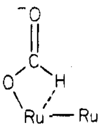
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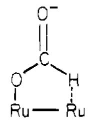
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to propose a process (Scheme I) that proceeds via a transition state (3), which is consistent with the available data, e.g., CO loss from $HRu_3(CO)_{11}^-$ is faster than CO_2 insertion. Indeed the insertion reaction described in Scheme I is retarded in the presence of a carbon monoxide atmosphere. However, intimate mechanistic detail of reaction 6 must await further experimental observations. These experiments are presently in progress in our laboratories.

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 80-09233 is greatly appreciated.

Registry No. $[PPN][\mu\text{-}HCO_2Ru_3(CO)_{10}]$, 86528-72-5; $[PPN][\mu\text{-}CH_3CO_2Ru_3(CO)_{10}]$, 86528-74-7; $[HRu_3(CO)_{11}][PPN]$, 71936-70-4; $Ru_3(CO)_{12}$, 15243-33-1; CO_2, 124-38-9; CO, 630-08-0.

Supplementary Material Available: Lists of structure factor amplitudes, tables of thermal parameters, positional parameters for hydrogen atoms, and bond lengths and angles in the cation, and ORTEP drawing of cation PPN (20 pages). Ordering information is given on any current masthead page.

Reaction of Thioesters and Thiolactones with Cyclopentadienylmetal Dicarbonyl Dimers

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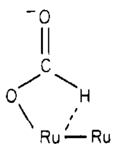
Complexes containing a metal–metal triple bond, $(RC_5H_4)_2M_2(CO)_4$ (R = H, CH_3; M = Mo, W), react with thioesters and thiolactones to give compounds of type (thioester or thiolactone) $M_2(CO)_4(C_5H_4R)$. Analytical and spectral data, together with an X-ray analysis of the (thiobutyrolactone)molybdenum complex, revealed that the sulfur is bonded to both molybdenum atoms and that a semibridging carbonyl group is present. There is no evidence for bonding of the oxygen, of the organic ligand, to a metal atom. Crystal data for $[(C_5H_5)_2Mo_2(CO)_4(SC_4H_6O)]$: tetragonal space group $P4_2bc$, a = 19.872 (3) Å, c = 9.643 (2) Å, V = 3808.0 Å^3, Z = 8. The intensities of 1384 reflections with $I > 2.3\sigma(I)$, collected by counter methods with Mo Kα radiation, were used in the least-squares refinement. Final R_F = 0.021 and R_{wF} = 0.025. The bridgehead C atom is bonded to one Mo atom while S bridges between both Mo atoms: Mo(1)–Mo(2) = 3.138 (1) Å, Mo(2)–C = 2.235 (6) Å, Mo(1)–S = 2.402 (1) Å, Mo(2)–S = 2.385 (2) Å, and S–C = 1.807 (6) Å. There is a semibridging carbonyl group: Mo(2)–C(21) = 1.944 (6) Å, Mo(1)···C(21) = 2.764 (8) Å, and Mo(2)–C(21)–O(21) = 162.7 (7)°.

Introduction

Much work has been done on the chemistry of metal–metal multiple bonds, including complexes bearing carbonyl ligands.[2,3] Some recent examples include the reaction of the in situ generated cyclopentadienylmolybdenum (or tungsten) dicarbonyl dimer 1 which contains a triple bond between the metal atoms, with $M(CO)_2(NO)(C_5H_5)$ (M = Mo, W) affording homonuclear and heteronuclear metal cluster nitrides 2;[4] with α-halo ketones to give the dehalogenated ketone 3 and the organomolybdenum tricarbonyl halide 4;[5] and with nitro compounds to form high oxidation state molybdenum and tungsten complexes having bridging and terminal oxygen ligands (5).[6]

In 1979, one of us[7] reported a new class of thione complexes (7) obtained by the reaction of 1 with thioketones 6 under mild conditions. Such complexes have the thione function bonded to one metal atom, with the sulfur donor bound to the other metal atom, and a semibridging carbonyl group is also present. It seemed of interest to learn the effect of a heteroatom on (a) the course of the complexation reaction and (b) the bonding parameters assuming complexes of structural type 7 were formed. Therefore, a series of thioesters and thiolactones were treated with the metal–metal triple bonded complexes 1. A previous study in the area of orthometalation showed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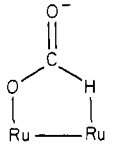
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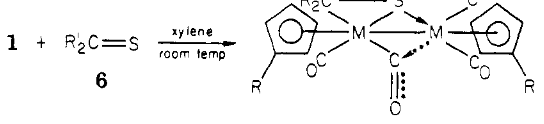

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(1) (a) University of Ottawa. (b) Simon Fraser University.

