Alkyne complexes of molybdenum(II) and tungsten(II) containing acyclic and cyclic thioether ligands; crystal structures of [WI2(CO)-{MeS(CH2)2S(CH2)2SMe-S,S'}(η2-PhC2Ph)], [MoI(CO)([9]aneS3-S,S',S'')(η2-PhC2Ph)]I and [WI(ttoc-S,S',S'')(η2-PhC2Ph)2]I3 (ttoc = 2,5,8-trithia[9]orthocyclophane)

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Reaction of equimolar quantities of [MX2(CO)(NCMe)(η2-RC2R)2] and MeS(CH2)2S(CH2)2SMe (ttn) in CH2Cl2 at room temperature gave the complexes [MI(CO)(ttn-S,S',S'')(η2-RC2R)]I·Et2O (M = Mo, X = I, R = Me 1 or Ph 3; M = W, X = I, R = Me 2; M = W, X = Br, R = Ph 4), as the only isolated products, whereas treatment of equimolar amounts of [WI2(CO)(NCMe)(η2-PhC2Ph)2] with ttn initially gave the crystallographically characterised complex [WI2(CO)(ttn-S,S')(η2-PhC2Ph)] 5, which after reflux in CH2Cl2 afforded [WI(CO)(ttn-S,S',S'')-(η2-PhC2Ph)]I 6. The crystal structure of 5 showed that the ttn ligand is attached to the tungsten by two adjacent sulfur atoms, leaving the third unco-ordinated. Equimolar quantities of 5 and [FeI(CO)2(η-C5H5)] gave the bimetallic complex [WI2(CO){MeS(CH2)2S(CH2)2SMe-S,S',S''}(η2-PhC2Ph){Fe(CO)2(η-C5H5)}]I 7. Reaction of equimolar quantities of [MoI2(CO)(NCMe)(η2-PhC2Ph)2] and Ph2P(S)CH2P(S)Ph2 yielded the neutral complex [MoI2(CO){Ph2P(S)CH2P(S)Ph2-S,S'}(η2-PhC2Ph)] 8. Treatment of equimolar amounts of [MoI2(CO)(NCMe)-(η2-RC2R)2] with 1,4,7-trithiacyclononane ([9]aneS3) gave [MoI(CO)([9]aneS3-S,S',S'')(η2-RC2R)2]I (R = Me 9 or Ph 10). Complex 10 was crystallographically characterised and shows a molybdenum atom bonded to the three sulfurs of [9]aneS3. Its geometry is best considered as a distorted octahedron with the diphenylacetylene occupying one site. Reaction of [MX2(CO)(NCMe)(η2-RC2R)2] with an equimolar amount of 2,5,8-trithia[9]-orthocyclophane (ttoc) afforded the salt complexes [MX(CO)(ttoc-S,S',S'')(η2-RC2R)]X 11–15 (M = Mo or W; X = I, R = Me or Ph; M = W, X = Br, R = Ph). The complex [WI(CO)(ttoc-S,S',S'')(η2-PhC2Ph)]I 14 was transformed in CH2Cl2 in the presence of PhC2Ph to give the crystallographically characterised [WI(ttoc-S,S',S'')-(η2-PhC2Ph)2]I3 16 in very low yield. The structure is best considered as a distorted octahedron with the diphenylacetylenes each occupying one site. The shortest W–S bond is for the unique sulfur atom of ttoc *trans* to iodide.

Although halogenocarbonyl alkyne complexes of molybdenum(II) and tungsten(II) have been extensively studied over the years,[1,2] very few examples containing neutral sulfur donor ligands have been described. The only examples to be reported are derived from the reactions of [WI2(CO)(NCMe)(η2-RC2R)2] (R = Me or Ph) with thiourea,[3] N,N,N',N'-tetramethylthiourea,[3] thioacetamide,[3] SPPh3[4] and R'(R'')CNNHCSNH2 (R = R' = Me or Et; R' = H, R'' = Ph; R' = Me, R'' = Prn, But or Ph),[5] and the reactions of [{W(μ-I)(CO)(dppm)(η2-MeC2Me)}2]-[BF4]2[6] and [WI(CO)(NCMe)(dppm)(η2-MeC2Me)][BF4][7,8] with thiourea[7] and thiosemicarbazones[8] and related ligands.

The crystal structure of the active site of nitrogenase[9–11] has highlighted the importance of the study of molybdenum complexes containing three sulfur donor atoms to help understand the function of this enzyme. In this regard, since nitrogenase under certain conditions can reduce alkynes to alkenes, the study of the chemistry of molybdenum complexes containing both alkynes and three sulfur donor atoms is of interest. Herein we describe the reactions of [MX2(CO)(NCMe)(η2-RC2R)2] with MeS(CH2)2S(CH2)2SMe (ttn), Ph2P(S)CH2P(S)Ph2, 1,4,7-

trithiacyclononane ([9]aneS3) and 2,5,8-trithia[9]orthocyclophane (ttoc). The molecular structures of [WI2(CO)(ttn-S,S')-(η2-PhC2Ph)]I, [MoI(CO)([9]aneS3-S,S',S'')(η2-PhC2Ph)]I and [WI(ttoc-S,S',S'')(η2-PhC2Ph)2]I3 are also described. Some preliminary results of this research have been reported.[12]

Results and Discussion

MeS(CH2)2S(CH2)2SMe and Ph2P(S)CH2P(S)Ph2 complexes

Treatment of [MX2(CO)(NCMe)(η2-RC2R)2][13–15] with 1 equivalent of MeS(CH2)2S(CH2)2SMe in CH2Cl2 gave the complex salts [MX(CO){MeS(CH2)2S(CH2)2SMe-S,S',S''}(η2-RC2R)]-X·Et2O (M = Mo, X = I, R = Me 1 or Ph 3; M = W, X = I, R = Me 2; M = W, X = Br, R = Ph 4) in good yield, *via* displacement of an acetonitrile, an alkyne and a halide ligand. Complexes 1–4 have been characterised by elemental analysis and conductivity measurements (Table 1), IR and 1H NMR spectroscopy (Table 2); they are 1:1 electrolytes, soluble in CH2Cl2, CHCl3 and acetonitrile. They were confirmed as Et2O solvates by repeated elemental analysis (C, H and S) and 1H NMR spectroscopy. All are air-sensitive in the solid state and very air-sensitive in solution, but can be stored under an inert

