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MOLYBDENUM ALKYL- AND ARYL-THIOLATES

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Summary

The reaction between $[(\eta^5\text{-}C_5H_5)MoH(CO)_3]$ and disulphides gives dimeric or trimeric complexes depending upon the conditions. The syntheses of the novel trinuclear molybdenum carbonyl complex $[\{Mo(\eta^5\text{-}C_5H_5)(SR)(\mu\text{-}CO)(CO)\}_3]$ (R = Me), and dinuclear compounds $[Mo_2(\eta^5\text{-}C_5H_5)(\mu\text{-}SR)_3(CO)_4]$ (R = Me) and $[Mo_2(\eta^5\text{-}C_5H_5)_2(SR)_2(CO)_2(\mu\text{-}SR)(\mu\text{-}Br)]$ (R = Me or Ph) are reported.

Alkylthio- and arylthio-metallates have been previously formed by reactions involving disulphides, the products containing terminal or bridging SR groups [1,2]. We show in this paper that the products of such reactions depend markedly upon the reaction conditions. The reaction between $[(\eta^5\text{-}C_5H_5)MoH(CO)_3]$ and dimethyldisulphide [2] is known to give $[(\eta^5\text{-}C_5H_5)Mo(CO)_2SMe]_2$ (I) as the major product. In tetrahydrofuran at 40°C, in addition to the dimer $[(\eta^5\text{-}C_5H_5)Mo(CO)_2SMe]_2$ (I) a trimeric derivative is formed, which we formulate as (II) on the basis of its spectroscopic data (Table 1) and by analogy with previous trimeric derivatives of molybdenum [3] together with $[(\eta^5\text{-}C_5H_5)Mo(CO)SMe]_2$ (III), which probably has multiple Mo-Mo bonding with bridging SMe or carbonyl groups. The same reaction in the presence of tungsten hexacarbonyl gives similar products but II is obtained in higher yield.

In the presence of $Mo(CO)_6$ there is formation of a complex $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(SMe)_3]$ (IV), which we formulate with three bridging MeS groups analogous to the structure formed from $[Mo_2(CO)_2L(\mu\text{-}S\text{—}t\text{-}Bu)_3(\eta^7\text{-}C_7H_7)]$ where L = $P(OMe)_3$ [4] or CO [5].

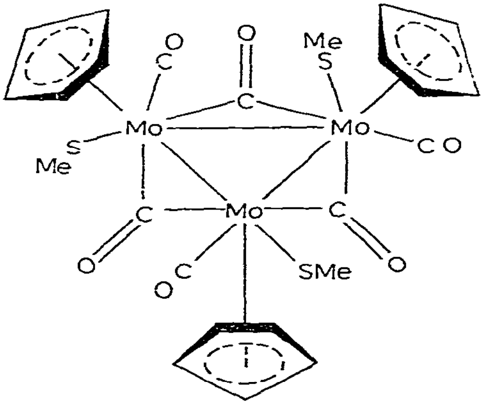
The reaction between $[(\eta^5\text{-}C_5H_5)MoH(CO)_3]$ and R-S-S-R (R = Me, Ph) in the presence of allyl bromide at medium temperature gives compounds V, for-

