841 (4)	0.2269 (2)
C(211)	0.4702 (5)	0.3322 (5)	0.1003 (2)
C(212)	0.5353 (4)	0.3450 (5)	0.1819 (2)
C(213)	0.4612 (5)	0.1759 (7)	0.2036 (2)
C(214)	0.3464 (5)	0.0508 (5)	0.1361 (3)
C(215)	0.3522 (4)	0.1484 (6)	0.0701 (2)
H(111)	−0.007 (4)	0.525 (4)	0.347 (2)
H(112)	−0.131 (4)	0.207 (4)	0.294 (2)
H(113)	−0.183 (4)	0.178 (4)	0.133 (2)
H(114)	−0.078 (4)	0.485 (4)	0.109 (2)
H(115)	0.023 (4)	0.699 (4)	0.238 (2)
H(211)	0.497 (4)	0.420 (5)	0.075 (2)
H(212)	0.611 (4)	0.453 (4)	0.212 (2)
H(213)	0.489 (5)	0.170 (6)	0.252 (2)
H(214)	0.277 (5)	−0.074 (5)	0.122 (2)
H(215)	0.299 (5)	0.111 (5)	0.022 (2)
H(52)	0.652 (3)	0.702 (3)	0.321 (1)
H(53)	0.916 (3)	0.836 (3)	0.409 (1)
H(55)	0.695 (3)	0.379 (4)	0.521 (2)
H(56)	0.422 (3)	0.245 (3)	0.432 (1)
H(542A)	1.130 (4)	0.928 (4)	0.525 (2)
H(542B)	1.250 (4)	0.864 (4)	0.549 (2)
H(542C)	1.176 (4)	0.861 (4)	0.454 (2)

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Table III. Selected Bond Lengths (Å)^a and Angles (deg)

Bond Lengths

Mo(1)-Mo(2)	3.245 (1), 3.252^b		
Mo(1)-P	2.326 (1), 2.331^b	Mo(2)-P	2.451 (1), 2.459^b
Mo(1)-C(111)	2.300 (3), 2.314^c	Mo(2)-C(211)	2.302 (3), 2.332^c
Mo(1)-C(112)	2.348 (3), 2.363^c	Mo(2)-C(212)	2.341 (3), 2.372^c
Mo(1)-C(113)	2.387 (3), 2.404^c	Mo(2)-C(213)	2.336 (3), 2.376^c
Mo(1)-C(114)	2.340 (3), 2.361^c	Mo(2)-C(214)	2.292 (3), 2.332^c
Mo(1)-C(115)	2.302 (3), 2.319^c	Mo(2)-C(215)	2.280 (3), 2.311^c
Mo(1)-C(11)	1.974 (3), 1.985^c	Mo(2)-C(21)	1.968 (3), 1.973^b
Mo(1)-C(12)	1.938 (3), 1.949^c	Mo(2)-C(22)	1.973 (3), 1.982^c
Mo(1)···C(21)	2.864 (3), 2.871^b	Mo(2)-S	2.567 (1), 2.576^b
C(11)-O(11)	1.153 (3), 1.171^d	C(21)-O(21)	1.158 (3), 1.167^d
C(12)-O(12)	1.151 (4), 1.163^d	C(22)-O(22)	1.151 (3), 1.163^d
S-P	2.022 (1), 2.026^c	P-C(51)	1.810 (2), 1.810^c
C(51)-C(52)	1.384 (3)	C(51)-C(56)	1.390 (3)
C(52)-C(53)	1.381 (3)	C(56)-C(55)	1.370 (3)
C(53)-C(54)	1.378 (3)	C(55)-C(54)	1.385 (4)
C(54)-O(541)	1.366 (3)	O(541)-C(542)	1.413 (4)

