

Synthesis and Reactions of Tungsten(II) Norbornadiene (nbd) Complexes. The Crystal and Molecular Structure of $[\text{WBr}(\text{SC}_6\text{F}_5)(\text{CO})_2(\text{nbd})]^\dagger$

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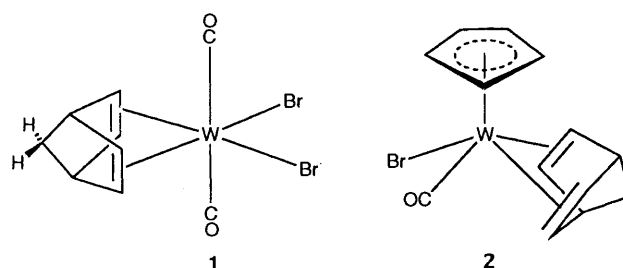
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The reaction of $[\text{WBr}_2(\text{CO})_2(\text{nbd})]$ **1** (nbd = norbornadiene) with $\text{Ti}(\text{C}_5\text{H}_5)$ gave a monocarbonyl derivative $[\text{WBr}(\text{CO})(\text{nbd})(\eta^5\text{-C}_5\text{H}_5)]$ **2**. With $\text{Ti}(\text{O}_2\text{CMe})$ and $\text{Ti}[\text{O}(\text{S})\text{CMe}]$, complex **1** gave monosubstituted derivatives $[\text{WBr}(\text{O}_2\text{CMe})(\text{CO})_2(\text{nbd})]$ **3a** and $[\text{WBr}\{\text{O}(\text{S})\text{CMe}\}(\text{CO})_2(\text{nbd})]$ **3b** which appear to be seven-co-ordinate according to IR data. In contrast **1** and $\text{Ti}(\text{SC}_6\text{F}_5)$ (1 : 1 molar ratio) gave the six-co-ordinate complex $[\text{WBr}(\text{SC}_6\text{F}_5)(\text{CO})_2(\text{nbd})]$ **4**. An X-ray diffraction study of **4** established that it has a distorted-octahedral structure with *trans* W–CO bonds approximately perpendicular to a plane containing the W, Br and S atoms and the midpoints of the nbd C=C bonds. Simple electronic arguments provide a rationalisation of many of the structural features of **4**. Reaction of **1** with 2 molar equivalents of $\text{Ti}(\text{SC}_6\text{F}_5)$ gave the bis(thiolate) derivative $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{nbd})]$ **5** again with a *trans* arrangement of CO ligands. The reactions of **5** with $\text{L} = \text{PEt}_3$, PMe_2Ph or $\text{P}(\text{OMe})_3$ gave the six-co-ordinate complexes $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2\text{L}_2]$ **6** which exist in two isomeric forms, red or green. Dynamic NMR studies have been used to characterise the isomeric behaviour and fluxional processes in the complexes.

An interesting feature of divalent molybdenum and tungsten chemistry is the ability of the metal to form either seven-co-ordinate 18-electron complexes which may be mono- or dinuclear or alternatively co-ordinatively unsaturated six-co-ordinate derivatives with a formal 16-electron configuration.¹ Although steric factors might be expected to play an important role in determining the relative stability of six- and seven-co-ordinate derivatives, electronic factors may also be important. For example, formally electron-deficient six-co-ordinate complexes could, in principle, be stabilised by π donation from certain anionic ligands, *e.g.* halides or oxygen-donor ligands. Previously we reported evidence for sulfur→metal π donation in complexes $[\text{M}(\text{SC}_6\text{F}_5)(\text{CO})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ² and decided to attempt synthesis of SC_6F_5 complexes of W^{II} by replacement of bromide ligands in the six-co-ordinate complex $[\text{WBr}_2(\text{CO})_2(\text{nbd})]$ (nbd = norbornadiene) **1** we reported previously.³ We now report the results of these studies in addition to details of other bromide-substitution reactions. During the course of this work syntheses of molybdenum and tungsten thiolate complexes were reported^{4,5} which provide an interesting comparison with our work.

Results and Discussion

The reaction of complex **1** with $\text{Ti}(\text{C}_5\text{H}_5)$ was carried out in an attempt to isolate a σ - or η^3 - C_5H_5 derivative. However, loss of one molecule of carbon monoxide occurs readily in diethyl ether since the red crystalline product **2** has the stoichiometry $[\text{WBr}(\text{CO})(\text{nbd})(\text{C}_5\text{H}_5)]$ according to mass spectroscopy ($m/z = 449$, M^+). However, attempts to obtain completely satisfactory data for carbon were unsuccessful (calc. 34.8, found 33.5%) despite the fact that hydrogen analysis was acceptable and the complex was recrystallised several times. The ¹H NMR spectrum showed no trace of impurities and is also



consistent with the above stoichiometry showing a $\eta^5\text{-C}_5\text{H}_5$ singlet and five norbornadiene resonances, integrated ratio 2:2:1:1:2. The IR spectrum as expected shows one $\nu(\text{CO})$ mode at 1928 cm^{-1} . Interestingly, attempts to isolate complexes of this type from the reaction of $[\text{MCl}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$ or W) with norbornadiene were unsuccessful,⁶ although butadiene (C_4H_6), $[\text{Mo}(\text{CO})_2(\text{C}_4\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)]^+$, $[\text{MCl}(\text{CO})(\text{C}_4\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$ or W) and $[\text{MoMe}(\text{CO})(\text{C}_4\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)]$ ⁷ and duroquinone (2,3,5,6-tetramethylcyclohexa-2,5-diene-1,4-dione) complexes $[\text{MoCl}(\text{CO})(\text{C}_6\text{Me}_4\text{O}_2)(\eta^5\text{-C}_5\text{H}_5)]$ ⁸ are known. The structure of **2** is presumably related to the latter with η^4 co-ordination of the norbornadiene ligand resulting in an 18-electron configuration at the metal. Significantly we note that the ¹H NMR data are incompatible with η^2 co-ordination since the alkene CH proton signals appear in the region δ 3.6–4.7 consistent with approach to sp^3 hybridisation as expected for co-ordinated alkene carbons.

The reaction of $[\text{WBr}_2(\text{CO})_2(\text{nbd})]$ **1** with 1 molar equivalent of the thallium(I) derivatives $\text{Ti}(\text{O}_2\text{CMe})$ and $\text{Ti}[\text{O}(\text{S})\text{CMe}]$ affords brown or yellow complexes which analyse as monosubstituted derivatives $[\text{WBr}(\text{O}_2\text{CMe})(\text{CO})_2(\text{nbd})]$ **3a** and $[\text{WBr}\{\text{O}(\text{S})\text{CMe}\}(\text{CO})_2(\text{nbd})]$ **3b**. Interestingly, monosubstituted complexes were obtained even when an excess of thallium salt was used. In contrast $[\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2]$ has been found to react with $\text{Na}[\text{O}(\text{S})\text{CR}]$ ($\text{R} = \text{Me}$ or Ph) to give successively $[\text{MoBr}\{\text{O}(\text{S})\text{CR}\}(\text{CO})_2(\text{PPh}_3)_2]$ and

