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A Novel Class of Thioketone Complexes. Crystal Structure of Bis(η^5-cyclopentadienyl)(thiocamphor)-tetracarbonyldimolybdenum[1]

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Abstract: Diaryl, aralkyl, and cycloalkyl thioketones react with dicyclopentadienylhexacarbonyldimolybdenum or -ditungsten to give a new class of thione complexes. These complexes, of formula $(R_2CS)M_2(CO)_4(C_5H_4R')_2$ (M = Mo, W), can also be synthesized by a very facile reaction of thioketones with the metal–metal triple-bonded complexes $[(C_5H_4R')M(CO)_2]_2$. The structures of these organosulfur compounds were elucidated on the basis of elemental analyses and infrared and magnetic resonance (^{1}H, ^{13}C) data, as well as an X-ray analysis of the thiocamphor molybdenum complex. The X-ray analysis reveals novel bonding of the thioketone function, as well as the existence of one semibridging [Mo(1)–C(2)–O(2) angle of 161.9°] and three terminal carbonyl groups. The molybdenum–molybdenum bond distance is 3.145 Å. Several of the complexes undergo equilibration in solution.

Introduction

There has been considerable interest, in recent years, in thioketone complexes of transition metals. Two classes of thione complexes have been reported in the literature: (1) sulfur-donor ligand ortho-metalated complexes with a transformed (e.g., **1**)[3,4] or retained (e.g., **2**)[5,6] thiocarbonyl function; (2) n-donor ligand complexes utilizing a lone pair of sulfur in bonding to a metal (e.g., **3**).[7-12]

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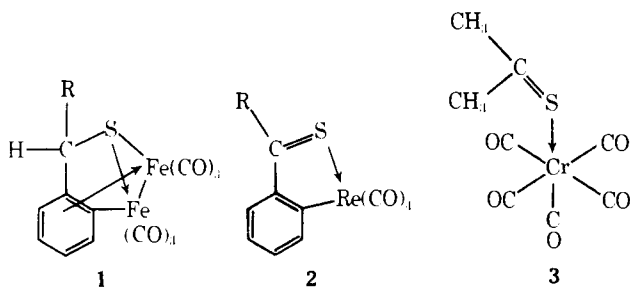
We decided to extend our investigations of thione–metal carbonyl chemistry to the reaction of the organosulfur compounds with the binuclear metal carbonyls, dicyclopentadi-

enylhexacarbonyldimolybdenum and -ditungsten. It was anticipated that ligand substitution would take place, giving complexes capable of undergoing cis–trans isomerism (**4** ⇌ **5**).[13,14] Such complexes were not formed, but rather this study


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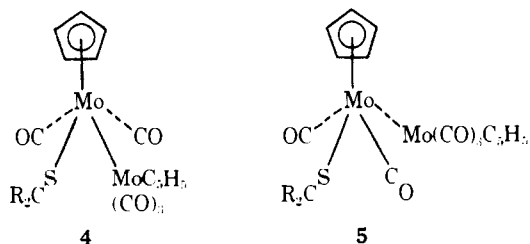
has led to the isolation and characterization by X-ray crystal-structure analysis of a third, and novel, class of thioketone complexes.

Results and Discussion

Synthesis of the Complexes. Treatment of a series of diaryl, aralkyl, and cycloalkyl thioketones (**6**) with the dimer of cyclopentadienylmolybdenum or -tungsten tricarbonyl (**7**, M = Mo, W; R' = H) affords $(R_2CS)M_2(CO)_4(C_5H_4R')_2$ (**8**), with the disubstituted complex **9** being formed in several instances.
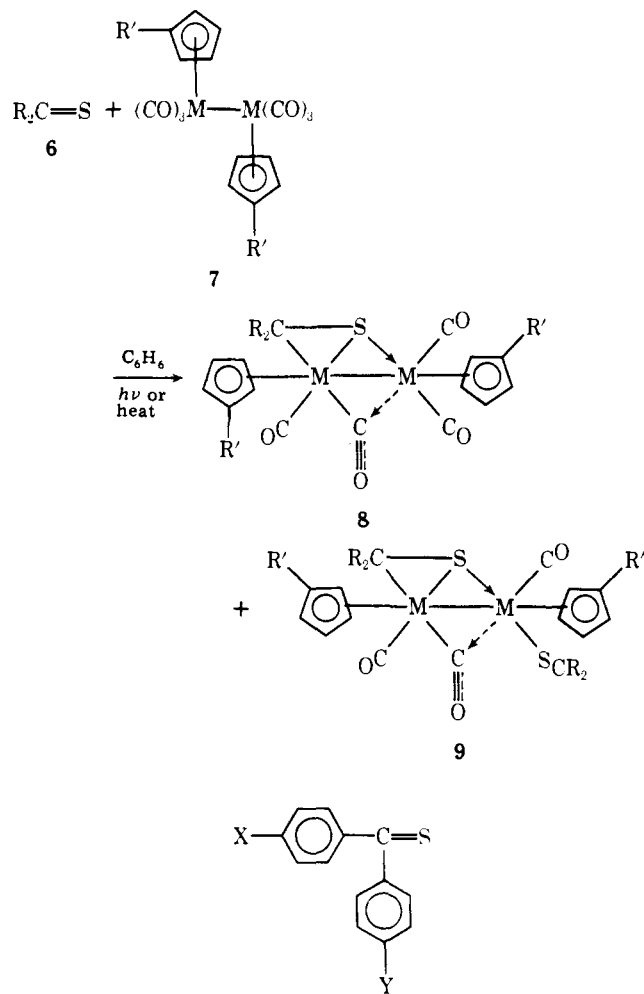
X = Y = OCH₃ (a), CH₃ (b), F (c), H (d), N(CH₃)₂ (e)
X = OCH₃, Y = H (f)
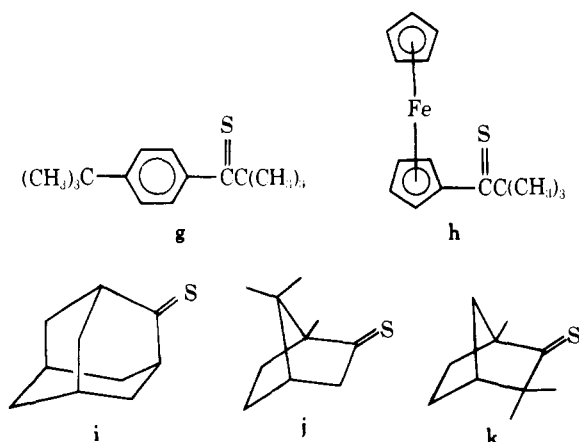
These reactions were effected either photolytically (3000 Å) or thermally, in benzene solution, for a minimum of 35 h. The yields and melting points for **8** and **9** are listed in Table I.

