been reported by us and other workers.[1,3,4,29]

The magnetic susceptibility of 5.2 μ_B for **3** (Evans method)[30,31] is higher than the values reported for similar Mn(II) systems (3.0–3.9 μ_B).[15,23,29] This is probably due to the longer Mn–Mn distances in **3**. For example, $Mn_3(mesityl)_6$ has a magnetic moment of 3.65 μ_B at 299 K.[23] The complex $Mn_2\{N(SiMe_3)_2\}_4$ has a Mn–Mn distance of 2.811 (1) Å at 140 K (2.841 (1) Å at room temperature) and has a magnetic moment of 3.34 μ_B.[15,32]

In summary, the $t\text{-}Bu_2CHO^-$ group can be employed as a bridging group to permit the stabilization of low-coordinate multinuclear metal complexes. The ligand can be introduced into metal complexes by (i) treating the lithium alkoxide with metal halides, (ii) by exchange with metal amides, or (iii) by the conversion of $t\text{-}Bu_3CO^-$ into $t\text{-}Bu_2CHO^-$ via the cleavage of a C–C bond and subsequent production of C_4H_8.

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Registry No. 1, 93684-91-4; **3**, 93684-92-5; $[Cr\{OC\text{-}t\text{-}Bu_3\}_2\cdot LiCl(THF)_2]$, 89189-87-7; $[Mn\{N(SiMe_3)_2\}(THF)]$, 69900-28-3; $HOC\text{-}t\text{-}Bu_3$, 41902-42-5.

Supplementary Material Available: Tables of bond distances and angles, structure factors, and calculated positional and thermal parameters for **1** and **3** (56 pages). Ordering information is given on any current masthead page.

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Novel Organosulfur Metal Complexes Derived from Dithioesters

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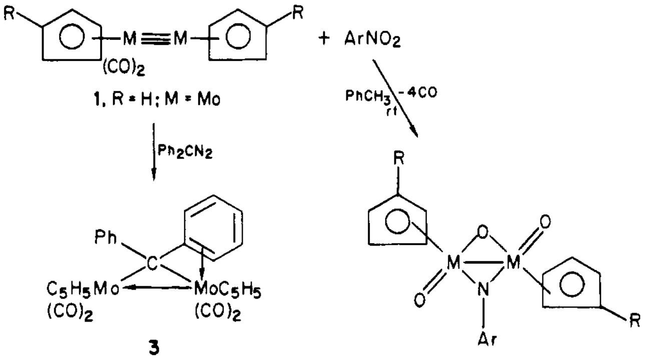
Abstract: Dithioesters react with complexes containing a metal–metal triple bond, in refluxing toluene or xylene, to give a novel class of organosulfur complexes. A single-crystal X-ray analysis of one such complex $[(CH_3C_5H_4)_2Mo_2(CO)_2(SCCH_3)(SC_2H_5)]$ confirms the presence of a symmetrically bridging thioacyl function, a bridging thioalkyl group, and a molybdenum–molybdenum single-bond distance of 2.806 (1) Å. When the reaction was effected at room temperature, a complex with a retained dithioester unit was obtained. As established by an X-ray analysis of $[Cp_2Mo_2(CO)_4(CH_3C(S)SC_2H_5)]$, the thiocarbonyl group is bonded to one molybdenum atom with the sulfur atom also donor bound to the other metal atom. A semibridging carbonyl group is also present.

One of the most exciting areas of research in inorganic chemistry is the chemistry of compounds containing metal–metal multiple bonds.[2] Significant work has been done on the reactivity of cyclopentadienylmolybdenum dicarbonyl dimer [**1**, R = H; M = Mo] and related complexes containing a metal–metal triple bond.[3,4] Interesting reactions have been observed on treatment of **1** with organonitrogen and sulfur compounds. Regarding nitrogen-containing substrates, nitro compounds react with **1** affording complexes **2** in a high-oxidation state.[5] Diazo compounds undergo several types of reactions,[6–10] including the loss of nitrogen with the formation of **3** (from diphenyldiazomethane) which contains a formal metal–metal donor bond.[6]



1, R = H; M = Mo

3

2

Treatment of thioketones with **1** at room temperature results in the isolation of complexes **4** with the thione function bonded to one metal atom, the sulfur donor bound to the other metal atom, and a semibridging carbonyl group.[11] Thioesters and thiolactones (RC(=S)OR′) form complexes formally of the same type as **4**, but with interesting differences in structural details. There is no evidence for participation of the oxygen atom in bonding to a metal atom.[12]

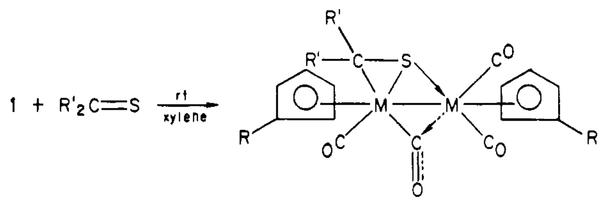


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Table I. Crystal Data[a]

formula	$C_{18}H_{22}Mo_2O_2S_2$	$C_{19}H_{22}Mo_2O_5S_2 \cdot 0.5CH_2Cl_2$
fw	526.38	628.86
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	*Pbcn*
a, Å	14.067 (1)	25.380 (2)
b, Å	9.864 (1)	12.747 (4)
c, Å	14.948 (2)	14.394 (2)
β, deg	111.851 (8)	
V, Å^3	1925.09	4656.8
Z	4	8
ρ_{calcd}, g cm^{-3}	1.816	1.794
ρ_{obsd},[b] g cm^{-3}	1.80	1.72[c]
μ, cm^{-1}	14.89	13.67

[a] At 18 ± 1 °C. [b] Flotation in aqueous $ZnBr_2$ solution. [c] Crystals used in the density determination had been stored under dry N_2 for several months. The low observed density suggests that they lost some CH_2Cl_2 solvate during this time. $\rho_{calcd}(C_{19}H_{22}Mo_2O_5S_2) = 1.673$ g cm^{-3}.

The complexation of dithioesters by metals has been studied extensively.[13] The utilization of these ligands in reaction with **1** results in the formation of a novel class of complexes. We now report the results of this investigation.

Results and Discussion

The required dithioesters were prepared by the known reaction of thioesters with Lawesson's reagent [i.e., the dimer of (*p*-methoxyphenyl)thionophosphine sulfide].[14] Treatment of **1** (R = H, CH_3; M = Mo) with ethyl dithioacetate [R′ = CH_3; R″ = C_2H_5] or *p*-methoxybenzyl dithiophenylacetate [R′ = $PhCH_2$; R″ = *p*-$CH_3OC_6H_4CH_2$] in refluxing toluene or xylene afforded the binuclear dimolybdenum complex **5**. This complex, having an unusual symmetrically bridged thioacyl function as well as a bridging thioalkyl group, was identified on the basis of analytical, spectral data, and an X-ray analysis of **5**, (R = R′ = CH_3;R″ = C_2H_5).