[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

[Mo{O(S)CR}₂(CO)₂(PPh₃)₂].⁹ The spectroscopic properties of **3a** and **3b** are unexpectedly simple with one very weak and one very strong band in the ν(CO) region in the IR spectra somewhat similar to the behaviour of precursor **1**.³ The CO ligands in **3** presumably have an approximately *trans* configuration with a OC–W–CO angle slightly less than 180° (*cf.* **1**). The ¹H NMR spectra are also very simple, each giving one methyl resonance in addition to three norbornadiene peaks at room temperature, integrated ratio 2:1:1. The bridgehead CH₂ appears as a pseudo-quartet, *i.e.* two doublets with second-order distortion. At lower temperatures the peak due to the four equivalent hydrogens shows distinct asymmetry but does not split into clearly resolved separate peaks, even at –80 °C. This would appear to indicate a high-symmetry structure possibly similar to that of complex **1**. However, other spectral data suggest otherwise. In principle, six- or seven-co-ordinate structures are possible for these complexes depending on whether the O₂CMe and O(S)CMe ligands are mono- or bi-dentate. Aforementioned molybdenum derivatives [MoBr{O(X)CMe}(CO)₂(PPh₃)₂] (X = O or S) have been assigned seven-co-ordinate structures on the basis of infrared spectroscopic studies.⁹ The difference (Δ) between ν_{asym}(CO₂) and ν_{sym}(CO₂) is considered to be useful in distinguishing between mono- and bi-dentate carboxylate ligands.¹⁰ If Δ is similar to or smaller than that for Na(CO₂R) then bidentate behaviour can be assumed. In the case of **3a** ν(CO₂) modes were observed at 1490 cm⁻¹ and 1538 cm⁻¹, *i.e.* Δ = 48 cm⁻¹, thus indicating a chelate structure and therefore seven-co-ordination. We assume that **3b** has a similar structure in view of the comparable spectroscopic properties. This is consistent with the presence of a ν(CO) mode at 1470 cm⁻¹ which compares with 1480 cm⁻¹ for the seven-co-ordinate complex [MoBr{O(S)CPh}(CO)₂(PPh₃)₂].⁹

Different isomeric forms are possible for seven-co-ordinate structures but the limited data available do not allow us to comment further. Unfortunately, attempts to obtain suitable crystals for X-ray diffraction studies were unsuccessful. However, we note that seven-co-ordinate structures are frequently fluxional, in many cases with very low energy barriers to rearrangement.¹ This explains the ¹H NMR data where exchange processes may be responsible for the simple appearance of the spectra. Alternatively this may arise from the accidental degeneracy of two or more resonances and studies currently in progress on related derivatives will hopefully resolve this matter.

The reaction of [WBr₂(CO)₂(nbd)] **1** with 1 molar equivalent of Ti(SC₆F₅)₃ in dichloromethane affords a brown crystalline complex which analyses as the monosubstituted derivative [WBr(SC₆F₅)(CO)₂(nbd)] **4**. The IR spectrum of **4** shows two ν(CO) modes, a very weak band near 2050 cm⁻¹ and a strong mode near 1975 cm⁻¹ which compares closely with the spectrum of the dibromo precursor **1**. X-Ray diffraction studies of **1** have established a structure which is basically octahedral with *trans* carbonyl and *cis* bromine ligands.¹¹ The octahedron is distorted with a OC–W–CO angle of 172.9(4)°. Consequently the strong asymmetric stretch of the *trans* CO ligands is accompanied by a weak, high-frequency symmetric stretch activated by the structural distortion. A similar structure is therefore possible for **4** in which the octahedron is distorted as a result of the d⁴ configuration of the metal.¹² The *trans* arrangement of the CO groups is in contrast with the *trans, cis* geometry of [Mo(SBu⁺)(CO)₂(bipy)]⁵ (bipy = 2,2'-bipyridine) and [Mo(OBu⁺)₂(CO)₂(py)₂]¹³ (py = pyridine) where the *cis* carbonyls give rise to two strong bands at significantly lower frequencies. *trans*-Thiolate ligands have also been found in [Mo(SBu⁺)₂(dppe)]¹⁴ whereas a *cis* arrangement of anionic ligands has been established in [Mo(SBu⁺)₂(CNBu⁺)₄]¹⁵ and [MoH(SR)(dppe)]₂ (R = C₆H₄Pr⁺₃-2,4,6; dppe = Ph₂PCH₂CH₂PPh₂)¹⁶ by X-ray diffraction studies.

Although a distorted-octahedral structure seems reasonable for complex **4**, the fact that complexes **3** appear to be seven-co-ordinate raised the possibility that a seven-co-ordinate dimeric

structure with bridging thiolates was also possible. Consequently X-ray diffraction studies of the complex were carried out. These established a monomeric, six-co-ordinate structure for complex **4** (see Fig. 1 and Table 1). Moreover, there is virtually no change in the highly distorted octahedral coordination of the metal atom in [WBr₂(CO)₂(nbd)] **1** when a bromine atom is replaced by a pentafluorobenzenethiolato ligand. Thus, in **4** the carbonyl ligands are *trans* [C(7)–W–C(8) 172.7(8)° and C(nbd1) and C(nbd2), the midpoints of the nbd double bonds C(11)–C(12) and C(14)–C(15), together with the atoms W, Br and S are coplanar to within ±0.04 Å. Within this plane the deviations of the angles subtended at tungsten from ideal values of 90 or 180° [note especially Br–W–S 108.2(2), C(nbd1)–W–C(nbd2) 64, Br–W–C(nbd1) 155 and S–W–C(nbd2) 160°] are both substantial and nearly identical to corresponding angles in **1**.¹¹

The W–Br bond length in complex **4** [2.521(3) Å], though longer than the corresponding distances in **1** [2.489(1) and 2.493(1) Å],¹¹ is still relatively short compared with values of 2.559(4)–2.571(4) Å found in [WBr₂(CO)₂(PPh₃)₂] where the W atom adopts a non-octahedral co-ordination,^{11,17} of 2.640(1) Å in [WBr(S₂CNMe₂)(CO)(nbd)(PMe₂Ph)] where the W atom is seven-co-ordinate,¹⁸ and with 2.619 Å, an average W–Br distance derived from the Cambridge Structural

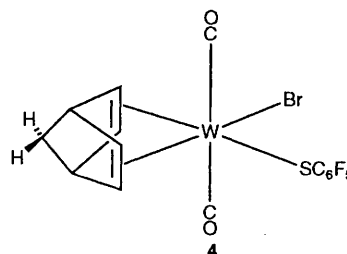


Table 1 Selected bond lengths (Å), angles and torsion angles (°) in [WBr(SC₆F₅)(CO)₂(nbd)] **4**