Compounds containing metal–metal multiple bonds undergo some fascinating addition reactions.[15] It was found that the metal–metal triple-bonded complexes, dicyclopentadienyl-tetracarbonyldimolybdenum[16] and -ditungsten (**10**, M = Mo, W; R' = H), reacted with the thioketones at room temperature to give the novel complex **8** in yields which were significantly superior to those obtained by the use of dicyclopentadienyl-hexacarbonyldimolybdenum or -ditungsten (**7**, M = Mo, W; R' = H). In addition, it was possible to realize the synthesis of several of the complexes which could not be obtained by the

Table I. Yields and Melting Points for Complexes Obtained from Reactions of Thioketones (**6**) with **7** and **10**[h]

thioketone 6a–k	7 or 10, M =, R' =	products	color[a]	yield, %	mp (dec), °C
6a	7, Mo, H	8[b]	B-G	64	130
	10, Mo, H	8		78	
	7, W, H	8	Gr	27	172
6b	7, Mo, H	8[c]	G	56	127
	10, Mo, H	8		66	
	10, W, H	8	Gr	84	140
6c	7, Mo, H	9	P	6	
	10, Mo, H	9	P	9	170
		8	G	73	175
6d	7, Mo, H	8	B	12	
		9	P	46	150
	10, Mo, H	8		81	145
	10, W, H	8	B	64	182
6e	7, Mo, H	8	YB		
6f	7, Mo, H	8	B	15	102
	10, Mo, H	8		77	
	10, Mo, CH₃	8	B	53	137
	10, W, H	8	Gr-B	26	149
6g	10, Mo, H	8	B	3	180
6h	10, Mo, H	8	B		
6i	7, Mo, H	8	G	5[d]	122
		9	P	14[e]	150
	10, Mo, H	8		98	
6i	10, Mo, CH₃	8	G	85	178
	10, W, H	8	G	73	232
6j	7, Mo, H[f]	8	B	32	190
		9	P	17[g]	248
	10, Mo, H	8		75	
	7, Mo, CH₃	8	G	75	189
	7, W, H	8	R	29	198
6k	7, Mo, H	8	V	15	143

[a] B = brown, G = green, Gr = gray, P = purple, V = violet, R = red. [b] Mol wt (osmometry, C₆H₆) found, 691 (calcd, 692.5). [c] A small amount of impure **9b** was also formed. [d] Mol wt (C₆H₆) found, 610 (calcd, 600). [e] Mol wt (CHCl₃) found, 746 (calcd, 766). [f] Yields of **8j** and **9j** are for the thermal reaction. Complex **8j** was formed in 74% yield, by irradiation of the thione with **7**, M = Mo; R' = H. [g] Found: Mo, 24.55 (calcd, 24.90). [h] Satisfactory C, H, and S analyses were obtained for all products, and the analytical data was made available to the referees.

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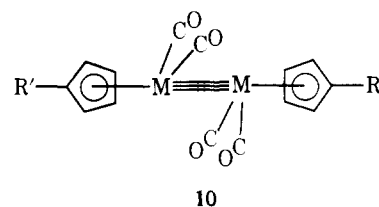
use of **7** (e.g., **8c**). Furthermore, the reaction of **10** with **6** is exceedingly facile, being essentially complete after mixing of the reactants. Sluggish reactions were encountered only when the sterically hindered thioketones, *p-tert*-butylthiopivalophenone and thiopivaloylferrocene, were used as reactants. Several methylcyclopentadienyl complexes, **8**, were also synthesized from the appropriate thioketone and **7** or **10**, R' = CH₃.

