

Six-co-ordinate 1,2-dithiolene complexes of tungsten(II) of the type $[W(S-S)(CO)_2L_2]$ [$S-S = C_3S_5$, benzene-1,2-dithiolate or maleonitriledithiolate; $L_2 = (PPh_3)_2$, $(PEt_3)_2$ or $Ph_2P(CH_2)_2PPh_2$]

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Reaction of the complexes $[Wl_2(CO)_3L_2]$ [$L_2 = (PEt_3)_2$, $(PPh_3)_2$ or $Ph_2P(CH_2)_2PPh_2 = dppe$] with 1 equivalent of $Na_2[S-S]$ ($S-S = C_3S_5$ or maleonitriledithiolate) or H_2bdt (benzene-1,2-dithiol) in acetonitrile and ethanol at room temperature afforded good yields of the six-co-ordinate compounds $[W(S-S)(CO)_2L_2]$ by displacement of the iodide ligands and a carbonyl ligand. X-Ray crystallographic studies were carried out on $[W(S-S)(CO)_2L_2]$ [$S-S = C_3S_5$, $L_2 = (PEt_3)_2$; $S-S = bdt$, $L_2 = (PEt_3)_2$ or $L_2 = dppe$]. The three structures are all six-co-ordinate with geometries intermediate between octahedral and trigonal prismatic but closer to the latter.

The importance of transition-metal complexes containing dianionic delocalised sulfur-donor chelating ligands, such as $C_3S_5^{2-}$ (4,5-disulfanyl-1,3-dithiole-2-thionate) and *mnt* (*mnt* = maleonitriledithiolate), has increased in recent years. Many examples of solid-state materials derived from these complexes have been shown to conduct electric currents, display unusual magnetic properties and have non-linear optical properties.¹⁻³ Although many examples of square-planar complexes have been described such as β - $[NiMe_4][Pd(C_3S_5)_2]$, which is a superconductor at 2 K,⁴ few examples of organotransition-metal complexes containing C_3S_5 and *mnt* are known. Two early examples are the bis(cyclopentadienyl) complexes $[M(mnt)(cp)_2]$ ($M = Mo$ or W),⁵ and in 1970 Eisenberg⁶ comprehensively reviewed 1,1- and 1,2-dithiolato-chelate complexes, including their organotransition-metal complexes. Several molybdenum complexes containing *cp* or C_5Me_5 and dithiolene ligands have been recently studied including $[Mo(dmit)_2(\eta-C_5Me_5)]$ ⁷ and the charge-transfer salt $[Mo(ddd)(cp)_2][tcnq]$ ⁸ (*ddd* = 5,6-dihydro-1,4-dithiin-2,3-dithiolate, *tcnq* = tetracyanoquinodimethane) which display co-operative low-temperature magnetic phenomena. Other mixed *cp*-dithiolene complexes which have also recently been studied are complexes of Fe ,⁹ Co ,¹⁰ Ti ¹¹ and Ru .¹² Fewer examples exist of complexes containing dithiolene and phosphorus ligands; the adducts $[Co(S_2C_2X_2)(cp)L]$ ¹⁰ ($L =$ tributylphosphine or tributyl phosphite) and the cluster $[Au_{10}(mnt)_2(PPh_3)_7]$ ¹³ being rare examples. The organometallic square-planar platinum complex $[Pt(mnt)(CNMe)_2](NC)_2C_2S_2CNMe$ has recently been shown crystallographically to demonstrate costacking of neutral planar metal and organic molecules.¹⁴

Over the past ten years we have been investigating the chemistry of the highly versatile seven-co-ordinate complexes $[Ml_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W) and their derivatives.¹⁵ Continuing our exploration of the chemistry of these and related complexes, in this paper we describe the reactions of the seven-co-ordinate complexes $[Wl_2(CO)_3L_2]$ [$L_2 = (PEt_3)_2$, $(PPh_3)_2$ or $Ph_2PCH_2CH_2PPh_2$ (*dppe*)] with 1 equivalent of $Na_2[S-S]$ ($S-S = C_3S_5$ or *mnt*) or H_2bdt (*bdt* = benzene-1,2-dithiolate) to give the novel six-co-ordinate complexes $[W(S-S)(CO)_2L_2]$. The molecular structures of $[W(S-S)(CO)_2(PEt_3)_2]$ ($S-S = C_3S_5$ or *bdt*) and $[W(bdt)(CO)_2(dppe)]$ are also described.