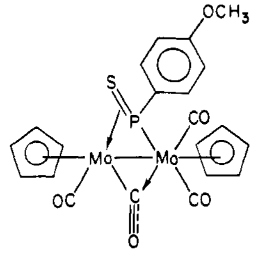
Bond Angles

Mo(1)-P-Mo(2)	85.53 (3)	Mo(1)-C(21)-Mo(2)	82.10 (8)
Mo(2)-Mo(1)-P	48.86 (2)	Mo(1)-Mo(2)-P	45.61 (2)
Mo(2)-Mo(1)-C(11)	85.06 (8)	Mo(1)-Mo(2)-C(21)	60.97 (8)
Mo(2)-Mo(1)-C(12)	123.21 (8)	Mo(1)-Mo(2)-C(22)	103.17 (9)
Mo(2)-Mo(1)-Cp(1)	117.37	Mo(1)-Mo(2)-Cp(2)	133.49
Mo(2)-Mo(1)-C(21)	36.92 (5)	Mo(1)-Mo(2)-S	78.39 (3)
P-Mo(1)-C(11)	106.79 (8)	P-Mo(2)-C(21)	106.56 (8)
P-Mo(1)-C(12)	84.53 (8)	P-Mo(2)-C(22)	114.58 (9)
P-Mo(1)-Cp(1)	125.15	P-Mo(2)-Cp(2)	113.69
P-Mo(1)-C(21)	85.77 (6)	P-Mo(2)-S	47.45 (3)
C(11)-Mo(1)-C(12)	79.26 (13)	C(21)-Mo(2)-C(22)	79.79 (12)
C(11)-Mo(1)-Cp(1)	126.16	C(21)-Mo(2)-Cp(2)	114.25
C(11)-Mo(1)-C(21)	68.80 (11)	C(21)-Mo(2)-S	125.12 (8)
C(12)-Mo(1)-Cp(1)	115.85	C(22)-Mo(2)-Cp(2)	122.16
C(12)-Mo(1)-C(21)	142.16 (10)	C(22)-Mo(2)-S	75.16 (9)
Cp(1)-Mo(1)-C(21)	99.54	Cp(2)-Mo(2)-S	120.48
Mo(1)-C(11)-O(11)	177.4 (2)	Mo(2)-C(21)-O(21)	166.0 (2)
Mo(1)-C(12)-O(12)	176.1 (2)	Mo(2)-C(22)-O(22)	178.6 (2)
Mo(1)-P-C(51)	133.60 (8)	Mo(2)-P-C(51)	119.21 (8)
Mo(1)-P-S	117.00 (5)	Mo(2)-P-S	69.29 (4)
Mo(1)-C(21)-O(21)	111.9 (2)	Mo(2)-S-P	63.27 (4)
S-P-C(51)	108.69 (9)	C(54)-O(541)-C(542)	118.1 (2)
P-C(51)-C(52)	120.0 (2)	P-C(51)-C(56)	122.1 (2)
C(51)-C(52)-C(53)	121.6 (2)	C(51)-C(56)-C(55)	120.8 (2)
C(52)-C(53)-C(54)	119.8 (2)	C(56)-C(55)-C(54)	120.8 (2)
C(53)-C(54)-C(541)	124.8 (2)	C(55)-C(54)-O(541)	116.1 (2)
C(52)-C(51)-C(56)	117.9 (2)	C(53)-C(54)-C(55)	119.1 (2)

[a] The first value is derived directly from the atomic coordinates, the second has been corrected for thermal motion. [b] Corrected for rigid-body motion. [c] Corrected for riding motion, the second-mentioned atom riding on the first. [d] Corrected for riding motion, both C and O atoms riding on the corresponding Mo.

The single-crystal analysis of **5**, R = H, M = Mo, confirmed the structure of the complex and provided details of the molecular geometry. Crystal data are given in Table I, atomic coordinates in Table II, and selected bond lengths and angles in Table III. Figure 1 shows a projected view of the molecule.

The Mo-Mo distance of 3.245 (1) Å indicates a single bond and is comparable with the length in $[(C_5H_5)Mo(CO_3)]_2$ (3.235 (1) Å)[13] but is shorter than in most related compounds with a bridging ligand.[2,14-18] The P atom of the ligand bridges the two Mo atoms, being 2.326 (1) Å from Mo(1) and 2.451 (1) Å from Mo(2) while the S atom is bonded to Mo(2) alone (2.567 (1) Å). This can be interpreted as $\sigma + \pi$-bond coordination with P being σ bonded to Mo(1) while P═S is π bonded to Mo(2).