TABLE 1

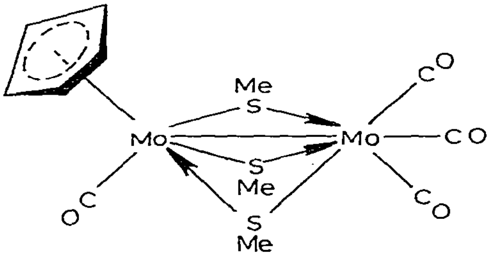
SPECTRAL DATA

Compound	IR frequencies (cm^{-1})[a]		^1H NMR δ (ppm/TMS)[b]
	ν(C≡O)	ν(CO) (bridging carbonyl)	
II	2005s	1790s[c]	6.00(s, 10 H; C_5H_5)[d]
	1975m(sh)		5.85(s, 5 H; C_5H_5)
	1900s	1775s	2.65(s, 3 H; Me)
			2.52(s, 3 H; Me)
			1.75(s, 3 H; Me)
III	1875(sh), 1850s		5.32(s, 10 H; C_5H_5)
			2.28(s, 3 H; Me)
IV[e]	2005s		5.38(s, 5 H; C_5H_5)
	1980s		2.63(s, 3 H; Me)
	1952m		2.60(s, 3 H; Me)
	1855ms		1.30(s, 3 H; Me)
Va	2010s		5.90(s, 10 H; C_5H_5)
	1970w(sh)		2.68(s, 6 H; Me)
			1.80(s, 3 H; Me)
Vb	2020s[c]		7.38(m, 15 H; C_6H_5)[f]
	1990mw		6.28(s, 10 H; C_5H_5)

[a] CH_2Cl_2 solution unless indicated otherwise; [b] $CDCl_3$ solution unless indicated otherwise; [c] Nujol; [d] $(CD_3)_2CO$; [e] ^{13}C NMR: 8.17, 26.30 and 26.56(Me); 91.25(C_5H_5); 219.88, 225.41, 226.18, 229.55 ppm (CO); [f] CD_3NO_2.

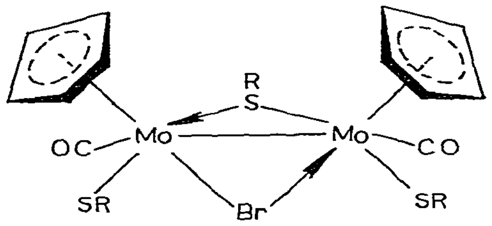


(II)



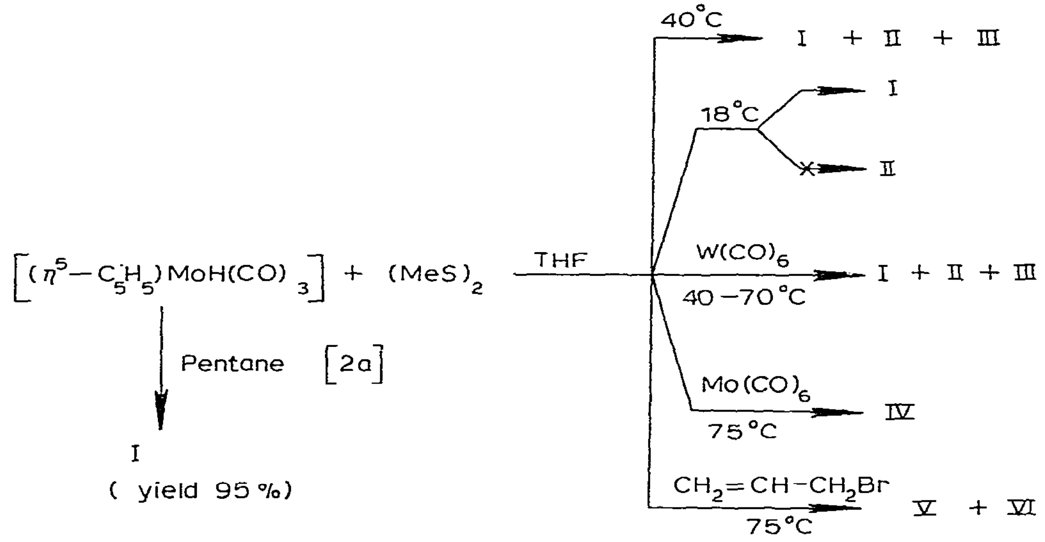
(IV)

mulated from spectroscopic studies and by analogy with the recently characterised dirhodium complex containing a bridging S—t-Bu and a bridging bromide [6]. The other major product from these reactions is $[(\eta^5\text{-}C_5H_5)MoBr(CO)_3]$ (VI), showing that allyl bromide is acting as a brominating reagent in these reactions.



(VI)

In none of the reactions described above is the fate of the hydrido group known.



Experimental

All preparations were carried out under nitrogen using Schlenk tubes or vacuum line techniques. Solvents were purified by standard methods and deoxygenated by purging with nitrogen. The hydrido(η^5-cyclopentadienyl)tricarbonylmolybdenum was prepared by published procedure [7]. The physical methods used are described elsewhere [8].

