The Formation, Structure, and Reversible Carbonylation of [(η^5-C_5H_5)-MM'$(CO)_7$(SR)] Complexes; Reactions of [(η^5-C_5H_5)MM'$(CO)_8$(SR)] with Hexafluorobut-2-yne

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The action of heat on [(η^5-C_5H_5)$(OC)_3$M(μ-SR)M'$(CO)_5$] (1) (M or M' = Cr, Mo, or W; R = Me or Ph) gives [(η^5-C_5H_5)$(OC)_2$M(μ-SR)M'$(CO)_5$] (2) containing a metal–metal bond. Photolysis of (2) in the presence of carbon monoxide regenerates (1) in an example of reversible cleavage of a M–M bond by carbon monoxide. The octacarbonyls (1) react with hexafluorobut-2-yne to give products of substitution at the (η^5-C_5H_5)M group. The spectroscopic parameters of the complexes and crystal-structure analyses of (1a; M = M' = W, R = Me), (2b; M = Mo, M' = W, R = Me), and [(η^5-C_5H_5)(OC)($CF_3C_2CF_3$)W(μ-SMe)W$(CO)_5$] (5) are discussed in terms of the electronic properties of the bridging thiolato-group and the metal centres.

As part of a general survey [1] of reactions of thiolatometal carbonyls with alkynes we have investigated the formation of some binuclear compounds of the chromium group, primarily for the characterisation of thiolato-derivatives but also to examine their reactions with polyfluoroalkynes. This work contributes to the general interest in research on polynuclear metal complexes with a view to the use of these compounds as models for homogeneous catalysis systems.[2]

The simplest polynuclear derivatives are the binuclear compounds which are the subject of the present work. The main possibilities for reaction are substitution, migration, oxidative addition, and elimination with oxidation and formation of metal–metal bonds. Some of the simpler compounds described here were first investigated by Earl and Vahrenkamp.[3]

RESULTS

Photolysis of 1 : 1 mixtures of the complexes [M$(CO)_3$(η^5-C_5H_5)(SR)] (M = Mo or W; R = Me or Ph) and [M'$(CO)_6$] (M' = Cr, Mo, or W) in tetrahydrofuran (thf) gives the binuclear complexes [(η^5-C_5H_5)$(OC)_3$M(μ-SR)M'$(CO)_5$] (1) in yields varying from 10 to 65%. Other products include the dimers [(η^5-C_5H_5)$(OC)_2$M(μ-SR)$_2$M$(CO)_2$(η^5-C_5H_5)], and binuclear [(η^5-C_5H_5)$(OC)_2$M(μ-SR)M'$(CO)_5$] (2) (derived by the action of heat from the u.v. lamp upon the mixture). Other binuclear products [(η^5-C_5H_5)M(μ-SR)$_4$M(η^5-C_5H_5)] and [(η^5-C_5H_5)(OC)M(μ-SR)$_3$M'$(CO)_3$] [4,5] are formed on the removal of volatiles, and these complexes have been identified spectroscopically. The structure of compound (1a; M = M' = W, R = Me) with a single SMe bridge unsupported by M–M' bonding has been confirmed by *X*-ray analysis (Figure 1). Other members of this series give very similar spectra and thus presumably have similar structures.

Complexes of type (1) are not obtained from thermal reactions which give dimeric [{M$(CO)_2$(η^5-C_5H_5)(SR)}$_2$], the trimeric complex [{M$(CO)_2$(η^5-C_5H_5)(SR)}$_3$], [5] [(η^5-C_5H_5)(OC)M(μ-SR)$_3$M'$(CO)_3$] (3), and *syn* and *anti* isomers of *trans*-[(η^5-C_5H_5)(OC)M(μ-SR)$_2$M(CO)(η^5-C_5H_5)] (4).[5,6] On standing a solution of the *syn* isomer changed slowly to the more stable *anti* isomer.

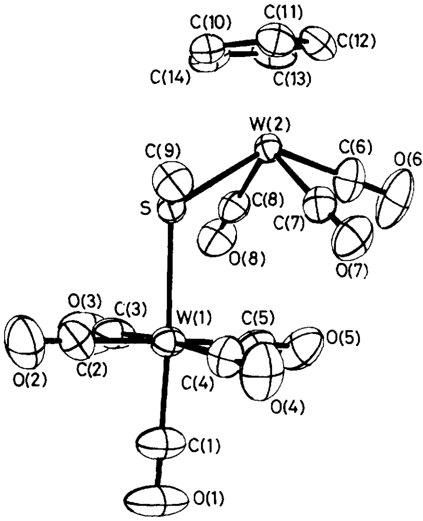
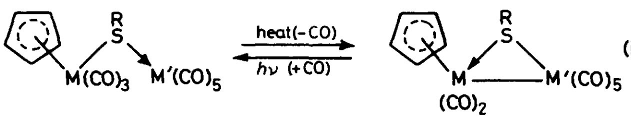


FIGURE 1 A perspective view of (1a). Here, and in Figures 2 and 3 unless otherwise stated, 50% probability ellipsoids are displayed and hydrogen atoms are omitted

On warming in dichloromethane compounds (1) lose CO and are converted into compounds (2) which contain a single bridging SR group and a metal–metal bond [equation (i)]. Compounds of type (2) have not been identified previously. Their structure has been established by an *X*-ray crystallographic study of the Mo–W complex [(η^5-C_5H_5)$(OC)_2$Mo(μ-SMe)W$(CO)_5$] (2b) (Figure 2). Photolysis of (2) under 1 atm † of carbon monoxide regenerates (1).



(1) (2) (i)

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† Throughout this paper: 1 atm = 101 325 N m^{-2}.

During these reactions there is some decomposition and $[M'(CO)_6]$, $[\{M(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$, and a small quantity of (3) are formed. Compound (3; R = Me) is also formed, along with other unidentified products, by the action of dimethyl disulphide upon (2; R = Me).