Crystal Structure of 8j (M = Mo; R' = H). The final atomic coordinates and temperature parameters are listed in Table A (supplementary material). A stereoscopic view of the complex as determined by the X-ray analysis is presented in Figure 1. The bond lengths and valence angles are given in Figure 2 and Table II. This structure has two particularly noteworthy features, viz., the novel coordination of the thioketone function and the semibridging between Mo(2) and one of the carbonyl groups.
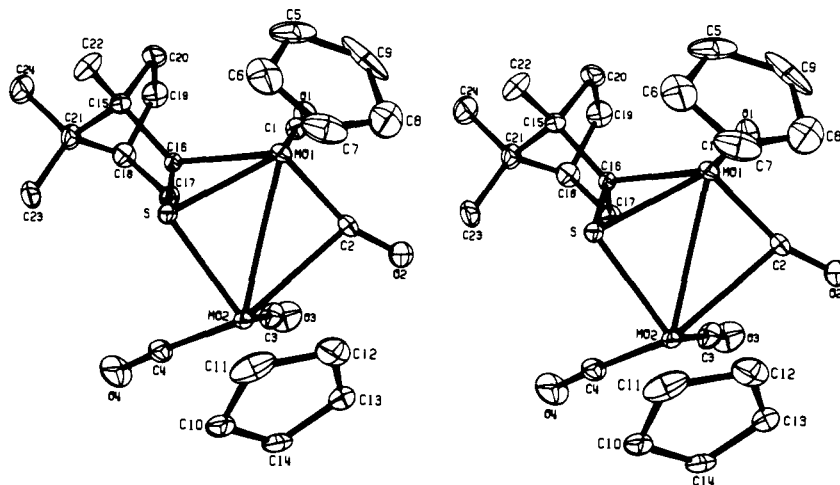
Figure 1. Stereoscopic view of the complex showing 20% probability ellipsoids.
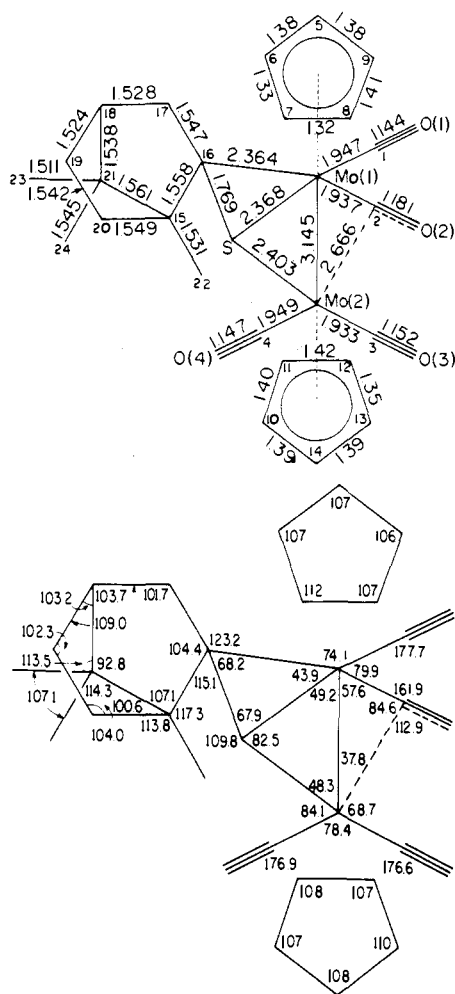

Figure 2. Bond lengths (Å) and valence angles (deg). The root mean squares of the estimated standard deviations of the bond lengths follow: Mo-Mo, 0.001; Mo-S, 0.002; Mo-C, 0.009; S-C, 0.006; C-O, 0.010; C-C, 0.012 in the bicyclic camphane and 0.02 Å in the cyclopentadienes. The corresponding values for the angles are 0.1° if the three atoms are Mo or S, 0.2° if two of the atoms are Mo or S, 0.4° if only one of the atoms is Mo or S, 0.7° for Mo-C-O and C-C-C of the bicyclic camphane, and 1° for C-C-C in the cyclopentadienes.

A variety of types of coordination to metals have been observed for thiocarbonyl ligands,[17] including the formation of a C-S-M three-membered ring, as was found in the case of a CS_2 ligand[18] and a thiocarboxamide group.[19] To our knowledge, the present structure represents the first instance of a

Table II. Bond Lengths (Å) and Bond Angles (deg) Not Listed in Figure 2

Mo(1)···C(5)	2.317(10)	S-Mo(1)-C(2)	106.4(2)
Mo(1)···C(6)	2.373(9)	C(2)-Mo(1)-C(16)	113.9(3)
Mo(1)···C(7)	2.375(8)	Mo(1)-Mo(2)-C(3)	90.2(2)
Mo(1)···C(8)	2.328(9)	Mo(1)-Mo(2)-C(4)	123.0(2)
Mo(1)···C(9)	2.291(13)	S-Mo(2)-C(2)	85.8(2)
Mo(2)···C(10)	2.322(7)	S·Mo(2)-C(3)	110.8(2)
Mo(2)···C(11)	2.364(9)	C(2)-Mo(2)-C(4)	139.3(3)
Mo(2)··C(12)	2.374(10)	C(16)-C(15)-C(20)	105.5(6)
Mo(2)···C(13)	2.315(9)	C(21)-C(15)-C(22)	115.8(7)
Mo(2)···C(14)	2.302(8)	Mo(1)-C(16)-C(15)	122.7(4)
Mo(2)-Mo(1)-C(1)	108.9(2)	S-C(16)-C(17)	120.3(4)
Mo(2)-Mo(1)-C(16)	75.6(1)	C(15)-C(21)-C(23)	115.2(7)
S-Mo(1)-C(1)	115.4(2)	C(18)-C(21)-C(24)	113.8(8)

thioketone being chelated in this fashion, i.e., both S and C(16) are bonded to Mo(1), with the sulfur atom also donor bound to Mo(2). The C-S bond in this ring (1.769 Å) is much longer than the corresponding bond length (1.599 Å) in a cyclobutanedithione,[20] and it is also longer by ~0.1 Å than the C-S bonds in the ligands mentioned above.[18,19] On the other hand, this bond is only 0.05 Å shorter than the single-bond value of 1.819 Å observed in ethylene sulfide.[21] The rehybridization of C(16) is also indicated by the fact that S and Mo(1) are displaced by >1 Å on opposite sides of the plane defined by C(15), C(16), C(17). The C-S bond, therefore, appears to be predominantly σ with some π character. Conversely, the Mo(1)-S bond of 2.368 Å is substantially shorter than the sum (2.65 Å) of the covalent radii, thus indicating considerable contribution of π bonding. The remaining Mo(1)-C(16) bond is about equal in length to the Mo-C distances in the cyclopentadienes or between Mo and the central carbon in an allylic ligand.[22] This three-membered ring is therefore best described as a metallothiocyclopropane with some π character in each bond.