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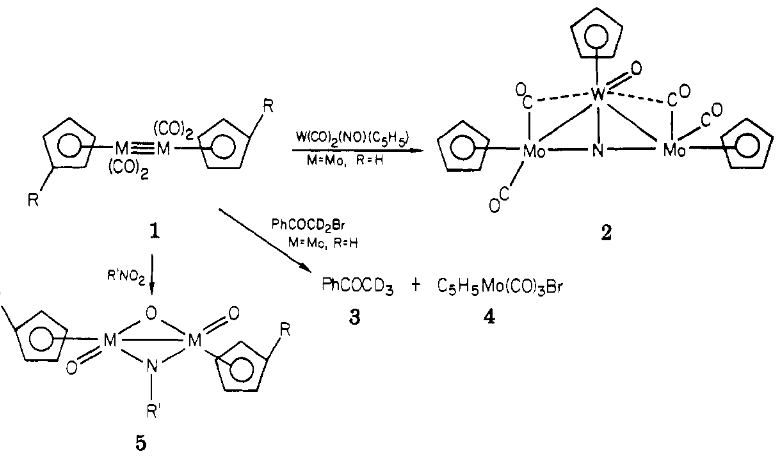
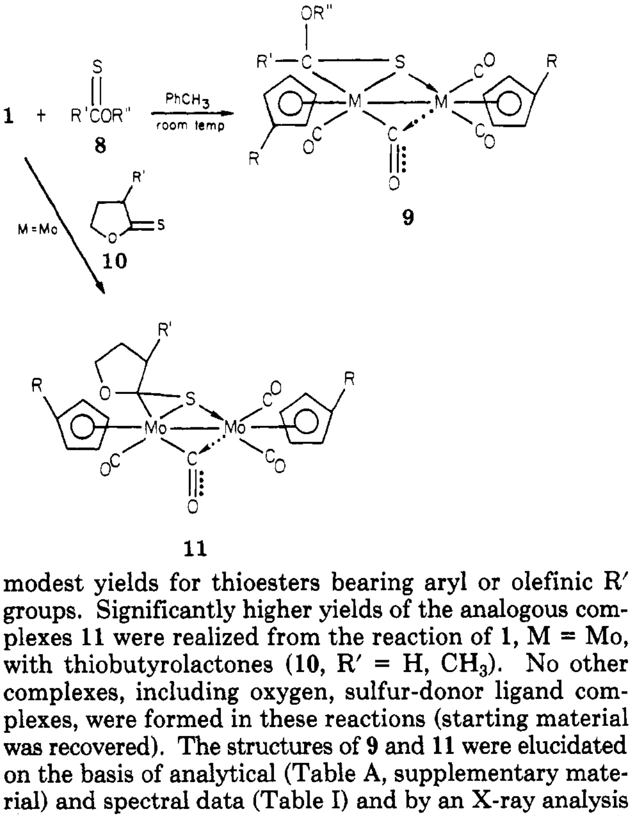


that, while thioketones were readily cyclometalated with diiron enneacarbonyl, thioesters afforded oxygen, sulfur-donor diiron hexacarbonyl complexes, with the orthometalated species formed as a byproduct.[8]

Results and Discussion

Synthesis and Spectral Properties of the Complexes. Reaction of *O*-alkyl thioesters 8 with 1 afforded complexes of structural type 9. The reaction occurred in modest yields for thioesters bearing aryl or olefinic R′ groups. Significantly higher yields of the analogous complexes 11 were realized from the reaction of 1, M = Mo, with thiobutyrolactones (10, R′ = H, CH_3). No other complexes, including oxygen, sulfur-donor ligand complexes, were formed in these reactions (starting material was recovered). The structures of 9 and 11 were elucidated on the basis of analytical (Table A, supplementary material) and spectral data (Table I) and by an X-ray analysis of the (thiobutyrolactone)dimolybdenum complex 11, R = R′ = H.