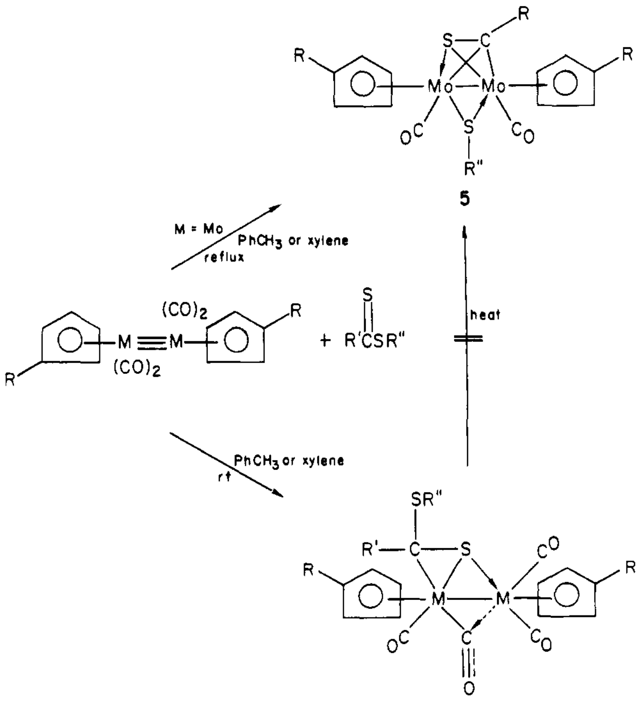

Table II. Data Collection and Refinement

diffractometer	Nonius CAD4F	
radiation	Mo Kα[a]	
scan mode	coupled ω–2θ	
	5	**6**
scan width,[b,c] deg in ω	0.55	0.70
scan speed,[d] deg in ω	4.02–0.44	4.02–0.69
2θ range, deg	0–50	0–45
total no. of reflns	3380	3045
no. of obsd reflns[e]	3140	2082
no. of variables	306	256
final R_1[f]	0.019	0.045
final R_2[g]	0.030	0.054
final GOF[h]	1.32	1.47

[a] Graphite monochromator, λ = 0.70930 Å (α_1), 0.71359 Å (α_2). [b] Also corrected for Kα_1–Kα_2 dispersion. [c] Scan extended by 25% on each side for background measurement. [d] Variable scan speed determined from intensity of reflection obtained in prescan. [e] Reflections where $I > 2.3\sigma(I)$. [f] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [g] $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2}$. [h] GOF = $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$; m = no. of observations, n = no. of variables.

Table III. Final Atomic Coordinates for **6**

atom	*x*	*y*	*z*	B_{iso}/B[a]
Mo(1)	0.27789 (1)	0.17131 (2)	0.23587 (1)	2.115 (10)
Mo(2)	0.21902 (1)	−0.05548 (2)	0.11432 (1)	2.171 (10)
S(1)	0.39127 (4)	0.04462 (6)	0.17644 (4)	2.83 (3)
C(2)	0.3367 (2)	−0.0307 (2)	0.2521 (2)	2.50 (9)
C(3)	0.3927 (2)	−0.1299 (3)	0.3304 (2)	3.38 (12)
S(2)	0.11867 (4)	0.04578 (6)	0.19809 (4)	2.67 (3)
C(4)	0.1167 (2)	−0.0617 (3)	0.2974 (2)	3.93 (14)
C(5)	0.0851 (4)	0.0178 (4)	0.3669 (3)	5.82 (23)
C(6)	0.3383 (2)	0.1354 (3)	0.3722 (2)	3.33 (12)
O(6)	0.3758 (2)	0.1176 (2)	0.4547 (1)	4.99 (13)
C(7)	0.1641 (2)	0.0880 (2)	0.0168 (2)	2.79 (10)
O(7)	0.1291 (2)	0.1602 (2)	−0.0471 (1)	4.16 (11)
C(11)	0.3451 (2)	0.3843 (2)	0.2191 (2)	3.36 (12)
C(12)	0.2626 (2)	0.3551 (2)	0.1323 (2)	3.56 (14)
C(13)	0.1735 (2)	0.3499 (2)	0.1526 (2)	3.18 (13)
C(14)	0.2006 (2)	0.3747 (3)	0.2516 (2)	3.50 (13)
C(15)	0.3077 (2)	0.3993 (2)	0.2934 (2)	3.16 (11)
C(16)	0.3673 (3)	0.4447 (4)	0.3947 (3)	4.74 (18)
C(21)	0.2027 (2)	−0.1982 (3)	−0.0105 (2)	3.56 (14)
C(22)	0.1073 (2)	−0.1946 (3)	0.0010 (2)	3.61 (14)
C(23)	0.1211 (2)	−0.2527 (3)	0.0905 (2)	4.13 (16)
C(24)	0.2244 (2)	−0.2929 (3)	0.1338 (2)	3.58 (14)
C(25)	0.2759 (2)	−0.2601 (2)	0.0714 (2)	3.21 (11)
C(26)	0.3842 (3)	−0.2948 (4)	0.0870 (3)	4.82 (19)
H(3A)	0.419 (2)	−0.209 (3)	0.305 (2)	3.9 (6)
H(3B)	0.350 (2)	−0.163 (3)	0.369 (2)	4.6 (7)
H(3C)	0.456 (2)	−0.084 (3)	0.381 (2)	5.0 (7)
H(4A)	0.189 (3)	−0.089 (4)	0.335 (3)	8.1 (11)
H(4B)	0.074 (3)	−0.140 (4)	0.269 (2)	5.7 (8)
H(5A)	0.073 (3)	−0.039 (4)	0.409 (3)	8.3 (12)
H(5B)	0.025 (3)	0.062 (4)	0.336 (3)	6.8 (11)
H(5C)	0.134 (3)	0.090 (5)	0.392 (3)	7.4 (11)
H(11A)	0.414 (2)	0.394 (3)	0.225 (2)	4.2 (6)
H(12A)	0.268 (2)	0.346 (3)	0.073 (2)	4.6 (7)
H(13A)	0.106 (2)	0.331 (3)	0.105 (2)	4.4 (7)
H(14A)	0.163 (2)	0.378 (3)	0.281 (2)	4.2 (7)
H(16A)	0.435 (5)	0.426 (6)	0.422 (4)	11.5 (17)
H(16B)	0.340 (3)	0.415 (4)	0.446 (3)	6.5 (9)
H(16C)	0.381 (4)	0.545 (5)	0.398 (4)	10.5 (15)
H(21A)	0.215 (2)	−0.171 (3)	−0.064 (2)	3.9 (7)
H(22A)	0.045 (3)	−0.160 (4)	−0.037 (2)	6.2 (9)
H(23A)	0.077 (2)	−0.265 (3)	0.117 (2)	4.1 (7)
H(24A)	0.251 (2)	−0.336 (3)	0.188 (2)	4.1 (7)
H(26A)	0.411 (2)	−0.232 (3)	0.056 (2)	4.5 (7)
H(26B)	0.417 (3)	−0.296 (4)	0.150 (3)	6.7 (10)
H(26C)	0.387 (3)	−0.383 (5)	0.063 (3)	8.2 (11)

[a] $B_{iso} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$ for non-hydrogen atoms.