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Table 1 Physical and analytical data * for complexes **1**–**16**

| Complex | Colour | Yield (%) | Analysis (%) | | | Λ/S cm^2 mol^{-1} |
			C	H	S	
1 [MoI(CO)(ttn-S,S',S'')(η^2-MeC$_2$Me)]I·Et$_2$O	Green	49	27.4 (26.2)	3.9 (4.4)	13.8 (14.0)	149
2 [WI(CO)(ttn-S,S',S'')(η^2-MeC$_2$Me)]I·Et$_2$O	Green	53	23.6 (23.2)	3.1 (4.4)	12.0 (12.4)	142
3 [MoI(CO)(ttn-S,S',S'')(η^2-PhC$_2$Ph)]I·Et$_2$O	Green	38	36.9 (36.9)	4.4 (4.2)	11.5 (11.8)	152
4 [WBr(CO)(ttn-S,S',S'')(η^2-PhC$_2$Ph)]Br·Et$_2$O	Green	44	38.2 (37.2)	4.0 (4.2)	11.6 (11.9)	156
5 [WI$_2$(CO)(ttn-S,S')(η^2-PhC$_2$Ph)]	Green	67	29.9 (30.5)	2.7 (2.9)	11.1 (11.6)	49
6 [WI(CO)(ttn-S,S',S'')(η^2-PhC$_2$Ph)]I	Green	64	30.1 (30.5)	2.5 (2.9)	11.3 (11.6)	138
7 [WI$_2$(CO)(ttn-S,S',S'')(η^2-PhC$_2$Ph){Fe(CO)$_2$(η-C$_5$H$_5$)}]I	Black	30	29.6 (29.8)	2.8 (2.6)	9.1 (8.5)	—
8 [MoI$_2$(CO){Ph$_2$P(S)CH$_2$P(S)Ph$_2$-S,S'}(η^2-PhC$_2$Ph)]	Gold	56	47.3 (47.8)	3.1 (3.2)	6.4 (6.4)	—
9 [MoI(CO)([9]aneS$_3$-S,S',S'')(η^2-MeC$_2$Me)]I	Green	70	21.0 (21.6)	3.2 (3.0)	15.9 (15.7)	152
10 [MoI(CO)([9]aneS$_3$-S,S',S'')(η^2-PhC$_2$Ph)]I	Green	48	34.0 (34.3)	3.4 (3.0)	13.8 (13.1)	154
11 [MoI(CO)(ttoc-S,S',S'')(η^2-MeC$_2$Me)]I	Green	42	29.0 (29.7)	3.1 (3.2)	14.0 (14.0)	142
12 [WI(CO)(ttoc-S,S',S'')(η^2-MeC$_2$Me)]I	Lime green	40	26.3 (26.3)	2.4 (2.9)	12.9 (12.4)	145
13 [MoI(CO)(ttoc-S,S',S'')(η^2-PhC$_2$Ph)]I	Green	60	41.4 (39.9)	3.0 (3.2)	11.7 (11.8)	140
14 [WI(CO)(ttoc-S,S',S'')(η^2-PhC$_2$Ph)]I	Lime green	55	36.4 (36.0)	2.7 (2.9)	11.5 (10.7)	141
15 [WBr(CO)(ttoc-S,S',S'')(η^2-PhC$_2$Ph)]Br	Green	47	39.8 (40.2)	3.1 (3.3)	11.8 (11.9)	160

* Calculated values in parentheses.

Table 2 Infrared ^{a} and ^{1}H NMR ^{b} data for complexes **1**–**15**

Complex	$\tilde{\nu}$(C≡O)/cm^{-1}	^{1}H NMR (δ, J/Hz)
1	1971s	3.5 (q, 4 H, CH$_2$O), 3.2 (s, 6 H, C$_2$Me), 2.8 (br m, 8 H, CH$_2$S), 2.25 (m, 3 H, CH$_3$S), 2.2 (s, 3 H, CH$_3$S), 1.2 (t, 6 H, CH_3CH$_2$O)
2	1954s	3.5 (q, 4 H, CH$_2$O), 3.4 (s, 6 H, C$_2$Me), 3.3 (br m, 8 H, CH$_2$S), 2.2 (s, 3 H, CH$_3$S), 2.15 (s, 3 H, CH$_3$S), 1.2 (t, 6 H, CH_3CH$_2$O)
3	1984s	7.5–7.3 (br m, 10 H, Ph), 3.5 (q, 4 H, CH$_2$O), 2.9 (br m, 8 H, CH$_2$S), 2.3 (s, 3 H, CH$_3$S), 2.25 (s, 3 H, CH$_3$S), 1.2 (t, 6 H, CH_3CH$_2$O)
4	1967s	7.5–7.3 (br m, 10 H, Ph), 3.5 (q, 4 H, CH$_2$O), 2.9 (br m, 8 H, CH$_2$S), 2.1 (s, 6 H, CH$_3$S), 1.2 (t, 6 H, CH_3CH$_2$O)
5	1968s	7.5–7.3 (br m, 10 H, Ph), 3.2 [br m, 4 H, CH$_2$SCH$_2$(co-ord)], 3.1 [s, 3 H, CH$_3$(co-ord)], 2.6 [m, 2 H, CH$_2$SCH$_3$(co-ord)], 2.35 [m, 2 H, CH$_2$SCH$_3$(unco-ord)], 2.2 [s, 3 H, CH$_3$(unco-ord)]
6	1974s	7.5–7.3 (br m, 10 H, Ph), 3.1 (br m, 8 H, CH$_2$S), 2.2 (s, 3 H, CH$_3$S), 2.15 (s, 3 H, CH$_3$S)
7	1960s, 1998s, 2045s	7.5–7.3 (br m, 10 H, Ph), 5.1 (s, 5 H, C$_5$H$_5$); 3.4 (br m, 4 H, CH$_2$SCH$_2$), 3.2 (br m, 2 H, CH_2SCH$_3$), 3.1 (br m, 3 H, SCH$_3$), 2.8 (br m, 5 H, CH$_2$SCH$_3$)
8	1973s	8.0–7.3 (br m, 30 H, Ph), 4.2 (t, 2 H, CH$_2$)
9	1970s	4.0 (br m, 12 H, SCH$_2$CH$_2$S), 3.2 (s, 6 H, C$_2$Me)
10	1980s	7.5–7.3 (br m, 10 H, Ph), 4.0 (br m, 12 H, SCH$_2$CH$_2$S)
11	1983s	7.5–7.3 (br m, 4 H, C$_6$H$_4$), 4.8, 4.4 (2d, 4 H, PhCH_2S, J = 12), 3.2 (s, 6 H, C$_2$Me), 2.9 (m, 8 H, SCH$_2$CH$_2$S)
12	1970s	7.5–7.3 (br m, 4 H, C$_6$H$_4$), 3.6 (s, 6 H, MeC$_2$), 4.2, 3.5 (2d, 4 H, PhCH_2S), 2.4 (m, 8 H, SCH$_2$CH$_2$S)
13	1992s	7.5–7.3 (br m, 14 H, C$_6$H$_4$, Ph), 4.6, 4.1 (2d, 4 H, PhCH_2S, J = 16), 3.4 (m, 8 H, SCH$_2$CH$_2$S)
14	1972s	7.7–7.3 (br m, 14 H, C$_6$H$_4$, Ph), 4.4, 3.8 (2d, 4 H, PhCH_2S), 2.5 (m, 8 H, SCH$_2$CH$_2$S)
15	1966s	7.7–7.3 (br m, 14 H, C$_6$H$_4$, Ph), 4.1, 3.9 (2d, 4 H, PhCH_2S), 2.6 (m, 8 H, SCH$_2$CH$_2$S)

^{a} All spectra were recorded in CH$_2$Cl$_2$ between NaCl plates; s = strong. ^{b} All spectra run in CDCl$_3$ at 25 °C and referenced to tetramethylsilane; s = singlet, br = broad, d = doublet, m = multiplet.

atmosphere in the solid state for several days at room temperature. The IR spectra all have single carbonyl bands below 2000 cm^{-1}, with the diphenylacetylene complexes having slightly higher frequencies than their but-2-yne counterparts. It is interesting that the reaction of equimolar amounts of [WI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] and MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe in CH$_2$Cl$_2$ at room temperature for 72 h gave the neutral complex [WI$_2$(CO)(ttn-S,S')(η^2-PhC$_2$Ph)] **5**. Subsequent reflux of **5** in CH$_2$Cl$_2$ for 6 h gave the expected complex salt [WI(CO)(ttn-S,S',S'')(η^2-PhC$_2$Ph)]I **6** via displacement of the iodide ligand.