Reactions of $[(\eta^5\text{-}C_5H_5)MoH(CO)_3]$

a) Dimethyldisulphide. An excess of dimethyldisulphide is added to a solution of hydridomolybdenum complex dissolved in tetrahydrofuran. Overnight stirring at 40°C gives a red-brown precipitate (II) which is separated by filtration, washed twice by THF and dried (yield: 25%). The brown filtrate is evaporated and the residue chromatographed on a Florisil column, two compounds, (I) (yield: 35%) and III, are separated. Recrystallization of the complex III gives green crystals (yield: 6%).

Compound II is slightly soluble in acetone and methylene chloride. Anal.

Found: C, 36.1; H, 3.0; Mo, 36.4; S, 12.1, Calcd. for $C_{24}H_{24}Mo_3O_6S_3$: C, 36.3; H, 3.0; Mo, 36.4; S, 12.1%. Melting point: 160—161°C (dec.).

Compound III is soluble in the usual organic solvents. Anal. Found: C, 35.8; H, 3.5; Mo, 40.5; S, 13.3, Calcd. for $C_{14}H_{16}Mo_2O_2S_2$: C, 35.6; H, 3.4; Mo, 40.6; S, 13.5%. Mass spectrum (*m/e*): 472 (*M*); 444 (*M* — CO); 416 (*M* — 2CO); 322 (Cp_2Mo_2).

b) Dimethyldisulphide in presence of W(CO)$_6$. This reaction is carried out as described above with $(MeS)_2$. Similar complexes are obtained, with yields as follows: I, 21%; II, 50% and III 2%.

c) Dimethyldisulphide in presence of Mo(CO)$_6$. Compound IV is obtained by refluxing for three days a mixture of hydridomolybdenum complex (6×10^{-3} mol), dimethyldisulphide (in excess) and $Mo(CO)_6$ (6×10^{-3} mol) dissolved in THF. IV is purified by chromatography on a Florisil column and is obtained in a low yield (15%).

IV is a dark-green complex, soluble in the usual organic solvents. Anal. Found: C, 28.2; H, 2.8; Mo, 36.3; S, 18.5; Calcd. for $C_{12}H_{14}Mo_2O_4S_3$: C, 28.2; H, 2.8; Mo, 37.6; S, 18.8. Mass spectrum (*m/e*): 510 (*M*); 482 (*M* — CO); 454 (*M* — 2 CO); 426 (*M* — 3 CO); 398 (*M* — 4 CO); Molecular weight (osmometry): 516 (calc. 510). Melting point: 158—160°C.

d) Dimethyldisulphide or diphenyldisulphide in presence of allyl bromide. Similarly, compounds V are obtained by refluxing $[(\eta^5\text{-}C_5H_5)MoH(CO)_3]$ ($\sim 1.4 \times 10^{-2}$ mol) and allyl bromide ($\sim 1.4 \times 10^{-2}$ mol) with an excess of alkyl- or aryl-disulphide in THF. Compounds V are insoluble in THF and are separated from $[(\eta^5\text{-}C_5H_5)MoBr(CO)_3]$ (VI) [yield: 14% (methyl); 75% (phenyl)] by filtration, washed by THF and dried [yield: 68% (Va); 3% (Vb)]. The orange-brown compounds V are soluble in methylene chloride, chloroform, acetone.

Va (methyl): Anal. Found: C, 30.0; H, 3.2; Br, 13.3; Mo, 31.6; S, 15.9, Calcd. for $C_{15}H_{19}BrMo_2O_2S_3$: C, 30.0; H, 3.2; Br, 13.3; Mo, 32.0; S, 16.0%. Molecular weight (osmometry): 583 (calcd. 599). Melting point: 190°C (dec.).

Vb (phenyl): Anal. Found: C, 45.8; H, 3.2; Br, 10.2, Calcd. for $C_{30}H_{25}BrMo_2O_2S_3$: C, 45.8; H, 3.2; Br, 10.2%. Mass spectrum (*m/e*): 758 (*M* — CO); 730 (*M* — 2 CO); 649 (*M* — CO — SPh); 459 $[Mo(C_5H_5)Br(SPh)_2]$; 270 $[Mo(C_5H_5)SPh]$.

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