Synthesis of the Cationic Bis(but-2-yne) Complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ and its Reactions with Neutral Bidentate Donor Ligands (L–L) to give $[W(CO)(S_2CNC_4H_8)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]BF_4$: *X*-ray Crystal Structure Determination of $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ †

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Silver tetrafluoroborate reacts with an equimolar quantity of $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ in acetonitrile at room temperature to give the cationic mono(acetonitrile) compound $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ (**1**) in good yield. Equimolar quantities of (**1**) and L–L [L–L = $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2), $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, 2,2′-bipyridine, 1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, or $S_2CP(C_6H_{11})_3$] react in CH_2Cl_2 at room temperature to give the highly coloured mono(but-2-yne) complexes $[W(CO)(S_2CNC_4H_8)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]BF_4$ (**2**)—(**8**) in high yield. The structure of $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ (**2**) was determined by *X*-ray crystallography. Crystals of (**2**) are monoclinic, space group $P2_1/c$ with a = 11.638(1), b = 12.400(2), c = 25.165(3) Å, and β = 90.40(1)°. The structure was refined to R = 0.069 (R' = 0.094) for 2 031 reflections with $F_o > 5\sigma(F_o)$. The geometry about the tungsten atom in (**2**) can be described as pseudo-octahedral, with the but-2-yne ligand *trans* to one of the phosphorus atoms of the $Ph_2PCH_2PPh_2$ ligand. The other phosphorus atom, the two sulphur atoms of the dithiocarbamate ligand, and the carbon monoxide ligand all lie approximately in the equatorial plane. The barrier to rotation of the but-2-yne ligand in complexes (**2**)—(**6**) was determined by variable-temperature ^1H n.m.r. spectroscopy. The results are discussed in terms of the steric and electronic effects of the bidentate donor ligands in (**2**)—(**6**). Carbon-13 n.m.r. spectroscopy suggests that the two but-2-yne ligands in (**1**) are donating a total of six electrons to the metal whereas the but-2-yne ligand in (**2**)—(**8**) acts as a four-electron donor to the metal centre.

Since alkyne ligands have two perpendicular filled $p\pi$ orbitals they can donate from two to four electrons to a transition-metal centre. This idea has been explored by both theoretical studies [1] and experimental results.[2] Since the report of Bottrill and Green [3] on the synthesis of the cationic bis(alkyne) molybdenum complexes $[Mo(CO)(\eta^2\text{-}RC_2R')_2(\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7)]BF_4$ in 1977, cationic alkyne complexes of molybdenum(II) and tungsten(II) have received considerable attention.[4]

In 1988 [5] we described the synthesis and structures of the neutral bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph). These complexes were prepared by reacting the seven-co-ordinate compound $[WI_2(CO)_3(NCMe)_2]$ with RC_2R in CH_2Cl_2. They react with, for example, S_2CX^- [X = NMe_2, NEt_2, $N(CH_2Ph)_2$, NC_4H_8, NC_5H_{10}, or OEt] to give the mono(iodo) compounds $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$.[6] In this paper we report the reaction of $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ with $AgBF_4$ in acetonitrile to give the new cationic bis(alkyne) compound $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ and describe its reaction with a series of bidentate ligands. The *X*-ray crystal structure of $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]BF_4$ is also described.

Results and Discussion

Equimolar quantities of $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ and $AgBF_4$ react in acetonitrile to give the new cationic complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ (**1**) in good yield. Complex (**1**) is very hygroscopic and it was difficult to obtain good analytical data for this compound. However, (**1**) reacts with an equimolar quantity of a bidentate ligand L–L [L–L = $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2), $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 5,6-dimethyl-1,10-phenanthroline (dmphen), or $S_2CP(C_6H_{11})_3$] to afford the highly coloured mono(but-2-yne) compounds $[W(CO)(S_2CNC_4H_8)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]BF_4$ (**2**)—(**8**) in high yield; these complexes are much less hygroscopic than (**1**). Complexes (**1**)—(**8**) have been fully characterised by elemental analysis (C, H, and N), i.r. spectroscopy (Table 1), and ^1H and ^{13}C n.m.r. spectroscopy (Tables 2 and 3). All the compounds are soluble in chlorinated solvents such as $CHCl_3$ and CH_2Cl_2, acetonitrile, and acetone, but are insoluble in hydrocarbon solvents and diethyl ether.