The molecular structure of the neutral complex **5** has been crystallographically determined, and shows a distorted octahedral geometry with cis-iodo ligands. The diphenylacetylene and the terminal sulfur of the ttn ligand complete the equatorial plane, whilst the carbon monoxide and the central sulfur atom of ttn occupy the two axial sites. As has often been observed in d^4 systems,[1,2,14,15] the alkyne ligand is parallel to the W–CO axis (Fig. 1, Table 3) and trans to an iodide ligand, which optimises both the π-acceptor and σ-donor properties of the diphenylacetylene. The IR spectra of both the neutral complex **5** and the salt **6** have very similar carbonyl bands at 1968 and 1974 cm^{-1} respectively, which suggests that displacing iodide by a thioether sulfur atom does not change the electron density at the tungsten atom significantly.

Table 3 Bond lengths (Å) and angles (°) for complexes **5**, **10** and **16**

Complex **5**

I(1)–W	2.848(2)	I(2)–W	2.785(2)
W–C(1)	1.931(10)	W–C(9)	2.021(10)
W–C(8)	2.031(10)	W–S(1)	2.470(3)
W–S(2)	2.574(3)	S(1)–(16)	1.808(10)
S(1)–C(17)	1.819(9)	S(2)–C(18)	1.832(10)
S(2)–C(19)	1.831(10)	S(3)–C(21)	1.770(11)
S(3)–C(20)	1.795(10)	C(2)–C(7)	1.367(14)
O–C(1)	1.177(11)	C(3)–C(4)	1.35(2)
C(2)–C(3)	1.428(13)	C(5)–C(6)	1.378(13)
C(4)–C(5)	1.36(2)	C(7)–C(8)	1.438(13)
C(6)–C(7)	1.398(14)	C(9)–C(10)	1.472(13)
C(8)–C(9)	1.319(12)	C(10)–C(11)	1.405(14)
C(10)–C(15)	1.381(13)	C(12)–C(13)	1.328(14)
C(11)–C(12)	1.341(13)	C(14)–C(15)	1.384(14)
C(13)–C(14)	1.39(2)	C(19)–C(20)	1.508(13)
C(17)–C(18)	1.545(13)		

C(1)–W–C(9)	111.6(4)	C(1)–W–C(8)	73.7(4)
C(9)–W–C(8)	38.0(3)	C(1)–W–S(1)	102.1(3)
C(9)–W–S(1)	85.3(3)	C(8)–W–S(1)	93.9(3)
C(1)–W–S(2)	167.7(3)	C(9)–W–S(2)	80.0(3)
C(8)–W–S(2)	117.8(3)	S(1)–W–S(2)	82.19(10)
C(1)–W–I(2)	89.8(3)	C(9)–W–I(2)	97.9(3)
C(8)–W–I(2)	97.3(3)	S(1)–W–I(2)	165.58(6)
S(2)–W–I(2)	84.54(8)	C(1)–W–I(1)	79.2(3)
C(9)–W–I(1)	167.1(3)	C(8)–W–I(1)	152.2(3)
S(1)–W–I(1)	85.59(9)	S(2)–W–I(1)	89.73(9)
I(2)–W–I(1)	88.74(7)	C(16)–S(1)–C(17)	98.9(5)
C(16)–S(1)–W	119.4(3)	C(17)–S(1)–W	104.8(3)
C(18)–S(2)–C(19)	102.7(5)	C(18)–S(2)–W	102.9(3)
C(19)–S(2)–W	114.2(3)	C(21)–S(3)–C(20)	103.4(5)
C(21)–S(3)–C(20)	144.2(4)	C(7)–C(2)–C(3)	121.7(10)
O–C(1)–W	178.6(9)	C(3)–C(4)–C(5)	122.2(10)
C(4)–C(3)–C(2)	117.8(10)	C(5)–C(6)–C(7)	121.7(10)
C(4)–C(5)–C(6)	119.2(11)	C(2)–C(7)–C(8)	124.8(10)
C(2)–C(7)–C(6)	117.2(9)	C(9)–C(8)–C(7)	135.5(10)
C(6)–C(7)–C(8)	117.8(10)	C(7)–C(8)–W	152.9(7)
C(9)–C(8)–W	70.6(6)	C(8)–C(9)–W	71.4(6)
C(8)–C(9)–C(10)	137.8(10)	C(15)–C(10)–C(11)	117.8(9)
C(10)–C(9)–W	149.5(7)	C(11)–C(10)–C(9)	118.7(9)
C(15)–C(10)–C(9)	123.5(9)	C(13)–C(12)–C(11)	123.4(11)
C(12)–C(11)–C(10)	119.4(10)		
C(12)–C(13)–C(14)	119.5(10)	C(15)–C(14)–C(13)	118.2(11)
C(14)–C(15)–C(10)	121.3(10)	C(18)–C(17)–S(1)	108.7(6)
C(17)–C(18)–S(2)	111.8(6)	C(20)–C(19)–S(2)	110.3(7)
C(19)–C(20)–S(3)	113.7(7)		

Complex **10**

I(1)–Mo	2.758(3)	Mo–S(1)	2.449(5)
Mo–C(100)	1.97(2)	Mo–S(7)	2.545(6)
Mo–C(11)	2.03(2)	Mo–S(4)	2.607(6)
Mo–C(21)	2.039(17)		

C(100)–Mo–C(11)	112.5(8)	C(11)–Mo–S(4)	164.7(6)
C(100)–Mo–C(21)	76.5(7)	C(21)–Mo–S(4)	157.2(6)
C(11)–Mo–C(21)	36.5(7)	S(1)–Mo–S(4)	79.96(18)
C(100)–Mo–S(1)	94.4(6)	S(7)–Mo–S(4)	81.14(18)
C(11)–Mo–S(1)	95.5(6)	C(100)–Mo–I(1)	90.3(6)
C(21)–Mo–S(1)	92.7(4)	C(11)–Mo–I(1)	101.2(6)
C(100)–Mo–S(7)	163.7(5)	C(21)–Mo–I(1)	107.9(4)
C(11)–Mo–S(7)	83.8(6)	S(1)–Mo–I(1)	159.37(15)
C(21)–Mo–S(7)	119.7(6)	S(7)–Mo–I(1)	86.67(15)
S(1)–Mo–S(7)	83.14(17)	S(4)–Mo–I(1)	80.78(13)
C(100)–Mo–S(4)	82.6(5)		