Instead of the expected five carbonyl groups, the X-ray analysis has revealed only four, with three terminal and having approximately similar geometry, and the fourth in a semibridging position. The latter carbonyl has a significantly longer C(2)-O(2) bond of 1.181 Å compared to a mean length of 1.148 Å in the others, and a much smaller Mo(1)-C(2)-O(2) angle of 161.9° than the average of 177.1° in the others. Also, the C(2) atom of this carbonyl group makes a short contact of 2.666 Å with Mo(2), indicating some degree of semibridging between them which is accompanied by a weakening of the C(2)-O(2) bond. The relationship between the bridge asymmetry and the Mo-C-O angle (161.9°) is in good agreement

with the correlation established by Klingler et al.[16] Also, the spectral properties, discussed later, are in accord with the presence of such a carbonyl group.

The Mo(1)-Mo(2) distance of 3.145 Å is significantly shorter than the value of 3.235 Å found in 7, R′ = H; M = Mo.[23] This distance is influenced not only by the effect of the semibridging carbonyl group but also by the coordination number and the type of bridging ligands.[15,16]

The central ring formed by S, Mo(1), Mo(2) makes dihedral angles of 171.7 and 115.0° with the planes of the rings formed by Mo(1), Mo(2), C(2) and S, Mo(1), C(16), respectively. Each of the cyclopentadiene rings is planar, χ^2 = 1.0 and 2.0, and their nearest Mo atoms are at normal distance of 2.012 and 2.026 Å from them. The bond lengths and angles in the bicyclic camphane system are normal within experimental errors, and there are no significant distortions in the torsion angles.[24]

Spectral Properties. The infrared spectra of these complexes displayed bands at 1946-1969 (w), 1910-1942 (vs), and 1847-1870 (s) cm^{-1} due to stretching vibrations of the terminal metal carbonyl groups (Table III). The semibridging carbonyl group gave an absorption at 1788-1826 (w) cm^{-1} which is in the same region as that reported for other complexes possessing this type of carbonyl group.[25,26] Electronic effects of substituent groups influence the position of the carbonyl stretching bands, as witnessed by the occurrence of these absorptions at considerably higher frequency for the 4,4′-difluorothiobenzophenone complex, **8c**, as compared to the 4,4′-bis(dimethylamino)thiobenzophenone complex, **8e**.

With the exception of the complex derived from 4-methoxythiobenzophenone (**8f**), all of the aromatic cyclopentadienyl thioketone complexes gave singlet signals at δ 4.63-4.75 and 5.23-5.38, which are assigned one to each of the two cyclopentadienyl rings. For a complex of a nonaromatic thione such as thiofenchone (**8k**), the cyclopentadienyl resonances are closer together (δ 5.31, 5.43).

The fully decoupled carbon-13 magnetic resonance spectrum of **8a**, the 4,4′-dimethoxythiobenzophenone complex, exhibited peaks at δ 93.60 and 95.83 for the two different sets of carbons of the cyclopentadienyl rings, δ 233.41, 234.65, and 236.93 for the terminal metal carbonyl carbons, δ 244.45 for the semibridging carbonyl group, and δ 106.93 due to the sulfur-bearing carbon. Note, in addition, that the carbons of the two methoxy groups are slightly different (δ 55.17, 55.33), indicative of the existence of the aromatic rings in different environments.

The NMR spectra for the complexes of 4-methoxythiobenzophenone (**8f**), adamantanethione (**8i**), and thiocamphor (**8j**) were especially intriguing. The room temperature proton magnetic resonance spectra of **8f, 8i,** and **8j** (R′ = H; M = Mo, W) showed four singlets (owing to overlap, three were observed in several cases) for the cyclopentadienyl ring protons at similar chemical shifts to the two signals for the same kind of protons in other complexes. Similarly, the methylcyclopentadienyl complexes (**8f,i,j**, M = Mo; R′ = CH$_3$) also exhibit four singlets (or three overlapping singlets) for the methyl groups of the two species. The fully decoupled carbon magnetic resonance spectrum of **8j**, M = Mo; R′ = H, gave four signals for the cyclopentadienyl ring carbons and more than four carbonyl carbon absorptions. There are two signals assigned to the sulfur-bearing carbons of the two thiocamphor complexes (δ 104.84, 114.94), but only one semibridging carbonyl carbon resonance (δ 245.3). These results clearly indicate the presence, in solution, of two similar but distinct species. We believe that in these cases equilibration of **8f,i,j** occurs with an isomer lacking a semibridging carbonyl group (**11**).