Three terminal metal carbonyl stretching frequencies were observed in the infrared region at 1945–1965 (s), 1910–1933 (vs), and 1840–1875 (vs) cm^{-1}, while the band for the semibridging carbonyl group occurred at 1793–1816 cm^{-1}. These bands are in the same regions as those for the thioketone complexes 7, except that the highest and lowest of the four absorptions are much more intense in the case of 9 and 11.

In the proton magnetic resonance spectra, the two cyclopentadienyl rings of 9 and 11 (R = H) gave two distinct singlet signals at δ 5.00–5.42 since the rings are in different environments. An exception was 9, R = H, R′ = *trans*-PhCH=CH, R″ = C_2H_5, M = Mo, where the protons of the two five-membered rings give rise to an apparent singlet. In the latter complex, as well as for the methylcyclopentadienyl analogue, the geometry of the olefinic group is trans (or *E*) since the *J* values of 16 Hz for spin–spin coupling of the olefinic protons are consistent with such a stereochemical arrangement. Note that there is no evidence for complexation of the carbon–carbon double in these examples.

The carbon-13 magnetic resonance spectra of 9 and 11 displayed several interesting features. The five carbons of the two cyclopentadienyl rings gave singlet signals in the δ 92.93–95.22 region of the spectrum. Similarly, in the case of complexes containing methylcyclopentadienyl ligands, the two methyl carbons are different. However, it was surprising to observe that all ring carbons of the two $C_5H_4CH_3$ ligands of 9, R = CH_3, R′ = *p*-BrC_6H_4, R″ = CH_3, M = Mo, and of 11, R = CH_3, R′ = H, were nonequivalent. The resonance for the thiocarbonyl carbon appeared in the narrow range of δ 160.78–165.12. Although this represents an upfield shift on complexation (the free ligand thiocarbonyl carbon occurs at δ 212.28–223.30), the magnitude of the shift is significantly less than in the case of thioketone complexes [e.g., 4,4′-dimethoxythiobenzophenone δ(CS) 233.30; complex 7 of 4,4′-dimethoxythiobenzophenone δ(CS) 106.93].[7] These data imply that there is more π-bonding character in the carbon–sulfur bond of 9 or 11 than of 7. Finally, there are four signals for the carbonyl carbons in the δ 212.50–248.75 region.

The mass spectrum of 11, R = R′ = H, did show $[M - CO]^+$ and $[M - 4CO]^+$ fragments. However attempts to record mass spectra of all the other complexes proved fruitless as decomposition of 9 or 11 occurred in the mass spectrometer.

Crystal Structure of 11, R = R′ = H (11a). Crystal data are given in Table II and atomic coordinates in Table III and selected bond lengths and angles in Table IV. An ORTEP diagram of the molecule is shown in Figure 1.

The structure closely resembles that of the thiocamphor derivative of 7, 7a.[7] The S atom of the ligand bridges both Mo atoms, and the bridgehead C, which has rehybridized from sp^2 in the parent to predominantly sp^3,[9] is bonded to just one Mo. The Mo–Mo and corresponding Mo–S

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[9] Mo(2) is 1.008 Å above the plane of C(55), C(51), O(52) and S is 1.270 (2) Å below this plane. The plane of S,C(51),Mo(2) is perpendicular to C(55),C(51),O(52).

Table I. Yields, Melting Points, and Spectral Data for 9 and 11[a]