Complex **16**

W–C(41)	2.041(14)	W–S(11)	2.493(5)
W–C(31)	2.048(16)	W–S(14)	2.589(4)
W–C(51)	2.052(17)	W–S(19)	2.606(5)
W–C(61)	2.092(16)	W–I(1)	2.800(3)

C(41)–W–C(31)	35.5(6)	S(11)–W–S(14)	79.62(14)
C(41)–W–C(51)	106.8(6)	C(41)–W–S(19)	83.9(5)
C(31)–W–C(51)	93.9(6)	C(31)–W–S(19)	85.0(4)
C(41)–W–C(61)	97.9(6)	C(51)–W–S(19)	159.7(4)
C(31)–W–C(61)	107.5(6)	C(61)–W–S(19)	161.1(5)
C(51)–W–C(61)	36.8(6)	S(11)–W–S(19)	79.80(14)
C(41)–W–S(11)	79.9(5)	S(14)–W–S(19)	90.71(16)
C(31)–W–S(11)	114.9(5)	C(41)–W–I(1)	120.0(4)
C(51)–W–S(11)	118.5(4)	C(31)–W–I(1)	86.3(5)
C(61)–W–S(11)	82.0(5)	C(51)–W–I(1)	83.9(4)
C(41)–W–S(14)	159.5(5)	C(61)–W–I(1)	118.3(4)
C(31)–W–S(14)	163.7(5)	S(11)–W–I(1)	145.98(11)
C(51)–W–S(14)	84.7(4)	S(14)–W–I(1)	77.41(11)
C(61)–W–S(14)	80.9(4)	S(19)–W–I(1)	75.75(11)
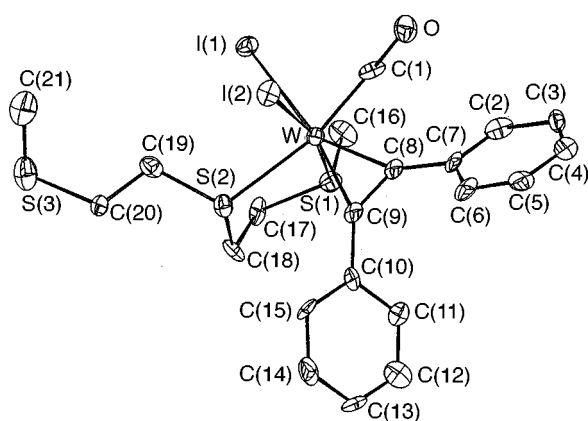
Fig. 1 Crystal structure of $[WI_2(CO)\{MeS(CH_2)_2S(CH_2)_2SMe\text{-}S,S'\}(\eta^2\text{-}PhC_2Ph)]$ **5**, showing the atom numbering scheme

We have previously described the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with 1 equivalent of, for example, $NCCH_2(3\text{-}C_4H_3S)$ which gave $[WI_2(CO)\{NCCH_2(3\text{-}C_4H_3S)\}\text{-}(\eta^2\text{-}MeC_2Me)_2]$,[16] with retention of configuration. We also know the structure of the bidentate ttn ligand in complex **5** (Fig. 1), of η^3-co-ordinated ttn in the carbonyl analogue of **5**, $[WI_2(CO)_2(ttn\text{-}S,S',S'')]$,[17] where the central sulfur is *trans* to CO and η^3-co-ordinated [9]aneS₃ in the complex [MoI(CO)-

$([9]aneS_3\text{-}S,S',S'')(\eta^2\text{-}PhC_2Ph)]I$ **10** (see Fig. 3 later). Based on these data a picture, Scheme 1, can be drawn for the reaction of equimolar amounts of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ and ttn to give eventually $[WI(CO)(ttn\text{-}S,S',S'')(\eta^2\text{-}PhC_2Ph)]I$. We suggest that this process involves initial displacement of MeCN by the central sulfur atom of the ttn ligand, since this is the most direct route to the stereochemistry shown for complex **5**, with CO *trans* to the central sulfur atom of the ttn ligand. Space-filling molecular models suggest that there is little difference in the steric requirements of monodentate ttn whether bound through the central or terminal sulfurs. The ¹H NMR spectra of complexes **1**–**6** all conform with the structures shown in Fig. 1 and Scheme 1.

Reaction of equimolar quantities of the neutral complex $[WI_2(CO)(ttn\text{-}S,S')(\eta^2\text{-}PhC_2Ph)]$ **5** and $[FeI(CO)_2(\eta\text{-}C_5H_5)]$ in CH_2Cl_2 gave the novel bimetallic complex $[WI_2(CO)(ttn\text{-}S,S',S'')(\eta^2\text{-}PhC_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}]I$ **7** in 30% yield (Tables 1 and 2). This complex is soluble in chlorinated solvents, and can be stored under nitrogen at room temperature for several days. The IR spectrum shows three carbonyl bands at 1960, 1998 and 2045 cm⁻¹. It is likely the band at 1960 cm⁻¹ is due to the carbonyl on the tungsten (1968 cm⁻¹ for compound **5**) and those at 1998 and 2045 cm⁻¹ to the carbonyls on the iron atom. The ¹H NMR spectrum shows a single isomer in solution, and hence the most likely structure of this complex is given in Fig. 2.

Reaction of equimolar amounts of $[MoI_2(CO)(NCMe)\text{-}(\eta^2\text{-}PhC_2Ph)_2]$ and $Ph_2P(S)CH_2P(S)Ph_2$ gave the neutral mono-
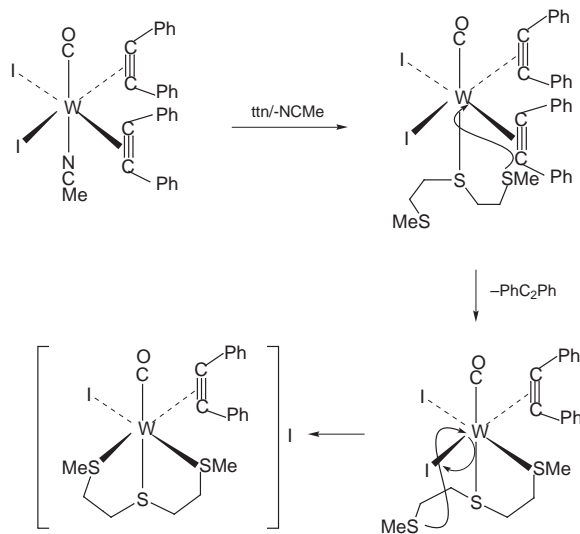
Scheme 1
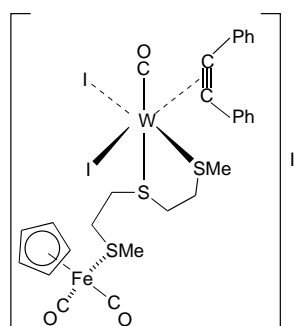
Fig. 2 Proposed structure for [WI$_2$(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-PhC$_2$Ph){Fe(CO)$_2$(η-C$_5$H$_5$)}]I **7**