Crystal Structure and Spectral Properties of 5 (R = R′ = CH_3; R″ = C_2H_5). An ORTEP diagram for this wine-red complex is illustrated in Figure 1, and Tables I–IV list crystal data and data collection, atomic coordinates, as well as selected bond lengths and angles.

The structure of **5** reveals a $(CO)(C_5H_4CH_3)Mo–Mo(C_5H_4CH_3)(CO)$ skeleton with two different, sulfur-containing ligands

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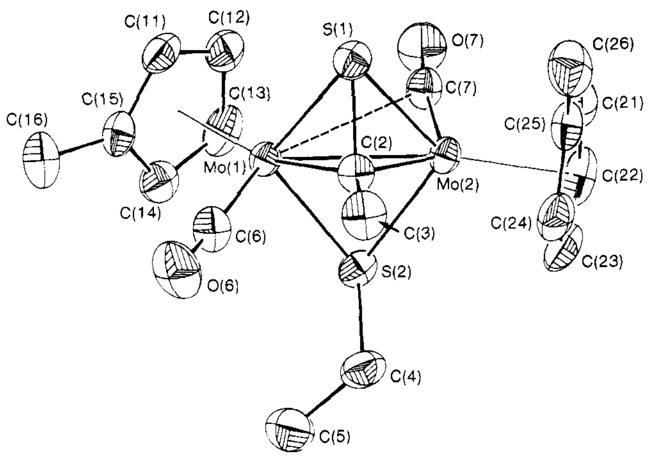

Figure 1. ORTEP diagram of $[(CH_3C_5H_4)_2Mo_2(CO)_2(SCCH_3)(SC_2H_5)]$ (**5**) showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels and hydrogen atoms have been deleted, here and in Figure 3.

bridging the Mo atoms (i.e., cleavage of the dithioester ligand occurred on forming **5**). One of these is a $(CH_3CS)^{3-}$ moiety which is located perpendicular to the Mo–Mo bond with both the S and αC atoms bonded to each Mo atom, and the other is a $(C_2H_5S)^-$ group in which the S atom alone bridges the Mo atoms. The Mo–Mo distance of 2.806 (1) Å is shorter than the values which have been reported for related metal carbonyl compounds[3-12,15-18] which range from 2.95 to 3.25 Å. As has been pointed out previously,[19] the length of lower order metal–metal bonds depends strongly on the number, size, arrangement, and character of the bridging groups, and **5** is unique in all of these respects. In addition, the Mo atoms in **5** have a formal oxidation state of III whereas all but one of the others have I. It is true that non-carbonyl complexes containing two or more bridging sulfur functionalities have Mo–Mo distances similar to that of **5**.[20]

All four Mo–S distances are similar [Mo(1)–S(1) = 2.439 (1) Å, Mo(2)–S(1) = 2.456 (1) Å, Mo(1)–S(2) = 2.435 (1) Å, Mo(2)–S(2) = 2.424 (1) Å]. In a strict, crystallographic sense, there is a significant difference in the Mo–S distances for each S atom, but from a chemical point of view, both S atoms are best regarded as being symmetrically bound and the same applies to C(2) of the $(CH_3CS)^{3-}$ group. This group acts as a five-electron donor. The S–C distance of 1.751 (2) Å is shorter than the thioethylate's 1.834 (2) Å, suggesting significant double-bond character in the former and that $(\sigma + \pi)$-bonded arrangements[16] should be considered along with purely σ-bonded forms in resonance arguments. To a lesser degree, this can be seen in the thiocamphor[11] and thiolactone[12] complexes [C–S = 1.769 (6) and 1.807 (6) Å, respectively]. The thioethylate group is conventionally σ-bonded to each Mo atom via S(2) with angles around the S atom approximating to tetrahedral.

At first glance, the carbonyl group C(7)–O(7) appears to be in a semibridging mode: The angle Mo(1)–Mo(2)–C(7) is 81.15 (7)° and angle Mo(2)–C(7)–O(7) is bent from linear [172.4 (2)°] with O(7) directed away from Mo(1). However, the Mo(1) ··· C(7) distance of 3.171 (2) Å is very long so this carbonyl is, at most, borderline between true semibonding and single terminal bonding. While the infrared spectra (KBr) of **5** (Experimental Section) shows three rather than two carbonyl stretching bands, none are in the region of 1800 cm^{-1}.[11,12] There are two distinct carbonyl carbon signals in the ^{13}C NMR spectra. Any interaction that may exist between Mo(1) and C(7) would result more from steric considerations than from a need to balance an unequal charge distribution.[21,22] Nevertheless, it does play an important role in the disposition of the bridging ligands in the plane perpendicular to the Mo–Mo bond as shown in Figure 2. Here **5** shows a strong structural similarity with μ-S_2 complexes such as $(C_5Me_5)_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$[23] and $Mo_2(\mu\text{-}S_2)[S_2C_2(C_6H_5)_2]_4$.[24]

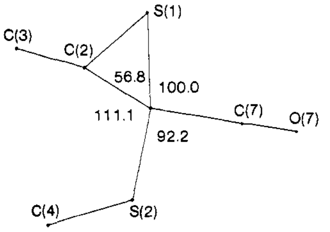

Figure 2. View down the Mo(1)–Mo(2) vector showing dihedral angles (deg) between planes of the type Mo(1), Mo(2), X (esd's < 0.1°).

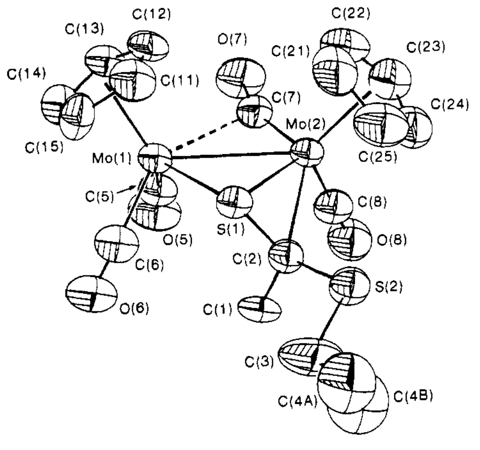

Figure 3. ORTEP diagram of $[Cp_2Mo_2(CO)_4(CH_3C(S)SC_2H_5)]$ (**6**) showing the atom-labeling scheme.

Least-squares-plane calculations through the five ring atoms of the methylcyclopentadienyl groups show that, in each case, the substituent methyl group is bent out-of-plane away from the center of the molecule. The deviation is larger for C(16) as this methyl eclipses C(6)–O(6) whereas C(26) is staggered with respect to the atoms on Mo(2). The wide range in Mo(C) (cyclopentadienyl) distances [2.280 (3) to 2.388 (2) Å] is common for such compounds[3,4,11,12,15-18] and stems largely from steric factors.