9 or 11	yield,[b] %	mp, °C (dec)	IR ν_{CO},[c] cm^{-1}	^{1}H NMR,[d] δ	^{13}C NMR,[d] δ
9, R = H, R′ = Ph, R″ = CH_3, M = Mo	15	158–159	1952 s, 1918 vs, 1859 vs, 1808 s	3.02 (s, 3 H, OCH_3), 5.00 (s, 5 H, C_5H_5), 5.25 (s, 5 H, C_5H_5), 7.20–7.60 (m, 5 H, Ph)	62.87 (OCH_3), 93.84 (C_5H_5), 96.24 (C_5H_5), 123.82, 126.76, 128.18 (benzenoid CH), 149.04 (benzenoid quarternary carbon), 165.12 (CS)[e,f]
9, R = H, R′ = Ph, R″ = CH_3, M = W	11	171–173	1947 s, 1911 vs, 1844 vs, 1799 ms	3.07 (s, 3 H, OCH_3), 5.17 (s, 5 H, C_5H_5), 5.42 (s, 5 H, C_5H_5), 7.20–7.70 (m, 5 H, Ph)	
9, R = H, R′ = p-BrC_6H_4, R″ = CH_3, M = Mo	15	163–166	1962 s, 1933 vs, 1863 vs, 1796 s	3.03 (s, 3 H, OCH_3), 5.00 (s, 5 H, C_5H_5), 5.21 (s, 5 H, C_5H_5), 7.35 (s, 4 H, p-BrC_6H_4)	61.91 (OCH_3), 92.93 (C_5H_5), 95.22 (C_5H_5), 119.35 (Br–C), 124.41, 130.29 (benzenoid CH), 147.07 (other benzenoid quarternary carbon), 163.67 (CS), 212.50, 230.96, 235.37, 244.64 (carbonyl carbons)
9, R = CH_3, R′ = p-BrC_6H_4, R″ = CH_3, M = Mo	19	124–126	1960 s, 1924 vs, 1875 vs, 1816 s	1.73 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 3.07 (s, 3 H, OCH_3), 4.80–5.30 (m, 8 H, C_5H_4), 7.37 (s, 4 H, p-BrC_6H_4)	13.20 (CH_3), 14.29 (CH_3), 62.75 (OCH_3), 91.66, 93.19, 94.31, 94.43, 94.75, 95.61, 97.02, 97.97 (CH of C_5H_4R rings), 109.15, 114.96 (quarternary carbons of C_5H_4 R rings), 120.26 (Br–C), 125.62, 131.21 (benzenoid CH), 148.06 (other benzenoid quarternary carbon), 165.06 (CS) 233.27, 236.07, 238.21, 246.81 (carbonyl carbons)
9, R = H, R′ = PhCH=CH, R″ = C_2H_5, M = Mo	27	134–136	1968 s, 1928 vs, 1845 vs, 1814 s	1.28 (t, 3 H, $\mathit{CH_3}CH_2$), 4.18 (q, 2 H, CH_2CH_3), 5.20 (s (br), 10 H, C_5H_5), 6.37 (d, 1 H, J = 16 Hz, CH=), 7.22 (m, 5 H, Ph), 7.36 (d, 1 H, J = 16 Hz, CH=)	
9, R = CH_3, R′ = PhCH=CH, R″ = C_2H_5, M = Mo	41	88–90	1956 s, 1917 vs, 1852 vs, 1809 s	1.22 (t, 3 H, $\mathit{CH_3}CH_2$), 1.88 (s, 3 H, CH_3), 2.00 (s, 3 H, CH_3), 4.08 (q, 2 H, $CH_3\mathit{CH_2}$), 5.12 (m, 8 H, C_5H_4), 6.28 (d, 1 H, J = 16 Hz, CH=), 7.15 (m, 5 H, Ph), 7.55 (d, 1 H, J = 16 Hz, CH=)	
11, R = R′ = H[g]	65	147–150	1949 s, 1910 vs, 1840 vs, 1814 s	2.07 (m, 2 H, CH_2), 2.67 (m, 2 H, CH_2CSMo), 3.87 (m, 2 H, CH_2O), 5.18 (s, 5 H, C_5H_5), 5.40 (s, 5 H, C_5H_5)	27.29 (CH_2), 49.72 ($\mathit{CH_2}CSMo$), 71.56 (CH_2O), 93.17 (C_5H_5), 94.53 (C_5H_5), 164.80 (CS), 227.79, 236.28, 245.17, 248.75 (carbonyl carbons)[h]
11, R = CH_3, R′ = H	58	110–111	1945 s, 1912 vs, 1865 vs, 1794 s	1.87 (s, 3 H, CH_3), 2.03 (m, 2 H, CH_2), 2.07 (s, 3 H, CH_3), 2.60 (m, 2 H, CH_2CSMo), 3.83 (m, 2 H, CH_2O), 4.70–5.30 (m, 8 H, C_5H_4)	13.52 (CH_3), 14.34 (CH_3), 27.02 (CH_2), 49.42 ($\mathit{CH_2}CSMo$), 71.54 (CH_2O), 89.26, 92.13, 92.58, 93.00, 94.14, 94.24, 96.63 (CH of C_5H_4 rings), 108.53, 115.44 (quarternary carbons of C_5H_4 rings), 165.00 (CS), 228.83, 237.21, 238.46, 247.28 (carbonyl carbons)
11, R = H, R′ = CH_3	52	139–141	1967 s, 1921 vs, 1859 vs, 1793 s		20.38 (CH_3), 31.41 (CH_2), 38.54 (CH_2), 61.18 (CH), 93.55 (C_5H_5), 94.89 (C_5H_5), 160.78 (CS)[e]