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This is analogous to the isocyanide ligand in $(C_5H_5)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-CNPh})$,[17] with one difference being that in the isocyanide complex, the terminal atom of the ligand bridges Mo atoms while in **5** it is the second atom that bridges. The S-P distance of 2.022 (1) Å suggests some double-bond character, which supports this proposal.[19]

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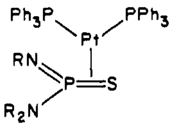
The cyclopentadienyl rings occur on opposite sides of the Mo_2P plane, in common with most related compounds.[2] There are some variations in the Mo–C distances to the cyclopentadienyl rings (they range from 2.300 (3)–2.387 (3) Å for Mo(1) and 2.280 (3)–2.341 (3) Å for Mo(2)), but there is no evidence for other than η^5 coordination. The rings are planar and there is no observable increase in bond order between the C atoms closest to the Mo atoms. The variations most likely result from nonbonding interactions with adjacent ligands, i.e., steric crowding around the Mo atoms. In both rings the longer Mo–C contacts are associated with the C atoms nearest the bridging ligand, a feature also observed for $(C_5H_5)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-CNPh})$ and **2**.

Carbonyl C(21)–O(21) is semibridging with Mo(2)–C(21) = 1.968 (3) Å and Mo(1)···C(21) = 2.864 (5) Å. The asymmetry of the semibridge and the Mo(2)–C(21)–O(21) angle (166.0 (2)°) place this complex precisely on the curve proposed by Klingler et al.[20] for two-electron donation from the C atom rather than four-electron donation from the C≡O π system. In **2** the Mo···C distance is 2.666 (9) Å and Mo–C–O = 161.9 (7)°. These facts, coupled with the higher infrared stretching frequency of the semibridging carbonyl group of **5** as compared to that of **2** (noted above), indicate there is a weaker interaction between the semibridging carbonyl group and Mo(1) in **5** than in **2**.

The methylcyclopentadienylmolybdenum complex **1**, M = Mo, R = CH_3, and the tungsten complex **1**, M = W, R = H, also reacted with Lawesson's reagent to give **5**, M = Mo, R = CH_3, and **5**, M = W, R = H, respectively. Spectral data for these complexes are given in the Experimental Section.

π Complexes of phosphine sulfides are known (e.g., **7**).[21] A recent attempt to synthesize a phosphinothioylidene complex of iron, $(\mu\text{-RPS})Fe_2(CO)_6$, from $RP(S)Cl_2$ and triiron dodecarbonyl gave instead the cluster $(\mu_3\text{-S})(\mu_3\text{-RP})Fe_3(CO)_9$.[22] The present work has resulted in the isolation and characterization of binuclear molybdenum and tungsten complexes of a phosphinothioylidene.



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Finally, it should be noted that all attempts to determine the fate, in these reactions, of the remaining fragment of Lawesson's reagent (i.e., $p\text{-}CH_3OC_6H_4PS_3$) have been unsuccessful.

Experimental Section

General Data. Infrared spectral determinations were made by using a Nicolet MX-1 Fourier transform infrared spectrometer. Varian T60 and EM360 spectrometers were used for recording proton magnetic resonance spectra. Melting points were recorded on a Gallenkamp apparatus. Elemental analyses were carried out by Canadian Microanalytical Service, Limited, Vancouver, Canada, and by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Lawesson's reagent and dicyclopentadienyldimolybdenum hexacarbonyl were commercial products and were used as received. Literature procedures[23] were used to prepare $(C_5H_4CH_3)_2Mo_2(CO)_6$ and $(C_5H_5)_2W_2(CO)_6$. Solvents were purified by standard methods.

All reactions were effected under a dry nitrogen atmosphere by using vacuum line and Schlenk techniques.

Reaction of 1, M = Mo, R = H, with Lawesson's Reagent (4). Complex **1**, M = Mo, R = H, was generated by heating a stirred solution of 2.0 g (4.0 mmol) of $(C_5H_5)_2Mo_2(CO)_6$ in dry degassed toluene (30 mL) at 120 °C for 17 h.[12] The solution was cooled to room temperature, Lawesson's reagent (1.6 g, 4.0 mmol) was added, and the reaction mixture was heated overnight at 70 °C. The solution was cooled, Florisil was added, and toluene was removed by rotary evaporation. The Florisil containing the crude product was added to the top of a Florisil chromatography column. Elution with hexane gave recovered $(C_5H_5)_2Mo_2(CO)_6$. Elution with 4:1 hexane–methylene chloride afforded **5**, M = Mo, R = H. Analytically pure brown product was obtained by crystallization from hexane–methylene chloride: yield 0.75 g (31%); mp 208 °C dec; IR (KBr) ν_{CO} 1961 (s), 1922 (vs), 1866 (vs), 1848 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (s, 3 H, OCH_3), 4.86 (s, 5 H, C_5H_5), 5.10 (s, 5 H, C_5H_5), 6.90–7.90 (m, 4 H, aromatic protons).