In the proton magnetic resonance spectrum of **5**, signals are observed for the protons of each of the cyclopentadienyl rings except in the case of **5** (R = H; R′ = $PhCH_2$; R″ = p-$CH_3OC_6H_4CH_2$). Similarly, separate groups of signals appeared, in the carbon magnetic resonance spectrum, for the cyclopentadienyl carbons of **5**, (R = R′ = CH_3; R″ = C_2H_5).

Reaction at Room Temperature. When **1** (R = H, CH_3; M = Mo, W) was reacted with ethyl dithioacetate at room temperature, the brown complexes **6** were obtained, with the dithioester unit intact. Complex **6** is not a precursor to **5** since none of the latter was detected on heating **6** in refluxing xylene. An X-ray crystal determination of **6** (R = H; R′ = CH_3; R″ = C_2H_5; M = Mo) established the structure of the complex. The ORTEP diagram for **6** is shown in Figure 3 [Tables I, II, V, and VI list relevant crystal

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Table IV. Selected Interatomic Distances (Å) and Angles (deg) for **5**^{a,b}

Mo(1)–Mo(2)	2.8056 (3), 2.810^{c}		
Mo(1)–S(1)	2.4391 (6), 2.442^{c}	Mo(2)–S(1)	2.4563 (6), 2.462^{c}
Mo(1)–S(2)	2.4345 (6), 2.440^{c}	Mo(2)–S(2)	2.4236 (6), 2.427^{c}
Mo(1)–C(2)	2.136 (2), 2.139^{c}	Mo(2)–C(2)	2.122 (2), 2.127^{c}
Mo(1)–C(6)	1.927 (3), 1.935^{d}	Mo(2)–C(7)	1.971 (2), 1.975^{d}
Mo(1)–C(11)	2.355 (2), 2.362^{e}	Mo(2)–C(21)	2.280 (3), 2.287^{e}
Mo(1)–C(12)	2.341 (3), 2.350^{e}	Mo(2)–C(22)	2.289 (3), 2.297^{e}
Mo(1)–C(13)	2.334 (2), 2.343^{e}	Mo(2)–C(23)	2.333 (3), 2.341^{e}
Mo(1)–C(14)	2.334 (3), 2.342^{e}	Mo(2)–C(24)	2.358 (3), 2.364^{e}
Mo(1)–C(15)	2.388 (2), 2.394^{e}	Mo(2)–C(25)	2.347 (2), 2.352^{e}
Mo(1)···C(7)	3.171 (2), 3.177^{f}		
S(1)–C(2)	1.751 (2), 1.754^{c}	S(2)–C(4)	1.834 (2), 1.842^{d}
C(2)–C(3)	1.505 (3), 1.517^{d}	C(4)–C(5)	1.494 (4), 1.516^{d}
C(6)–O(6)	1.161 (3), 1.171^{g}	C(7)–O(7)	1.146 (3), 1.155^{g}
C(15)–C(11)	1.402 (4), 1.412^{h}	C(25)–C(21)	1.411 (4), 1.421^{h}
C(11)–C(12)	1.411 (4), 1.419^{h}	C(21)–C(22)	1.415 (5), 1.423^{h}
C(12)–C(13)	1.395 (4), 1.404^{h}	C(22)–C(23)	1.401 (5), 1.410^{h}
C(13)–C(14)	1.404 (4), 1.413^{h}	C(23)–C(24)	1.409 (4), 1.417^{h}
C(14)–C(15)	1.420 (4), 1.429^{h}	C(24)–C(25)	1.416 (4), 1.424^{h}
C(15)–C(16)	1.501 (4), 1.504^{h}	C(25)–C(26)	1.493 (4), 1.497^{h}
Mo(2)–Mo(1)–S(1)	55.32 (2)	Mo(1)–Mo(2)–S(1)	54.75 (2)
Mo(2)–Mo(1)–S(2)	54.54 (2)	Mo(1)–Mo(2)–S(2)	54.91 (1)
Mo(2)–Mo(1)–C(2)	48.56 (6)	Mo(1)–Mo(2)–C(2)	49.01 (6)
Mo(2)–Mo(1)–C(6)	116.51 (8)	Mo(1)–Mo(2)–C(7)	81.15 (7)
Mo(2)–Mo(1)–Cp(1)	132.19	Mo(1)–Mo(2)–Cp(2)	166.52
S(1)–Mo(1)–S(2)	108.95 (2)	S(1)–Mo(2)–S(2)	108.74 (2)
S(1)–Mo(1)–C(2)	44.39 (6)	S(1)–Mo(2)–C(2)	44.23 (6)
S(1)–Mo(1)–C(6)	101.55 (8)	S(1)–Mo(2)–C(7)	92.92 (7)
S(1)–Mo(1)–Cp(1)	119.71	S(1)–Mo(2)–Cp(2)	124.62
S(2)–Mo(1)–C(2)	80.55 (6)	S(2)–Mo(2)–C(2)	81.09 (6)
S(2)–Mo(1)–C(6)	99.08 (8)	S(2)–Mo(2)–C(7)	86.70 (7)
S(2)–Mo(1)–Cp(1)	113.87	S(2)–Mo(2)–Cp(2)	120.81
C(2)–Mo(1)–C(6)	73.08 (10)	C(2)–Mo(2)–C(7)	125.75 (9)
C(2)–Mo(1)–Cp(1)	163.25	C(2)–Mo(2)–Cp(2)	119.62
C(6)–Mo(1)–Cp(1)	111.04	C(7)–Mo(2)–Cp(2)	112.01
Mo(1)–S(1)–Mo(2)	69.93 (2)	Mo(1)–C(2)–Mo(2)	82.43 (8)
Mo(1)–S(1)–C(2)	58.59 (8)	Mo(2)–S(1)–C(2)	57.69 (7)
Mo(1)–C(2)–S(1)	77.02 (9)	Mo(2)–C(2)–S(1)	78.08 (9)
Mo(1)–C(2)–C(3)	139.8 (2)	Mo(2)–C(2)–C(3)	132.4 (2)
Mo(1)–S(2)–Mo(2)	70.55 (2)		
Mo(1)–S(2)–C(4)	113.35 (11)	Mo(2)–S(2)–C(4)	111.57 (9)
S(1)–C(2)–C(3)	123.3 (2)	S(2)–C(4)–C(5)	110.9 (2)
Mo(1)–C(6)–O(6)	178.1 (2)	Mo(2)–C(7)–O(7)	172.5 (2)
C(15)–C(11)–C(12)	109.1 (2)	C(25)–C(21)–C(22)	108.9 (3)
C(11)–C(12)–C(13)	107.7 (2)	C(21)–C(22)–C(23)	107.8 (3)
C(12)–C(13)–C(14)	108.0 (2)	C(22)–C(23)–C(24)	107.8 (3)
C(15)–C(14)–C(15)	108.7 (2)	C(23)–C(24)–C(25)	109.0 (3)
C(14)–C(15)–C(11)	106.4 (2)	C(24)–C(25)–C(21)	106.4 (2)
C(14)–C(15)–C(16)	126.7 (3)	C(24)–C(25)–C(26)	126.0 (3)
C(11)–C(15)–C(16)	126.7 (3)	C(21)–C(25)–C(26)	127.4 (3)