[a] Satisfactory C, H, and S analyses were obtained for 9 and 11 (Table A, supplementary material). [b] Yields are of analytically pure materials. [c] Recorded as KBr disks. [d] $CDCl_3$ solution with $(CH_3)_4Si$, as internal standard. [e] The chemical shift for the carbonyl carbons was not determined. [f] ^{13}C of 8, R = Ph, R″ = CH_3, δ 212.28 (CS). [g] Mass spectrum, m/e 508 $[M - CO]^+$, 424 $[M - 4\ CO]^+$. [h] ^{13}C of 10, R′ = H, δ 223.30 (CS).

Table II. Crystal Data

$C_{18}H_{16}Mo_2O_5S$
cryst system: tetragonal
space group $P4_2bc$
a = 19.872 (3) Å
c = 9.643 (2) Å
V = 3807.99 Å^3

Z = 8
fw 536.27
ρ_{calcd} = 1.871 g cm^{-3}
ρ_{obsd} = 1.880 g cm^{-3}
μ = 14.25 cm^{-1}

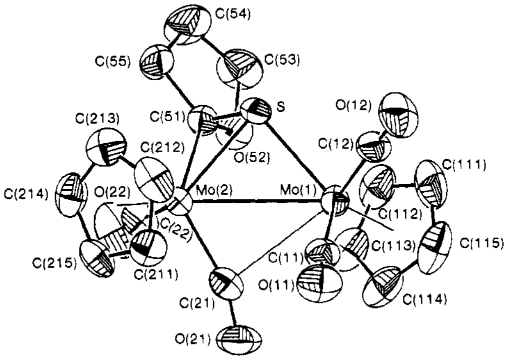

Figure 1. ORTEP diagram of $[(C_5H_5)_2Mo_2(CO)_4(SC_4H_6O)]$ showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been deleted from the diagram.

bond distances are very similar for these compounds, being respectively 3.138 (1) Å [3.145 (1) Å], 2.402 (2) Å [2.403 (2) Å], and 2.385 (2) Å [2.368 (2) Å] for **11a** (and **7a**). However, the Mo–C(51) bond in **11a** is 2.235 (6) Å which is considerably shorter than the corresponding bond in **7a** [2.364 (9) Å] while the C(51)–S bond is significantly longer (1.807 (6) Å in **11a**, cf. 1.769 (6) Å in **7a**). This indicates that there is an increase in the strength of the metal–C bond at the expense of some π-bonding between the C and S atoms. C–S bonds can be as long as 1.916 (1) Å[10] so an appreciable amount of π-bonding still remains in the C–S bond. The bond length found for **11a** is comparable with that in ethylene sulfide (1.819 (2) Å)[11] which also has the S atom in a three-membered ring.

The five-membered heterocyclic ring has an envelope conformation, with C(51) being the atom out-of-plane from the others. The flap angle is 27.7°. The endocyclic O atom is not coordinated to the metal atoms of this or of adjacent molecules (intramolecular distance to Mo(1) = 3.619 (4) Å; intermolecular (Mo atom) contacts > 4.58 Å).

The Mo(2)–C(21)–O(21) angle of the semibridging carbonyl in **11a** (162.7 (7)°) is similar to the corresponding angle in **7a** (161.9 (7)°) but the C(21)···Mo(1) distance is longer (2.764 (8) Å in **11a**, cf. 2.666 (9) Å in **7a**). However it is still of such a length as to allow some bonding between the two atoms.

In conclusion, thioesters and thiolactones react with complexes containing a metal–metal triple bond to give complexes containing a C–S–Mo unit and a semibridging carbonyl group. While the complexes formed from these and the thioketone ligands are of the same type, these are some interesting differences in structural detail. The oxygen atom of the thioketone or thiolactone does not participate in bonding to a metal atom.

Experimental Section

General Data. Melting points were recorded on a Gallenkamp apparatus. 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 were determined on a VG Micromass 7070E spectrometer. Elemental analyses were carried out by Canadian Microanalytical Service, Limited, Vancouver, Canada.