The ^1H n.m.r. spectrum of (**1**) shows four different but-2-yne methyl resonances which suggests the asymmetric structure as shown in Figure 1, *i.e.* similar to the solid-state structure of the complex $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ which has been determined crystallographically.[6] The ^{13}C n.m.r. spectrum shows four but-2-yne contact carbon resonances between 183.29 and 162.89 p.p.m. which suggests [7] that the two but-2-yne ligands in (**1**) are donating a total of six electrons to the metal.

The structure of the bis(diphenylphosphino)methane complex $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ (**2**) has been determined by *X*-ray crystallography. The structure of

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† Bis(diphenylphosphino)methane(η^2-but-2-yne)carbonyl(pyrrolidine-1-carbodithioato)tungsten(II) tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Physical, analytical, and i.r. data for the complexes $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ and $[W(CO)(S_2CNC_4H_8)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]BF_4$

Complex	Colour	Yield (%)	Analysis[a] (%) C	H	N	I.r.[b] (cm^{-1}) ν(CO)	ν(C≡C)
(1) $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$[c]	Yellow-brown	63	31.2 (32.3)	3.5 (3.9)	3.8 (4.7)	2 080s	1 850vw
(2) $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$	Red	65	47.8 (47.6)	4.4 (4.1)	1.6 (1.6)	1 939s	1 645w
(3) $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}MeC_2Me)]BF_4$	Red	65	48.0 (48.2)	4.5 (4.3)	1.2 (1.6)	1 937s	*d*
(4) $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_2PhP(CH_2)_2PPh_2\text{-}PP'\}(\eta^2\text{-}MeC_2Me)]BF_4$	Red	59	51.3 (51.1)	5.0 (4.6)	1.1 (1.4)	1 942s	1 620vw
(5) $[W(CO)(S_2CNC_4H_8)(bipy)(\eta^2\text{-}MeC_2Me)]BF_4$	Red	65	36.4 (36.7)	3.6 (3.4)	6.0 (6.4)	1 935s	1 635vw
(6) $[W(CO)(S_2CNC_4H_8)(phen)(\eta^2\text{-}MeC_2Me)]BF_4$	Red	63	38.7 (38.9)	3.4 (3.3)	5.9 (6.2)	1 938s	1 644vw
(7) $[W(CO)(S_2CNC_4H_8)(dmphen)(\eta^2\text{-}MeC_2Me)]BF_4$	Red	62	40.4 (40.8)	3.7 (3.7)	5.7 (5.9)	1 934s	*d*
(8) $[W(CO)(S_2CNC_4H_8)\{S_2CP(C_6H_{11})_3\}(\eta^2\text{-}MeC_2Me)]BF_4$	Red-brown	53	40.7 (40.7)	5.8 (5.5)	1.3 (1.6)	1 942s	*d*

[a] Calculated values in parentheses. [b] Spectra recorded in $CHCl_3$ as thin films between NaCl plates; s = strong, vw = very weak. [c] ν(C≡N) at 2 325w and 2 300w cm^{-1}. [d] ν(C≡C) was not observed.