The kinetics of equilibration of **8f** $\rightleftharpoons$ **11f** and **8j** $\rightleftharpoons$ **11j** in CDCl$_3$ were followed at four temperatures using proton magnetic resonance spectroscopy (signals for the η^5-C$_5$H$_5$ protons). At the lowest temperature only **8** was initially present

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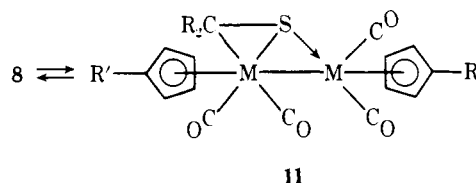
(i.e., only two singlets for the cyclopentadienyl rings of **8f** or **8j** were observed when the spectrum was recorded immediately after addition of the complex to CDCl$_3$ at −30 °C). The rates for the forward and reverse processes and the equilibrium constants (**11/8**) are given in Table B. The rate of equilibration for the aromatic thioketone complex **8f** is greater than that for the complex derived from thiocamphor (**8j**). This is reflected in the smaller activation energy (E_a) for **8f** (21.13 ± 4.49 kcal/mol) when compared with **8j** (24.61 ± 4.72 kcal/mol). The thermodynamic parameters ΔH (2.4 ± 0.28 kcal/mol for **8f**, 2.7 ± 0.16 kcal/mol for **8j**), ΔG (−0.20 ± 0.32 kcal/mol for **8f**, +0.20 ± 0.20 kcal/mol for **8j**), and ΔS (8.9 ± 0.96 cal/mol·K for **8f**, 8.6 ± 0.76 cal/mol·K for **8j**) were similar for **8f** and **8j**.

An alternative explanation for the solution behavior of **8f** and **8j** is the possible existence of these complexes in diastereomeric forms. It is not apparent, however, how the diastereomeric concept would apply in the case of the complex of the symmetrical thione, adamantanethione (**8j**).

Work is in progress on the chemistry of these novel complexes. We expect that these complexes will be useful precursors to important organic compounds of biological interest.

Experimental Section

General Data. Infrared spectra were obtained using a Unicam SP1100 spectrometer, equipped with a calibration standard. ^{1}H NMR spectra were recorded on a Varian T60 or HA100 spectrometer, using tetramethylsilane as internal standard. Carbon magnetic resonance spectra were recorded in the fully and partially decoupled modes using a Varian FT-80 spectrometer. Mass spectral analyses were determined on an AEI MS902 spectrometer. A Fisher-Johns apparatus was used for melting point determinations. Elemental analyses were performed by the Butterworth Microanalytical Consultancy, Ltd., Teddington, Great Britain, M-H-W Laboratories, Phoenix, Ariz., and Drs. F. and E. Pascher, Bonn, West Germany.

Dicyclopentadienylhexacarbonyldimolybdenum was purchased from Pressure Chemical Co. or synthesized according to the procedure described by Wilkinson.[27] Literature procedures were also employed for the preparation of the tungsten analogue as well as for di-(methylcyclopentadienyl)hexacarbonyldimolybdenum.[27] The metal-metal triple-bonded complexes (**10**) were obtained by thermolysis of the single-bonded analogues (**7**) in *m*- or *p*-xylene, benzene, *n*-octane, or toluene.[28] They were either isolated prior to reaction with the thioketone or used in situ, with the same results.

4,4′-Dimethoxythiobenzophenone and 4,4′-bis(dimethylamino)thiobenzophenone were commercial products. 4,4′-Dimethylthiobenzophenone,[29] thiobenzophenone,[29] 4,4′-difluorothiobenzophenone,[30] 4-methoxythiobenzophenone,[31] thiopivaloylferrocene,[6] adamantanethione,[32] thiocamphor,[33] and thiofenchone[33] were all synthesized from the corresponding ketones by procedures described in the literature. The method of Scheeren and co-workers[29] was used to prepare *p-tert*-butylthiopivalophenone.

Solvents were purified and dried by standard methods. All reactions were effected under a dry nitrogen atmosphere. Irradiation experiments were carried out with a Rayonet photoreactor, using 3000-Å lamps. The following procedures are typical.

Reaction of 4,4′-Dimethoxythiobenzophenone (6a) with (a) 7, R′ = H; M = Mo. A mixture of the thioketone (0.258 g, 1.0 mmol) and **7**, R′ = H; M = Mo (0.24 g, 0.50 mmol) in degassed benzene (70 mL) was photolyzed for 39 h. The color of the solution changed from purple-blue to brown. The solution was concentrated to a small volume and then chromatographed on Fisher alumina. Elution with 5:1 hexane/benzene gave 0.11 g of recovered thioketone. Elution with benzene gave a brown, viscous solid. Crystallization of the latter from 4:1 hexane/ether, at −78 °C, afforded 0.22 g (64% yield) of complex **8a**, R′ = H; M = Mo.