W–Br	2.521(3)	W–S	2.322(5)
W–C(7)	2.040(18)	W–C(8)	1.975(19)
W–C(11)	2.233(21)	W–C(12)	2.279(19)
W–C(14)	2.397(18)	W–C(15)	2.380(17)
W–C(nbd1)	2.148	W–C(nbd2)	2.282
S–C(1)	1.774(17)	O(1)–C(7)	1.138(21)
O(2)–C(8)	1.167(23)	C(9)–C(10)	1.574(29)
C(9)–C(13)	1.510(32)	C(10)–C(11)	1.551(26)
C(10)–C(15)	1.494(28)	C(11)–C(12)	1.382(27)
C(12)–C(13)	1.520(26)	C(13)–C(14)	1.489(28)
C(14)–C(15)	1.408(26)		
Br–W–S	108.2(2)	Br–W–C(7)	85.1(6)
Br–W–C(8)	89.6(6)	Br–W–C(nbd1)	155.2
Br–W–C(nbd2)	91.5	S–W–C(7)	91.8(5)
S–W–C(8)	85.2(5)	S–W–C(nbd1)	96.6
S–W–C(nbd2)	160.1	C(7)–W–C(8)	172.7(8)
C(7)–W–C(nbd1)	94.3	C(7)–W–C(nbd2)	92.5
C(8)–W–C(nbd1)	92.7	C(8)–W–C(nbd2)	92.6
C(nbd1)–W–C(nbd2)	63.7	W–S–C(1)	110.6(6)
S–C(1)–C(2)	123.0(12)	S–C(1)–C(6)	121.2(15)
C(2)–C(1)–C(6)	115.8(16)	W–C(7)–O(1)	176.5(16)
W–C(8)–O(2)	174.8(16)	C(10)–C(9)–C(13)	92.5(16)
C(9)–C(10)–C(11)	101.3(15)	C(9)–C(10)–C(15)	100.3(16)
C(11)–C(10)–C(15)	100.9(16)	C(10)–C(11)–C(12)	103.8(15)
C(11)–C(12)–C(13)	108.1(16)	C(9)–C(13)–C(12)	101.0(17)
C(9)–C(13)–C(14)	102.6(17)	C(12)–C(13)–C(14)	101.8(15)
C(13)–C(14)–C(15)	105.3(17)	C(10)–C(15)–C(14)	106.5(15)
Torsion angles			
Br–W–S–C(1)	–87.4(7)	W–S–C(1)–C(2)	–84.7(15)
C(7)–W–S–C(1)	–2.0(8)	W–S–C(1)–C(6)	94.9(15)
C(8)–W–S–C(1)	–175.4(8)		

C(nbd1) and C(nbd2) are the midpoints of the C(11)–C(12) and C(14)–C(15) bonds.

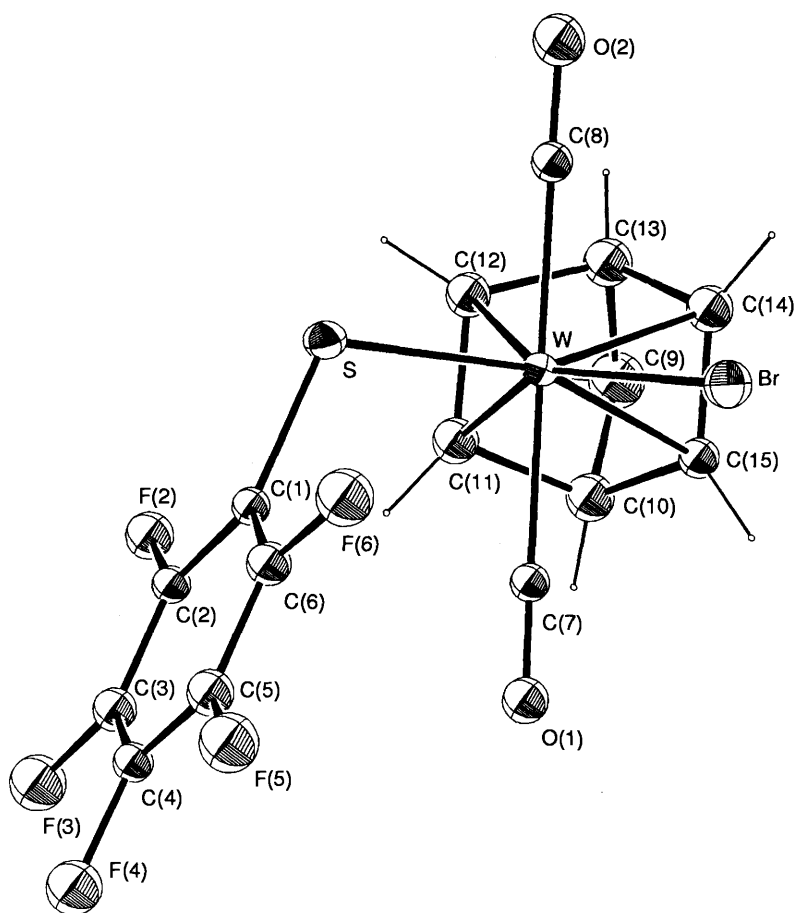


Fig. 1 A view of a molecule of $[\text{WBr}(\text{SC}_6\text{F}_5)(\text{CO})_2(\text{nbd})]$ **4** showing 20% vibrational ellipsoids except for hydrogen atoms which are represented by spheres of arbitrary size

Database.¹⁹ A survey of W–Br distances in 37 structures containing Br bonded to six-co-ordinate W confirms that the great majority are longer than that in **4**.²⁰ In contrast the W–CO distances in **4** [1.98(2) and 2.04(2) Å], like those in **1** [2.03(1) and 2.05(1) Å], seem relatively long: a mean value of 1.936 Å has been derived for such distances¹⁹ and values of 1.92(3)–1.974(7) Å have been found in $[\text{WBr}_2(\text{CO})_2(\text{PPh}_3)_2]$,^{11,17} $[\text{WBr}(\text{S}_2\text{CNMe}_2)(\text{CO})(\text{nbd})(\text{PMe}_2\text{Ph})]$ ¹⁸ and $[\text{W}(\text{SC}_6\text{H}_2\text{Pr}^i_{3-2,4,6})_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$.⁴ In the last compound the tungsten co-ordination is trigonal prismatic and this may partly explain why the W–S(thiolate) bond lengths [2.460(2) and 2.395(2) Å] are so much longer than the corresponding distance of 2.322(5) Å in **4**. However, we consider that strong S→W π donation is the major reason for the shortness of the W–S bond in **4**. We have previously rationalised variations in W^{IV} –S(thiolate) bond lengths in a similar way.²¹

The most notable structural difference between complexes **1** and **4** lies in the asymmetry shown by the W–C(nbd) distances in the latter. The W–C(11) and W–C(12) bond lengths [2.23(2) and 2.28(2) Å] are comparable with values in other $\text{W}^{\text{II}}(\text{nbd})$ complexes {e.g. 2.26(1)–2.30(1) Å in **1** and 2.266(5)–2.324(5) Å in $[\text{WBr}(\text{S}_2\text{CNMe}_2)(\text{CO})(\text{nbd})(\text{PMe}_2\text{Ph})]$ ^{11,18}} whereas the W–C(14) and W–C(15) bond lengths [2.40(2) and 2.38(2) Å] are much longer, implying that the thiolate ligand exerts a greater *trans* influence than does bromide.