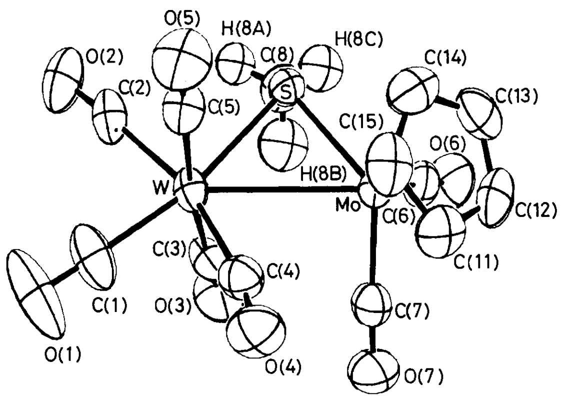


FIGURE 2 A perspective view of (2b). Methyl hydrogen atoms are shown since the data permitted unconstrained refinement of their positions

No well identified compound was isolated from the reaction between (1) and trifluoropropyne, but with hexafluorobut-2-yne (1a; M = M′ = W, R = Me) gives (5) (Figure 3) which is a binuclear derivative with a single SMe bridge unsupported by metal–metal bonding with substitution of alkyne into the tricarbonyl(cyclopentadienyl)-tungsten group [equation (ii)]. In addition to the binuclear alkyne complex (5), the heterocyclic derivative $[(\eta^5\text{-}C_5H_5)(OC)_2\overline{WC(F_3C){=}C(CF_3)C(O)S}Me]$,[1] $[W(CO)_6]$, and $[W(CO)_5(thf)]$ are also found. Compound (5) is only formed in trace yield by the thermal reaction between (1) and hexafluorobut-2-yne. Complex (1; R = Ph) reacts with hexafluorobut-2-yne to give (6) which is formulated as a mononuclear π-alkyne complex on the basis of spectroscopy;[7] a binuclear species $[(\eta^5\text{-}C_5H_5)(OC)(CF_3C_2CF_3)W(\mu\text{-}SPh)W(CO)_5]$ appears to be formed in this reaction but has not been obtained pure.

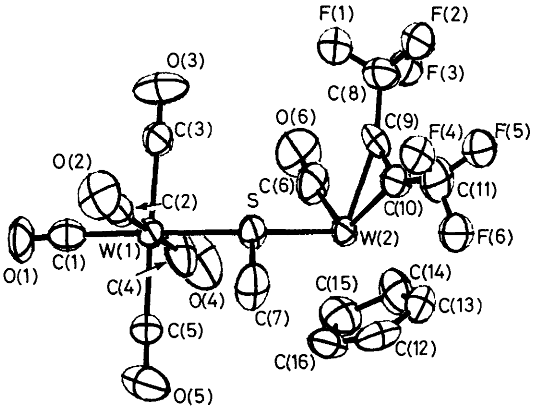
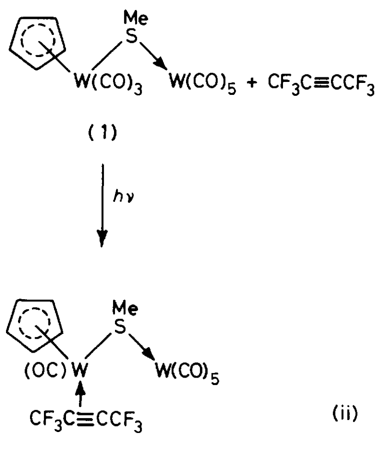


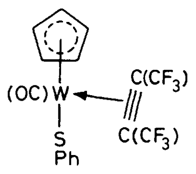
FIGURE 3 A perspective view of (5). For clarity the fluorine atoms are represented by spheres of arbitrary radius. The temperature factors of the fluorine atoms indicate large torsional motions of the CF_3 about the C–C bonds



(1)

(5)

(ii)



(6)

DISCUSSION

The complexes (1) are presumably formed by attack of $[M(CO)_3(\eta^5\text{-}C_5H_5)(SR)]$ on $[M'(CO)_5(thf)]$, the latter intermediate being formed photolytically. The structure of (1) implies that the sulphur atom in the corresponding mononuclear parent complex $[M(CO)_3(\eta^5\text{-}C_5H_5)(SR)]$ retains sufficient Lewis basicity to act as a two-electron donor to $M'(CO)_5$. The ^{13}C chemical shifts (Table 1) of the $M'(CO)_5$ group in (1) suggest that the electronic effect of the $(\eta^5\text{-}C_5H_5)M(CO)_3(SR)$ donor group is similar to that of trialkylphosphines which are considered better σ-donors and poorer π-acceptors than carbon monoxide.[8] This conclusion is consistent with the slight shortening of the W(1)–C(1) bond *trans* to S, compared with the *cis* bonds, in (1a). Comparison of the ^{13}C and ^{1}H n.m.r. spectra of (1) (*e.g.* M = W) with those of the parent mononuclear species reveals major changes in the chemical shifts of the thiolato-carbon and hydrogen atoms as would be expected from their different electronic environments. Additionally, the ^{13}C chemical shifts of the carbonyls of the $(\eta^5\text{-}C_5H_5)M(CO)_3(SR)$ groups show that two (presumably cisoid) carbon atoms are deshielded relative to the mononuclear parent species whereas one (transoid) carbon atom is shielded. There are no obvious trends in bond lengths which would explain this but the conformation in the solid is such as to bring the cisoid carbon atoms closer to the tungsten atom of the $W(CO)_5$ group and this conformation may persist in solution. The cyclopentadienyl groups in (1) appear to have undergone only slight changes in chemical shift and thus in electron density as compared with the parent mononuclear species.