Table 2. Proton n.m.r. data* (δ, *J* in Hz) for the complexes $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ and $[W(CO)(S_2CNC_4H_8)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]BF_4$

Complex	
(1)	3.92 (t, 2 H, NCH_2, *J* 6.23); 3.62 (t, 2 H, NCH_2, *J* 6.73); 3.02, 2.98, 2.94, 2.85 (4 × s, 12 H, ≡CMe); 2.09 (s, 3 H, NCMe); 1.99 (br m, 4 H, CH_2)
(2)	7.35 (m, 20 H, Ph); 4.62 (m, 2 H, PCH_2P); 3.45 (m, 4 H, NCH_2), 2.9 (s, 6 H, ≡CMe); 1.85 (m, 4 H, CH_2)
(3)	7.5 (m, 20 H, Ph); 3.40 (m, 4 H, NCH_2); 2.7 (s, 6 H, ≡CMe); 1.90 (m, 4 H, CH_2); 1.75 (m, 4 H, CH_2)
(4)	7.45 (m, 25 H, Ph); 3.45 (m, 4 H, NCH_2); 2.72 (s, 6 H, ≡CMe); 1.80 (m, 4 H, CH_2); 1.45 (m, 8 H, CH_2)
(5)	8.75—7.25 (m, 8 H, bipy); 3.65 (m, 4 H, NCH_2); 3.42 (s, 6 H, ≡CMe); 2.25 (m, 4 H, CH_2)
(6)	8.8—7.65 (m, 8 H, phen); 3.95 (m, 4 H, NCH_2); 3.45 (s, 6 H, ≡CMe); 2.15 (m, 4 H, CH_2)
(7)	9.7—7.75 (m, 6 H, dmphen); 3.95 (m, 4 H, NCH_2); 3.55 (s, 6 H, ≡CMe); 2.82 (s, 3 H, CH_3); 2.75 (s, 3 H, CH_3); 2.05 (m, 4 H, CH_2)
(8)	3.5 (m, 4 H, NCH_2); 3.0 (s, 6 H, ≡CMe); 2.1 (m, 4 H, NCH_2); 1.84, 1.60, 1.45 (m, 33 H, C_6H_{11})

* Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$: s = singlet, t = triplet, m = multiplet, and br = broad multiplet.

Table 3. Carbon-13 n.m.r. data[a] (δ/p.p.m., *J*/Hz) for the complexes $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ and $[W(CO)(S_2CNC_4H_8)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]BF_4$

Complex	
(1)	207.46 (s, C≡O); 193.29 (s, CS_2); 183.29, 174.9, 173.8, 162.89 (s, C≡C); 126.75 (s, N*C*Me); 50.59 (s, NCH_2); 50.32 (s, NCH_2); 24.93 (s, CH_2); 24.61 (s, CH_2); 19.16, 19.13, 18.36, 17.0 (4 × s, ≡C*Me*); 4.0 (s, *Me*CN)
(2)	223.8 (s, C≡C); 206.7 (s, C≡O); 202.5 (s, CS_2); 133.15—126.49 (m, Ph); 50.98 (s, NCH_2); 49.9 (s, NCH_2); 30.43 [t, PCH_2P, *J*(P–C) 26.1]; 24.84 (s, CH_2); 24.4 (s, CH_2); 19.61 (s, ≡C*Me*)
(3)	222.9 (s, C≡C); 208.8 (s, C≡O); 203.5 (s, CS_2); 134.7—126.84 (m, Ph); 50.5 (s, NCH_2); 49.5 (s, NCH_2); 28.84 [d, PCH_2, *J*(P–C) 13]; 28.29 [d, PCH_2, *J*(P–C) 12.89]; 24.61 (s, CH_2); 24.35 (s, CH_2); 19.76 (s, ≡C*Me*)
(4)	223.4 (s, C≡C); 207.6 (s, C≡O); 203.1 (s, CS_2); 137.08—123.5 (m, Ph); 50.3 (s, NCH_2); 49.4 (s, NCH_2); 29.67 (m, PCH_2); 24.61 (s, CH_2); 24.16 (s, CH_2); 19.51 (s, ≡C*Me*)
(5)	218.9 (s, C≡C); 209.9 (s, C≡O); 205.3 (s, CS_2); 153.14, 153.0, 151.3, 148.4, 141.7, 140.1, 127.4, 126.2, 125.1, 124.5 (m, bipy); 51.87 (s, NCH_2); 50.5 (s, NCH_2); 22.3 (s, ≡C*Me*)
(6)	225.66 (s, C≡C); 205.94 (s, CS_2); 152.65, 149.0, 143.7, 143.4, 140.1, 138.5, 130.7, 130.5, 127.9, 127.7, 126.9, 125.3 (m, phen); 52.1 (s, NCH_2); 50.5 (s, NCH_2); 24.91 (s, CH_2); 24.5 (s, CH_2); 22.42 (s, ≡C*Me*)
(7)	226.8 (s, C≡C); 205.94 (s, CS_2); 152.3, 149.8, 144.8, 144.2, 143.2, 140.1, 138.9, 138.3, 132.7, 132.4, 131.9, 127.8, 126.6 (m, dmphen); 51.9 (s, NCH_2), 50.8 (s, NCH_2); 24.3 (s, CH_2); 22.38 (s, ≡C*Me*); 19.95 (s, CH_3); 19.74 (s, CH_3)
(8)	221.9 (s, C≡C); 209.4 (s, C≡O); 201.62 (s, CS_2); 195 (s, CS_2); 50.21 (s, NCH_2); 49.71 (s, NCH_2); 28.42—24.08 (m, CH_2);[b] 19.72 (s, ≡C*Me*)