Most of the significant structural features of complex **4** can be accounted for by an extension of the arguments advanced by Cotton and Meadows¹¹ to explain the bonding in **1**. In this approach the distortions from octahedral co-ordination are ignored in considering the d-orbital splitting of the tungsten(II) ion which is assigned a $d_{xz}^2d_{yz}^2d_{xy}^0$ configuration [x , y and z axes in **4** being taken approximately parallel to the W–Br, W–S and C(7) vectors]. Thereby all four metal d electrons are

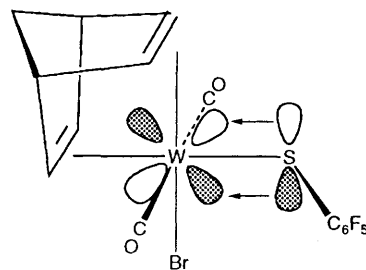


Fig. 2 Orbital overlap in $[\text{WBr}(\text{SC}_6\text{F}_5)(\text{CO})_2(\text{nbd})]$ **4** showing π donation from sulfur to tungsten

available for donation into π -acceptor carbonyl and nbd orbitals. The empty d_{xy} orbital is thus freed for π donation from S and Br. The structure of **4** is best understood if S→W π donation predominates (see Fig. 2). The C(7)–W–S–C(1) and W–S–C(1)–C(2) torsion angles of $-2.0(8)$ and $-85(2)^\circ$ indicate, on the supposition of sulfur sp^2 hybridisation, that the filled sulfur p-orbital is aligned in the xy plane. It is thus able to make a maximum overlap with the W d_{xy} acceptor orbital whereas it is virtually normal to, and hence unable to interact with, the C_6F_5 π system. The orientation of the thiolate ligand with respect to the metal, the shortness of the W–S bond and the slightly greater length of the W–Br bond in **4** compared with **1** are all consistent with this bonding scheme. Furthermore, the high *trans* influence of the thiolate ligand in **4** can be explained by a simple electrostatic argument: the W–C(nbd1) and W–C(nbd2) σ -donor bonds are respectively perpendicular and parallel to the direction of S→W charge transfer which should therefore exert a greater weakening effect on W–C(nbd2).

The variable-temperature ^1H and ^{19}F NMR spectra of

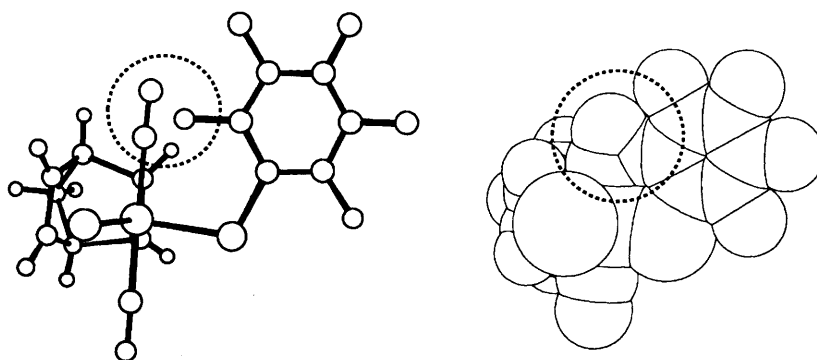
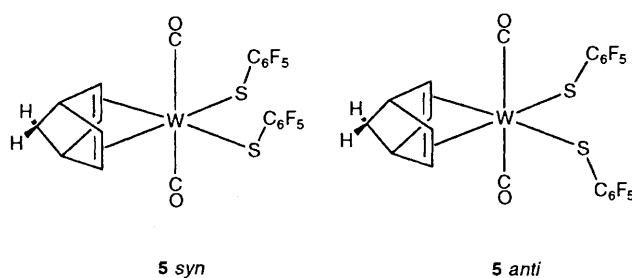


Fig. 3 Space-filling and ball-and-stick diagrams of $[\text{WBr}(\text{SC}_6\text{F}_5)(\text{CO})_2(\text{nb})]$ **4** showing interaction of a C_6F_5 *o*-fluorine with the CO ligand (circled)

complex **4** can be interpreted in terms of the structure found in the solid state. Below -20°C (CDCl_3) the ^1H spectrum shows six equal intensity resonances at δ 3.5–4.7 and a bridgehead CH_2 peak at δ 0.98. In theory the latter should be split due to inequivalence of the two protons but we assume their distance from the Br and SC_6F_5 ligands results in a single peak. As the temperature is raised the bridgehead CH_2 peak shows little change but the other six broaden (*ca.* 10°C) and collapse to give three broad resonances integrated 1:1:1 at *ca.* 35°C . In deuteriated toluene a total of four well resolved peaks are observed at $+65^\circ\text{C}$. These data are consistent with structure **4** which is rigid at low temperatures and where the $\text{C}_6\text{F}_5\text{S}$ ligand adopts a particular orientation with respect to the rest of the molecule, presumably that observed in the solid state. We have observed this previously in pseudo-six-co-ordinate perfluorothioloate derivatives of Mo^{II} and W^{II} , $[\text{M}(\text{SR})(\text{CO})(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$ or W , $\text{R} = \text{CF}_3$ or C_6F_5) where two isomers are observed at low temperature in the ^{19}F NMR spectra due to restricted rotation about the $\text{M}-\text{SR}$ bond.² We also note that the $\text{SC}_6\text{H}_2\text{Pr}^1_{3-2,4,6}$ ligand in the related complex $[\text{MoH}(\text{SC}_6\text{H}_2\text{Pr}^1_{3-2,4,6})(\text{dppe})_2]$ ¹⁶ adopts a comparable orientation to that of the SC_6F_5 group in **4** by lying parallel to the MoPSP plane. At higher temperatures rotation about the $\text{W}-\text{SC}_6\text{F}_5$ bond in **4** will result in equivalence of three sets of hydrogens leading to three non-bridgehead peaks in the ^1H NMR spectra, as is observed.

The ^{19}F NMR spectrum of complex **4** is also temperature dependent, the most definitive information being obtained from the *o*-fluorine region near δ -130 . At room temperature (CD_2Cl_2) a sharp multiplet is observed but below -40°C this broadens and splits into two broad peaks at -90°C . The *m*-fluorine resonance is also broad at this temperature whereas the *para* resonance remains sharp throughout this temperature range. This is also consistent with the existence of one C_6F_5 environment in addition to which a preferred C_6F_5 orientation also appears to be adopted at low temperatures as a consequence of a barrier to rotation about the $\text{C}_6\text{F}_5\text{-S}$ bond. We have observed this previously in $[\text{M}(\text{SC}_6\text{F}_5)\text{O}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$ or W) where steric interactions were held to be responsible.² As with the latter case, molecular graphics studies²² of **4** revealed steric interactions between the C_6F_5 *o*-fluorines and the adjacent CO ligand as the former is allowed to rotate about the $\text{S}-\text{C}_6\text{F}_5$ bond (see Fig. 3). Not surprisingly these are at their greatest when the C_6F_5 group is rotated by *ca.* 90° relative to the position found in the solid state. The preferred orientation is presumably that observed in the solid state which would account for the separate environments observed for the five fluorines of the C_6F_5 ring at low temperatures.