TABLE 1

N.m.r. shifts in $CDCl_3$ with reference to $SiMe_4$

	$\delta(^1H)$/p.p.m.		$\delta(^{13}C)$/p.p.m.					
					$M'(CO)_5$		$M(CO)_n$ (n = 2 or 3)	
Compound	C_5H_5	SCH_3	SCH_3	C_5H_5	CO (eq.)	CO (ax.)	CO *trans*	CO *cis*
(1a)	5.68	2.52	31.14	93.64	198.56	200.57	222.33	215.26
(1b)	5.57	2.42	30.81	95.17	198.24	201.0	234.27	225.32
$[W(CO)_3(\eta^5\text{-}C_5H_5)(SMe)]$	5.68	2.05	17.73	93.50			225.4	212.5
(2a)	5.55	3.22	35.55	93.07	193.4 198.5	199.2	230.8	
(2b)	5.40	3.05	32.81	94.4	196.4	200.8	240.4	
(5)	5.85	2.91	46.9	94.8	198.4	200.2		

The thermal reaction of (1) to give (2) would seem to involve initial loss of carbonyl from the $(\eta^5\text{-}C_5H_5)M(CO)_3$ group and subsequent formation of a single M–M' metal–metal bond, so that there is an increase in the formal oxidation state of M' from 0 to +II. The reaction is reversed on irradiation in the presence of carbon monoxide. There is ample precedent for the induction of metal–metal bonding by decarbonylation and the conversion of (2) back to (1) is a clear example of cleavage of a metal–metal bond by a reaction involving only carbon monoxide. The closest parallel would appear to be the use of phosphine or phosphite addition to break metal–metal bonds.[9]

The formation of (3) during the thermal decarbonylation of (1) to give (2) can proceed by oxidative addition of a disulphide to (2) but there is no proof that this is the main method of formation of the complex and the intermediate formation of substantial quantities of disulphide does not seem likely.

TABLE 2

Selected distances (Å) and angles (°) in $[(\eta^5\text{-}C_5H_5)(OC)_3W(\mu\text{-SMe})W(CO)_5]$ (1a)

(*a*) Bond lengths

W(1)–S	2.596(1)	W(2)–S	2.541(1)
W(1)–C(1)	1.979(7)	W(2)–C(6)	1.980(7)
W(1)–C(12)	2.065(6)	W(2)–C(7)	2.003(6)
W(1)–C(3)	2.036(7)	W(2)–C(8)	1.990(6)
W(1)–C(4)	2.025(6)	W(2)–C(10)	2.377(6)
W(1)–C(5)	2.041(6)	W(2)–C(11)	2.364(6)
S–C(9)	1.830(6)	W(2)–C(12)	2.306(7)
C–O	1.09(1)—1.16(1)	W(2)–C(13)	2.293(7)
C–C	1.39(1)—1.44(1)	W(2)–C(14)	2.336(6)

(*b*) Bond angles

S–W(1)–C(1)	177.1(2)	C(3)–W(1)–C(4)	177.2(3)
S–W(1)–C(2)	88.0(2)	C(3)–W(1)–C(5)	91.0(3)
S–W(1)–C(3)	89.1(2)	C(4)–W(1)–C(5)	89.9(2)
S–W(1)–C(4)	93.4(2)	S–W(2)–C(6)	133.1(2)
S–W(1)–C(5)	92.8(2)	S–W(2)–C(7)	76.7(2)
C(1)–W(1)–C(2)	90.1(3)	S–W(2)–C(8)	78.5(2)
C(1)–W(1)–C(3)	88.7(3)	C(6)–W(2)–C(7)	74.0(3)
C(1)–W(1)–C(4)	88.7(3)	C(6)–W(2)–C(8)	77.2(3)
C(1)–W(1)–C(5)	89.2(3)	C(7)–W(2)–C(8)	108.5(2)
C(2)–W(1)–C(3)	90.8(3)	W(1)–S–W(2)	119.7(1)
C(2)–W(1)–C(4)	88.2(2)	W(1)–S–C(9)	105.0(2)
C(2)–W(1)–C(5)	178.0(2)	W(2)–S–C(9)	106.4(2)
W–C–O	175(1)—179(1)	C–C–C	107(1)—109(1)

TABLE 3

Selected distances (Å) and angles (°) in $[(\eta^5\text{-}C_5H_5)(OC)_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}}(CO)_5]$ (2b)

(*a*) Bond lengths

W–Mo	3.131(1)	Mo–S	2.407(1)
W–S	2.492(1)	Mo–C(6)	1.930(5)
W–C(1)	2.012(7)	Mo–C(7)	1.960(6)
W–C(2)	2.058(5)	Mo–C(11)	2.319(5)
W–C(3)	2.041(5)	Mo–C(12)	2.275(6)
W–C(4)	2.028(6)	Mo–C(13)	2.280(7)
W–C(5)	2.050(6)	Mo–C(14)	2.362(6)
S–C(8)	1.824(6)	Mo–C(15)	2.392(5)
C–C	1.37(1)—1.41(1)	C–O	1.11(1)—1.16(1)

(*b*) Bond angles

S–W–Mo	49.1(1)	C(2)–W–C(3)	92.5(2)
S–W–C(1)	166.7(2)	C(2)–W–C(4)	161.8(2)
S–W–C(2)	84.4(2)	C(2)–W–C(5)	87.8(2)
S–W–C(3)	89.1(2)	C(3)–W–C(4)	93.2(2)
S–W–C(4)	113.0(2)	C(3)–W–C(5)	173.0(2)
S–W–C(5)	83.9(2)	C(4)–W–C(5)	88.6(2)
Mo–W–C(1)	144.1(2)	W–Mo–S	51.5(1)
Mo–W–C(2)	133.1(2)	W–Mo–C(6)	115.6(2)
Mo–W–C(3)	82.5(1)	W–Mo–C(7)	88.1(2)
Mo–W–C(4)	64.9(2)	S–Mo–C(6)	84.3(2)
Mo–W–C(5)	92.1(1)	S–Mo–C(7)	120.4(2)
C(1)–W–C(2)	82.4(2)	C(6)–Mo–C(7)	76.2(2)
C(1)–W–C(3)	91.2(2)	W–S–Mo	79.4(1)
C(1)–W–C(4)	80.2(2)	W–S–C(8)	110.3(2)
C(1)–W–C(5)	95.7(2)	Mo–S–C(8)	114.3(2)
W–C(4)–O(4)	167.5(5)	C–C–C	107.0(6)—108.7(5)
W–C–O *	175.7(5)—177.9(5)	Mo–C–O	176.1(5)—178.1(5)

* Excluding W–C(4)–O(4).