Results and Discussion

The starting materials for this research, namely $[Wl_2(CO)_3L_2]$

[$L_2 = (PEt_3)_2$ ¹⁶ $(PPh_3)_2$ ¹⁷ or *dppe*¹⁸] were prepared by treating $[Wl_2(CO)_3(NCMe)_2]$ with 2 equivalents of $L = PEt_3$ or PPh_3 or 1 equivalent of *dppe*. The complexes $[Wl_2(CO)_3L_2]$ react at room temperature with 1 equivalent of $Na_2[S-S]$ ($S-S = C_3S_5$ or *mnt*) or H_2bdt to give good yields of the six-co-ordinate complexes $[W(S-S)(CO)_2L_2]$ **1-9** by the displacement of the iodide ligands and loss of a carbonyl ligand. All the new complexes have been fully characterised by elemental analysis (C, H and N), infrared (Table 1) and ¹H NMR spectroscopy (Table 2); **2**, **3** and **8** were also characterised by ³¹P NMR spectroscopy (Table 2). Complexes **2**, **5** and **6** were also crystallographically characterised. Although the solid-state crystal structure of the complex $[W(bdt)(CO)_2(dppe)]$ **6** occurs as a 0.5CH₂Cl₂ solvate, the bulk material did not show a 0.5CH₂Cl₂ solvate in the ¹H NMR spectrum and repeated elemental analysis agreed with the non-solvate formulation. The FAB mass spectra of the complexes $[W(C_3S_5)(CO)_2L_2]$ [$L_2 = (PEt_3)_2$ or *dppe*] show their molecular ions at *m/z* 672 [$L_2 = (PEt_3)_2$] and 834 [$L_2 = dppe$]. Magnetic susceptibility measurements have shown complexes **1-9** to be diamagnetic. The bis(triethylphosphine) complexes are soluble in diethyl ether and chlorinated solvents, whereas the $(PPh_3)_2$ and *dppe* complexes were considerably less soluble but were soluble in polar chlorinated solvents such as CH₂Cl₂ and CHCl₃. All the complexes were stable when stored under nitrogen, however they decomposed in solution when exposed to air.

The characteristic absorption bands for the dithiolene ligands are present in the infrared spectra; comparison of the bands arising from the C=C and the C-S bonds of the metal-bound dithiolene and the free dithiolene show only a slight change in frequency. The stretching frequency of the C-S bond in the ligated dithiolene is slightly lower than in the free dithiolene, as would be expected when bound in a bidentate manner to a metal complex. It has been observed that the C=C stretching mode in square-planar dithiolene complexes reduces in frequency as the charge on the molecule is decreased consistent with a reduction in bonding electron density at this position. The detection of this band at about 1430 cm⁻¹ for the complexes described here is suggestive of highly negatively charged dithiolene ligands bearing approximately a full double negative charge.¹⁹ The absorption bands in the regions 1937-1961 and 1863-1889 cm⁻¹ correspond to the two *cis*-carbonyl groups attached to the tungsten centre. The capping carbonyl bands observed in the infrared spectra of the tungsten complexes $[Wl_2(CO)_3L_2]$ [$L_2 = (PPh_3)_2$, $(PEt_3)_2$ or *dppe*] at ca. 2000 cm⁻¹ are no longer present. This is supported by the crystal struc-

Table 1 Physical, analytical^a and IR^b data for the complexes [W(S-S)(CO)₂L₂]

Complex	Colour	Yield (%)	Analysis (%)			IR (cm ⁻¹)	
			C	H	N	ν(CO)	ν(CS)
1 [W(C ₃ S ₅)(CO) ₂ (PPh ₃) ₂]	Dark brown	78	50.0 (51.3)	3.4 (3.8)	—	1943 1863	1062
	2 [W(C ₃ S ₅)(CO) ₂ (PEt ₃) ₂]	Brown-black	79	30.4 (30.4)	4.6 (4.5)	—	1950 1879
3 [W(C ₃ S ₅)(CO) ₂ (dppe)]				Dark brown	48	43.6 (44.6)	3.3 (2.9)
	4 [W(bdt)(CO) ₂ (PPh ₃) ₂]	Dark brown	37			57.8 (58.4)	3.9 (3.7)
5 [W(bdt)(CO) ₂ (PEt ₃) ₂]				Brown	50	38.8 (39.0)	5.6 (5.5)
	6 [W(bdt)(CO) ₂ (dppe)]	Dark brown	44			53.3 (52.4)	3.9 (3.6)
7 [W(mnt)(CO) ₂ (PPh ₃) ₂]				Brown	65	55.5 (55.8)	3.7 (3.3)
	8 [W(mnt)(CO) ₂ (PEt ₃) ₂]	Brown-black	70			34.9 (35.1)	5.0 (4.9)
9 [W(mnt)(CO) ₂ (dppe)]				Brown	69	49.2 (49.4)	3.0 (3.1)