(alkyne) complex [MoI$_2$(CO){Ph$_2$P(S)CH$_2$P(S)Ph$_2$-S,S'}(η^2-PhC$_2$Ph)] **8** in 56% yield. The complex is reasonably air-stable in the solid state, but very air-sensitive in solution. The IR spectrum shows, as expected, a single carbonyl band at 1973 cm^{-1}, *i.e.* close to that of the crystallographically characterised neutral complex **5** (1968 cm^{-1}). The spectrum of **8** also shows a P=S band at 560 cm^{-1}, which is lower than for free Ph$_2$P(S)CH$_2$-P(S)Ph$_2$ [ν(P=S) 626 cm^{-1}]. A number of other attempted reactions of Ph$_2$P(S)CH$_2$P(S)Ph$_2$ or the dithioether ligands RS(CH$_2$)$_2$SR (R = Ph or *p*-tolyl) with [MI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] were carried out without success. In fact no reaction occurred with the dithioethers RS(CH$_2$)$_2$SR even after prolonged periods of time under reflux conditions; only starting materials were isolated.

[9]aneS$_3$ and ttoc complexes

Reaction of equimolar quantities of [MoI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] (R = Me or Ph) and [9]aneS$_3$ in CH$_2$Cl$_2$ gave the complex salts [MoI(CO)([9]aneS$_3$-S,S',S'')(η^2-RC$_2$R)]I **9** (R = Me) and **10** (R = Ph) (Tables 1 and 2). Conductivity measurements show both to be 1 : 1 electrolytes in acetonitrile. The complexes are soluble in solvents such as CH$_2$Cl$_2$, CHCl$_3$ and acetonitrile and are air-sensitive in both the solid state and in solution. The IR carbonyl stretching bands at 1970 and 1980 cm^{-1} for **9** and **10** respectively reflect the better donor ability of the but-2-yne ligand in **9**.

The crystal structure of the diphenylacetylene complex [MoI(CO)([9]aneS$_3$-S,S',S'')(η^2-PhC$_2$Ph)]I **10** is shown in Fig. 3, together with the atomic numbering scheme. The molybdenum atom is bonded to [9]aneS$_3$, together with an iodide, a carbonyl and a diphenylacetylene ligand. The geometry around the metal can be considered as essentially octahedral, assuming
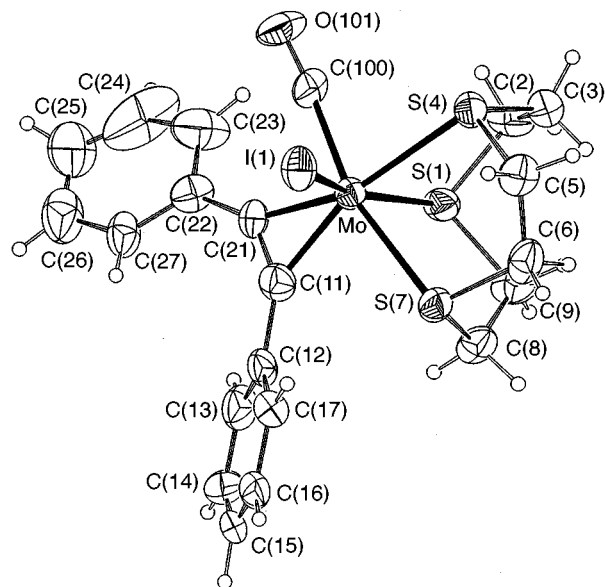

Fig. 3 Structure of the cation of [MoI(CO)([9]aneS$_3$-S,S',S'')(η^2-PhC$_2$Ph)]I **10**, together with the atomic numbering scheme. Ellipsoids are shown at 30% probability, hydrogen atoms as small circles of arbitrary radii

that the alkyne occupies one site only. The three Mo–S distances are very different with the bond *trans* to iodine the shortest at 2.449(5), next longest is the bond *trans* to carbonyl at 2.545(6) Å and the longest the bond *trans* to the alkyne at 2.607(6) Å. The bond lengths to iodide [2.758(3)], carbonyl [1.97(2)] and the alkyne [2.03(2), 2.04(2) Å] are as expected. The geometry has some similarity with that found for the cation [WI(CO)$_3$([9]aneS$_3$)]$^+$ but that structure, having four monodentate ligands *trans* to the [9]aneS$_3$, is best described as a capped octahedron.[18] Indeed the geometry of **10** has close similarity with that found for the six-co-ordinate octahedral structure [Mo(CO)$_3$([9]aneS$_3$)].[19] The [9]aneS$_3$ ligand has the expected distorted C_3 symmetry with torsion angles very similar to those found in the three structures mentioned above.

The ^{1}H NMR spectra of complexes **9** and **10** conform with the structure shown in Fig. 3. The ^{13}C NMR spectrum of **9** shows alkyne carbon resonances at δ 225.7 and 226.2 which indicate[20] that the but-2-yne ligand is essentially donating four electrons to the metal. A carbonyl resonance at δ 215.3 was observed together with six resonances for the [9]aneS$_3$ ligand between δ 34.9 and 44.7 and a broad resonance at δ 22.3 for the methyl groups of the but-2-yne ligand. Similarly, the ^{13}C NMR spectrum of the diphenylacetylene complex **10** shows six resonances each for the [9]aneS$_3$ ligand and the phenyl carbons, and a carbonyl resonance at δ 212.5. The alkyne carbon chemical shifts again suggest[20] the alkyne is donating four electrons to the molybdenum, giving an 18-electron complex.

Several attempts were made to isolate the S$_2$-bonded complexes [MoI$_2$(CO)([9]aneS$_3$-S,S')(η^2-RC$_2$R)] by treating the starting materials for short periods of time, but without success. This is perhaps not surprising in view of the significant macrocyclic effect[21] for [9]aneS$_3$ and ttoc (see below) compared to the open-chain analogue ttn.

Reaction of equimolar amounts of [MX$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] and the macrocyclic ligand ttoc gave the complexes [MX(CO)(ttoc-S,S',S'')(η^2-RC$_2$R)]X **11–15** (M = Mo or W; X = I; R = Me or Ph; M = W, X = Br, R = Ph). These were characterised in the normal manner (Tables 1 and 2) and are all 1 : 1 electrolytes in acetonitrile solution (Table 1). Since their carbonyl stretching frequencies and ^{1}H NMR properties are similar to those of the crystallographically characterised complex **10**, it is likely they will have a similar structure to that shown in Fig. 3.
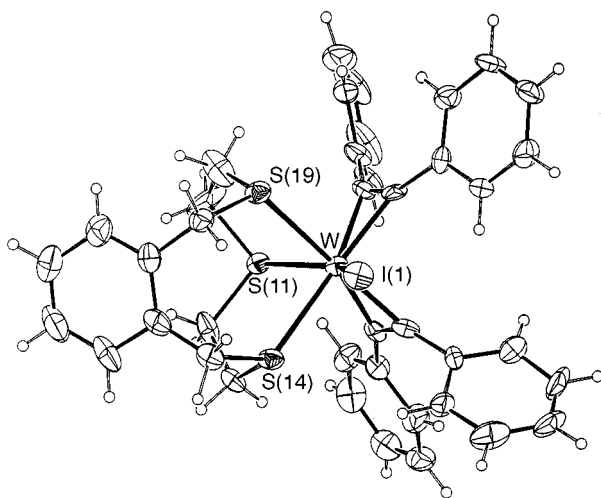
Fig. 4 Structure of the cation of [WI(ttoc-S,S',S'')(η^2-PhC$_2$Ph)$_2$]I$_3$ **16**. Details as in Fig. 3