[a] Spectra recorded in $CDCl_3$ (+25 °C) referenced to $SiMe_4$: s = singlet, m = multiplet, and d = doublet. [b] Complex resonances structure which leads to non-assignment of each individual resonance of $P(C_6H_{11})_3$ and CH_2 groups of pyrrolidine ring.

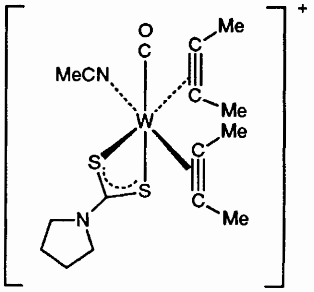

Figure 1. Proposed structure in solution for complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ **(1)**

(2) is shown in Figure 2 with selected bond lengths and angles in Table 4. The geometry about the metal atom is conveniently described as strongly distorted octahedral if the but-2-yne ligand is considered to occupy one site only. This ligand would seem to bond in a slightly asymmetric fashion [W–C 2.01(3), 2.08(4) Å] but the low precision of the structure determination does not allow one to attach any real significance to the difference. On the other hand, the asymmetry in the $Ph_2PCH_2PPh_2$ ligand chelation [W–P 2.491(8), 2.627(10) Å] is almost certainly real, with the longer bond *trans* to the but-2-yne ligand. Similarly, asymmetry in the dithiocarbamate chelation [W–S 2.443(8), 2.541 (11) Å] is explained by the *trans* positioning of S(2) to the carbonyl.

The energy barriers to but-2-yne rotation of complexes **(2)**—**(6)** were determined using variable-temperature ^1H n.m.r. spectroscopy. The spectra of the but-2-yne methyl protons of $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ **(2)** at various temperatures are shown in Figure 3. The values of

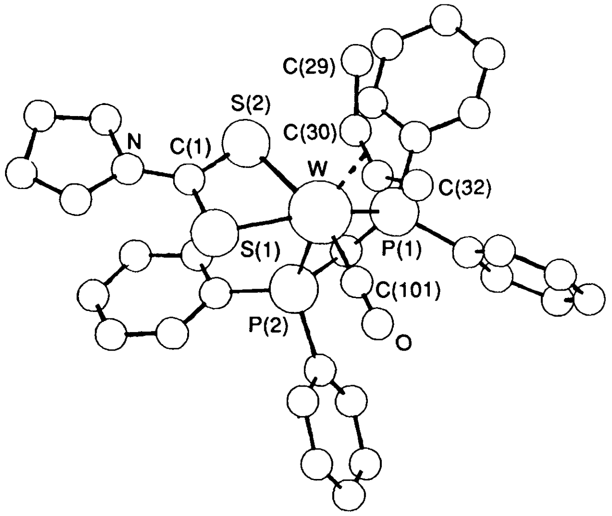

Figure 2. *X*-ray crystal structure of the cation in $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ (**2**)