The bis(thiolato) complex $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{nb})]$ **5**, obtained from **1** with 2 molar equivalents of $\text{Ti}(\text{SC}_6\text{F}_5)_3$, forms dark red crystals which are soluble in polar organic solvents such as acetone and dichloromethane. The IR spectrum is



almost identical to those of **1** and **4** showing a weak $\nu(\text{CO})$ mode at 2040 cm^{-1} accompanied by a strong band at 1969 cm^{-1} , again indicating a *trans* disposition of CO ligands with a non-linear $\text{OC}-\text{W}-\text{CO}$ arrangement. This dictates a *cis* arrangement of the thiolato ligands which interestingly contrasts with the *trans* structure revealed by X-ray diffraction studies of the related complexes $[\text{Mo}(\text{SBU}^t)_2(\text{dppe})]$ ¹⁴ and $[\text{Mo}(\text{SC}_6\text{H}_3\text{Ph}_2-2,6)_2(\text{CO})_2(\text{bipy})]$.²³

The ^1H and ^{19}F NMR spectra of complex **5** are temperature dependent, again indicating restricted rotation about the $\text{C}_6\text{F}_5\text{-S}$ and $\text{C}_6\text{F}_5\text{S}-\text{W}$ bonds. However, the situation is also complicated by isomerism as will now be described. If we assume the existence of sulfur-metal π donation as described earlier for **4** (Fig. 2) it is clear that two isomers are possible, the *syn* and *anti* forms. The ^1H and ^{19}F NMR spectra provide evidence for both forms at low temperature but free rotation about the $\text{W}-\text{SC}_6\text{F}_5$ bonds results in isomer exchange at higher temperatures. At 20°C (CD_2Cl_2) the ^1H NMR spectrum exhibits the three norbornadiene NMR signals, integrated 4:2:2, expected for such a structure. At lower temperatures the two non-bridgehead signals broaden and split into five separate peaks, one of which is composed of overlapping multiplets (Fig. 4). Detailed analysis of these peaks, in particular their integrated intensities, indicates that two isomeric forms are present, ratio 3:4; the *syn* gives rise to four non-bridgehead resonances ratio 2:2:1:1 and the *anti* isomer to three of equal intensity. The ^{19}F NMR spectrum (CD_2Cl_2) accordingly shows one C_6F_5 environment at 20°C but two, ratio 3:4 (one *anti* and one *syn*), at -70°C . Subsequent broadening and splitting of the *o*-fluorine peaks at lower temperatures reveals evidence for restricted rotation about the $\text{C}_6\text{F}_5\text{-S}$ bonds in both isomers. In contrast distinct peaks due to the *syn* and *anti* forms of the related complex *cis*- $[\text{Mo}(\text{SBU}^t)_2(\text{CNBu}^t)_4]$ could not be detected in the ^1H and ^{13}C NMR spectra as low as -100°C ¹⁴ suggesting a much lower barrier to exchange compared with **5**.

Previously we have observed that $[\text{WBr}_2(\text{CO})_2(\text{diene})]$ react with an excess of ligand L to give $[\text{WBr}_2(\text{CO})\text{L}_2(\text{diene})]$ [diene = nbd, L = PMe_2Ph or $\text{P}(\text{OMe})_3$] whereas with diene = cycloocta-1,5-diene or cyclooctatetraene substitution occurs to give seven-co-ordinate complexes $[\text{WBr}_2(\text{CO})_2\text{L}_3]$ [L = CNBu^t , $\text{P}(\text{OMe})_3$ or PMe_2Ph].³ Accordingly reactions of

$[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{nbd})]$ with PEt_3 , PMe_2Ph or $\text{P}(\text{OMe})_3$ were carried out. Complex **5** reacts smoothly with an excess of phosphine in diethyl ether or dichloromethane at room temperature to give green ($\text{L} = \text{PEt}_3$ or PMe_2Ph) or red ($\text{L} = \text{P}(\text{OMe})_3$) solutions from which the dicarbonyl complexes $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2\text{L}_2]$ ($\text{L} = \text{PEt}_3$ **6a**, PMe_2Ph **6b** or $\text{P}(\text{OMe})_3$ **6c**) were isolated. The green and red complexes **6a** and **6c** appear to be relatively stable in solution, whereas the green form of the PMe_2Ph complex **6b** appears to rearrange in solution to give a mixture of red and green forms after *ca.* 30 min according to NMR studies.

These results are similar to those reported for related thiolate complexes $[\text{M}(\text{SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ ($\text{M} = \text{Mo}$ or W , $\text{R} = \text{Me}$ or Pr^i) which also exist in red and/or green isomeric forms.⁴ X-Ray diffraction studies of the red complexes $[\text{M}(\text{SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ ($\text{M} = \text{Mo}$ or W) revealed an unusual distorted trigonal-prismatic structure **7a** with one $\text{SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6}$, one PMe_2Ph and one CO ligand occupying each triangular face. However, NMR data indicate that the structure is closer to octahedral in solution, possibly with the *cis*, *trans*, *cis* structure **7b**. The red-brown bipyridyl complex $[\text{Mo}(\text{SCMe}_3)_2(\text{CO})_2(\text{bipy})]$ has also been assigned a *trans*, *cis*, *cis* octahedral structure on the basis of spectroscopic

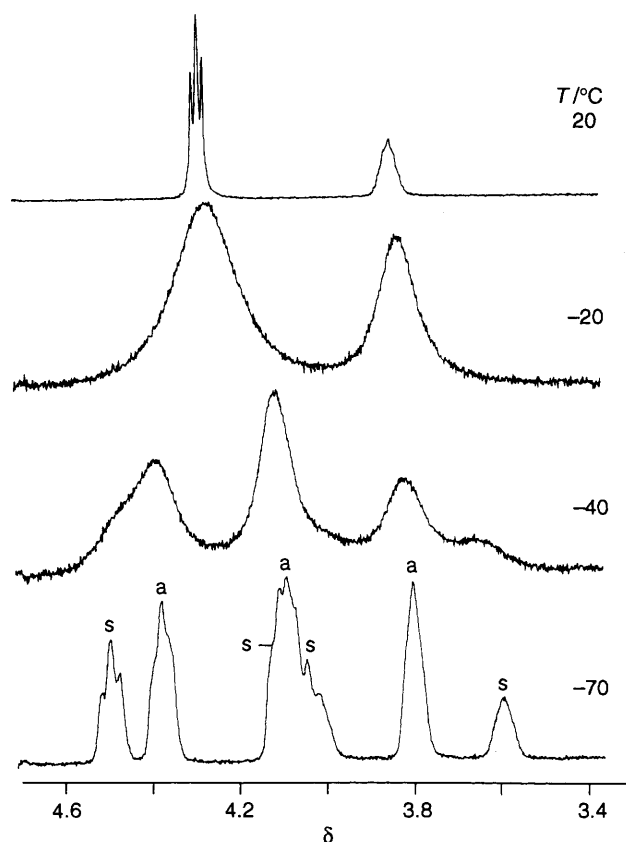
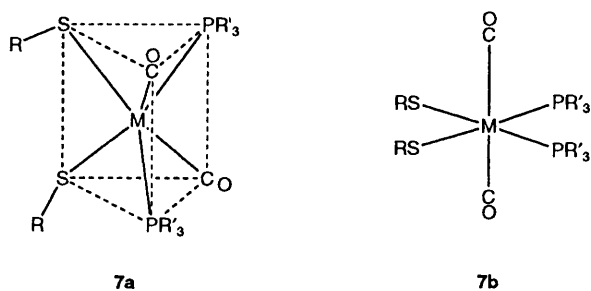


Fig. 4 Variable-temperature ^1H NMR spectra of $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{nbd})]$ **5** in CD_2Cl_2 (*s* = *syn*, *a* = *anti*)



data.⁵ Related six-co-ordinate thiolate complexes $[\text{Ru}(\text{SR})_2(\text{CO})_2(\text{PR}'_3)_2]$ ²⁴ and $[\text{Os}(\text{SR})_2(\text{CO})_2(\text{PR}'_3)_2]$ ²⁵ are known which have been assigned octahedral geometries.