Table III. Pertinent Spectral Data for **8**

8a-k, M =, R' =	IR, $\nu_{C\equiv O}$, cm^{-1} (solvent)^a	^{1}H NMR, δ ppm	^{13}C NMR, δ ppm
8a, Mo, H	1963 w, 1938 vs, 1862 s, 1810 w (CHCl$_3$)	3.77 (s, 6 H, OCH$_3$), 4.68 (s, 5 H, C$_5$H$_5$), 5.30 (s, 5 H, C$_5$H$_5$), 6.67 (d, J = 9 Hz, protons on carbons ortho to the methoxy-bearing carbons), 7.19 (d, 4 H, other aromatic protons)	55.17, 55.33 (methoxy carbons), 93.60 (C$_5$H$_5$ ring), 95.83 (C$_5$H$_5$ ring), 106.93 (sulfur-bearing carbon), 112.66, 126.14, 135.62, 136.44, 147.08, 157.25, 158.85 (benzenoid carbons), 233.41, 234.65, 236.93 (terminal carbonyl carbons), 244.45 (semibridging carbonyl carbon)
8a, W, H	1946 w, 1924 vs, 1847 s, 1804 w (CCl$_4$)	3.75 (s, 6 H, OCH$_3$), 4.75 (s, 5 H, C$_5$H$_5$), 5.38 (s, 5 H, C$_5$H$_5$), 6.69 (d, 4 H, J = 9 Hz, protons on carbons ortho to the methoxy-bearing carbons), 7.21 (d, 4 H, other aromatic protons)	
8b, Mo, H	1960 w, 1934 vs, 1858 s, 1808 w (CHCl$_3$)	2.27 (s, 3 H, CH$_3$), 2.30 (s, 3 H, CH$_3$), 4.63 (s, 5 H, C$_5$H$_5$), 5.23 (s, 5 H, C$_5$H$_5$), 6.76-7.28 (m, 8 H, aromatic protons)	
8b, W, H	1955 wm, 1929 vs, 1853 s, 1813 w (CCl$_4$)	2.28 (s, 3 H, CH$_3$), 2.31 (s, 3 H, CH$_3$), 4.74 (s, 5 H, C$_5$H$_5$), 5.38 (s, 5 H, C$_5$H$_5$), 6.70-7.40 (m, 8 H, aromatic protons)	
8c, Mo, H	1962 w, 1941 vs, 1872 s, 1826 w (CCl$_4$)	4.66 (s, 5 H, C$_5$H$_5$), 5.26 (s, 5 H, C$_5$H$_5$), 6.68-7.48 (m, 8 H, aromatic protons)	
8d, Mo, H	1959 w, 1938 vs, 1864 s, 1816 w (CHCl$_3$)	4.58 (s, 5 H, C$_5$H$_5$), 5.25 (s, 5 H, C$_5$H$_5$), 6.94-7.41 (m, 10 H, aromatic protons)	
8d, W, H	1954 w, 1926 vs, 1851 s, 1811 w (CCl$_4$)	4.72 (s, 5 H, C$_5$H$_5$), 5.38 (s, 5 H, C$_5$H$_5$), 7.13 (s (br), 10 H, aromatic protons)	
8e, Mo, H	1950 m, 1927 vs, 1849 s, 1805 w (CHCl$_3$)		
8f, Mo, H	1960 w, 1933 vs, 1858 s, 1808 w (CHCl$_3$)	3.73 (s, 3 H, OCH$_3$), 4.61, 4.67, 5.23, 5.27 (singlets, 10 H, C$_5$H$_5$ rings), 6.58-7.42 (m, 9 H, aromatic)	
8f, Mo, CH$_3$	1952 w, 1934 vs, 1859 s, 1808 w (CHCl$_3$)	1.68, 1.76, 1.97 (singlets, 6 H, CH$_3$, 1.76 twice the height of the other two), 3.74 (s, 3 H, OCH$_3$), 4.00-4.43, 4.83-5.53 (m (br), 8 H, C$_5$H$_4$ rings), 6.65 (d, 2 H, J = 8 Hz, protons on carbons ortho to the methoxy-bearing carbon), 6.78-7.57 (m, 7 H, other aromatic protons)	
8f, W, H	1952 w, 1926 vs, 1849 s, 1809 w (CCl$_4$)	3.78 (s, 3 H, OCH$_3$), 4.73, 4.77, 5.36, 5.41 (singlets, 10 H, C$_5$H$_5$ rings), 6.72 (d, 2 H, J = 9 Hz, protons on carbons ortho to the methoxy-bearing carbon), 6.93-7.40 (m, 7 H, other aromatic protons)	
8g, Mo, H	1965 mw, 1942 vs, 1870 s, 1808 w (CCl$_4$)	1.34 (s, 18 H, *tert*-butyl groups), 4.99 (s, 5 H, C$_5$H$_5$), 5.80 (s, 5 H, C$_5$H$_5$), 7.25 (d, 2 H, J = 3 Hz, protons on carbons ortho to the *tert*-butyl-bearing carbon), 7.72 (d, 2 H, other aromatic protons)	
8h, Mo, H	1957 w, 1934 vs, 1864 s, 1815 w (CCl$_4$)		
8i, Mo, H	1958 m, 1910 vs, 1859 s, 1799 w (CHCl$_3$)	1.5-2.61 (m, 14 H, adamantane protons), 5.25, 5.32, 5.35 (singlets, 10 H, C$_5$H$_5$ rings)	93.23, 93.58, 94.10, 94.82 (C$_5$H$_5$ rings)
8i, Mo, CH$_3$	1969 s, 1925 vs, 1878 m, 1819 w (C$_6$H$_{14}$)	1.3-2.8 (m, 14 H, adamantane protons), 2.04, 2.10, 2.13, 2.21 (singlets, 6 H, CH$_3$), 4.86-5.63 (m, 8 H, C$_5$H$_4$ rings)	
8i, W, H	1960 w, 1916 vs, 1859 s, 1808 w (CCl$_4$)	1.5-2.9 (m, 14 H, adamantane protons), 5.39, 5.43, 5.47, 5.50 (singlets, 10 H, C$_5$H$_5$ rings)	91.73, 92.43, 93.90 (C$_5$H$_5$ rings)
8j, Mo, H	1958 s, 1920 vs, 1860 s, 1795 wm (CHCl$_3$)	0.70, 0.92, 0.97, 1.03 (singlets, 9 H, methyl of both isomers), 0.68-1.95 (m, 7 H, other protons of thiocamphor ligand), 5.23, 5.27,	14.21, 19.05, 19.56, 20.57, 26.65, 37.94, 38.69, 41.10, 44.01, 44.78, 45.56 (thiocamphor carbons, except sulfur-bearing carbon), 92.43, 93.08,

Table III (*Continued*)