^a Calculated values in parentheses. ^b Recorded in CH₂Cl₂ as thin films between NaCl plates.

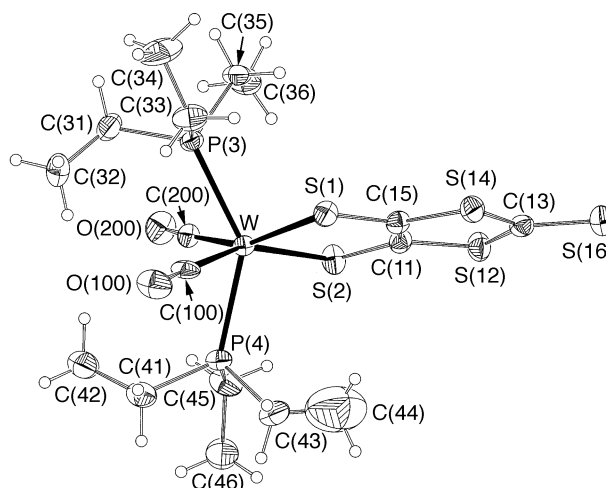
Table 2 Proton and selected ³¹P NMR data * for the complexes [W(S-S)(CO)₂L₂]

Complex	¹ H, δ(J/Hz)	³¹ P, δ(J _{WP} / Hz)
1	7.5 (m, 18 H, <i>m</i> -, <i>p</i> -H of Ph), 7.8 (m, 12 H, <i>o</i> -H of Ph)	—
2	1.1 (dt, 18 H, <i>J</i> _{PH} = 15.4, <i>J</i> _{HH} = 7.7, CH ₃), 1.8 (qnt, 12 H, <i>J</i> _{PH} = <i>J</i> _{HH} = 7.0, CH ₂)	23.0 (s, 87)
3	2.5 (br m, 2 H, CH ₂), 2.7 (br m, 2 H, CH ₂), 7.4 (m, 12 H, <i>m</i> -, <i>p</i> -H of Ph), 7.8 (m, 8 H, <i>o</i> -H of Ph)	32.3 (s, 58)
4	7.5 (m, 18 H, <i>m</i> -, <i>p</i> -H of Ph), 7.7 (m, 16 H, <i>o</i> -H of Ph, bdt)	—
5	1.4 (dt, 18 H, <i>J</i> _{HH} = 11.4, <i>J</i> _{PH} = 5.6, CH ₃), 2.4 (qnt, 12 H, <i>J</i> _{PH} = <i>J</i> _{HH} = 7.1, CH ₂), 7.7 (m, 4 H, bdt)	—
6	2.5 (br m, 4 H, CH ₂), 7.3 (m, 20 H, Ph), 7.7 (m, 4 H, bdt)	—
7	7.4–7.7 (m, Ph)	—
8	1.3 (dt, 18 H, <i>J</i> _{HH} = 11.6, <i>J</i> _{PH} = 5.8, CH ₃), 2.5 (qnt, 12 H, <i>J</i> _{PH} = <i>J</i> _{HH} = 7.1, CH ₂)	28.6 (s, 87)
9	2.4 (br m, 2 H, CH ₂), 2.5 (br m, 2 H, CH ₂), 7.4 (m, 20 H, Ph)	—

* Spectra run in CDCl₃ (+25 °C): s = singlet, br = broad, dt = doublet of triplets, m = multiplet, qnt = quintet.

tures (see Figs. 1–3) which show only the two *cis*-carbonyls to be present in the products **2**, **5** and **6**. The near-infrared spectrum of [W(C₃S₅)(CO)₂(PPh₃)₂] **1** shows two absorption bands at 2325 nm and a broad band at 900–700 nm. The latter band is usually observed for C₃S₅ complexes.