[a] Bond lengths corrected for thermal motion are given following the corresponding uncorrected value. [b] Cp(*n*) is the centroid of C(*n*1)–C(*n*5). [c] Rigid body: Mo(1), Mo(2), S(1), S(2), C(2). [d] Riding motion of the second-mentioned atom on the first. [e] Rigid body: Mo(*n*), C(*n*1)–C(*n*6). [f] Rigid body: Mo(1), Mo(2), S(1), S(2), C(2), C(7). [g] From the distance Mo···O (corrected for motion of O riding on Mo), the distance Mo–C (corrected for motion of C riding on Mo) and the angle Mo–C–O. [h] Rigid body: C(*n*1)–C(*n*6).

data]. The ethyldithioacetate group bridges the Mo atoms with S(1) bonded to both Mo(1) and Mo(2) and C(2) to Mo(2) alone. In this respect, it resembles the thiocamphor[11] and thiolactone[12] complexes we have studied previously. The Mo–S bond lengths are comparable with the values found for these compounds, and the feature that the bond between S(1) and Mo(1) is slightly longer than that to Mo(2) is also observed here [2.395 (3) and 2.372 (3) Å, respectively]. The Mo(2)–C(2) distance in **6** is considerably shorter than that in the thiocamphor and thiolactone [2.178 (10) Å cf. 2.235 (6) and 2.364 (9) Å, respectively]. This may result from the delocalization of electron density throughout the S(1)–C(2)–S(2) portion of the ligand which is shown by equal C(2)–S(1) and C(2)–S(2) bond lengths of 1.790 (11) and 1.786 (12) Å.

Carbonyl C(7)–O(7) is in a genuine semibridging arrangement and bears the normal relationship between asymmetry of the M–C distances and M–C–O angles.[25] The position of the infrared band for the semibridging carbonyl group of **6** is similar to that for the related thioester complexes.[12]

As mentioned previously, the Mo–Mo distance is very sensitive to changes in the bridging ligands. These distances in **6** and the thiocamphor and thiolactone derivatives [3.163 (1), 3.145 (1), and 3.138 (1) Å, respectively] are reasonably similar as a result of the strong parallels in their bonding.

In conclusion, dithioesters react with compounds containing a metal–metal triple bond to give expected (**6**) and novel (**5**) complexes. The latter class of organosulfur compounds have a number of unique features including a symmetrically bridged thioacyl unit and a short metal–metal bond.

Experimental Section

General Data. A Fisher-Johns apparatus was used for melting point determinations. Infrared spectra were obtained by using a Nicolet MX-1 Fourier transform infrared spectrometer. Proton NMR spectral determinations were made with a Varian T-60 or EM360 spectrometer, while carbon-13 spectra were recorded in the fully and partially decoupled modes by using a Varian FT-80 spectrometer. Mass spectral analyses

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Table V. Final Atomic Coordinates of Non-Hydrogen Atoms for **6**

atom	*x*	*y*	*z*	B_{iso}/B^a
Mo(1)	0.26141 (4)	0.09598 (8)	0.21768 (6)	3.45 (5)
Mo(2)	0.38107 (4)	0.13819 (8)	0.16884 (6)	3.45 (5)
S(1)	0.31562 (12)	0.24868 (22)	0.23413 (19)	3.8 (1)
S(2)	0.41416 (14)	0.33004 (28)	0.31536 (24)	5.6 (2)
C(1)	0.3618 (5)	0.1673 (10)	0.3997 (7)	5.2 (8)
C(2)	0.3705 (5)	0.2204 (9)	0.3081 (7)	4.0 (6)
C(3)	0.3831 (8)	0.4101 (16)	0.4104 (12)	10.4 (15)
C(4A)[b]	0.4079 (15)	0.5078 (35)	0.4220 (28)	12.2 (10)
C(4B)[b]	0.4289 (31)	0.4310 (68)	0.4640 (53)	15.9 (24)
C(5)	0.2820 (5)	−0.0258 (10)	0.2904 (8)	4.4 (7)
O(5)	0.2916 (4)	−0.0993 (7)	0.3354 (6)	6.6 (7)
C(6)	0.2385 (5)	0.1340 (9)	0.3415 (9)	4.7 (8)
O(6)	0.2235 (4)	0.1525 (7)	0.4155 (6)	6.9 (7)
C(7)	0.3470 (5)	0.0009 (11)	0.1487 (8)	4.7 (7)
O(7)	0.3411 (4)	−0.0843 (7)	0.1210 (6)	6.5 (6)
C(8)	0.4205 (5)	0.0587 (10)	0.2614 (9)	4.7 (7)
O(8)	0.4448 (4)	0.0130 (8)	0.3145 (6)	6.6 (6)
C(11)	0.2196 (6)	0.1799 (12)	0.0943 (11)	6.0 (10)
C(12)	0.2383 (6)	0.0859 (15)	0.0596 (8)	6.2 (12)
C(13)	0.2150 (5)	0.0028 (11)	0.1069 (8)	5.0 (7)
C(14)	0.1796 (5)	0.0456 (11)	0.1704 (9)	4.9 (8)
C(15)	0.1825 (5)	0.1553 (12)	0.1606 (10)	5.6 (9)
C(21)	0.3801 (7)	0.2292 (22)	0.0254 (12)	7.9 (15)
C(22)	0.3963 (9)	0.1271 (19)	0.0088 (10)	7.6 (14)
C(23)	0.4422 (9)	0.1110 (16)	0.0531 (13)	7.8 (13)
C(24)	0.4569 (7)	0.1969 (23)	0.0993 (11)	7.5 (15)
C(25)	0.4202 (11)	0.2736 (14)	0.0842 (13)	8.0 (15)
C(71)[c]	0.0412 (14)	0.2874 (30)	0.1224 (27)	14.2
C(72)[c]	0.0282 (19)	0.2722 (42)	0.2001 (44)	14.2
C(73)[c]	0.0103 (20)	0.1978 (49)	0.1399 (37)	14.2
C(74)[c]	0.0000	0.1394 (64)	0.2500	14.2
C(75)[c]	0.0431 (20)	0.2224 (39)	0.2782 (34)	14.2
C(76)[c]	0.0316 (24)	0.0873 (52)	0.1634 (43)	14.2

[a] $B_{iso} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$ (in Å^2). [b] Fixed partial occupancies: C(4A), 0.62; C(4B), 0.38. [c] Refined occupancies: C(71), 0.82 (5); C(72), 0.62 (5); C(73), 0.53 (4); C(74), 0.51 (6); C(75), 0.60 (4); C(76), 0.53 (4).

were determined on a VG Micromass 7070E spectrometer. Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ, and by Schwarzkopf Laboratories, Woodside, NY. Dicyclopentadienyldimolybdenum hexacarbonyl was purchased from Strem or Pressure Chemicals and used as received. The tungsten analogue and bis(methylcyclopentadienyl)dimolybdenum hexacarbonyl were prepared according to literature procedures.[25] The dithioesters were synthesized from thioesters following procedures developed by Lawesson and co-workers.[14]

Solvents were dried and purified by standard methods. All reactions were effected under a dry nitrogen atmosphere with use of vacuum line and Schlenk techniques.