Table III. Fractional Atomic Coordinates of the Non-Hydrogen Atoms

atom	*x*	*y*	*z*
Mo(1)	0.21975 (2)	0.00480 (2)	0.50000 (...)
Mo(2)	0.30119 (2)	−0.02199 (2)	0.22671 (7)
S	0.29658 (7)	−0.08364 (7)	0.43876 (17)
C(11)	0.2674 (3)	0.0904 (3)	0.4934 (7)
O(11)	0.2948 (2)	0.1411 (2)	0.4991 (5)
C(12)	0.2749 (3)	0.0046 (3)	0.6658 (7)
O(12)	0.3056 (3)	0.0050 (3)	0.7658 (5)
C(111)	0.1276 (4)	−0.0269 (4)	0.6338 (8)
C(112)	0.1185 (3)	−0.0598 (3)	0.5041 (9)
C(113)	0.1108 (3)	−0.0112 (3)	0.4043 (8)
C(114)	0.1156 (3)	0.0520 (3)	0.4670 (9)
C(115)	0.1250 (4)	0.0435 (4)	0.6099 (9)
C(21)	0.2290 (3)	0.0441 (3)	0.2257 (8)
O(21)	0.1941 (2)	0.0887 (2)	0.1948 (6)
C(22)	0.2465 (3)	−0.0608 (3)	0.0778 (7)
O(22)	0.2151 (2)	−0.0850 (3)	−0.0086 (5)
C(51)	0.2647 (3)	−0.1246 (3)	0.2848 (6)
O(52)	0.1969 (2)	−0.1427 (2)	0.2850 (4)
C(53)	0.1933 (4)	−0.2124 (4)	0.3216 (9)
C(54)	0.2582 (4)	−0.2438 (3)	0.2877 (10)
C(55)	0.3036 (3)	−0.1871 (3)	0.2452 (8)
C(211)	0.3781 (3)	0.0679 (3)	0.2121 (8)
C(212)	0.4104 (3)	0.0183 (4)	0.2877 (7)
C(213)	0.4190 (3)	−0.0381 (3)	0.2038 (8)
C(214)	0.3910 (3)	−0.0236 (3)	0.0758 (7)
C(215)	0.3656 (3)	0.0423 (3)	0.0796 (6)

Dicyclopentadienyldimolybdenum hexacarbonyl was purchased from Strem Chemicals and used as received. The tungsten analogue and bis(methylcyclopentadienyl)dimolybdenum hexacarbonyl were prepared according to literature procedures.[12] Esters and lactones were commercial products, as was Lawesson's reagent (the dimer of (*p*-methoxyphenyl)thionophosphine sulfide). Procedures developed by Lawesson and co-workers were used for the preparation of *O*-alkyl thioesters[13,14] and thiolactones.[15]

Standard methods were used for the drying and purification of solvents. All reactions were effected under a dry nitrogen atmosphere using vacuum line and Schlenk techniques.

General Procedure for the Reaction of Thioesters and Thiolactones with 1. The metal–metal triple bonded complex was generated by refluxing $(RC_5H_4)_2M_2(CO)_6$ (1–3 mmol) in toluene (20–30 mL) for 18–24 h.[16] Complexes of structure **1** were characterized by infrared and NMR spectroscopy and isolated (if desired) prior to reaction with **8** and **10**. An equimolar amount of **8** or **10**, in toluene (5 mL), was then added to **1** at room temperature, and the reaction mixture was then stirred for 19–26 h. The solvent was removed by rotary evaporation, and the resulting crude product was dissolved in 4:1 hexane–methylene chloride and chromatographed on Florisil. Elution with 4:1 hexane–methylene chloride afforded unreacted **8** or **10** followed by red $(RC_5H_4)_2M_2(CO)_6$. Elution with 1:1 hexane–methylene chloride gave **9** or **11**, usually as brown or green-brown crystals.

X-ray Analysis. Orange-red crystals of **11** (R = R′ = H) were examined, and a needle segment 0.11 × 0.07 × 0.36 mm was selected and mounted on the end of a glass fiber with its longest dimension parallel to the fiber axis. Oscillation, Weissenberg, and precession X-ray photographs were taken by using Cu Kα radiation and revealed tetragonal 4/*mmm* Lane symmetry.