The structural (Tables 2 and 3) and n.m.r. results (Table 1) permit some comparisons to be made regarding the bonding in (1) and (2). Deshielding of the ^{13}C and ^1H nuclei of the bridging thiolato-group in (2) relative to (1) implies a reduction in electron density on the sulphur substituent, most probably by participation of the sulphur orbitals in the metal–metal bonding. The M–S bond lengths in (2b) are shorter than corresponding bonds in (1a). The S–W(CO)$_5$ distance decreases from 2.596(1) to 2.492(1) Å whereas the $(\eta^5\text{-}C_5H_5)M\text{–}S$ bonds show a larger change, from 2.541(1) Å (M = W) to 2.407(1) Å (M = Mo). This might be expected since the M carries one less carbonyl in (2) but the comparison is complicated by the change of M from W to Mo. Interestingly, the shrinkage of the mean Mo–S bridging distances from 2.54 Å in $[\{Mo(CO)_2(\eta^5\text{-}C_5H_5)(\mu\text{-SPh})\}_2]$, where the metal atoms are not directly bonded, to 2.42 Å in the Mo=Mo double-bonded species $[\{Mo(CO)(\eta^5\text{-}C_5H_5)(\mu\text{-SBu}^t)\}_2]$ is[6] practically identical to that shown by the $(\eta^5\text{-}C_5H_5)M\text{–}S$ distances in (1a) and (2b). The M–S–M' angle decreases sharply, from 119.7(1) to 79.4(1)°, on going from (1a) to (2b) whereas the M– and M′–S–CH_3 angles show only a slight change (means 106 and 112°).

Two further structural features of (2b) merit comment. First, although several multiple Mo–W bond lengths have been determined[10] this is the first measurement of the length of a single Mo–W bond. Its value [3.131(1) Å] is comparable with those of single Mo–Mo and W–W bonds.[11,12] Secondly, the $SW(CO)_5$ unit in (2b) possesses an essentially octahedral geometry, albeit somewhat distorted compared with (1a), with the Mo atom occupying a site roughly midway along the S · · · C(4) edge of the octahedron. The semi-bridging nature of the C(4)–O(4) carbonyl is apparent from the Mo · · · C(4) distance of 2.921(7) Å and the W–C(4)–O(4) angle of 167.5(5)° [*cf.* 176—178° for other W–C–O angles in (2b)]. The existence of a similar semi-bridging carbonyl in $[(\eta^5\text{-}C_5H_5)(OC)_2Mn(\mu\text{-}AsMe_2)Mn(CO)_4]$, which resembles (2b) structurally, has been explained in terms both of steric[13] and electronic[14] effects. Complex (2) appears to retain its semi-bridged structure in CH_2Cl_2 solution: there are carbonyl bands between 1 855 and 1 870 cm^{-1} and the ^{13}C n.m.r. spectra are complex, with two signals again consistent with semi-bridging.[12]

The π-alkyne complex (5) is derived by replacement of two carbonyls by hexafluorobut-2-yne at the $(\eta^5\text{-}C_5H_5)W(CO)_3$ centre of (1a). This would seem to imply greater susceptibility to photochemical activation at $(\eta^5\text{-}C_5H_5)W(CO)_3$ than at $W(CO)_5$. Indeed, in the present series of reactions the $M(CO)_5$ group displays considerable stability. The conversion of (1a) into (5) seems to be analogous to the addition of hexafluorobut-2-yne to mononuclear $[M(CO)_3(\eta^5\text{-}C_5H_5)(SR)]$ complexes to give π-alkyne species analogous to (6). When R = perfluoroalkyl an analogue of (6) is the only product isolated[7] but when R = alkyl the reaction proceeds through a complex series of heterocyclic intermediates. With (1; R = Ph) and hexafluorobut-2-yne there is evidence for an intermediate binuclear derivative although (6) remains the ultimate product.

Species such as (6) and, by analogy, the alkyne-substituted metal centre in (5), have been regarded as co-ordinatively unsaturated 16-electron systems, with the alkyne acting as a two-electron donor.[1,15] In the mononuclear case the appearance of a 16-electron species as the ultimate product could be rationalised by entropy effects. For the binuclear complexes it is more surprising, since metal–metal bond formation could give, in place of (5), a complex derived from (2) by substitution of carbonyl by a two-electron donor alkyne or formation of a 1,2-dimetallated ethene derivative. The structure of (5) (Table 4) permits a discussion of this problem. The W(2) co-ordination in (5) is octahedral, with three facial sites occupied by CO, S, and the midpoint of the hexafluorobut-2-yne C≡C bond, and the remaining three by the $\eta^5\text{-}C_5H_5$ ring. The geometry of the complex can then be rationalised[7,16,17] by assuming that the W(2) atom has a d^4 configuration and an empty acceptor d_{xy} orbital in the plane defined by the W–S and W–alkyne bonds. This arrangement permits maximum back donation to carbonyl and also allows donation both from sulphur and from an alkyne π orbital into the metal d_{xy} acceptor orbital. This bonding scheme is consistent with (*i*) the η^2-C≡C and W–CO bonds being parallel and coplanar [C(9)–C(10)–W(2)–C(6) 1.4(9)°], (*ii*) the W–C(alkyne) bond lengths which are closer to the values considered typical of four- rather than two-electron donor alkyne–tungsten bonding,[16] and (*iii*) the drastic shortening of the W(2)–S bond from 2.541(1) Å in (1a) to 2.337(3) Å in (5). By comparison the S–$W(CO)_5$ distances in (1a) and (5) differ by only 0.04 Å. The variations in the W–S bond lengths in (1a) and (5) correlate with the n.m.r. parameters of the complexes in that the H_3CS signals differ considerably whereas those of the $W(CO)_5$ groups change very little. The shorter W(2)–S bond in (5), compared with (1a) is compensated for by a more obtuse W–S–W angle [131.5(1)°] so that the W · · · W non-bonded distances are similar in the two complexes [4.442(1) and 4.459(1) Å in (1a) and (5) respectively].