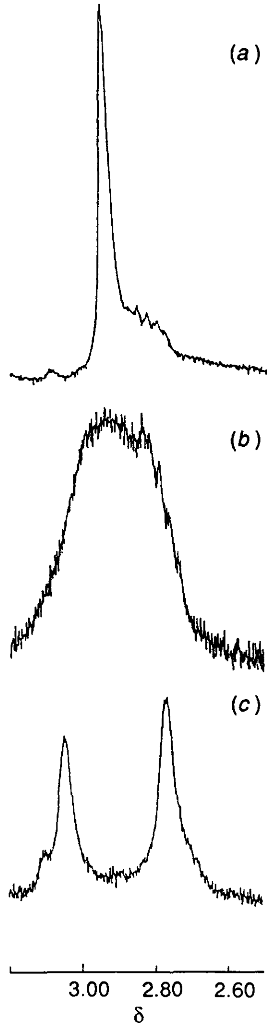

Figure 3. But-2-yne methyl ^1H n.m.r. resonances at various temperatures for the complex $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ (**2**); 295 (*a*), 248 (*b*), and 233 K (*c*)

Table 4. Selected bond lengths (Å) and angles (°) for complex (**2**)

S(1)–W	2.443(8)	S(2)–W	2.541(11)
P(1)–W	2.491(8)	P(2)–W	2.627(10)
C(101)–W	1.974(32)	C(30)–W	2.007(33)
C(31)–W	2.079(35)	C(25)–S(1)	1.769(29)
C(25)–S(2)	1.684(27)	C(6)–P(1)	1.835(20)
C(12)–P(1)	1.818(19)	C(34)–P(1)	1.849(27)
C(18)–P(2)	1.836(22)	C(24)–P(2)	1.847(20)
C(34)–P(2)	1.863(27)	C(25)–N	1.327(33)
C(26)–N	1.555(39)	C(29)–N	1.511(37)
O–C(101)	1.115(31)	C(27)–C(26)	1.506(49)
C(28)–C(27)	1.458(54)	C(29)–C(28)	1.495(45)
C(31)–C(30)	1.360(44)	C(32)–C(30)	1.530(42)
C(33)–C(31)	1.476(44)		
S(2)–W–S(1)	71.3(3)	P(1)–W–S(1)	146.5(2)
P(1)–W–S(2)	90.4(3)	P(2)–W–S(1)	84.4(3)
P(2)–W–S(2)	80.7(3)	P(2)–W–P(1)	64.7(3)
C(101)–W–S(1)	94.6(9)	C(101)–W–S(2)	162.7(8)
C(101)–W–P(1)	96.9(9)	C(101)–W–P(2)	88.2(9)
C(30)–W–S(1)	115.3(10)	C(30)–W–S(2)	84.1(11)
C(30)–W–P(1)	89.3(10)	C(30)–W–P(2)	149.6(10)
C(30)–W–C(101)	111.6(12)	C(31)–W–S(1)	144.4(9)
C(31)–W–S(2)	121.3(10)	C(31)–W–P((1)	99.0(9)
C(31)–W–P(2)	154.0(9)	C(31)–W–C(101)	73.1(13)
C(31)–W–C(30)	38.8(12)	C(25)–S(1)–W	87.7(9)
C(25)–S(2)–W	86.4(10)	C(6)–P(1)–W	117.3(8)
C(12)–P(1)–W	120.8(7)	C(12)–P(1)–C(6)	103.2(9)
C(34)–P(1)–W	99.6(9)	C(34)–P(1)–C(6)	106.6(11)
C(34)–P(1)–C(12)	108.4(11)	C(18)–P(2)–W	121.8(8)
C(24)–P(2)–W	116.9(7)	C(24)–P(2)–C(18)	105.4(9)
C(34)–P(2)–W	94.6(9)	C(34)–P(2)–C(18)	109.7(11)
C(34)–P(2)–C(24)	107.0(10)	C(26)–N–C(25)	119.8(23)
C(29)–N–C(25)	126.6(26)	C(29)–N–C(26)	113.7(22)
O–C(101)–W	179.2(27)	C(1)–C(6)–P(1)	119.8(6)
C(5)–C(6)–P(1)	120.1(6)	C(7)–C(12)–P(1)	118.4(6)
C(11)–C(12)–P(1)	121.1(6)	C(13)–C(18)–P(2)	118.9(6)
C(17)–C(18)–P(2)	120.9(6)	C(19)–C(24)–P(2)	117.8(5)
C(23)–C(24)–P(2)	122.0(5)	S(2)–C(25)–S(1)	114.5(15)
N–C(25)–S(1)	120.0(21)	N–C(25)–S(2)	125.5(22)
C(27)–C(26)–N	99.4(26)	C(28)–C(27)–C(26)	108.1(35)
C(29)–C(28)–C(27)	110.7(33)	C(28)–C(29)–N	100.1(26)
C(31)–C(30)–W	73.5(20)	C(32)–C(30)–W	149.5(25)
C(32)–C(30)–C(31)	136.5(33)	C(30)–C(31)–W	67.7(22)
C(33)–C(31)–W	148.7(24)	C(33)–C(31)–C(30)	143.5(32)
P(2)–C(24)–P(1)	95.3(13)		