The crystal structures contain discrete molecules of complexes **2**, **5** and **6**, illustrated in Figs. 1, 2 and 3 together with the atomic numbering scheme. The structures of **2** and **5** are very similar, in particular with regard to the geometry of the co-ordination sphere. The two carbonyl groups are mutually *cis* albeit with angles in excess of 90° [106.5(4), 108.2(5) in **2** and 107.0(6)° in **5**] (Table 3) and *trans* to the bidentate C₃S₅ or bdt ligand, though the angles are very much distorted from 180°. This *cis*-arrangement of two carbonyl ligands is usually found in dicarbonyl structures because their strong π acidity makes the *trans* arrangement unfavourable. The two triethylphosphine monodentate ligands are also *trans* to each other though the angles are significantly distorted from linear [142.3(1), 140.2(1) in **2**, 141.1(1) in **5**]. The geometry of the co-ordination sphere can be considered to be intermediate between octahedral and trigonal prismatic, though closer to the latter.

**Fig. 1** Structure of complex **2**. Thermal ellipsoids are drawn at 40% probability. The hydrogen atoms are shown with small arbitrary radii

Distortions in six-co-ordinate dicarbonyl complexes of molybdenum(II) and tungsten(II) have recently been analysed.^{20,21} Apart from the structures only slightly distorted from the ideal forms of octahedron and trigonal prism, there is a complete range of intermediate geometries characterised by the twist angle between the two triangular faces. This is 60° for the octahedron and 0° for the trigonal prism. These angles are 23, 23° in **2** and 20° in **5**. These structures conform to the pattern of geometries noted in refs. 20 and 21.

By contrast in the structure of complex **6** there is a bidentate phosphine ligand so that the phosphorus atoms are mutually *cis* subtending an angle of 76.2(1)° at the metal atom. The two carbonyl groups are mutually *cis* but subtending an angle of 76.6(7)° at the metal. According to the classification described above,^{20,21} when the angle between carbonyl groups is less than 90°, then the structure will be octahedral, but that is not the case here. Indeed the structure is unique in that the angle between carbonyl groups is significantly less than 90° but yet the structure is significantly distorted towards the trigonal prism. The twist angle in this structure is only 12°, so this structure is very close to being an ideal trigonal prism.

The bond lengths in the three structures are as expected. In **2** and **5**, tungsten–carbonyl distances are 1.94(2)–1.97(2), W–S