TABLE 4

Selected distances (Å) and angles (°) in
$[(\eta^5\text{-}C_5H_5)(OC)(CF_3C_2CF_3)W(\mu\text{-}SMe)W(CO)_5]$ (5)

(*a*) Bond lengths

W(1)–S	2.553(3)	W(2)–C(14)	2.259(15)
W(1)–C(1)	2.035(13)	W(2)–C(15)	2.337(16)
W(1)–C(2)	2.038(12)	W(2)–C(16)	2.396(15)
W(1)–C(3)	2.033(12)	S–C(7)	1.831(11)
W(1)–C(4)	2.053(16)	F(1)–C(8)	1.23(2)
W(1)–C(5)	2.020(13)	F(2)–C(8)	1.33(2)
W(2)–S	2.337(3)	F(3)–C(8)	1.32(2)
W(2)–C(6)	2.020(14)	F(4)–C(11)	1.20(3)
W(2)–C(9)	2.062(11)	F(5)–C(11)	1.16(2)
W(2)–C(10)	2.033(11)	F(6)–C(11)	1.21(3)
W(2)–C(12)	2.371(14)	C(9)–C(10)	1.299(16)
W(2)–C(13)	2.322(12)	C(8)–C(9)	1.448(19)
C–O	1.12(2)—1.17(2)	C(10)–C(11)	1.441(19)
C–C(C_5H_5)	1.39(2)—1.44(2)		

(*b*) Bond angles

S–W(1)–C(1)	175.0(3)	S–W(2)–C(6)	89.5(4)
S–W(1)–C(2)	86.7(3)	S–W(2)–C(9)	103.4(3)
S–W(1)–C(3)	90.3(3)	S–W(2)–C(10)	103.4(3)
S–W(1)–C(4)	93.9(4)	C(6)–W(2)–C(9)	78.9(5)
S–W(1)–C(5)	89.5(4)	C(6)–W(2)–C(10)	115.9(5)
C(1)–W(1)–C(2)	88.7(5)	W(1)–S–W(2)	131.5(1)
C(1)–W(1)–C(3)	91.7(5)	W(1)–S–C(7)	107.6(5)
C(1)–W(1)–C(4)	90.7(5)	W(2)–S–C(7)	110.6(5)
C(1)–W(1)–C(5)	89.0(5)	W(2)–C(9)–C(10)	70.3(7)
C(2)–W(1)–C(3)	90.6(5)	W(2)–C(9)–C(8)	149.7(10)
C(2)–W(1)–C(4)	178.2(6)	C(8)–C(9)–C(10)	139.9(11)
C(2)–W(1)–C(5)	95.0(5)	W(2)–C(10)–C(9)	72.7(7)
C(3)–W(1)–C(4)	87.7(6)	W(2)–C(10)–C(11)	150.4(10)
C(3)–W(1)–C(5)	174.3(5)	C(9)–C(10)–C(11)	136.7(12)
C(4)–W(1)–C(5)	86.6(6)	C–C–F	113(2)—117(2)
W–C–O	171(2)—180(2)	F–C–F	99(2)—115(2)
C–C–C(C_5H_5)	107(2)—110(2)		

EXPERIMENTAL

The thiolates $[M(CO)_3(\eta^5\text{-}C_5H_5)(SR)]$ were prepared according to the literature;[18] metal hexacarbonyls were commercial products. Analyses were by Centre de Microanalyse du CNRS, Lyon. Mass spectra were recorded on a M.S. 12 mass spectrometer, n.m.r. spectra in $CDCl_3$ on a

JEOL FX100 spectrometer (^{1}H and ^{13}C in p.p.m. with reference to $\mathrm{SiMe_4}$, ^{19}F in p.p.m. with reference to $\mathrm{CCl_3F}$), and i.r. spectra (in $\mathrm{CH_2Cl_2}$) on a Pye-Unicam SP2000 spectrophotometer.

Preparation of Complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{M}(\mu\text{-SR})\text{M}'(\text{CO})_5]$ (1).—In a typical preparation the thiolate $[\text{M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)(\text{SR})]$ (5 mmol) was photolysed with $[\text{M}'(\text{CO})_6]$ (5 mmol) in tetrahydrofuran for about 48 h. The solvent was evaporated, and the product dissolved in the minimum of dichloromethane for chromatography on Florisil. The complexes were eluted with a mixture of hexane–dichloromethane–acetone (6 : 3 : 1) and separated from the dimers $[\{\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)(\text{SR})\}_2]$ (yield 0—60%) and minor products.

If the gaseous products of the reaction are removed periodically the yields of (1) are very small and the yields of complexes such as $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu\text{-SMe})_4\text{Mo}(\eta^5\text{-C}_5\text{H}_5)]$ (5—10%) and $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})\text{M}(\mu\text{-SR})_3\text{M}'(\text{CO})_3]$ (3) rise [in particular for M = Mo, M′ = W, R = Ph the yield of (3) can rise to 35%].

Thermal reactions between $[\text{M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)(\text{SR})]$ and $[\text{M}'(\text{CO})_6]$ in tetrahydrofuran give no appreciable quantities of (1) but yield complexes which we have already described [5] and *syn-trans*-$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})\text{Mo}(\mu\text{-SR})_2\text{Mo}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$ in a 13% yield formed from $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)(\text{SR})]$ and $[\text{Mo}(\text{CO})_6]$.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{W}(\mu\text{-SMe})\text{W}(\text{CO})_5]$ (1a). Orange-red solid, yield 50% (Found: C, 24.3; H, 1.4; S, 4.9; W, 52.2. Calc. for $\mathrm{C_{14}H_8O_8SW_2}$: C, 23.9; H, 1.1; S, 4.6; W, 52.2%). The mass spectrum shows a parent ion at *m/e* 704 and ions corresponding to $[M - n\text{CO}]^+$ (n = 1—8), $[\text{W}(\text{CO})_6]^+$, and $[\text{C}_5\text{H}_5\text{W}]^+$. The i.r. spectrum shows carbonyl peaks at 2 070m, 2 040(sh), 2 036s, 1 956vs, 1 928vs, and 1 894(sh) cm^{-1}. M.p. 112—113 °C.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo}(\mu\text{-SMe})\text{W}(\text{CO})_5]$ (1b). Red solid, yield 30% (Found: C, 27.8; H, 1.3; Mo, 15.1; S, 5.2. Calc. for $\mathrm{C_{14}H_8MoO_8SW}$: C, 27.3; H, 1.3; Mo, 15.5; S, 5.2%). I.r.: 2 090(sh), 2 080mw, 2 050m, 1 965s, 1 938s, and 1 900(sh) cm^{-1}. M.p. 86—88 °C (decomp.).