8a–k, M = R′ =	IR, $\nu_{C\equiv O}$, cm⁻¹ (solvent)[a]	¹H NMR, δ ppm	¹³C NMR, δ ppm
		5.41, 5.43 (singlets, 10 H, C₅H₅ rings)	93.41, 94.08 (carbons of C₅H₅ rings), 104.84, 114.94 (sulfur-bearing carbons), 234.7, 235.9, 236.4, 237.5, 238.9, 239.5 (terminal carbonyl carbons), 245.3 (semibridging carbonyl carbon)
8j, Mo, CH₃	1954 s, 1916 vs, 1859 m, 1801 w (CHCl₃)	0.71, 0.91, 0.97, 1.01 (singlets, 9 H, methyls of both isomers), 0.69–1.89 (m, 7 H, other protons of thiocamphor ligand), 2.08, 2.21, 2.25 (singlets, 6 H, methyl of cyclopentadienyl rings, 2.08 is twice the height of the others), 4.96–5.53 (m, 8 H, C₅H₄ rings)	
8j, W, H	1950 ms, 1917 vs, 1849 s, 1788 w (CHCl₃) 1942 ms, 1910 vs, 1839 vs, 1786 m (KBr)	0.68–1.72 (m, 16 H, thiocamphor protons), 5.34, 5.40, 5.55, 5.57 (singlets, 10 H, C₅H₅ rings)	
8k, Mo, H	1950 m, 1918 vs, 1852 s, 1810 w (CHCl₃)	0.73–2.20 (m, 16 H, thiofenchone protons), 5.31 (s, 5 H, C₅H₅), 5.43 (s, 5 H, C₅H₅)	

[a] vs = very strong, s = strong, ms = medium-strong, m = medium, mw = medium-weak, w = weak. [b] CDCl₃ solution with (CH₃)₄Si as internal standard.

(b) 7, R′ = H; M = W. The thioketone (0.40 g, 1.5 mmol) and **7**, R′ = H; M = W (1.00 g, 1.5 mmol) were refluxed in benzene (70 mL) for 29 h. Evaporation of the solution (at ca. 30 Torr) gave a solid which was dissolved in benzene (10 mL) and chromatographed on Baker silica gel. Elution with 1:1 benzene/hexane afforded 0.214 g of unreacted **7**, R′ = H; M = W. Further elution with benzene/hexane or with benzene gave crude **8a**, R′ = H; M = W. Purification of the latter was achieved by dissolution in a minimum amount of ether, addition of an equal volume of hexane, and slow evaporation of the solution, yield 0.297 g (27%).

(c) 10, R′ = H; M = Mo. To the molybdenum–molybdenum triple-bonded complex **10**, R′ = H; M = Mo, generated by refluxing 1.50 g (2.0 mmol) of **7**, R′ = H; M = Mo, in *m*-xylene (50 mL) and then cooling to room temperature (isolating **10** if desired), was added the thioketone (0.60 g, 2.3 mmol). Thin layer chromatography after 6 min showed no thioketone. The mixture was stirred at room temperature for 1 h and then worked up as described for **7**, R′ = H; M = Mo, to give 1.24 g (78%) of **8a**, R′ = H; M = Mo.

Reaction of Adamantanethione (6i) with (a) 7, R′ = H; M = Mo. A mixture of adamantanethione (0.332 g, 2.00 mmol) and [C₅H₅Mo(CO)₃]₂ (0.980 g, 2.00 mmol) in benzene (40 mL) was refluxed for 36 h. The solution was cooled, evaporated (at ca. 30 Torr), and then chromatographed on Baker silica gel. Elution with 1:1 hexane/benzene gave unreacted **7**, R′ = H; M = Mo, followed by a purple solid. The latter was then subjected to preparative thin layer chromatography (EM silica gel) using 4:1 hexane/ether as the developer. In this way, complex **9i**, R′ = H; M = Mo, was isolated in 14% yield (0.102 g): mp 150°C dec; IR (CHCl₃) ν_{CO} 1930 (s), 1760 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 1.25–2.25 (m, 14 H, adamantanoid protons), 5.22 (s, 5 H, C₅H₅), 5.32 (s, 5 H, C₅H₅).

Continuation of the column chromatography gave 0.0566 g (5.0%) of complex **8i**.

(b) 10, R′ = H; M = Mo. To 1.3 mmol of [C₅H₅Mo(CO)₂]₂ in *m*-xylene (40 mL) was added 0.44 g (2.6 mmol) of adamantanethione. The solution was stirred for 10 min, rotary evaporated to a small volume, and then chromatographed on silica gel as described in part (a). Yield of **8i**, R′ = H; M = Mo, was 0.763 g (98%).

X-ray Analysis. The complex C₂₄H₂₆O₄Mo₂S, M_r = 602.4, forms brown, prismatic crystals which are monoclinic, space group $P2_1$, with a = 15.607 (2) Å, b = 10.280 (2) Å, c = 7.993 (2) Å, β = 109.86 (3)°, V = 1206.1 Å³, Z = 2, D_c = 1.66 g cm⁻³, D_m = 1.69 g cm⁻³ (by flotation in bromobenzene/iodobenzene), $F(000)$ = 604, μ(Cu Kα) = 97.10, μ(Mo Kα) = 11.24 cm⁻¹.