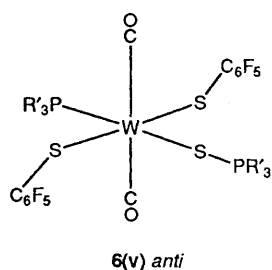
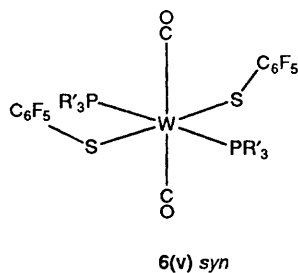
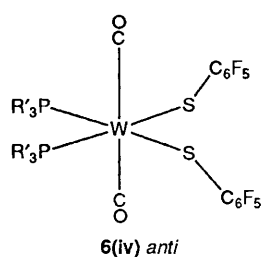
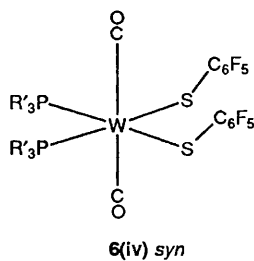
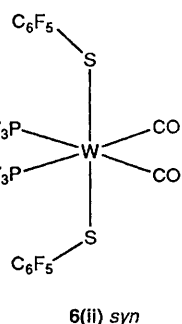
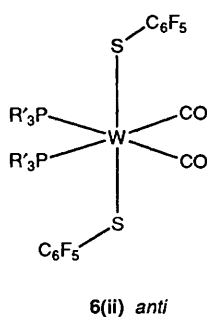
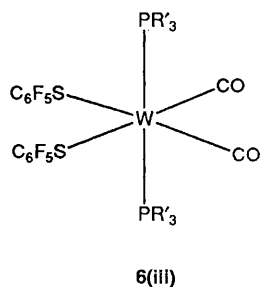
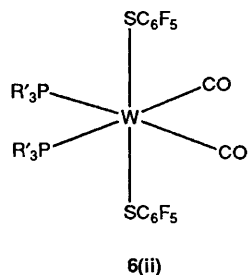
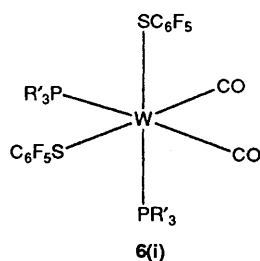
It seems reasonable to assign a similar solid-state structure **7a** to **6c** and the red form of **6b** in view of the similar colour and stoichiometry to the red complexes $[\text{M}(\text{SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$. However, in solution the spectroscopic data are more consistent with an octahedral geometry and a *cis* OC–W–CO arrangement. For example, the solution IR spectrum of $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ **6c** shows a medium and a strong $\nu(\text{CO})$ band at 1978 and 1905 cm^{-1} . This compares with 1940 and 1867 cm^{-1} for **6b** and 1921 and 1830 cm^{-1} for $[\text{W}(\text{SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$. These differences presumably reflect differences in the donor properties of the thiolate ligands and the phosphorus-donor ligands. Exceptionally low $\nu(\text{CO})$ values (1908, 1768 cm^{-1}) found with $[\text{Mo}(\text{O}i\text{Bu})_2(\text{CO})_2(\text{py})_2]$ have been interpreted in terms of significant π donation by the alkoxide ligands to the metal.¹³

Based on a distorted-octahedral geometry, three forms with *cis* carbonyls are possible, **6(i)**, **6(ii)** and **6(iii)**. Two of these have been identified in the solid state previously, **6(ii)** in the aforementioned *trans*, *cis*, *cis*- $[\text{Mo}(\text{O}i\text{Bu})_2(\text{CO})_2(\text{py})_2]$ ¹³ and **6(iii)** in *cis*, *cis*, *trans*- $[\text{MoBr}_2(\text{CO})_2(\text{PPh}_3)_2]$.²⁶ Moreover isomeric forms of all three (*syn* and *anti*) are also possible as a consequence of preferred $\text{C}_6\text{F}_5\text{S}$ orientations. However, at room temperature only one set of $\text{P}(\text{OMe})_3$, C_6F_5 and CO signals are observed in ^1H , ^{19}F , ^{31}P and ^{13}C NMR spectra of **6c** thus eliminating the less-symmetric isomer **6(i)**.

The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of complex **6c** shows one $\text{P}(\text{OMe})_3$ methyl peak and a triplet for the carbonyl-carbon resonance $J_{\text{P-C}}$ 73.5 Hz, consistent with either **6(ii)** or **6(iii)** in solution. However, the ^1H NMR spectrum exhibits the distinctive 'filled in doublet' observed for *cis*- $\text{P}(\text{OMe})_3$ methyls when intermediate values of $J_{\text{P-P}}$ are present indicating that **6(ii)** is the preferred isomeric form.²⁷ The ^{19}F NMR spectrum also shows one set of C_6F_5 resonances at room temperature but these broaden at lower temperatures and separate into two sets of peaks, integrated 2:1, at -60°C in CD_2Cl_2 . It appears that two isomers exist at this temperature, the minor one with equivalent C_6F_5 groups, **6(ii)** *syn* and the major species with two C_6F_5 environments, **6(ii)** *anti*. This is supported by the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum where the singlet observed at 20°C splits into one sharp and one broad peak at -60°C . This structural proposal differs from that suggested for red $[\text{W}(\text{SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ where structure **7b** is proposed despite the fact that the IR spectrum indicates *cis* carbonyls.⁴

Possible structures of the green complexes $[\text{M}(\text{SC}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ ($\text{M} = \text{Mo}$ or W) have been discussed in detail by Richards and co-workers⁴ but no clear conclusion could be reached except that in solution inequivalent CO and phosphine ligands appear to be present. Similarly we are unable to propose structures with any degree of certainty for the green complexes **6a** and **6b** isolated in the present work. The triethylphosphine complex **6a** appears to have a non-linear *trans* arrangement of the two CO ligands about the metal centre since the IR spectrum shows one weak and one strong $\nu(\text{CO})$ mode near 1900 cm^{-1} , *cf.* **1**, **4** and **5**. Based on a distorted-octahedral geometry, two isomeric forms with a symmetric arrangement of the SC_6F_5 and PEt_3 are possible *cis*, **6(iv)**, or *trans*, **6(v)**, each of which can have *syn* and *anti* forms. The ^1H and ^{19}F NMR each show one set of ligand resonances indicating that only one of the two possible forms is present in solution. The ^{19}F NMR spectrum however shows additional peaks on cooling to -50°C , perhaps indicating the freezing out of *syn* and *anti* forms at low temperatures. However, these were not sufficiently well resolved for unambiguous conclusions to be reached.