In an attempt to grow X-ray-quality crystals of [WI(CO)-(ttoc-S,S',S'')(η^2-PhC$_2$Ph)]I **14**, during a period of several weeks in the presence of PhC$_2$Ph, a CH$_2$Cl$_2$–Et$_2$O (90:10) solution of **14** at −17 °C gave three very well formed single crystals of the non-carbonyl-containing product [WI(ttoc-S,S',S'')(η^2-PhC$_2$Ph)$_2$]I$_3$ **16** which was crystallographically characterised. The molecular structure is shown in Fig. 4, together with the atomic numbering scheme. The tungsten atom is bonded to the ttoc ligand together with an iodide and two diphenylacetylene ligands. Again the geometry can best be considered as essentially octahedral with the two acetylenes each occupying one site, though in this case the distortion from octahedral is significantly increased by comparison with **10** no doubt because of the steric crowding induced by two diphenylacetylene ligands rather than one. Rather surprisingly in this structure the shortest W–S bond is to S(11) at 2.493(5) Å, *trans* to iodide, while the other two bonds which are *trans* to the diphenylacetylene ligands are equivalent at 2.589(4) and 2.606(5) Å. This pattern could well be due to the presence of the rigid phenyl group in the ttoc ligand; in fact a similar, though less marked, variation in bond lengths was observed in the complex [Mo(CO)$_3$(ttoc)].[22] The geometry of the triiodide anion is as expected.

These conditions proved very difficult to reproduce and attempts to prepare complex **16** in higher yield were unsuccessful.

Conclusion

We have investigated the co-ordination chemistry of the sulfur donors ttn, Ph$_2$P(S)CH$_2$P(S)Ph$_2$, [9]aneS$_3$ and ttoc at molybdenum(II) and tungsten(II) halogenocarbonyl complexes containing alkyne ligands, prompted by the S$_3$ co-ordination of molybdenum in the active site of nitrogenase. Further investigation of the synthesis and characterisation of important non-carbonyl-containing complexes exemplified by [MoI(ttoc-S,S',S'')(η^2-PhC$_2$Ph)$_2$]I$_3$ (Fig. 4) will be the subject of further study. We have also established the use of [WI$_2$(CO)(ttn-S,S')(η^2-PhC$_2$Ph)] as a ligand to form the bimetallic complex [WI$_2$(CO)(ttn-S,S',S'')(η^2-PhC$_2$Ph){Fe(CO)$_2$(η-C$_5$H$_5$)}]I, and further study of the synthesis of multimetallic complexes of this type is being undertaken.

Experimental

All reactions described in this paper were carried out under an atmosphere of dry nitrogen using standard Schlenk-line techniques. The solvents were all dried and degassed before use. Dichloromethane was refluxed over phosphorus pentaoxide

and diethyl ether was dried over sodium wire. The starting complexes [MX$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] (M = W, X = Br, R = Ph;[13] M = Mo, X = I, R = Me or Ph;[14] M = W, X = I, R = Me or Ph[15]) were prepared according to the published methods; MeS(CH$_2$)$_2$S(CH$_2$)$_s$SMe,[17] Ph$_2$P(S)CH$_2$P(S)Ph$_2$,[23] [9]aneS$_3$[18,24,25] and ttoc[18] were prepared by variations of the literature methods. All other chemicals were obtained from commercial sources and used without further purification.

Elemental analyses (C, H and S) were determined using a Carlo Erba MOD 1108 instrument (helium carrier gas) by Mr. K. Jones (Bangor). Conductivities were measured using a Portland Electronics conductivity bridge. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer, proton NMR spectra on a Bruker AC 250 instrument (University of Wales, Bangor) and ^{13}C NMR spectra on a JEOL GS 270 instrument (NFL, Norwich) referenced to tetramethylsilane.

Preparations

[MoI(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-MeC$_2$Me)]-I·Et$_2$O 1 and [MoI(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-PhC$_2$Ph)]I·Et$_2$O 3. To a solution in CH$_2$Cl$_2$ (50 cm^3) of [MoI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] (0.46 g, 0.59 mmol) was added an equimolar amount of ttn (0.11 g, 0.59 mmol). The solution was stirred at room temperature for 12 h and the solvent removed *in vacuo* to give the green complex [MoI(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-PhC$_2$Ph)]I **3** (yield = 0.18 g). Similarly, equimolar amounts of MeS(CH$_2$)$_2$-S(CH$_2$)$_2$SMe (0.21 g, 1.16 mmol) and [MoI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$] (0.61 g, 1.16 mmol) were stirred in CH$_2$Cl$_2$ (50 cm^3) at room temperature for 12 h. Removal of the solvent *in vacuo* gave [MoI(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-MeC$_2$-Me)]I **1** (yield = 0.39 g). Both complexes **1** and **3** were recrystallised from a CH$_2$Cl$_2$–Et$_2$O mixture before drying *in vacuo* followed by analysis.

[WI(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-MeC$_2$Me)]-I·Et$_2$O 2, [WI$_2$(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S'}(η^2-PhC$_2$-Ph)] 5 and [WI(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-PhC$_2$Ph)]I 6. To a solution of [WI$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] (0.28 g, 0.32 mmol) in CH$_2$Cl$_2$ (45 cm^3) was added an equimolar amount of ttn (0.06 g, 0.33 mmol) and the solution stirred for 72 h. The resulting solution was filtered over Celite and the solvent removed *in vacuo* to give the green complex [WI$_2$(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S'}(η^2-PhC$_2$Ph)] **5** (yield = 0.18 g). Recrystallisation of complex **5** from CH$_2$Cl$_2$–Et$_2$O at 0 °C gave green crystals of suitable quality for X-ray crystallography. A similar reaction but followed by a further reflux of the solution in CH$_2$Cl$_2$ (45 cm^3) for 6 h gave a green solid on removal of solvent. Recrystallisation of this solid from CH$_2$Cl$_2$–Et$_2$O at 0 °C gave the green crystalline complex [WI(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-PhC$_2$Ph)]I **6** (yield = 0.17 g).

To a solution of the yellow complex [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$] (0.25 g, 0.41 mmol) in CH$_2$Cl$_2$ (45 cm^3) was added an equimolar amount of MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe (0.08 g, 0.41 mmol) and the solution was stirred for 72 h. The resulting solution was filtered over Celite and the solvent removed *in vacuo* to give the green complex [WI(CO){MeS(CH$_2$)$_2$-S(CH$_2$)$_2$SMe-S,S',S''}(η^2-MeC$_2$Me)]I·Et$_2$O **2** (yield = 0.17 g), which was recrystallised from CH$_2$Cl$_2$–Et$_2$O before drying *in vacuo* prior to analysis.