The X-ray measurements were carried out on a four-circle Picker diffractometer using a crystal fragment, 0.10 × 0.26 × 0.44 mm, mounted along *b**. The unit cell parameters were derived from the angular settings of six high-order axial reflections measured with Cu radiation [λ(Kα₁) = 1.540 50, λ(Kα₂) = 1.544 34 Å]. The intensity data were measured with Nb-filtered Mo radiation using the θ–2θ scan procedure at a 2θ speed of 2° min⁻¹. The 2θ scan ranges were 1.9° for 2θ < 10°, 2.0° for 2θ = 10–50°, and 2.4° for 2θ = 50–55°, and the background was measured for 10 s at the start and end of each scan. The (003) and (400) reflections were monitored at regular intervals for scaling, and showed a variation of less than 3%. Reflections with net counts <100 or <5% of their background counts were categorized as unobserved. Thus, of the 2932 independent reflections with 2θ ≤ 55°, 2690 (92%) were observed. The net intensities were corrected for Lorentz and polarization effects and for absorption.

The structure was determined by the heavy-atom method and the atomic parameters were refined by block-diagonal least squares. All hydrogen atoms, except one from each of the three methyl groups, were located on difference Fourier maps and their parameters were refined isotropically. The C–H bonds are in the range of 0.69–1.16 Å, with an average value of 0.94 (13) Å. All these bond lengths are within two standard deviations of the values normally obtained from X-ray analyses. Equally, only one bond angle deviates by more than two standard deviations from the expected geometry. Scattering factors were taken from the "International Tables for X-ray Crystallography"[34] and the molybdenum and sulfur curves were corrected for anomalous dispersion. Throughout the refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized and the following weighting scheme was used during the final stages: $w = w_1 w_2$, where w_1 = 1 for $|F_o|$ ≤ 35, w_1 = 35/$|F_o|$ for $|F_o|$ > 35, w_2 = sin² θ/0.07 for sin² θ < 0.07, w_2 = 1 for sin² θ ≥ 0.07. Two very strong reflections, (020) and (110), and all unobserved reflections were assigned zero weights. After the final cycle the average parameter shift equaled 0.1σ and the largest one 1.2σ. The agreement index R ($\Sigma|\Delta F|/\Sigma|F_o|$) is 0.034 and the weighted index R' ($\Sigma w \Delta F^2/\Sigma w F_o^2$) is 0.032 for the 2690 observed reflections. The absolute configuration assumed in the refinement and shown in the figures is that derived from *d*-camphor. The final difference Fourier map showed no distinctive features. A list of observed and calculated structure amplitudes is available (Table C—see paragraph at end of paper regarding supplementary material).

Supplementary Material Available: Final atomic coordinates and

temperature parameters (Table A), rates for the forward and reverse processes and equilibrium constants (Table B), and a list of observed and calculated structure amplitudes (Table C) (15 pages). Ordering information is given on any current masthead page.

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Dimolybdenum Tetraacetate and the Octachlorodimolybdate(II) Anion as Reagents for Preparing Mononuclear Molybdenum(II) Complexes. Geometry of the Hepta(methylisocyano)molybdenum(II) Cation

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Abstract: The reactions of $Mo_2(O_2CCH_3)_4$ and $K_4Mo_2Cl_8$ with alkyl isocyanides causes scission of the Mo—Mo quadruple bond to give $[Mo(CNR)_7]^{2+}$ ions, where R = CH_3, $(CH_3)_3C$, or C_6H_{11}, which can be isolated by using large anions such as BF_4^- and PF_6^-. For the case where R = CH_3, we have structurally characterized the product $[Mo(CNCH_3)_7](BF_4)_2$. The structure of this compound has been determined by X-ray crystallography. It crystallizes in space group *Pbcn* with unit cell dimensions of $a = 11.660$ (4) Å, $b = 18.733$ (4) Å, $c = 22.610$ (5) Å, and $Z = 8$. The $[Mo(CNCH_3)_7]^{2+}$ cation possesses no crystallographic symmetry. It comes closest to having a capped octahedral (CO) arrangement, although there are two orientations that can be viewed as distorted forms of the capped trigonal prismatic structure, and one that is a distorted form of 4:3 coordination. This is the first example of a homoleptic ML_7 species with a CO structure.

Introduction

The reactions of multiply bonded dimetal species, such as $Mo_2(O_2CCH_3)_4$, may all be classified as either (A) those in which the M-M multiple bond is retained, possibly with some change in bond order, or (B) those in which the metal atoms become separated. We include under B cases where a binuclear structure is retained but only by virtue of bridging ligands, with the M-M bond order being reduced, effectively to zero, as when $Re_2Cl_8^{2-}$ reacts[2] with ligands such as $SC(NH_2)_2$ and $Ph_2PCH_2CH_2PPh_2$.

Reactions of type B are not only interesting because of their bearing on the nature of the M-M multiple bonds but for the practical reason that they can afford efficient synthetic methods to prepare more conventional complexes. In some cases, entirely new kinds of complexes have been so obtained, such as the 14-electron metal nitrosyls $Mo_2(OR)_6(NO)_2$, which are prepared[3] by the action of NO on $Mo_2(OR)_6$, and the 17-electron species *trans*-$Re(CO)_2Cl_2(PR_3)_2$ which are formed[4] upon reacting CO with $Re_2Cl_4(PR_3)_4$. In other cases, multiply bonded M_2 species which are themselves easy to prepare and handle provide excellent starting materials for new synthetic routes to previously known compounds.

We report here an exemplary case of a class B reaction leading to a compound that is of considerable interest in its own right. In 1973, Novotny and Lippard[5] reported the preparation of $[Mo(CNR)_7]^{2+}$ ions by the reaction of $Mo(CO)_6$ with the isocyanide and iodine, or by alkylation of $[Mo(CN)_8]^{4-}$, and later Lewis and Lippard carried out an X-ray crystallographic