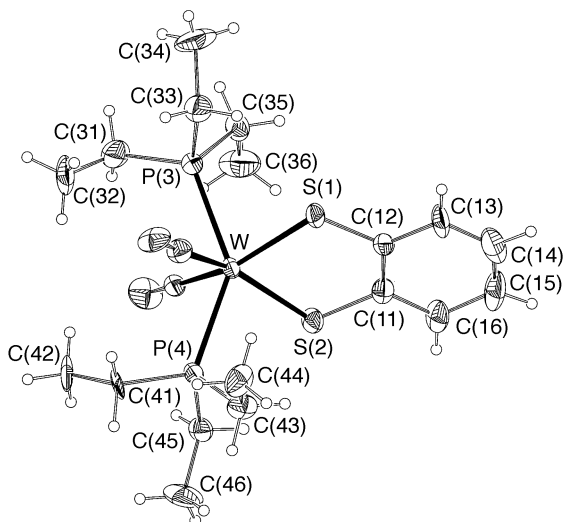


Fig. 2 Structure of complex 5. Details as in Fig. 1

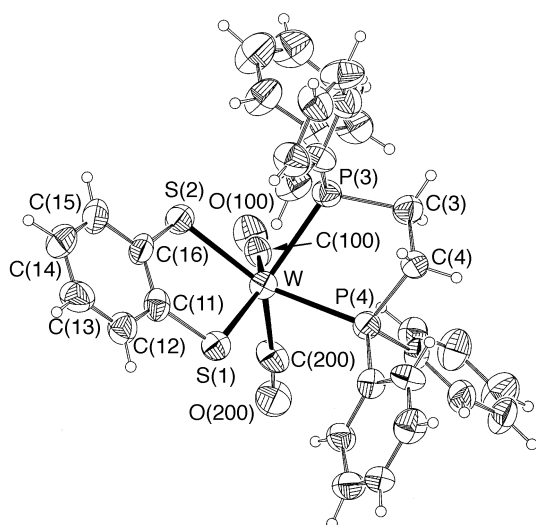


Fig. 3 Structure of complex 6. Details as in Fig. 1

2.386(3)–2.405(3) in **2** and 2.383(3), 2.405(4) Å in **5** and W–P 2.458(3)–2.467(3) in **2** and 2.475(3), 2.483(3) Å in **5**. There seems to be little difference between the effects therefore of C_3S_5 and bdt on the co-ordination sphere. In **6**, while the geometry is different because of the bidentate phosphorus ligand, there are no major differences in dimensions with W–C 1.95(2), 1.99(2), W–S 2.369(4), 2.392(4) and W–P 2.472(5), 2.504(4) Å.

The 1H NMR spectra of complexes **1–9** conform with the structures shown in Figs. 1–3. The $^{31}P\{-H\}$ NMR spectra of the complexes $[W(S-S)(CO)_2L_2]$ [$S-S = C_3S_5$, $L_2 = (PEt_3)_2$ **2** or dppe **3**; $S-S = mnt$, $L_2 = (PEt_3)_2$ **8**] show a singlet resonance with tungsten satellites, see Table 2.

Complex **1** is six-co-ordinate, having lost the capping carbonyl observed in the original diiodo complex $[Wl_2(CO)_3(PPh_3)_2]$. Attempts to reintroduce a third carbonyl ligand by saturating a solution of complex **1** in dichloromethane with carbon monoxide were unsuccessful.

In conclusion, we have successfully prepared and characterised the first examples of mono(dithiolene) complexes of tungsten(II), and are currently exploring their non-linear optical properties.

Experimental

The preparation and purification of complexes **1–9** were carried out under an atmosphere of dry nitrogen using Schlenk-line

Table 3 Dimensions (distances in Å, angles in °) in the metal co-ordination spheres of the three structures

Complex 2	Molecule A	Molecule B
W(1)–C(200)	1.958(10)	1.967(11)
W(1)–C(100)	1.971(12)	1.936(13)
W(1)–S(2)	2.386(3)	2.397(3)
W(1)–S(1)	2.397(3)	2.405(3)
W(1)–P(3)	2.460(3)	2.467(3)
W(1)–P(4)	2.466(3)	2.458(3)
C(200)–W(1)–C(100)	106.5(4)	108.2(5)
C(200)–W(1)–S(2)	155.4(3)	157.4(3)
C(100)–W(1)–S(2)	87.5(3)	87.0(3)
C(200)–W(1)–S(1)	90.0(3)	88.0(3)
C(100)–W(1)–S(1)	155.2(3)	155.5(3)
S(1)–W(1)–S(2)	84.26(10)	83.78(9)
C(200)–W(1)–P(3)	78.4(3)	77.9(3)
C(100)–W(1)–P(3)	79.6(3)	78.6(3)
S(2)–W(1)–P(3)	124.79(10)	122.51(9)
S(1)–W(1)–P(3)	86.06(9)	87.30(11)
C(200)–W(1)–P(4)	78.4(3)	80.4(3)
C(100)–W(1)–P(4)	79.0(3)	77.1(3)
S(2)–W(1)–P(4)	84.79(11)	87.11(8)
S(1)–W(1)–P(4)	123.22(10)	124.86(11)
P(3)–W(1)–P(4)	142.28(9)	140.22(10)

Complex 5

W–C(100)	1.969(11)	W–S(2)	2.405(4)
W–C(200)	2.01(2)	W–P(3)	2.475(3)
W–S(1)	2.383(3)	W–P(4)	2.483(3)
C(100)–W–C(200)	107.0(6)	S(1)–W–P(3)	84.23(11)
C(100)–W–S(1)	152.2(4)	S(2)–W–P(3)	126.52(13)
C(200)–W–S(1)	90.6(4)	C(100)–W–P(4)	78.2(3)
C(100)–W–S(2)	90.0(4)	C(200)–W–P(4)	79.3(4)
C(200)–W–S(2)	153.4(4)	S(1)–W–P(4)	127.17(11)
S(1)–W–S(2)	82.46(12)	S(2)–W–P(4)	84.44(12)
C(100)–W–P(3)	78.9(3)	P(3)–W–P(4)	141.09(12)
C(200)–W–P(3)	77.8(4)		