General Procedure for the Thermal Reaction of Dithioesters with 1. Compound **1** was generated by refluxing a toluene or xylene solution (20–30 mL) of $(RC_5H_4)_2M_2(CO)_6$ [1.0–2.0 mmol] overnight and analyzing the mixture by infrared spectroscopy. An equimolar amount of the dithioester was added, and the reaction mixture was refluxed with stirring overnight. The solution was cooled to room temperature and concentrated by rotary evaporation, and silica gel column chromatography [49:1 hexane:ether] afforded **5** as wine red crystals. The melting points and pertinent spectral data are given in Table VII.

General Procedure for the Room-Temperature Reaction of Dithioesters with 1. The above reaction and workup procedure was used, except that the reaction mixture of **1** and the dithioester was stirred at room temperature rather than under reflux conditions. Pertinent data for other products (**6**) are listed in Table VII.

X-ray Analysis. Single crystals of **5** (0.45 × 0.20 × 0.30 mm) and **6** (0.06 × 0.31 × 0.33 mm) were selected and mounted on the end of glass fibres with their largest dimensions parallel to the fibre axes. X-ray photographs of **5** taken by using Cu Kα radiation revealed $2/m$ Laue symmetry and systematic extinctions $h0l$ ($l = 2n + 1$), $0k0$ ($k = 2n + 1$), uniquely determining the space group $P2_1/c$; mmm Laue symmetry and systematic extinctions $0kl$ ($k = 2n + 1$), $h0l$ ($l = 2n + 1$), $hk0$ ($h + k = 2n + 1$) uniquely determined the space group of **6** to be *Pbcn*.

The crystals were transferred to a Nonius CAD4F diffractometer. Accurate cell dimensions and orientation matrices were determined in each case by least-squares analyses of the setting angles of 25 reflections (27°–2θ–31° for **5**; 24°–2θ–27° for **6**) which were accurately centered on the counter. Crystal data are given in Table I. The intensities of unique data sets ($h,k,\pm l$, for **5**; h,k,l for *6*) were measured as outlined in Table II. Two standards, measured at regular intervals, showed a small decrease in intensity (≈2%) over the duration of the data collection of **5**, and data were scaled accordingly. During the data collection of **6**, however, the intensities of both standards decreased constantly to final values which were 42% of the original. Data were consequently rescaled with respect to the intensities of the standards (see below). Analytic absorption corrections were applied to the data ($T = 0.69$–0.76 for **5** and 0.68–0.92 for **6**).

The structure of **5** was solved by standard heavy-atom techniques.[27] All non-hydrogen atoms were located and refined, initially with individual isotropic temperature factors and then with anisotropic temperature factors. An inner-data difference map at this stage revealed all H atoms. The H atoms were included in the refinement with isotropic temperature factors. An extinction correction also was determined.[28] The structure was refined until all shift:error ratios were 0.1.

The data of **6** were intially scaled linearly. The structure was solved by heavy-atom techniques which located most of the non-hydrogen atoms of the dimolybdenum molecule which were refined with isotropic temperature factors and then anisotropically. A different map at this stage revealed two positions for C(4) and also 6 peaks on or close to the twofold axis $(0,y,1/4)$. The two C(4) positions were given occupancies proportional to their peak heights. In following least-squares refinement, their occupancies were allowed to vary while their isotropic temperature factors were held fixed at a common value and then the occupancies were held at these refined values and the temperature factors were allowed to refine. The other 6 peaks were separate from the dimolybdenum molecule and presumably indicate a disordered solvent molecule(s). A low-temperature mass spectrum had exhibited major peaks at 84 and 86 m/e of appropriate intensities to suggest that CH_2Cl_2 was present in the crystals. However, it was not found possible to construct a simple model of disordered CH_2Cl_2 to fit the observed peaks so the peaks were regarded as C atoms with isotropic temperature factors fixed arbitrarily at $U = 0.18$ Å^2 and occupancies which were initially set proportional to their peak heights and which were then allowed to vary in subsequent least-squares refinement. H atoms for the cyclopentadienyl group were included at calculated positions but were not refined. The structure was refined to convergence at $R_1 = 0.066$.

Examination of R_1 and $w\Delta^2$ as a function of k index revealed a disturbing systematic trend which was traced back to the linear scaling of the data (k was the index collected slowest). A plot of the standard reflections showed that the decomposition curve was basically exponential in nature so linear scaling gave only an approximate fit. A five-point smoothed curve was found to be much better and was used to rescale the data.

The parameters of the atoms of the dimolybdenum molecule obtained above were used with the rescaled data. Once again a difference map revealed a region of disorder about $0,y,{}^1/_4$ so the procedure outlined above was repeated. A subsequent inner-data difference map revealed the methyl hydrogens around C(1) which were included in structure factor calculations but were not refined. This time the structure converged to $R_1 = 0.045$, confirming the superiority of the five-point smoothed curve over the linear fit for scaling the data. The total number of electrons involved in the region of the "solvent molecule", as derived from the refined occupancies, is 40.2 e cf. 42 e for CH_2Cl_2. There are only 4 "solvent molecules" in the unit cell.

Refinement for both structures was by full-matrix least-squares analysis, minimizing the function $\sum w(F_0 - F_c)^2$, where $w = 1$ in the early stages and $w = 1/[(\sigma(F))^2 + pF^2]$ in the final cycles ($p = 0.0004$ for **5** and 0.0006 for **6**). The biggest features in final difference maps were around the Mo atom(s) in each case. Neutral scattering factors with anomalous dispersion corrections were used throughout.[29] Computer programs[30] were run on VAX11/750 and IBM 370/155 machines. The atom-labeling schemes are displayed in Figures 1 and 3.