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Table IV. Selected Bond Lengths (Å) and Angles (deg)

Bond Distances

Mo(1)-Mo(2)	3.138 (1)	C(11)-O(11)	1.145 (7)	Mo(2)-C(215)	2.298 (6)
Mo(1)-S	2.402 (2)	C(12)-O(12)	1.140 (8)	Mo(2)-C(21)	1.944 (6)
Mo(1)-C(111)	2.327 (7)	S-C(51)	1.807 (6)	Mo(2)-C(22)	1.960 (6)
Mo(1)-C(112)	2.387 (6)	C(51)-O(52)	1.395 (7)	Mo(2)-C(51)	2.235 (6)
Mo(1)-C(113)	2.375 (7)	O(52)-C(53)	1.431 (8)	C(21)-O(21)	1.165 (7)
Mo(1)-C(114)	2.295 (6)	Mo(2)-S	2.385 (2)	C(22)-O(22)	1.146 (8)
Mo(1)-C(115)	2.294 (7)	Mo(2)-C(211)	2.356 (5)	C(51)-C(55)	1.512 (9)
Mo(1)-C(11)	1.948 (6)	Mo(2)-C(212)	2.387 (6)	C(55)-C(54)	1.501 (9)
Mo(1)-C(12)	1.939 (6)	Mo(2)-C(213)	2.373 (6)	C(54)-C(53)	1.469 (12)
Mo(1)···C(21)	2.764 (8)	Mo(2)-C(214)	2.304 (6)		

Bond Angles

Mo(1)-S-Mo(2)	81.92 (5)	Mo(1)-C(12)-O(12)	177.8 (6)	S-Mo(2)-C(51)	45.9 (2)
Mo(2)-Mo(1)-S	48.82 (4)	Mo(1)-S-C(51)	108.0 (2)	C(21)-Mo(2)-C(22)	81.5 (3)
Mo(2)-Mo(1)-C(11)	82.5 (2)	Mo(1)-C(21)-O(21)	114.8 (5)	C(21)-Mo(2)-Cp(2)	115.4
Mo(2)-Mo(1)-C(12)	113.6 (2)	C(51)-O(52)-C(53)	107.3 (5)	C(21)-Mo(2)-C(51)	112.2 (2)
Mo(2)-Mo(1)-Cp(1)	126.8	O(52)-C(53)-C(54)	108.2 (6)	C(22)-Mo(2)-Cp(2)	116.4
Mo(2)-Mo(1)-C(21)	37.8 (1)	C(53)-C(54)-C(55)	105.7 (6)	C(22)-Mo(2)-C(51)	69.2 (2)
S-Mo(1)-C(11)	108.8 (2)	C(54)-C(55)-C(51)	103.9 (6)	Cp(2)-Mo(2)-C(51)	132.4
S-Mo(1)-C(12)	80.9 (2)	Mo(1)-C(21)-Mo(2)	81.6 (2)	Mo(2)-C(21)-O(21)	162.7 (6)
S-Mo(1)-Cp(1)	128.4	Mo(1)-Mo(2)-S	49.27 (4)	Mo(2)-C(22)-O(22)	178.4 (6)
S-Mo(1)-C(21)	85.9 (1)	Mo(1)-Mo(2)-C(21)	60.6 (2)	Mo(2)-S-C(51)	62.7 (2)
C(11)-Mo(1)-C(12)	75.7 (3)	Mo(1)-Mo(2)-C(22)	113.3 (2)	Mo(2)-C(51)-S	71.4 (2)
C(11)-Mo(1)-Cp(1)	122.1	Mo(1)-Mo(2)-Cp(2)	128.7	Mo(2)-C(51)-O(52)	123.3 (4)
C(11)-Mo(1)-C(21)	72.0 (2)	Mo(1)-Mo(2)-C(51)	77.1 (2)	Mo(2)-C(51)-C(55)	121.3 (4)
C(12)-Mo(1)-Cp(1)	117.8	S-Mo(2)-C(21)	108.8 (2)	S-C(51)-O(52)	117.0 (4)
C(12)-Mo(1)-C(21)	138.8 (2)	S-Mo(2)-C(22)	113.9 (2)	S-C(51)-C(55)	113.5 (5)
Cp(1)-Mo(1)-C(21)	101.0	S-Mo(2)-Cp(2)	115.9	O(52)-C(51)-C(55)	106.4 (5)
Mo(1)-C(11)-O(11)	175.4 (6)				

Systematic extinctions indicated that the space group was $P4_2bc$ or $P4_2/mbc$.