Complex 6

W–C(200)	1.95(2)	W–S(2)	2.392(4)
W–C(100)	1.99(2)	W–P(3)	2.472(5)
W–S(1)	2.369(4)	W–P(4)	2.504(4)
C(200)–W–C(100)	76.6(7)	S(1)–W–P(3)	130.3(2)
C(200)–W–S(1)	89.6(5)	S(2)–W–P(3)	84.9(2)
C(100)–W–S(1)	146.2(5)	C(200)–W–P(4)	75.7(5)
C(200)–W–S(2)	133.2(5)	C(100)–W–P(4)	113.5(4)
C(100)–W–S(2)	84.6(4)	S(1)–W–P(4)	92.00(14)
S(1)–W–S(2)	82.84(14)	S(2)–W–P(4)	150.3(2)
C(200)–W–P(3)	131.3(5)	P(3)–W–P(4)	76.23(14)
C(100)–W–P(3)	79.3(5)		

techniques. Ethanol was dried over magnesium-iodine and distilled prior to use. Dichloromethane was dried over P_2O_5 and distilled before use. The complexes $[Wl_2(CO)_3L_2]$ [$L_2 = (PPh_3)_2$, $^{16} (PEt_3)_2$, 17 or dppe 18], $Na_5[C_3S_5]$ 22 and $Na_2[mnt]$ 23 were prepared according to the literature methods, and all the chemicals were obtained from commercial sources.

Elemental analyses (C, H and N) were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as the carrier gas) and 1H and ^{31}P NMR spectra on a Bruker AC/250 spectrometer (1H referenced to tetramethylsilane, ^{31}P to 85% H_3PO_4). Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer, the near-infrared spectrum on a Beckman DK-2A ratio-recording spectrophotometer. Magnetic susceptibilities were recorded on a Johnson-Matthey magnetic susceptibility balance. The FAB mass spectra were recorded on a VG-Autospec Instrument using Cs^+ ions at 25 kV bombarded onto a sample dissolved in a 3-nitrobenzyl alcohol matrix target (EPSRC Mass Spec. Instr., Swansea).

Table 4 Crystal data and structure refinement for complexes **2**, **5** and **6**

	2	5	6 ·0.5CH ₂ Cl ₂
Empirical formula	C ₁₇ H ₃₀ O ₂ PS ₆ W	C ₂₀ H ₃₄ O ₂ P ₂ S ₂ W	C _{34.5} H ₂₉ ClO ₂ P ₂ S ₂ W
<i>M</i>	673.59	616.38	820.94
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ /n
<i>a</i> /Å	11.117(9)	8.223(7)	8.047(8)
<i>b</i> /Å	12.776(9)	11.102(7)	18.581(14)
<i>c</i> /Å	17.901(14)	14.391(8)	23.070(14)
α /°	91.95(1)	97.21(1)	
β /°	91.09(1)	101.11(1)	93.22(1)
γ /°	94.06(1)	98.47(1)	
<i>U</i> /Å ³	2534	1259	3444
<i>Z</i>	4	2	4
<i>D</i> _c /Mg mm ⁻³	1.766	1.626	1.583
μ /mm ⁻¹	5.127	4.893	3.675
<i>F</i> (000)	1332	612	1620
Crystal size/mm	0.15 × 0.20 × 0.25	0.20 × 0.35 × 0.25	0.25 × 0.25 × 0.10
θ Range for data collection/°	5.46–24.72	2.66–24.03	2.08–25.20
<i>hkl</i> Ranges	–13 to 12, –14 to 14, 0–20	–9 to 9, –12 to 12, 0–15	0–9, –21 to 21, –27 to 27
Reflections measured	12 665	4725	9500
Independent reflection (<i>R</i> _{int})	6499 (0.0303)	2873 (0.0293)	5461 (0.0700)
Data, restraints, parameters	6499, 0, 501	2873, 0, 251	5461, 0, 388
Goodness of fit on <i>F</i> ²	1.111	1.094	0.992
<i>a</i> , <i>b</i> in weighting scheme *	0.0448, 23.659	0.130, 3.598	0.158, 0.000
Final <i>R</i> 1, <i>wR</i> 2 indices [<i>I</i> > 2 σ (<i>I</i>) (all data)]	0.0451, 0.1085 0.0568, 0.1158	0.0497, 0.1527 0.0550, 0.1603	0.0838, 0.2073 0.1471, 0.2458
Largest difference peak and hole/e Å ⁻³	1.052, –1.136	0.813, –1.824	2.464, –1.731