Table 5. Barriers to but-2-yne rotation for the complexes $[W(CO)(S_2CNC_4H_8)(L\text{–}L)(\eta^2\text{-}MeC_2Me)]BF_4$

Complex	T_c[a]/K	$\Delta\nu$[b]/Hz	$\Delta G^‡$ (T_c)/ kJ mol^{-1}
(**2**)	248	70	49.9
(**3**)	268	36.1	55.6
(**4**)	268	58.97	54.5
(**5**)	277	44.48	57.1
(**6**)	278	58.84	56.7

[a] T_c = Coalescence temperature. [b] $\Delta\nu$ = Separation of but-2-yne methyl signals undergoing collapse.

$\Delta G^‡$ for (**2**)—(**6**) were calculated using the Gutowsky–Holm equation[8] and are given in Table 5. It is interesting to note that the $Ph_2P(CH_2)_2PPh_2$ complex $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}MeC_2Me)]BF_4$ (**3**) has a higher barrier to but-2-yne rotation ($\Delta G^‡$ = 55.6 kJ mol^{-1}) compared to the $Ph_2PCH_2PPh_2$ compound (**2**) ($\Delta G^‡$ = 49.9 kJ mol^{-1}). This is likely to be due to the fact that the $Ph_2P(CH_2)_2PPh_2$ ligand occupies more space at the metal centre compared to $Ph_2PCH_2PPh_2$. The triphosphine complex $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_2PhP(CH_2)_2PPh_2\text{-}PP'\}(\eta^2\text{-}MeC_2Me)]BF_4$ (**4**) has a similar barrier to but-2-yne rotation (within