Thermal motion corrections[31] are reported for the bond lengths in

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Table VI. Selected Interatomic Distances (Å) and Angles (deg) for **6**[a,b]

Mo(1)–Mo(2)	3.1633 (14), 3.165[c]	Mo(2)–C(2)	2.178 (10), 2.282[c]
Mo(1)–S(1)	2.395 (3), 2.402[c]	Mo(2)–S(1)	2.372 (3), 2.375[c]
Mo(1)–C(5)	1.944 (13), 1.950[d]	Mo(2)–C(7)	1.974 (15), 1.981[d]
Mo(1)–C(6)	1.937 (13), 1.947[d]	Mo(2)–C(8)	1.951 (13), 1.961[d]
Mo(1)–C(11)	2.330 (13), 2.346[e]	Mo(2)–C(21)	2.369 (13), 2.378[e]
Mo(1)–C(12)	2.353 (12), 2.365[e]	Mo(2)–C(22)	2.340 (14), 2.354[e]
Mo(1)–C(13)	2.311 (11), 2.318[e]	Mo(2)–C(23)	2.304 (13), 2.324[e]
Mo(1)–C(14)	2.278 (12), 2.289[e]	Mo(2)–C(24)	2.295 (14), 2.315[e]
Mo(1)–C(15)	2.294 (12), 2.311[e]	Mo(2)–C(25)	2.335 (14), 2.348[e]
Mo(1)···C(7)	2.678 (12), 2.681[c]		
S(1)–C(2)	1.790 (11), 1.791[c]	S(2)–C(3)	1.879 (17)
C(2)–C(1)	1.50 (2), 1.51[d]	C(3)–C(4A)	1.41 (5)
C(2)–S(2)	1.786 (12), 1.787[c]	C(3)–C(4B)	1.42 (8)
C(5)–O(5)	1.16 (2), 1.18[f]	C(7)–O(7)	1.17 (2), 1.18[f]
C(6)–O(6)	1.16 (2), 1.17[f]	C(8)–O(8)	1.14 (2), 1.15[f]
C(11)–C(12)	1.38 (3), 1.40[e]	C(21)–C(22)	1.39 (4), 1.41[e]
C(12)–C(13)	1.39 (2), 1.41[e]	C(22)–C(23)	1.34 (3), 1.36[e]
C(13)–C(14)	1.39 (2), 1.41[e]	C(23)–C(24)	1.33 (4), 1.36[e]
C(14)–C(15)	1.41 (2), 1.42[e]	C(24)–C(25)	1.37 (4), 1.39[e]
C(15)–C(11)	1.38 (2), 1.39[e]	C(25)–C(21)	1.44 (4), 1.46[e]
Mo(2)–Mo(1)–S(1)	48.1 (7)	Mo(1)–Mo(2)–S(1)	48.75 (8)
		Mo(1)–Mo(2)–C(2)	76.7 (3)
Mo(2)–Mo(1)–C(5)	89.8 (4)	Mo(1)–Mo(2)–C(7)	57.4 (3)
Mo(2)–Mo(1)–C(6)	116.7 (4)	Mo(1)–Mo(2)–C(8)	104.6 (4)
Mo(2)–Mo(1)–Cp(1)	120.6	Mo(1)–Mo(2)–Cp(2)	134.1
		S(1)–Mo(2)–C(2)	45.2 (3)
S(1)–Mo(1)–C(5)	116.2 (4)	S(1)–Mo(2)–C(7)	106.1 (4)
S(1)–Mo(1)–C(6)	83.0 (4)	S(1)–Mo(2)–C(8)	113.4 (4)
S(1)–Mo(1)–Cp(1)	118.8	S(1)–Mo(2)–Cp(2)	118.4
		C(2)–Mo(2)–C(7)	119.1 (5)
		C(2)–Mo(2)–C(8)	72.5 (4)
		C(2)–Mo(2)–Cp(2)	129.3
C(5)–Mo(1)–C(6)	77.6 (5)	C(7)–Mo(2)–C(8)	82.2 (5)
C(5)–Mo(1)–Cp(1)	124.3	C(7)–Mo(2)–Cp(2)	111.5
C(6)–Mo(1)–Cp(1)	117.2	C(8)–Mo(2)–Cp(2)	118.4
Mo(1)–S(1)–Mo(2)	83.14 (10)		
Mo(1)–S(1)–C(2)	110.0 (4)	Mo(2)–S(1)–C(2)	64.6 (4)
S(1)–C(2)–C(1)	119.9 (9)	Mo(2)–C(2)–S(1)	70.2 (4)
S(1)–C(2)–S(2)	111.1 (6)	Mo(2)–C(2)–S(2)	109.8 (5)
C(1)–C(2)–S(2)	113.2 (8)	Mo(2)–C(2)–C(1)	125.7 (8)
C(2)–S(2)–C(3)	102.0 (7)	S(2)–C(3)–C(4A)	112 (2)
		S(2)–C(3)–C(4B)	99 (3)
Mo(1)–C(5)–O(5)	176 (1)	Mo(1)–C(7)–O(7)	159 (1)
Mo(1)–C(6)–O(6)	177 (1)	Mo(1)–C(8)–O(8)	178 (1)
C(15)–C(11)–C(12)	106.7 (12)	C(25)–C(21)–C(22)	105.1 (16)
C(11)–C(12)–C(13)	109.7 (12)	C(21)–C(22)–C(23)	108.6 (17)
C(12)–C(13)–C(14)	107.3 (13)	C(22)–C(23)–C(24)	110.7 (18)
C(13)–C(14)–C(15)	106.8 (12)	C(23)–C(24)–C(25)	108.5 (17)
C(14)–C(15)–C(11)	109.4 (12)	C(24)–C(25)–C(21)	107.1 (17)

[a] Bond lengths corrected for thermal motion are given following the corresponding uncorrected values. [b] Cp(*n*) is the centroid of C(*n*1)–C(*n*5). [c] Rigid body: Mo(1), Mo(2), S(1), C(2), S(2). [d] Riding motion of the second-mentioned atom on the first. [e] Rigid body: Mo(*n*), C(*n*1)–C(*n*5). [f] From the distance Mo···O (corrected for motion of O riding on Mo), the distance Mo–C (corrected for motion of C riding on Mo), and the angle Mo–C–O.

Table VII. Pertinent Data for **5** and **6**[a]

5 or **6**	mp, °C, dec	IR ν_{CO},[b] cm^{-1}	^{1}H NMR C_5H_4R,[c] δ
5 ($R = R' = CH_3$; $R'' = C_2H_5$[d])	84–86	1891 (s), 1882 (vs), 1859 (vs)	2.00 (s, 3 H, $C_5H_4CH_3$) 2.06 (s, 3 H, $C_5H_4CH_3$) 5.06–5.30 (m, 8 H, $C_5H_4CH_3$)
5 ($R = H$; $R' = CH_3$; $R'' = C_2H_5$)	86–90	1942 (s), 1884 (vs), 1842 (vs)	5.20 (s, 5 H, C_5H_5) 5.33 (s, 5 H, C_5H_5)
5 ($R = H$; $R' = PhCH_2$; $R'' = p\text{-}CH_3OC_6H_4CH_2$)	180–185	1951 (vs), 1923 (s), 1887 (vs)	5.34 (s, 10 H, C_5H_5)
6 ($M = Mo$; $R = H$; $R' = CH_3$; $R'' = C_2H_5$)	110–112	1960 (vs), 1940 (vs), 1918 (vs), 1841 (vs), 1806 (ms)	5.40 (s, 5 H, C_5H_5) 5.67 (s, 5 H, C_5H_5)
6 ($M = Mo$; $R = R' = CH_3$; $R'' = C_2H_5$)		1956 (vs), 1914 (s), 1905 (ms), 1869 (ms)[e]	1.93 (s, 3 H, $C_5H_4CH_3$) 2.00 (s, 3 H, $C_5H_4CH_3$) 4.90–5.40 (m, 8 H, $C_5H_4CH_3$)
6 ($M = W$; $R = R' = CH_3$; $R'' = C_2H_5$)	113–115	1942 (vs), 1902 (vs), 1827 (vs), 1791 (ms)	5.20 (s, 5 H, C_5H_5) 5.50 (s, 5 H, C_5H_5)