[WBr(CO){MeS(CH$_2$)$_2$S(CH$_2$)$_2$SMe-S,S',S''}(η^2-PhC$_2$Ph)]-Br·Et$_2$O 4 and [WBr(CO)(ttoc-S,S',S'')(η^2-PhC$_2$Ph)]Br 15. To a solution of [WBr$_2$(CO)(NCMe)(η^2-PhC$_2$Ph)$_2$] (0.51 g, 0.66 mmol) in CH$_2$Cl$_2$ (50 cm^3) was added an equimolar amount of ttn (0.12 g, 0.66 mmol). The resulting solution was stirred for 24 h, then filtered and the solvent removed to

Table 4 Crystal data and structure refinement for complexes **5**, **10** and **16**

		5	**10**	**16**
Empirical formula		$C_{21}H_{24}I_2OS_3W$	$C_{29}H_{22}Cl_2I_2MoO_{3.5}S_3$	$C_{40.166}H_{36.33}Cl_{0.33}I_4S_3W$
M		826.23	842.75	1318.47
T/K		120(2)	293(2)	293(2)
$\lambda(\text{Mo-K}\alpha)/\text{Å}$		0.710 69	0.710 73	0.710 73
Crystal system, space group		Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Trigonal, $P\bar{3}$
$a/\text{Å}$		8.458(2)	32.78(3)	23.80(2)
$b/\text{Å}$		13.494(12)	11.645(13)	23.80(2)
$c/\text{Å}$		22.03(3)	21.77(2)	12.999(13)
$\beta/°$		99.48(8)	125.78(1)	
$U/\text{Å}^3$		2480(4)	6742(12)	6379(11)
Z		4	8	6
$D_c/\text{Mg m}^{-3}$		2.213	1.707	2.059
μ/mm^{-1}		7.412	2.586	5.815
$F(000)$		1544	3352	3702
Crystal size/mm		$0.11 \times 0.11 \times 0.21$	$0.35 \times 0.30 \times 0.25$	$0.25 \times 0.25 \times 0.25$
θ Range for data collection (°)		2.44 to 22.76	2.89 to 25.05	2.32 to 24.95
Index ranges		$-6 < h < 8,$	$0 \leqslant h \leqslant 38,$	$-28 \leqslant h \leqslant 28,$
		$-10 < k < 14,$	$-12 \leqslant k \leqslant 13,$	$-27 < k < 27,$
		$-23 < l < 22$	$-25 \leqslant l \leqslant 20$	$-15 < l < 15$
Reflections collected		6633	8011	18 293
unique (R_{int})		2830 (0.067)	4969 (0.045)	7173 (0.052)
Weighting scheme		$1/[\sigma^2(F^2)]$	$a = 0.089, b = 388.29*$	$a = 0.028, b = 218.29*$
Data/restraints/parameters		2830/0/249	4969/0/295	7173/0/442
Final R indices $[I > 2\sigma(I)]$	$R1$	0.0349	0.0830	0.0825
	$wR2$	0.0684	0.1244	0.1673
R indices (all data)	$R1$	0.0602	0.1244	0.1131
	$wR2$	0.0743	0.1853	0.2461
Largest diff. peak and hole/e Å^{-3}		1.208, -0.742	1.606, -0.984	2.479, -1.555

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

give the green complex [WBr(CO){MeS(CH₂)₂S(CH₂)₂SMe-S,S',S''}(η²-PhC₂Ph)]Br·Et₂O **4** (yield = 0.21 g) which was recrystallised from CH₂Cl₂–Et₂O before drying *in vacuo* prior to analysis. Similarly, the reaction of [WBr₂(CO)(NCMe)(η²-PhC₂Ph)₂] (0.42 g, 0.55 mmol) with an equimolar amount of ttoc (0.14 g, 0.55 mmol) with stirring in CH₂Cl₂ (50 cm³) at room temperature for 24 h, followed by filtration and removal of solvent *in vacuo*, gave the green complex [WBr(CO)(ttoc-S,S',S'')(η²-PhC₂Ph)]Br **15** (yield = 0.21 g).

[WI₂(CO){MeS(CH₂)₂S(CH₂)₂SMe-S,S',S''}(η²-PhC₂Ph)-{Fe(CO)₂(η-C₅H₅)}]I 7. To a stirred solution in CH₂Cl₂ (50 cm³) of [WI₂(CO){MeS(CH₂)₂S(CH₂)₂SMe-S,S'}(η²-PhC₂Ph)] **5** (0.54 g, 0.63 mmol) was added [FeI(CO)₂(η-(C₅H₅)] (0.20 g, 0.63 mmol). The resulting solution was stirred for 4 h at room temperature and the solvent removed *in vacuo*. The resulting black solid was recrystallised from CH₂Cl₂ (15 cm³) to give [WI₂(CO){MeS(CH₂)₂S(CH₂)₂SMe-S,S',S''}(η²-PhC₂Ph)-{Fe(CO)₂(η-C₅H₅)}]I **7** (yield = 0.22 g).

[MoI₂(CO){Ph₂P(S)CH₂P(S)Ph₂-S,S'}(η²-PhC₂Ph)] 8. To a solution of [MoI₂(CO)(NCMe)(η²-PhC₂Ph)₂] (0.40 g, 0.52 mmol) in CH₂Cl₂ (50 cm³) at room temperature was added Ph₂P(S)CH₂P(S)Ph₂ (0.23 g, 0.52 mmol). The resulting solution was stirred for 10 h, filtered over Celite and the solvent removed *in vacuo* to give the gold coloured complex [MoI₂(CO)-{Ph₂P(S)CH₂P(S)Ph₂-S,S'}(η²-PhC₂Ph)] **8** (0.29 g). Further purification was carried out *via* recrystallisation from the minimum volume of CH₂Cl₂ at 0 °C.

[MoI(CO)([9]aneS₃-S,S',S'')(η²-PhC₂Ph)]I 10 and [MoI-(CO)([9]aneS₃-S,S',S'')(η²-MeC₂Me)]I 9. To a solution of [MoI₂(CO)(NCMe)(η²-PhC₂Ph)₂] (0.40 g, 0.52 mmol) in CH₂Cl₂ (50 cm³) at room temperature was added [9]aneS₃ (0.09 g, 0.52 mmol). The resulting solution was stirred for 20 h before filtration over Celite and removal of the solvent *in vacuo* gave the green complex [MoI(CO)([9]aneS₃-S,S',S'')(η²-PhC₂Ph)]I **10** (0.18 g). Recrystallisation from CH₂Cl–Et₂O at 0 °C gave green crystals of suitable quality for X-ray crystallography.

Similarly, addition of [9]aneS₃ (0.10 g, 0.57 mmol) to a solution of [MoI₂(CO)(NCMe)(η²-MeC₂Me)₂] (0.30 g, 0.57 mmol) in CH₂Cl₂ (50 cm³) at room temperature for 24 h gave the green complex [MoI(CO)([9]aneS₃-S,S',S'')(η²-MeC₂Me)]I **9** (0.24 g). Further purification was carried out *via* recrystallisation from the minimum volume of CH₂Cl₂ at 0 °C.