The green isomer of complex **6b** was isolated pure from the reaction mixture with short reaction times but on dissolving in



CD_2Cl_2 readily turns brown and eventually red. Infrared spectra taken in the solid state (Nujol) or immediately in solution (CCl_4) are similar to that of **6a**, but on placing under nitrogen two extra peaks at 1868s and 1938m cm^{-1} similar to those for **6c** are observed suggesting isomerisation to give a mixture of green and red forms. It did not prove possible to obtain NMR spectra of a completely pure form, red or green so that conclusions concerning the structure are not possible. Further studies in this area of chemistry are currently in progress and hopefully these will help clarify this and other unresolved problems.

Experimental

The NMR spectra were recorded on a Bruker WP 200SY

spectrometer at 200.13 (^1H), 188.3 (^{19}F), 81.0 (^{31}P) and 50.32 MHz (^{13}C). Chemical shifts are referenced to SiMe_4 (^1H , δ 0) and CCl_3F (^{19}F , δ 0). Infrared spectra were recorded as solutions on a Perkin Elmer 580 spectrophotometer with polystyrene as reference and mass spectra on a Vacuum Generators updated AEI MS 11 instrument. Reactions were carried out under dry, oxygen-free nitrogen using Schlenk techniques. Solvents were dried by refluxing over P_2O_5 (CH_2Cl_2), calcium hydride (hexane, diethyl ether) and distilled just before use. The complex $[\text{WBr}_2(\text{CO})_2(\text{nbd})]$ was synthesised as described previously.³

Reactions of $[\text{WBr}_2(\text{CO})_2(\text{nbd})]$ 1.—*With $\text{Tl}(\text{C}_5\text{H}_5)$.* A mixture of complex **1** (37 mg) and $\text{Tl}(\text{C}_5\text{H}_5)$ (20 mg) in Et_2O (10 cm^3) was stirred at room temperature for 18 h. The red-brown solution obtained after centrifuging was treated with hexane, concentrated *in vacuo* and cooled to -15°C to give red crystals of $[\text{WBr}(\text{CO})(\text{nbd})(\eta^5\text{-C}_5\text{H}_5)]$ **2** (13 mg, 38%) (Found: C, 33.5; H, 2.75. $\text{C}_{13}\text{H}_{13}\text{BrOW}$ requires C, 34.8; H, 2.9%; $m/z = 449, M^+$). IR (CHCl_3) 1928s cm^{-1} . ^1H NMR (CDCl_3): δ 5.44 (s, 5 H, C_5H_5), 3.60 (br m, 2 H, nbd), 3.49 (m, 2 H, nbd), 3.36 (m, 1 H, nbd), 2.65 (m, 1 H, nbd) and 1.11 (m, 2 H, nbd).

With $\text{Tl}(\text{O}_2\text{CMe})$, 1:2 molar ratio. A mixture of complex **1** (29 mg) and $\text{Tl}(\text{O}_2\text{CMe})$ (30 mg) in CH_2Cl_2 (3 cm^3) was stirred at room temperature for 3 h. The yellow solution obtained on centrifuging the mixture was treated with hexane and concentrated *in vacuo* to give brown crystals of $[\text{WBr}(\text{O}_2\text{CMe})(\text{CO})_2(\text{nbd})]$ **3a** (6 mg, 22%) (Found: C, 27.3; H, 2.4. $\text{C}_{11}\text{H}_{11}\text{BrO}_4\text{W}$ requires C, 28.1; H, 2.4%). IR (CCl_4): $\nu(\text{CO})$ 2056w and 1985s cm^{-1} . ^1H NMR (CDCl_3 , 20 $^\circ\text{C}$): δ 3.81 (br s, 4 H, nbd), 3.30 (br s, 2 H, nbd), 1.87 (s, 3 H, O_2CMe) and 1.14 (pseudo q, 2 H, nbd).

With $\text{Tl}[\text{O}(\text{S})\text{CMe}]$, 1:3 molar ratio. A mixture of complex **1** (57 mg) and $\text{Tl}[\text{O}(\text{S})\text{CMe}]$ (100 mg) in Et_2O (3 cm^3) was stirred at room temperature for 1 min. The yellow solution obtained on centrifuging was treated with hexane and concentrated *in vacuo* to give a yellow microcrystalline solid $[\text{WBr}\{\text{O}(\text{S})\text{CMe}\}(\text{CO})_2(\text{nbd})]$ **3b** (25 mg, 44%) (Found: C, 27.5; H, 2.3. $\text{C}_{11}\text{H}_{11}\text{BrO}_3\text{SW}$ requires C, 27.1; H, 2.3%; $m/z = 459, [M - \text{CO}]^+$). IR (CCl_4): $\nu(\text{CO})$ 2050w and 1982s cm^{-1} . ^1H NMR (CDCl_3): δ 3.85 (br s, 4 H, nbd), 3.24 (br s, 2 H, nbd), 2.09 [br s, 3 H, $\text{O}(\text{S})\text{CMe}]$ and 1.25 (pseudo q, 2 H, nbd).

With $\text{Tl}(\text{SC}_6\text{F}_5)$, 1:1 molar ratio. A mixture of complex **1** (49 mg) and $\text{Tl}(\text{SC}_6\text{F}_5)$ (42 mg) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 10 min. A yellow-brown solution was obtained on centrifuging and on treatment with hexane and concentrating *in vacuo* brown crystals of $[\text{WBr}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{nbd})]$ **4** were obtained (48 mg, 79%) (Found: C, 29.7; H, 1.4; S, 5.1. $\text{C}_{15}\text{H}_8\text{BrF}_5\text{O}_2\text{S}_2\text{W}$ requires C, 29.5; H, 1.3; S, 5.2%; $m/z = 583, [M - \text{CO}]^+$). IR (CCl_4): $\nu(\text{CO})$ 2055m and 1986s cm^{-1} . ^1H NMR (CDCl_3 , -50°C): δ 4.65 (br s, 1 H), 4.51 (br s, 1 H), 4.04 (br s, 1 H), 3.96 (br m, 1 H), 3.80 (br s, 1 H), 3.59 (br m, 1 H) and 0.98 (s, 2 H).

With an excess of $\text{Tl}(\text{SC}_6\text{F}_5)$. A mixture of complex **1** (42 mg) and $\text{Tl}(\text{SC}_6\text{F}_5)$ (81 mg) in CH_2Cl_2 (3 cm^3) was stirred at room temperature for 18 h. The dark red solution obtained on centrifuging was treated with hexane, concentrated *in vacuo* and cooled to -15°C to give red-brown crystals of $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{nbd})]$ **5** (40 mg, 67%) (Found: C, 34.3; H, 1.2. $\text{C}_{21}\text{H}_8\text{F}_{10}\text{O}_2\text{S}_2\text{W}$ requires C, 34.5; H, 1.1%; $m/z = 730, M^+$). IR (CCl_4): $\nu(\text{CO})$ 2040w and 1969s cm^{-1} . NMR (CDCl_3 , 20 $^\circ\text{C}$): δ 4.24 (t, J 2.5 Hz, 4 H), 3.84 (br s, 2 H) and 1.03 (s, 2 H); ^{19}F , δ -134.1 (m, 4F), -155.73 (t, 2F) and -161.86 (m, 4F).