[a] Satisfactory C, H analyses were obtained. [b] KBr disks. [c] $CDCl_3$ with tetramethylsilane as an internal standard. [d] ^{13}C NMR: δ_{CO} 234.93, 286.27. [e] Nujol mull.

Tables V and VI. Corrections to angles are small (±1 esd) and are not listed. Coordinates for the hydrogen atoms of **6**, anisotropic temperature factors for the non-hydrogen atoms, and bond lengths and angles involving the H atoms and within the "solvate" of **6** comprise supplementary Tables I–V and are deposited.

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Registry No. 1 (R = CH_3; M = Mo), 69140-73-4; **1** (R = H; M = Mo), 56200-27-2; **1** (R = CH_3; M = W), 92670-32-1; **5** (R = R′ = CH_3; R″ = C_2H_5), 92670-33-2; **5** (R = H; R′ = CH_3; R″ = C_2H_5), 92670-34-3; **5** (R = H; R′ = $PhCH_2$; R″ = p-$CH_3OC_6H_4CH_2$), 92670-35-4; **6** (M = Mo; R = H; R′ = CH_3; R″ = C_2H_5), 92670-36-5; **6**·$0.5CH_2Cl_2$ (M = Mo; R = H; R′ = CH_3; R″ = C_2H_5), 92760-84-4; **6** (M = Mo; R = R′ = CH_3; R″ = C_2H_5), 92670-38-7; $(CH_3C_5H_4)_2Mo_2(CO)_6$, 33056-03-0; $(C_5H_5)_2Mo_2(CO)_6$, 12091-64-4; $(CH_3C_5H_4)_2W_2(CO)_6$, 68111-11-5; ethyl dithioacetate, 870-73-5; p-methoxybenzyl benzenedithioacetate, 92670-39-8.

Supplementary Material Available: Tables of thermal and hydrogen atom parameters, temperature factors, additional bond lengths and angles, least-squares planes, and structure factors for **5** and **6** (55 pages). Order information is given on any current masthead page.

Electronic Coupling in Delocalized Mixed-Valence Dimers

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Abstract: The electronic absorption spectra of the Creutz–Taube mixed-valence ion and its osmium analogue have been reinvestigated, and a simple effective pair model has been developed. This model successfully interprets the anisotropy of the EPR g values and MCD spectra of the Creutz–Taube ion and provides an assignment of the visible and near-IR absorption spectra of the osmium analogue. Indications of further complexities in the Creutz–Taube ion are outlined.

The properties of the mixed-valence decaammine(μ-pyrazine-N,N')diruthenium(5+) (Creutz–Taube) ion have generated considerable debate with regard to its electronic structure, and a recent contribution has summarized and reviewed the evidence for and against a delocalized model.[1] The case for delocalization, based on analyses of the EPR and optical data, has been put by Hush et al.,[2,3] but the optical argument revolves around the width of the near-infrared absorption band, and, so far, no framework has been developed to interpret the polarized spectra of delocalized mixed-valence complex ions. Such a model should also be compatible with the EPR data so that both EPR and optical data can be treated within the same framework. Several attempts to model the system have been made; some concentrate on vibronic effects[4,5] while others work within a molecular orbital description,[6,7] intuitively more appealing from the viewpoint of inorganic chemistry. None of these deals satisfactorily with the polarization of the electronic absorption spectra.

We have found that magnetic circular dichroism (MCD) can be used to great advantage in understanding the near-infrared absorption spectra of many osmium(III) and ruthenium(III) complex ions.[8,9] A similar situation applies to mixed-valence complex ions involving these metals, and we have developed the simplest type of model that can be used to interpret the MCD of these materials. The approach arises naturally from the one we developed to interpret the electronic properties of the $(Ru,Os)^{3+}$ ions which have the t_2^5 configuration. Our model is based on an effective Hamiltonian for the $^2T_2$ term along with a consideration of the effective electric dipole transition moments associated with the odd parity potentials of the ligand field experienced by each metal ion. These potentials break down the Laporte restriction within each metal ion d shell and also provide for two-center excitations between the metal ions. The latter transition dipoles can interfere with the former and provide a net MCD signal when the external magnetic field lies transverse to the direction of the metal ions. This approach uses "transfer integrals" to describe the coupling between the two metal ions and enables a reinterpretation of the existing EPR data as well as the electronic absorption spectrum of the Creutz–Taube ion and the electronic spectrum of the osmium analogue. The present paper deals with these matters while another work[10] reports a corresponding analysis of the properties of the dinitrogen osmium 5+ mixed-valence ion.

Table I. Effective Single-Ion Hamiltonian and Energy Matrix (Units of λ)

$$\mathcal{H}_{\text{eff}} = \Delta(L_Z^2 - {}^2/_3) - \beta(L_X^2 - L_Y^2) - \lambda L\cdot S$$

$$\begin{array}{l|lll}
\pm 1/2 X_\pm & \Delta/3 + {}^1/_2 & 0 & -\beta \\
\mp 1/2 X_0 & 0 & -2\Delta/3 & 1/2^{1/2} \\
\pm 1/2 X_\mp & -\beta & 1/2^{1/2} & \Delta/3 - {}^1/_2
\end{array}$$

$$|\pm 1/2 X_\pm\rangle = |x_\pm^2 \overset{\pm}{x}_\mp x_0^2|$$

$$|\mp 1/2 X_0\rangle = -|x_\pm^2 x_\mp^2 \overset{\mp}{x}_0|$$

$$|\pm 1/2 X_\mp\rangle = |\overset{\pm}{x}_\pm x_\mp^2 x_0^2|$$

EPR Spectra

The original powder and glass measurements of Bunker et al.[11] were shown to be incomplete by Hush et al.[3] through their single-crystal study. Hush et al.[3] concluded that the Creutz–Taube ion has approximate tetragonal symmetry with the principal axis ($g_\parallel$) perpendicular to the pyrazine ring, not along the Ru–pyr–Ru axis. This accidental or pseudotetragonal description can occur if the tetragonal (Δ) and rhombic (β) field parameters (defined

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