Table 6. Fractional atomic co-ordinates (× 10^4) for complex **(2)**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	11 236(1)	2 301(1)	524(1)	C(17)	10 801(19)	2 857(17)	2 347(9)
S(1)	9 203(6)	2 588(8)	714(3)	C(18)	10 616(19)	3 559(17)	1 922(9)
S(2)	10 638(8)	1 019(7)	1 260(4)	C(19)	11 082(14)	5 556(17)	890(8)
P(1)	13 240(6)	2 324(8)	878(3)	C(20)	11 210(14)	6 662(17)	808(8)
P(2)	11 581(7)	3 564(7)	1 348(4)	C(21)	12 125(14)	7 212(17)	1 044(8)
N	8 438(22)	1 364(26)	1 520(12)	C(22)	12 912(14)	6 658(17)	1 363(8)
O	11 454(21)	4 318(22)	−189(10)	C(23)	12 784(14)	5 552(17)	1 445(8)
C(101)	11 375(26)	3 585(28)	65(14)	C(24)	11 869(14)	5 001(17)	1 209(8)
C(1)	14 797(17)	658(17)	664(7)	C(25)	9 334(25)	1 601(25)	1 218(13)
C(2)	15 297(17)	−352(17)	745(7)	C(26)	8 552(28)	482(29)	1 956(14)
C(3)	14 932(17)	−1 002(17)	1 163(7)	C(27)	7 301(46)	329(44)	2 086(23)
C(4)	14 066(17)	−643(17)	1 500(7)	C(28)	6 691(36)	1 316(37)	1 944(18)
C(5)	13 565(17)	367(17)	1 419(7)	C(29)	7 255(30)	1 862(29)	1 485(15)
C(6)	13 931(17)	1 017(17)	1 001(7)	C(30)	11 598(31)	941(29)	127(17)
C(7)	14 347(14)	3 131(16)	−7(8)	C(31)	11 564(31)	1 746(32)	−240(16)
C(8)	15 268(14)	3 592(16)	−277(8)	C(32)	11 714(32)	−289(32)	120(16)
C(9)	16 196(14)	4 017(16)	7(8)	C(33)	11 668(32)	1 980(30)	−813(16)
C(10)	16 203(14)	3 981(16)	561(8)	C(34)	12 981(25)	2 937(24)	1 536(12)
C(11)	15 282(14)	3 521(16)	831(8)	F(1)	3 200(28)	1 091(26)	2 624(14)
C(12)	14 354(14)	3 095(16)	547(8)	F(2)	3 778(29)	1 436(29)	3 472(15)
C(13)	9 648(19)	4 222(17)	1 913(9)	F(3)	4 575(30)	433(28)	2 975(15)
C(14)	8 864(19)	4 183(17)	2 329(9)	F(4)	4 334(28)	2 409(30)	2 820(13)
C(15)	9 049(19)	3 481(17)	2 755(9)	B	3 653(55)	1 479(56)	3 011(29)
C(16)	10 017(19)	2 818(17)	2 764(9)				

experimental error ±1 kJ mol^{-1}) to the $Ph_2P(CH_2)_2PPh_2$ complex **(3)** which suggests that the unco-ordinated $-CH_2CH_2PPh_2$ moiety on the triphosphine ligand is not affecting the barrier to but-2-yne rotation. The more electron-rich ligands bipy and phen have, as expected, the same barrier to but-2-yne rotation within experimental error since they have similar electronic and steric properties when co-ordinated as bidentate ligands to the metal.

The ^{13}C n.m.r. spectra of complexes **(2)**—**(8)** have but-2-yne resonances above 200 p.p.m. which indicates[7] that the but-2-yne is utilising both of its perpendicular $p\pi$ orbitals in electron donation to the tungsten. The highly coloured nature of these four-electron alkyne complexes is similar to other four-electron mono(alkyne) complexes of molybdenum(II) and tungsten(II).[9] The alkyne contact carbon resonances and the carbonyl resonances (both above 200 p.p.m. in ^{13}C n.m.r. spectra) were distinguished by the fact that the but-2-yne contact carbon resonances are approximately twice as intense as the carbonyl resonance, and the carbonyl resonances are lower in chemical shift than the alkyne resonances as has been previously observed for this type of compound.[4a,9d]

Experimental

The synthesis and purification of the compounds described were carried out under an atmosphere of nitrogen using standard vacuum/Schlenk-line techniques. The compound $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ was prepared by the published method.[6] All chemicals were purchased from commercial sources.

Microanalyses (C, H, and N) were determined by using a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1430 ratio-recording infrared spectrophotometer. The ^1H, variable-temperature ^1H, and ^{13}C n.m.r. spectra were recorded on a Bruker AC 250 CP/MAS n.m.r. spectrometer by Mr. E. Lewis of the Department of Chemistry, University of Wales, Bangor.