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{W}(\mu\text{-SPh})\text{W}(\text{CO})_5]$ (1c). Orange solid, yield 65% (Found: C, 31.5; H, 1.5; S, 4.2; W, 47.7. $\mathrm{C_{19}H_{10}O_8SW_2}$ requires C, 29.8; H, 1.3; S, 4.2; W, 48.0%). I.r.: 2 075w, 2 040m, 1 960s, 1 935s, and 1 900 cm^{-1}. ^{1}H N.m.r.: 7.28 ($\mathrm{SC_6H_5}$); 5.67 ($\mathrm{C_5H_5}$). M.p. 99 °C (decomp.).

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{W}(\mu\text{-SMe})\text{Mo}(\text{CO})_5]$ (1d). Yellow-orange solid, yield 10% (Found: C, 26.8; H, 1.5; S, 4.9; W, 30.6. $\mathrm{C_{14}H_8MoO_8SW}$ requires C, 27.2; H, 1.3; S ,5.2; W, 29.9%). The mass spectrum shows a parent ion at *m/e* 616 and ions corresponding to $[M - n\text{CO}]^+$ (n = 1—8). I.r.: 2 080m, 2 040ms, 1 960s, and 1 900m cm^{-1}. ^{1}H N.m.r.: 5.68 ($\mathrm{C_5H_5}$): 2.30 ($\mathrm{SCH_3}$).

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{Mo}(\mu\text{-SMe})\text{Mo}(\text{CO})_5]$ (1e). Orange-red solid, yield 15% (Found: C, 28.2; H, 1.7; Mo, 38.0; S, 6.5. $\mathrm{C_{14}H_8Mo_2O_8S}$ requires C, 31.8; H, 1.5; Mo, 36.4; S, 6.1%). I.r.: 2 080w, 2 045m, 1 970s, 1 910s, and 1 900m cm^{-1}. ^{1}H N.m.r.: 5.60 ($\mathrm{C_5H_5}$); 2.22 ($\mathrm{SCH_3}$).

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{W}(\mu\text{-SMe})\text{Cr}(\text{CO})_5]$ (1f). Orange-red solid, yield 10% (Found: C, 29.1; H, 1.6; Cr, 9.0; S, 5.5; W, 32.3. Calc. for $\mathrm{C_{14}H_8CrO_8SW}$: C, 29.4; H, 1.4; Cr, 9.0; S, 5.6; W, 32.1%). The mass spectrum shows a parent ion at *m/e* 572 and ions corresponding to $[M - n\text{CO}]^+$ (n = 1—8). I.r.: 2 075w, 2 045mw, 1 995(sh), 1 975s, 1 945, and 1 930m cm^{-1}. ^{1}H N.m.r.: 5.62 ($\mathrm{C_5H_5}$); 2.20 ($\mathrm{SCH_3}$).

syn-trans-$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})\text{Mo}(\mu\text{-SMe})_2\text{Mo}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$ (4). Chestnut-brown solid, yield 5% (Found: C, 35.1; H, 3.3; Mo, 38.9; S, 11.7. $\mathrm{C_{14}H_{16}Mo_2O_2S_2}$ requires C, 36.0; H, 3.2; Mo, 38.4; S, 12.8%). The mass spectrum shows a parent ion at *m/e* 472 and ions corresponding to $[M - n\text{CO}]^+$ (n = 1 or 2). I.r. (Nujol mull): 1 870(sh) and 1 830s cm^{-1}. ^{1}H N.m.r.: 5.50 and 5.32 ($\mathrm{C_5H_5}$); 2.38 ($\mathrm{SCH_3}$). On warming or standing this complex changes to the *anti-trans* complex.

Preparation of Complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\overline{\text{M}(\mu\text{-SMe})\text{M}'}(\text{CO})_5]$ (2).—Complexes (1) (5 mmol) were warmed in $\mathrm{CH_2Cl_2}$ at 45 °C for 72 h. The reaction mixture was chromatographed on Florisil and eluted with hexane–$\mathrm{CH_2Cl_2}$ (4 : 1). Complexes (2) were obtained in 50—60% yield.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\overline{\text{W}(\mu\text{-SMe})\text{W}}(\text{CO})_5]$ (2a). Black solid (Found: C, 23.5; H, 1.2; S, 4.6; W, 54.4. $\mathrm{C_{13}H_8O_7SW_2}$ requires C, 23.1; H, 1.2; S, 4.7; W, 54.4%). The mass spectrum shows a parent ion at *m/e* 676 and ions corresponding to $[M - n\text{CO}]^+$ (n = 1—7), $[M - 3\text{CO} - \text{CH}_3]^+$, $[M - 7\text{CO} - \text{SCH}_3]^+$, $[\text{C}_5\text{H}_5\text{W}(\text{CO})_2(\text{SCH}_3)]^+$, and $[\text{C}_5\text{H}_5\text{W}(\text{SCH}_3)]^+$. I.r.: 2 080w, 2 040w, 1 960s, 1 940ms, and 1 855w cm^{-1}.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}}(\text{CO})_5]$ (2b). Black solid (Found: C, 26.8; H, 1.4; Mo, 15.4; S, 5.6. $\mathrm{C_{13}H_8MoO_7SW}$ requires C, 26.6; H, 1.4; Mo, 16.3; S, 5.5%). The mass spectrum shows a parent ion at *m/e* 588 and ions corresponding to $[M - n\text{CO}]^+$ (n = 1—7) and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_n(\text{SCH}_3)]^+$ (n = 1—3). I.r.: 2 085m, 2 020w, 1 975s, 1 955(sh), 1 930m, and 1 870m cm^{-1}. M.p. 99 °C.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\overline{\text{Mo}(\mu\text{-SMe})\text{Mo}}(\text{CO})_5]$ (2c). Black solid. This complex has not been obtained pure; it is unstable and decomposes quickly. It has been characterised by its i.r. spectrum: 2 070w, 2 040w, 1 978ms, 1 940s, and 1 855mw cm^{-1}.