* $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Preparations

[W(C₃S₃)(CO)₂(PPh₃)₂] **1**. To sodium metal (0.032 g, 1.4 mmol) dissolved in dry ethanol was added 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (0.28 g, 0.3 mmol) with stirring under a stream of dinitrogen. The mixture was stirred under N₂ for 45 min. The deep red solution was added dropwise with stirring to a solution of [Wl₂(CO)₃(PPh₃)₂] (0.72 g, 0.7 mmol) in acetonitrile (10 cm³) and stirred for 16 h. The solvent was removed *in vacuo* and the dark, oily powder resolvated in dry, degassed CH₂Cl₂, filtered and the solvent removed *in vacuo*. This procedure was repeated several times to ensure removal of sodium iodide. The oily product was recrystallised from dry dichloromethane and hexane to give [W(C₃S₃)(CO)₂(PPh₃)₂] **1** (yield = 0.52 g, 78%. See Table 1 for physical and analytical data.

Complexes **2** and **3** were prepared in a similar manner. Analytically pure crystals suitable for X-ray crystallography were grown by resolvating **2** in CH₂Cl₂–hexane (4:1) at 0 °C.

[W(bdt)(CO)₂(PPh₃)₂] **4**. To a stirring suspension of H₂bdt (0.04 g, 0.3 mmol) in acetonitrile (5 cm³) was added dropwise a solution of [Wl₂(CO)₃(PPh₃)₂] (0.29 g, 0.3 mmol) in acetonitrile (10 cm³). The reaction was stirred for 16 h, filtered and the solvent removed *in vacuo*. The product was washed with acetone and recrystallised from CH₂Cl₂–acetone to yield [W(bdt)(CO)₂(PPh₃)₂] **4** (yield = 0.13 g, 37%).

Complexes **5** and **6** were prepared in a similar way, and purified by recrystallisation from acetonitrile. Analytically pure crystals suitable for X-ray crystallography were grown by resolvating **5** in CH₂Cl₂–hexane (4:1) and storing the solution at 0 °C. Analytically pure crystals suitable for X-ray crystallography of **6** were grown in a similar manner.

[W(mnt)(CO)₂(PPh₃)₂] **7**. To a stirring solution of [Wl₂(CO)₃(PPh₃)₂] (2.81 g, 2.7 mmol) in acetonitrile (10 cm³) was added a solution of Na₂[mnt] (0.5 g, 2.7 mmol) in acetonitrile (20 cm³) dropwise under dinitrogen. The mixture was stirred for 4 h and the solvent removed *in vacuo*. The dark brown oily product was resolvated in dry dichloromethane, filtered and the solvent removed *in vacuo*. This was repeated sev-

eral times. The product was recrystallised from acetonitrile to give [W(mnt)(CO)₂(PPh₃)₂] **7** (yield = 1.59 g, 65%). Complexes **8** and **9** were prepared in a similar manner.

X-Ray crystallography

Crystal data for complexes **2**, **5** and **6** are given in Table 4, together with refinement details. Data for all three crystals were collected at 293(2) K with Mo-K α radiation (λ 0.710 73 Å) using the MAR Research image-plate system. The crystals were positioned at 75 mm from the image plate. Ninety five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.²⁴ The three structures were solved by heavy-atom methods using SHELXS 86.²⁵ In **2** there were two molecules in the asymmetric unit with equivalent dimensions. For all three structures the non-hydrogen atoms were refined anisotropically and hydrogen atoms, included in calculated positions, were refined isotropically. In **6** there was a disordered dichloromethane solvent molecule refined with 50% occupancy. One chlorine occupied two possible positions, each given 25% occupancy. The solvent atoms were given isotropic thermal parameters. In all three structures hydrogen atoms were positioned geometrically and given thermal factors of 1.2 times those of the atom to which they were bonded. Methyl groups were refined as rigid groups. Empirical absorption corrections were carried out.²⁶ The final refinements were carried out on *F*² using SHELXL.²⁷

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/429.

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