$[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ **(1)**.—To $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$ (1.00 g, 1.68 mmol) dissolved in MeCN (40 cm^3) was added $AgBF_4$ (0.3282 g, 1.68 mmol) with continuous stirring under a stream of dry nitrogen. After stirring for 10 h the solvent was removed *in vacuo*. The crude product was then dissolved in CH_2Cl_2 (20 cm^3) and filtered to remove AgI. The solvent volume was reduced *in vacuo* to 2 cm^3 and dropwise addition of diethyl ether precipitated the yellow-brown cationic complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ **(1)** which on recrystallisation from MeCN yielded 0.63 g (63%).

$[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ **(2)**.—To $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ (0.4 g, 0.675 mmol) dissolved in CH_2Cl_2 (12 cm^3) was added $Ph_2PCH_2PPh_2$ (0.2593 g, 0.675 mmol) with continuous stirring under a stream of dry nitrogen. After 17 h the solution was filtered and the solvent volume reduced to 2 cm^3 *in vacuo*. Dropwise addition of diethyl ether precipitated the red cationic complex $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ **(2)** which on recrystallisation from CH_2Cl_2–Et_2O yielded 0.41 g (65%) of pure product, of which some of the crystals were suitable for *X*-ray crystallography.

Similar reactions of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]BF_4$ with $Ph_2P(CH_2)_2PPh_2$, $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, bipy, phen, dmphen, or $S_2CP(C_6H_{11})_3$ in CH_2Cl_2 afforded the analogous cationic complexes **(3)**—**(8)** respectively.

Crystal Structure Analysis of $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)]BF_4$ **(2)**.—The single crystal used for the *X*-ray examination was sealed under nitrogen in a capillary. Crystallographic data were obtained using a CAD4 diffractometer, operating in the ω—2θ scan mode and using graphite-monochromatised Mo-K_α radiation as previously described.[10]

Crystal data. $C_{35}H_{36}BF_4NOP_2S_2W$, $M = 884.426$, monoclinic, space group $P2_1/c$, $a = 11.638(1)$, $b = 12.400(2)$, $c = 25.165(3)$ Å, $\beta = 90.40(1)°$, $U = 3\,631.7(4)$ Å^3, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $\lambda(Mo\text{-}K_\alpha) = 0.7107$ Å, $\mu(Mo\text{-}K_\alpha) = 34.93$ cm^{-1}, $F(000) = 1.756$.

Cell dimensions were obtained by least-square refinement on setting angles of 25 well spaced reflections with $10.0 < \theta < 12.0°$. Intensity data were recorded on a crystal of dimensions $0.10 \times 0.12 \times 0.20$ mm in the range $1.5 \leqslant \theta \leqslant 25.0°$, with $-13 < h < 13$, $-14 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 14$. Monitoring of three standards shows that no significant deterioration of the crystal occurred (fluctuation <1.5%). The data were corrected for absorption empirically, using ψ-scan profiles. Of the 7 320 intensities measured, 6 372 were unique and only 2 031 observed $[I > 2.5\sigma(I)]$.

The structure was solved *via* the heavy atom method and refined by full-matrix least squares. Only the W, S, P, N, and O atoms were refined anisotropically, the remaining non-hydrogens isotropically; hydrogens were not located or included. Phenyl rings were treated as idealised hexagons with C–C 1.395 Å. The atoms of the BF_4^- ion showed considerable displacements. Computations were made with SHELX 80[11] using inlaid scattering factors (for C, H, S, P, N, O, B, and F) or as given in ref. 12 (for W). The final R,R' factors were 0.069, 0.094 respectively, for 177 parameters, with weights of $w = 1/\sigma^2(F) + 0.0067F_o^2]$ giving flat agreement analyses. The largest shift/estimated standard deviation was 1.4 U_{iso} for one of the F atoms. The residuals in the final difference map were −1.2 and 0.95 e $Å^{-3}$, the latter close to one of the F atoms.

The final atomic positions are given in Table 6. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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