Photolysis of complexes (2) (5 mmol) in thf was carried out for 48 h under 1 atm carbon monoxide. Complexes (1) were formed in 50% yield accompanied by other products (see Results). Complex (2b) $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\overline{\text{Mo}(\mu\text{-SMe})\text{W}}(\text{CO})_5]$ (5 mmol) was heated in thf at 60 °C with excess of dimethyl disulphide to give mainly $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})\overline{\text{Mo}(\mu\text{-SMe})_3\text{W}}(\text{CO})_3]$ (3), green solid (Found: C, 23.6; H, 2.3. $\mathrm{C_{12}H_{14}MoO_4S_3W}$ requires C, 24.0; H, 2.3%). I.r.: 1 995s, 1 965vs, 1 930s, and 1 840s cm^{-1}. ^{1}H N.m.r.: 5.58 ($\mathrm{C_5H_5}$); 2.73, 2.70, 1.38 ($\mathrm{SCH_3}$). M.p. 58 °C (decomp).

Reactions of $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_3\text{W}(\mu\text{-SR})\text{W}(\text{CO})_5]$ *with Alkynes*.—Complexes (1a) and (1c) (2 mmol) in thf were photolysed for 60 h with 4 mmol alkyne ($\mathrm{CF_3C_2H}$ or $\mathrm{CF_3C_2CF_3}$). Products were separated by chromatography on Florisil and eluted with hexane (80%) and $\mathrm{CH_2Cl_2}$ (20%).

$[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})(\text{CF}_3\text{C}_2\text{CF}_3)\text{W}(\mu\text{-SMe})\text{W}(\text{CO})_5]$ (5). Red solid, recrystallised from hexane, yield 30% (Found: C, 23.9; H, 1.0; F, 13.6; S, 4.0; W, 42.6. $\mathrm{C_{16}H_8F_6O_6SW_2}$ requires C, 24.9; H, 0.9; F, 13.2; S, 3.7; W, 42.5%). The mass spectrum shows a parent ion at *m/e* 810 and ions corresponding to $[M - n\text{CO}]^+$ (n = 2—6), $[(\text{C}_5\text{H}_5)(\text{C}_4\text{F}_6)\text{W}(\text{CO})(\text{SCH}_3)]^+$, and $[(\text{C}_5\text{H}_5)(\text{C}_4\text{F}_6)\text{W}(\text{SCH}_3)]^+$. I.r.: 2 080w, 2 020mw, 1 988vs, 1 946s, and 1 915(sh); 1 730mw (C≡C). ^{19}F N.m.r.: 56.2, 57.2 (quartets) [J(FF) 3 Hz]. M.p. 118—119 °C (decomp.).

$[\text{W}(\text{CF}_3\text{C}_2\text{CF}_3)(\text{CO})(\eta^5\text{-C}_5\text{H}_5)(\text{SC}_6\text{H}_5)]$ (6). Red solid, yield 60% (Found: C, 35.0; H, 1.8; F, 20.8; S, 5.3; W, 35.2. $\mathrm{C_{16}H_{10}F_6OSW}$ requires C, 35.0; H, 1.8; F, 20.8; S, 5.8; W, 33.6%). I.r.: 2 000s and 1 715mw cm^{-1} (C≡C). N.m.r.: ^{1}H, 7.25 ($\mathrm{SC_6H_5}$), 5.47 ($\mathrm{C_5H_5}$); ^{19}F,

57.45, 55.30 (quartets) [*J*(FF) 3.4 Hz]. M.p. 106—107 °C (decomp).

X-*Ray Crystal-structure Analyses*.—The crystal structures of (1a), (2b), and (5) were determined by standard methods (see ref. 19). Unit-cell dimensions (Table 5) and the intensities of Bragg reflections (θ—2θ scans) were measured with Mo-K_α radiation, λ = 0.710 69 Å, using an Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator. The intensities were corrected for Lorentz, polarisation, and [except for (5)] absorption effects, then scaled to allow for the minor variations in the intensities of standard reflections. After averaging duplicate intensities the analyses were carried out with the reflections for which $I \geqslant 3\sigma(I)$.

TABLE 5

Crystal data and agreement indices for (1a), (2b), and (5)

	(1a)	(2b)	(5)
Formula	$C_{14}H_8O_8SW_2$	$C_{13}H_8MoO_7SW$	$C_{16}H_8F_6O_6SW_2$
M	704.0	588.1	810.0
Space group [a]	*P*2₁/*c*	*C*2/*c*	*P*2₁/*n*
a/Å	8.053(1)	33.461(4)	8.217(3)
b/Å	17.749(2)	6.946(2)	15.024(5)
c/Å	12.566(2)	15.378(3)	17.194(3)
β/°	90.80(1)	111.08(2)	92.23(2)
U/Å^3	1 796	3 335	2 121
Z	4	8	4
D_c/g cm^{-3}	2.604	2.342	2.537
F(000)	1 279.6	2 191.3	1 479.6
μ(Mo-$K\alpha$)/cm^{-1}	124.1	74.3	105.5
A^* [b]	0.17—0.29	0.43—0.58	
$\theta_{max.}$(Mo-$K\alpha$)/°	30	28	25
$I > 3\sigma(I)$	3 895	2 542	2 747
Refined parameters	227	221	281
R	0.028	0.021	0.037
R′	0.036	0.026	0.051
R_M [c]	0.029	0.027	0.032

[a] Each crystal belongs to the monoclinic system. [b] Transmission factors on F^2 calculated by Gaussian integration; the irregular shape of the crystal of (5) precluded absorption correction. [c] *R* factor for merging equivalent $|F_o|$.