Reactions of $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{nbd})]$ 5.—*With PET_3 .* A solution of complex **5** (50 mg) in CH_2Cl_2 (10 cm^3) was treated with PET_3 (17 mg), when the colour changed from red to green. After 15 min hexane was added and the solution concentrated *in vacuo* to give green crystals of $[\text{W}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{PET}_3)_2]$ **6a** (44 mg, 89%) (Found: C, 35.4; H, 3.6. $\text{C}_{26}\text{H}_{30}\text{F}_{10}\text{O}_2\text{P}_2\text{S}_2\text{W}$ requires C, 35.7; H, 3.5%). IR (CDCl_3): 1974vw and 1866s cm^{-1} . NMR (CD_2Cl_2 , 20 $^\circ\text{C}$): ^1H , δ 1.95, 1.83 (overlapping multiplets,

Table 2 Fractional coordinates for [WBr(SC₆F₅)(CO)₂(nbd)] 4

Atom	x	y	z
W	-0.193 48(7)	0.230 35(6)	-0.241 49(5)
Br	-0.017 43(20)	0.361 28(18)	-0.204 40(17)
S	-0.349 6(4)	0.240 7(4)	-0.109 8(3)
F(2)	-0.393 4(9)	0.019 8(8)	-0.073 0(8)
F(3)	-0.318 0(11)	-0.088 4(10)	0.096 6(9)
F(4)	-0.188 1(11)	-0.004 1(9)	0.262 3(9)
F(5)	-0.129 9(13)	0.193 3(10)	0.256 8(9)
F(6)	-0.200 0(12)	0.302 7(10)	0.087 3(9)
O(1)	-0.005 5(12)	0.092 8(10)	-0.095 5(9)
O(2)	-0.371 4(13)	0.386 3(11)	-0.367 2(10)
C(1)	-0.300 4(16)	0.166 2(14)	0.001 4(12)
C(2)	-0.327 5(16)	0.064 6(14)	0.007 7(12)
C(3)	-0.289 5(17)	0.010 3(15)	0.094 2(14)
C(4)	-0.224 3(16)	0.053 4(15)	0.177 6(13)
C(5)	-0.194 1(18)	0.147 5(16)	0.172 8(15)
C(6)	-0.232 3(17)	0.206 4(15)	0.086 6(13)
C(7)	-0.073 9(16)	0.139 4(14)	-0.149 8(13)
C(8)	-0.304 4(17)	0.331 7(15)	-0.316 6(13)
C(9)	-0.195 8(22)	0.057 1(18)	-0.482 1(17)
C(10)	-0.128 7(19)	0.051 5(16)	-0.367 4(15)
C(11)	-0.248 3(19)	0.076 8(16)	-0.297 1(13)
C(12)	-0.324 3(18)	0.141 8(15)	-0.359 2(14)
C(13)	-0.252 6(19)	0.159 6(16)	-0.462 1(14)
C(14)	-0.133 3(18)	0.217 1(15)	-0.423 8(14)
C(15)	-0.054 9(16)	0.148 5(14)	-0.364 4(13)

12 H, CH₂) and 1.03 (apparent spt, 18 H, CH₃); ¹⁹F, δ -135.8 (m, 4F), 159.23 (t, 2F) and 163.60 (m, 4F).

With PMe₂Ph. A solution of complex **5** (50 mg) in CH₂Cl₂ (10 cm³) was treated with PMe₂Ph (20 mg) when the red colour slowly (10 min) turned green. Hexane (3 cm³) was added, the solution concentrated *in vacuo* and after cooling to -15 °C green crystals of [W(SC₆F₅)₂(CO)₂(PMe₂Ph)₂] **6b** were obtained (48 mg, 87%) (Found: C, 39.1; H, 2.4. C₃₀H₂₂F₁₀O₂P₂S₂W requires C, 39.4; H, 2.4%). IR (CCl₄): ν(CO) 1877s cm⁻¹. NMR (CDCl₃, 20 °C): ¹H, δ 7.6–7.2 (m, 10 H, Ph) and 2.0 (overlapping signals, 12 H, Me); ¹⁹F, δ -133.02 (m, 4F), -159.33 (t, 2F) and -165.20 (m, 4F).

With P(OMe)₃. A solution of complex **5** (40 mg, 0.056 mmol) in CH₂Cl₂ (4 cm³) was treated with P(OMe)₃ (10 mg, 0.08 mmol) in a sealed tube and warmed to 60 °C for 1.5 h. The resulting red solution was filtered, treated with hexane (4 cm³), concentrated *in vacuo* and on cooling to -15 °C orange-red crystals of [W(SC₆F₅)₂(CO)₂{P(OMe)₃}₂] **6c** were obtained (36 mg, 74%) (Found: C, 26.5; H, 1.9. C₂₀H₁₈F₁₀O₈P₂S₂W requires C, 27.1; H, 2.05%). IR (CCl₄): ν(CO) 1978m and 1905s cm⁻¹. NMR: ¹H(CDCl₃, 20 °C), δ 3.70 (filled in doublet, Me); ¹⁹F (CD₂Cl₂, 20 °C), δ -133.02 (m, 4F), -159.33 (t, 2F) and -165.20 (m, 4F); ¹³C-{¹H} (CDCl₃, 26 °C), δ 225.85 (t, J_{P-C} 73.5 Hz, CO), 150–135 (group of multiplets, C₆F₅) and 54.50 (s, Me); ³¹P-{¹H} (CD₃Cl₂, -60 °C), δ 145.2 (s) and 144.7 (br s).

Structure Analysis.—*Crystal data.* C₁₅H₈BrF₅O₂SW, *M* = 611.04, monoclinic, space group *P*2₁/*n*, *a* = 10.040(4), *b* = 13.379(3), *c* = 12.575(3) Å, β = 91.88(3)°, *U* = 1688.2(8) Å³, *Z* = 4, *D*_c = 2.404 g cm⁻³, *F*(000) = 1136, Mo-Kα X-rays, λ = 0.710 69 Å, μ = 95.1 cm⁻¹.

Measurements were made with a plate-shaped crystal of dimensions 0.36 × 0.16 × 0.02 mm mounted on an Enraf-Nonius CAD4 diffractometer. The intensities of 3794 reflections with 2 ≤ θ ≤ 24°, *h* 0–11, *k* -15 to 4 and *l* -14 to 14 were estimated from ω-2θ scans. Lorentz polarisation and empirical absorption corrections²⁸ (correction factors 0.80–1.30) were applied and equivalent reflections then merged (*R*_{int} = 0.063 for 1050 duplicate measurements) to give 2640 unique structure amplitudes of which 1587, with *I* ≥ 3σ(*I*), were used subsequently.

The structure was solved by Patterson and Fourier methods.

The final full-matrix least-squares refinement on *F* of 116 parameters, including anisotropic displacement parameters only for W, Br and S atoms, converged at *R* = 0.052 and *R*' = 0.057 with *w* = 1/σ²(*F*), see Table 2. Hydrogen atoms were placed in stereochemically acceptable positions and constrained to ride on their parent C atoms with C–H 0.96 Å and *U*(H) ≈ 1.2*U*(C). Final Δρ values were between 2.3 and -1.6 e Å⁻³. All calculations were performed with the GX package²⁹ using scattering factors and anomalous dispersion corrections from ref. 30.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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