Anal. Calcd for $C_{21}H_{17}Mo_2O_5PS$: C, 41.74; H, 2.84; P, 5.13. Found: C, 41.50; H, 2.35; P, 5.14.

Reaction of 1, M = Mo, R = CH_3, with Lawesson's Reagent (4). The same procedure was used as in the case of **1**, M = Mo, R = H. **5**, M = Mo, R = CH_3: yield 20%; mp 174 °C dec; IR (KBr) ν_{CO} 1957 (s), 1926 (vs), 1867 (vs), 1831 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70 (s, 3 H, CH_3), 2.00 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 4.55–5.37 (m, 8 H, C_5H_4 rings), 6.95, 7.80 (m, 4 H, aromatic protons).

Anal. Calcd for $C_{23}H_{21}Mo_2O_5PS$: C, 43.67; H, 3.32; P, 4.90. Found: C, 43.89; H, 3.02, P, 4.51.

Reaction of 1, M = W, R = H, with Lawesson's Reagent (4). Complex **5**, M = W, R = H, was obtained in 28% yield by using the same procedure as that described for the preparation of **5**, M = Mo, R = H: IR (KBr) ν_{CO} 1986 (s), 1939 (vs), 1863 (vs), 1827 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.73 (s, 3 H, OCH_3), 4.98 (s, 5 H, C_5H_5), 5.41 (s, 5 H, C_5H_5), 6.72, 7.40 (m, 4 H, aromatic protons).

Anal. Calcd for $C_{21}H_{17}O_5PSW_2$: C, 32.33; H, 2.20; P, 3.97. Found: C, 31.97; H, 1.92; P, 3.87.

X-ray Analysis. A large dark brown crystal of **5** was cleaved to produce a block 0.25 × 0.38 × 0.36 mm that was affixed to the end of a glass fiber. X-ray photographs taken with Cu Kα radiation (λ = 1.5418 Å) revealed only Laue $\bar{1}$ symmetry (indicating space group $P1$ or $P\bar{1}$) and gave approximate unit-cell parameters. A Delaunay reduction[24] gave the unit cell used in subsequent work but did not indicate higher symmetry.

The crystal was then transferred to a Picker FACS-I four-circle automated diffractometer employing graphite-monochromated Mo Kα radiation ($\lambda(K\alpha_1)$ = 0.70930 Å). The ambient temperature was maintained at 20 ± 1 °C. Accurate cell dimensions were determined by least-squares analysis of the setting angles of 26 reflections (with 2θ values ranging from 29 to 34°) widely separated in reciprocal space, which were accurately centered on the diffractometer detector. Crystal data are given in Table I.

The peak profiles of 3888 unique reflections $4° \le 2\theta \le 50°$ [(hkl), $(\bar{h}kl)$, $(\bar{h}k\bar{l})$, $(hk\bar{l})$] were measured with a θ–2θ scan running at 2° min^{-1} with scan width of $(1.4 + 0.692 \tan \theta)°$. Stationary-crystal–stationary-counter background counts of 10% of the scan time were taken at each side of the scan. Peak profile analysis using the method of Grant and Gabe[25] was performed on all reflections to derive the intensities, I, and the associated errors, $\sigma(I)$. Two standards were measured after every 70 reflections and showed that the crystal orientation did not move significantly during data collection and that no decomposition had taken place. A total of 3541 reflections with $I > 2.3\sigma(I)$ were regarded as observed and used in structure solution and refinement. Data were corrected for absorption (T = 0.66–0.74).[26] ψ Scans on several reflections near χ = 90° showed close agreement between the observed intensity curve and the calculated transmission coefficient curve.