[MoI(CO)(ttoc-S,S',S'')(η²-MeC₂Me)]I 11 and [MoI(CO)-(ttoc-S,S',S'')(η²-PhC₂Ph)]I 13. To a solution of [MoI₂-(CO)(NCMe)(η²-PhC₂Ph)₂] (0.43 g, 0.55 mmol) in CH₂Cl₂ (50 cm³) at room temperature was added ttoc (0.14 g, 0.55 mmol). The resulting solution was stirred for 20 h before filtration over Celite and removal of the solvent *in vacuo* gave the green complex [MoI(CO)(ttoc-S,S',S'')(η²-PhC₂Ph)]I **13** (0.27 g, 60%). Similarly, stirring a solution of ttoc (0.17 g, 0.65 mmol) plus [MoI₂(CO)(NCMe)(η²-MeC₂Me)₂] (0.34 g, 0.65 mmol) in CH₂Cl₂ (50 cm³) at room temperature for 24 h gave the green complex [MoI(CO)(ttoc-S,S',S'')(η²-MeC₂Me)]I **11** (0.19 g, 42%). Complexes **11** and **13** were recrystallised from CH₂Cl₂ solutions before final drying *in vacuo*.

[WI(CO)(ttoc-S,S',S'')(η²-PhC₂Ph)]I 14, [WI(ttoc-S,S',S'')(η²-PhC₂Ph)₂]I₃ 16 and [WI(CO)(ttoc-S,S',S'')(η²-MeC₂Me)]I 12. To a solution of [WI₂(CO)(NCMe)(η²-PhC₂Ph)₂] (0.30 g, 0.35 mmol) in CHCl₃ (50 cm³) was added ttoc (0.09 g, 0.35 mmol) and the solution was stirred at room temperature for 72 h. The resulting solution was filtered over Celite and the solvent removed *in vacuo* to give the lime-green crystalline complex [WI(CO)(ttoc-S,S',S'')(η²-PhC₂Ph)]I **14** (yield = 0.17 g). Further recrystallisation from CH₂Cl₂–Et₂O (90:10) in the presence of PhC₂Ph at −17 °C for 2 weeks gave more of the lime-green complex and also three very well formed dark green crystals. These crystals were characterised by X-ray crystallography as [WI(ttoc-S,S',S'')(η²-PhC₂Ph)₂]I₃ **16** (yield <1%).

The reaction of [WI₂(CO)(NCMe)(η²-MeC₂Me)₂] (0.30 g, 0.49 mmol) with ttoc (0.13 g, 0.49 mmol) with stirring in CH₂Cl₂ (50 cm³) at room temperature for 72 h gave a green

sticky oil after removal of the solvent *in vacuo*. Recrystallisation from CH_2Cl_2–Et_2O at $0\,°C$ gave the lime-green complex [WI(CO)(ttoc-*S*,*S'*,*S''*)(η^2-MeC$_2$Me)]I **12** (yield = 0.15 g).

Crystallography

Crystal data are given in Table 4, together with refinement details. Data for compound **5** were collected on a Delft Instrument FAST TV area detector[26] at the window of a rotating-anode generator, with a molybdenum target. An absorption correction was carried out using DIFABS.[27]

The structure was solved by heavy-atom methods (SHELXS[28]) and then subjected to full-matrix least-squares refinement based on F_o^2 (SHELXL 93[29]). Diagrams were drawn with SNOOPI.[30] Sources of scattering factor data are given in ref. 29.

Data for compounds **10** and **16** were collected using the MAR Research image plate system. The crystals were positioned 75 mm from the 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.[31] Both structures were solved using direct methods with SHELXS 86.[28] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions. Both structures contained some disordered solvent molecules. Absorption corrections were carried out using DIFABS and the structures were then refined on F^2 using SHELXL 93.

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References

1 J. L. Templeton, *Adv. Organomet. Chem.*, 1989, **29**, 1.
2 P. K. Baker, *Adv. Organomet. Chem.*, 1996, **40**, 45.
3 P. K. Baker and E. M. Armstrong, *Polyhedron*, 1989, **8**, 351.
4 P. K. Baker and S. D. Ridyard, *Polyhedron*, 1993, **12**, 915.
5 P. K. Baker and S. D. Ridyard, *Polyhedron*, 1993, **12**, 2105.
6 P. K. Baker and K. R. Flower, *Polyhedron*, 1990, **9**, 2135.
7 P. K. Baker, K. R. Flower, P. A. Bates and M. B. Hursthouse, *J. Organomet. Chem.*, 1989, **372**, 263.
8 P. K. Baker and K. R. Flower, *Z. Naturforsch.*, *Teil B*, 1993, **48**, 1715.
9 J. Kim and D. C. Rees, *Science*, 1992, **257**, 1677.
10 W. H. Orme-Johnson, *Science*, 1992, **257**, 1639.
11 J. Kim and D. C. Rees, *Nature* (*London*), 1992, **360**, 553.
12 P. K. Baker, A. I. Clark, S. J. Coles, M. B. Hursthouse and R. L. Richards, *J. Organomet. Chem.*, 1996, **518**, 235.
13 P. K. Baker, D. J. Muldoon, A. J. Lavery and A. Shawcross, *Polyhedron*, 1994, **13**, 2915.
14 N. Aimeloglou, P. K. Baker, M. G. B. Drew and M. M. Meehan, *Polyhedron*, in the press.
15 E. M. Armstrong. P. K. Baker and M. G. B. Drew, *Organometallics*, 1988, **7**, 319.
16 P. K. Baker, M. G. B. Drew, S. Edge and S. D. Ridyard, *J. Organomet. Chem.*, 1991, **409**, 207.
17 P. K. Baker, S. D. Harris, M. C. Durrant, D. L. Hughes and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1401.
18 P. K. Baker, S. J. Coles, M. C. Durrant, S. D. Harris, D. L. Hughes, M. B. Hursthouse and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4003.
19 M. T. Ashby and D. L. Lichtenberger, *Inorg. Chem.*, 1985, **24**, 636.
20 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 3288.
21 M. C. Durrant, B. Goerdt, C. Hauser, T. Krawinkel and R. L. Richards, *Transition Met. Chem.*, 1996, **20**, 583.
22 B. de Groot and S. J. Loeb, *Inorg. Chem.*, 1990, **29**, 4084.
23 A. Davison and D. L. Reger, *Inorg. Chem.*, 1971, **10**, 1967.
24 R. S. Glass, G. S. Wilson and W. N. Setzer, *J. Am. Chem. Soc.*, 1980, **102**, 5068.
25 M. C. Durrant and R. L. Richards, *Chem. Ind.*, (*London*), 1991, 474.
26 S. R. Drake, M. B. Hursthouse, K. M. A. Malik and S. A. S. Miller, *Inorg. Chem.*, 1993, **32**, 4653.
27 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
28 SHELX 86, G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
29 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.
30 K. Davies and K. C. Prout, University of Oxford, 1993.
31 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.