TABLE 6

Fractional atomic co-ordinates (× 10^5 for W and S, × 10^4 for O and C) for (1a)

Atom	*x*	*y*	*z*
W(1)	12 007(3)	2 810(1)	27 682(2)
W(2)	35 542(2)	20 408(1)	7 785(1)
S	35 822(15)	12 372(7)	24 518(9)
O(1)	−1 668(8)	−825(3)	3 266(6)
O(2)	3 071(8)	−258(3)	4 854(4)
O(3)	−804(8)	1 511(3)	4 067(6)
O(4)	2 910(8)	−1 067(3)	1 531(4)
O(5)	−731(7)	736(3)	646(5)
O(6)	1 251(11)	2 067(4)	−1 250(5)
O(7)	3 491(7)	404(3)	−148(4)
O(8)	47(5)	2 421(3)	1 683(4)
C(1)	−619(8)	−430(4)	3 084(6)
C(2)	2 459(9)	−64(3)	4 126(5)
C(3)	−22(9)	1 084(4)	3 608(6)
C(4)	2 352(8)	−557(4)	1 970(5)
C(5)	−28(7)	585(4)	1 403(5)
C(6)	2 101(10)	2 063(4)	−505(5)
C(7)	3 518(7)	986(3)	212(4)
C(8)	1 335(7)	2 271(3)	1 375(4)
C(9)	5 473(7)	666(4)	2 406(5)
C(10)	6 014(7)	2 552(4)	1 556(5)
C(11)	6 403(7)	2 292(4)	522(5)
C(12)	5 429(9)	2 718(4)	−209(5)
C(13)	4 460(8)	3 235(4)	404(6)
C(14)	4 832(7)	3 118(4)	1 477(6)

TABLE 7

Fractional atomic co-ordinates (× 10^5 for W, Mo, and S; × 10^4 for O and C) for (2b)

Atom	*x*	*y*	*z*
W	7 013(1)	10 105(3)	17 463(1)
Mo	16 902(1)	17 471(7)	25 881(3)
S	11 346(3)	38 466(19)	16 260(8)
O(1)	−30(2)	−2 011(10)	1 517(4)
O(2)	−87(1)	3 201(8)	292(3)
O(3)	944(2)	−999(7)	150(3)
O(4)	1 158(2)	−2 099(7)	3 280(3)
O(5)	553(2)	3 516(8)	3 333(3)
O(6)	2 131(1)	2 572(8)	1 174(3)
O(7)	1 844(1)	−2 280(7)	1 896(4)
C(1)	240(2)	−942(10)	1 625(4)
C(2)	200(2)	2 481(10)	794(3)
C(3)	855(2)	−316(9)	724(4)
C(4)	1 039(2)	−897(9)	2 737(4)
C(5)	600(2)	2 596(10)	2 772(4)
C(6)	1 959(2)	2 280(9)	1 695(4)
C(7)	1 772(2)	−807(9)	2 136(4)
C(8)	1 121(2)	4 104(11)	435(4)
C(11)	2 040(2)	795(9)	4 121(4)
C(12)	2 318(2)	1 863(11)	3 831(4)
C(13)	2 165(2)	3 712(10)	3 654(4)
C(14)	1 786(2)	3 843(10)	3 857(4)
C(15)	1 713(2)	2 027(12)	4 156(4)

TABLE 8

Fractional atomic co-ordinates (× 10^5 for W and S; × 10^4 for F, O, and C) for (5)

Atom	*x*	*y*	*z*
W(1)	17 007(5)	35 301(3)	44 646(2)
W(2)	6 810(4)	11 140(3)	30 203(2)
S	1 844(31)	21 274(18)	40 148(16)
F(1)	3 547(22)	−186(10)	4 461(11)
F(2)	2 111(18)	−1 359(8)	4 202(10)
F(3)	3 756(14)	−812(9)	3 484(8)
F(4)	−2 006(33)	−743(24)	4 154(11)
F(5)	−1 170(26)	−1 431(12)	3 399(18)
F(6)	−2 643(26)	−554(19)	3 082(21)
O(1)	3 209(12)	5 322(6)	5 110(5)
O(2)	−391(12)	3 434(7)	5 998(6)
O(3)	4 506(12)	2 378(9)	5 263(6)
O(4)	3 924(17)	3 570(9)	2 994(8)
O(5)	−759(16)	4 686(8)	3 455(7)
O(6)	4 455(10)	1 357(9)	3 216(8)
C(1)	2 743(14)	4 671(9)	4 883(7)
C(2)	366(15)	3 472(7)	5 438(7)
C(3)	3 475(14)	2 772(8)	4 989(7)
C(4)	3 108(22)	3 578(8)	3 504(8)
C(5)	64(16)	4 275(9)	3 846(7)
C(6)	3 097(17)	1 325(10)	3 190(9)
C(7)	−2 000(13)	2 351(10)	4 062(8)
C(8)	2 645(18)	−569(10)	3 978(9)
C(9)	1 376(15)	−25(7)	3 614(7)
C(10)	−175(13)	−55(8)	3 439(6)
C(11)	−1 477(20)	−688(10)	3 513(10)
C(12)	−1 590(16)	1 425(12)	2 171(8)
C(13)	−663(16)	747(10)	1 851(7)
C(14)	874(21)	1 105(10)	1 713(8)
C(15)	918(21)	2 002(11)	1 914(9)
C(16)	−620(20)	2 223(11)	2 211(8)

The structures were solved by the heavy-atom method and refined by difference-Fourier and full-matrix least-squares techniques [$w^{-1} = \sigma^2 + (0.02|F|)^2$ where σ is derived from counting statistics]. The final agreement indices were in accord with the internal consistency of the data as judged by the *R* factors for merging equivalent reflections (Table 5). Mean $w\Delta^2$ showed little variation with sinθ or $|F_o|$. In the final difference syntheses maximum $|\Delta\rho|$ values were, for (1a) 2.4 e Å^{-3} round W atoms and 0.7 e Å^{-3} elsewhere, and for (2b) and (5) 1.0 and 1.8 e Å^{-3} respectively. Fractional co-ordinates of the heavier atoms are given in Tables 6—8.* Scattering factors and anomalous dispersion corrections were taken from ref. 20. Hydrogen scattering was allowed for in the final calculations [except for methyl H in (1a)].

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* The anisotropic vibrational parameters and observed and calculated structure factors are available in Supplementary Publication No. SUP 23191 (57 pp.). For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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