The three-dimensional Patterson synthesis was used to determine the coordinates of the Mo atoms assuming space group

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$P\bar{1}$. Successful refinement of the structure confirms this choice of space group. Least-squares refinement and difference-Fourier syntheses revealed all remaining non-hydrogen atoms. At this stage, the non-hydrogen atoms were assigned anisotropic temperature factors and the cyclopentadienyl and phenyl H atoms were calculated geometrically (r_{C-H} = 0.95 Å)[27] and given isotropic temperature factors held invariant at 1.25U_{iso} of the C atoms to which they were attached. After several cycles of least-squares refinement of these parameters and a secondary extinction parameter,[28] an inner-data difference Fourier map revealed the methyl H atoms which were also included in the least-squares (U invariant). The structure was refined until all shift/error ratios were less than 0.2, the final residuals being R_F = 0.020 and R_{wF} = 0.028 for 323 variables. The final value for the extinction parameter was 1.4 (2) × 10^{-6}. Refinement throughout was by least-squares analysis, minimizing the function $\sum w(F_o| - |F_c|)^2$ In the early stages the least-squares analysis was by full-matrix using unit weights (w = 1). For the final cycles it was block-diagonal (Gauss–Siedel) with the weighting scheme $w = 1/[(\sigma(F))^2 + pF^2]$. The parameter p was varied to give minimum variation of the averaged $\sum w(|F_o| - |F_c|)^2$ with F_o and (sin θ)/λ; the best fit was obtained with $p = 5 \times 10^{-5}$. The biggest features in a final difference map were areas of negative electon density ($|\rho_{max}|$ = 0.36 (6) e Å^{-3}) around the Mo atoms. Neutral scattering factors with anomalous dispersion corrections for the non-hydrogen atoms were used.[29] Computer programs[30] were run on a PDP-8e computer.

Thermal motion corrections were calculated for the more precise bond lengths in Table III. Those involving the central core of the molecule [Mo(1), Mo(2), P, S, C(21)] were calculated from a rigid-body model of these atoms alone.[31] The remainder were based on a riding model.[32] The uncorrected bond lengths are cited in the discussion to be consistant with previously reported structures. The magnitude of some corrections (up to 7 esd's for the Mo–Mo distance) should be regarded as a warning when comparing bond lengths from different structure determinations. Corrections to angles are small (typically ≤1 esd) and are not reported.

Temperature factors, additional bond lengths and angles, and least-squares planes have been deposited as Tables SI, SII, and SIII, respectively.

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Registry No. 1, M = Mo, R = H, 56200-27-2; 1, M = Mo, R = CH_3, 69140-73-4; 1, M = W, R = H, 62853-03-6; 4, 19172-47-5; 5, M = Mo, R = H, 86392-82-7; 5, M = Mo, R = CH_3, 86392-83-8; 5, M = W, R = H, 86392-84-9; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Temperature factors, additional bond lengths and angles, least-squares planes, and a listing of observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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Electron Counting in Cluster Species. The Significance of the Structure and Isomerism of the Iron–Molybdenum–Sulfur Cluster Compound (Dicyclopentadienyldimolybdenum)diiron Octacarbonyl Disulfide, $(\eta^5\text{-}C_5H_5)_2Mo_2Fe_2(CO)_8S_2$, a Hexanuclear Species in Which Two Mo_2FeS Tetrahedra Share a Common Mo–Mo Edge

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The published structures of two isomers of the mixed-metal complex $(\eta^5\text{-}C_5H_5)_2(CO)_2Mo_2Fe_2(CO)_6S_2$, when viewed as Mo_2FeS tetrahedra sharing common Mo–Mo edges, are related in a particularly simple fashion. These clusters belong to a family of edge-sharing bitetrahedral electron-precise clusters of which several examples are already known. The skeletal electron requirements and scope for isomerism of mixed transition-metal–main-group element clusters of these types and their relationship to electron-deficient octahedral clusters are noted.

Recent elucidation of the structure of the mixed metal cluster compound $Cp_2Mo_2Fe_2(CO)_6(\mu_3\text{-}S)_2(\mu\text{-}CO)_2$ (**1**)[1] (Cp ≡ $\eta^5\text{-}C_5H_5$) showed this compound to have a planar arrangement of its four metal atoms. Tetranuclear transition-metal clusters with 62 valence shell electrons (VSE's) usually have butterfly-shaped structures,[2-4] as had already

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