The crystal was then transferred to a Picker FACS-I four-circle automated diffractometer (ambient temperature 20.6 °C) employing graphite-monochromated Mo Kα radiation. A total of 26 reflections with 2θ ranging from 24 to 29°, widely separated in reciprocal space, were accurately centered on the diffractometer counter, and accurate cell dimensions were determined by least-squares analysis of their setting angles ($\lambda(K\alpha_1) = 0.70930$ Å).

The peak profiles of 1798 unique reflections (*hkl*) with $k \leq h$, $4° \leq 2\theta \leq 50°$, 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 each scan. Peak-profile analysis[17] was performed on all reflections to derive the intensity, I, and the associated error, $\sigma(I)$. Two standards measured after every 75 reflections gave no indication of decomposition. A total of 1384 reflections with $I > 2.3\sigma(I)$ were regarded as observed and used in structure solution and refinement. An analytic absorption correction[18] was applied to the data ($T = 0.893$–0.908).

A three-dimensional Patterson synthesis was used to determine the coordinates of the Mo atoms, assuming the noncentrosymmetric space group $P4_2bc$ (justified subsequently by the structure analysis.) A structure factor calculation followed by a Fourier synthesis revealed most of the remaining non-hydrogen atoms. The rest were located after successive least-squares refinement and difference Fourier syntheses. A check on the chirality of the structure showed the original coordinates to be marginally better than the inverse. At this stage the non-hydrogen atoms were assigned anisotropic temperature factors for future refinement. The H atoms were calculated geometrically[19] and assigned isotropic temperature factors of 1.25 times that of the C atoms to which they were attached. The H atoms' scattering factor contributions were included in further least-squares cycles, but their parameters were not refined. The final residuals were $R_F = 0.021$ and $R_{wF} = 0.025$ for 234 variables. A final difference Fourier map showed no outstanding features ($|P_{max}| \leq 0.26\ (6)$ e Å^{-3}).

Refinement throughout was by least-squares analysis, minimizing the function $\sum w(|F_o| - |F_c|)^2$. Initially unit weights and full-matrix refinement was used, but for the final cycles the weighting scheme was $w = 1/[(\sigma(F))^2 + 0.0003F^2]$ with a Gauss–Siedel block diagonal procedure. The average of $w(|F_o| - |F_c|)^2$ did not vary significantly with F_o or $(\sin \theta)/\lambda$. Neutral scattering factors were used with anomalous dispersion corrections being applied to the non-hydrogen atoms.[20] Computation was carried out on a PDP-8e computer using the NRC program package.[21] The atomic labeling scheme is displayed in Figure 1. Thermal motion corrections[22] are reported for selected bond lengths in Table IV. The rigid-body model was based on the thermal parameters of Mo(1), Mo(2), S, C(51), and C(21). Temperature factors for the non-hydrogen atoms, the calculated parameters for the H atoms, additional bond lengths and angles, and least-squares planes comprise supplementary Tables B–E and are deposited.

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Registry No. 1 (R = H, M = Mo), 56200-27-2; 1 (R = CH_3, M = Mo), 69140-73-4; 1 (R = H, M = W), 62853-03-6; 8 (R′ = PhCH=CH, R″ = C_2H_5), 80095-81-4; 8 (R′ = Ph, R″ = CH_3), 5873-86-9; 8 (R′ = *p*-BrC_6H_4, R″ = CH_3), 86633-05-8; 9 (R = H, R′ = Ph, R″ = CH_3, M = Mo), 86645-69-4; 9 (R = H, R′ = Ph, R″ = CH_3, M = W), 86645-70-7; 9 (R = H, R′ = *p*-BrC_6H_4, R″ = CH_3, M = Mo), 86645-71-8; 9 (R = CH_3, R′ = *p*-BrC_6H_4, R″ = CH_3, M = Mo), 86645-72-9; 9 (R = H, R′ = PhCH=CH, R″ = C_2H_5, M = Mo), 86645-73-0; 9 (R = CH_3, R′ = PhCH=CH, R″ = C_2H_5, M = Mo), 86645-65-0; 10 (R′ = H), 39700-44-2; 10 (R′ = CH_3), 86633-04-7; 11 (R = R′ = H), 86645-66-1; 11 (R = CH_3, R′ = H), 86645-67-2; 11 (R = H, R′ = CH_3), 86645-68-3.

Supplementary Material Available: Table of analytical data and tables of temperature factors, hydrogen atom coordinates, additional bond lengths and angles, least-squares planes, and structure-factors for 11 (R = R′ = H) (15 pages). Ordering information is given on any current masthead page.

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