Preparation, Characterisation, and Reactions with Phosphite Donor Ligands of the New Cationic Monoalkyne Complexes $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$ (n = 1—6; R = Me or Ph). *X*-Ray Crystal Structure of $[WI(CO)\{P(OPr^i)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]_{0.5}[OH]_{0.5}\cdot0.5H_2O$ †

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Reaction of the complexes $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)]$ (n = 1—6; R = Me or Ph) with 1 equivalent of $Ag[BF_4]$ in acetonitrile at room temperature affords good yields of the highly coloured cationic alkyne compounds $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$ (**1**)—(**12**). The complex $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ reacts rapidly with 1 equivalent of $P(OR')_3$ (R′ = Me, Et, Pr^i, or Bu^n) in CH_2Cl_2 to afford the substituted products $[WI(CO)\{P(OR')_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (**13**)—(**16**). *X*-Ray single crystallographic studies were carried out on the compound $[WI(CO)\{P(OPr^i)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]_{0.5}[OH]_{0.5}\cdot0.5[H_2O]$ (**15**). Crystals of (**15**) are monoclinic space group $P2_1/n$, Z = 8, in a unit cell of dimensions a = 19.494(18), b = 19.634(12), c = 25.063(15) Å, and β = 101.3(1)°. The structure was refined to R = 0.080 for 3 987 reflections above background. There are two cations in the asymmetric unit with equivalent geometry. The co-ordination geometry about the tungsten atoms may be considered to be octahedral, with as expected the but-2-yne ligand *trans* to the iodide ligand. Carbon-13 n.m.r. chemical shifts of the alkyne contact carbons suggest that the alkyne ligand is donating four-electrons to the metal in compounds (**1**)—(**16**). The barrier to but-2-yne rotation in (**15**) is $\Delta G^{\ddagger} = 56.9 \pm 0.5$ kJ mol^{-1}.

The orthogonal p_π orbitals of alkyne ligands allow variable electron-donor interactions to a transition metal which can range from two to four electrons depending on the complex under consideration.[1] This variable electron-donor ability of alkynes has been supported by theoretical calculations[2] and experimental results.[3] A wide range of cationic alkyne complexes of molybdenum(II) and tungsten(II) containing cyclopentadienyl or indenyl ligands have been reported and their chemistry studied in detail.[4] Hitherto, very few cationic halogeno-alkyne complexes of molybdenum(II) and tungsten(II) have been published. The only examples to be reported are by Lippard and co-workers.[5] In 1977, they described the reductive coupling of two isonitrile ligands to give cationic halogeno-alkyne complexes of the type $[MoI(CNR)_4(RNHC_2NHR)]I$. Further reports of this work have been published in the 1980s by Lippard and co-workers.[6]

In recent years we have been investigating the chemistry of the versatile bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph).[7] The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ react with 1 equivalent of bidentate phosphine ligands (L_2) to give the monoalkyne compounds $[WI_2(CO)(L_2)(\eta^2\text{-}RC_2R)]$.[8] In this paper we report the reactions of $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)]$ (n = 1—6; R = Me or Ph) with 1 equivalent of $Ag[BF_4]$ in acetonitrile to give the novel cationic halogenoalkyne complexes $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$. We also report the reactions of $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ with 1 equivalent of $P(OR')_3$ (R′ = Me, Et, Pr^i, or Bu^n) to give the substituted products $[WI(CO)\{P(OR')_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$. The *X*-ray crystal structure of $[WI(CO)\{P(OPr^i)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]_{0.5}[OH]_{0.5}\cdot0.5H_2O$ is also described.

Results and Discussion

The monoalkyne complexes $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)]$ (n = 1—6, R = Me or Ph) react with 1 equivalent of $Ag[BF_4]$ in acetonitrile at room temperature to give good yields of the new, highly coloured cationic alkyne compounds $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$ [(**1**)—(**12**)]. The highly coloured nature of these compounds (Table 1) is similar to that observed for other cationic 'four-electron' alkyne complexes of the types $[Mo(CO)L(\eta^2\text{-}RC_2R')(\eta^5\text{-}C_5H_5$ or $C_9H_7)][BF_4]$ (L = PEt_3, PPh_3, or $P(C_6H_{11})_3$, R = R′ = Me; R = Bu^t, R′ = H; R = Ph, R′ = Me; R = Pr^i, R′ = H) reported by Green and co-workers.[4d]

The compounds $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$ (**1**)—(**12**) were fully characterised by elemental analysis (C, H, and N) and i.r. spectroscopy (Table 1), ^1H and ^{13}C n.m.r. spectroscopy (Tables 2 and 3). All the new compounds, (**1**)—(**12**), are soluble in polar solvents such as NCMe, CH_2Cl_2, and $CHCl_3$ but, as expected, since being salts they are insoluble in non-polar solvents such as diethyl ether and hydrocarbon solvents. The complexes are stable when stored in the solid state under nitrogen for prolonged periods of time. However, they decompose when exposed to air in solution.

The room-temperature ^{31}P n.m.r. spectra ($CDCl_3$, +25 °C) of complexes (**1**) and (**7**) show one pair of intensity-matched doublets at δ = −19.30 (d, $^2J_{P-P}$ = 29.03) and −35.34 p.p.m. (d, $^2J_{P-P}$ = 29.05 Hz) for (**1**), and −23.9 (d, $^2J_{P-P}$ = 26.36) and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. vii—xx.

Table 1. Physical, analytical,[a] and i.r.[b] data for the complexes $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$ and $[WI(CO)\{P(OR')_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$

			Analytical data/%			I.r. (cm^{-1})		
Compound	Colour	Yield/ %	C	H	N	ν(CO)	ν(CN)	ν(C≡C)
(**1**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Purple	70	42.2 (42.4)	3.7 (3.5)	1.3 (1.6)	1 960s	2 375w, 2 350w	1 680w
(**2**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Purple	68	43.1 (43.3)	3.8 (3.6)	1.8 (1.5)	1 960s	2 370w, 2 340w	1 660w
(**3**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Purple	65	43.9 (43.8)	3.7 (3.8)	1.8 (1.5)	1 950s	2 375w, 2 350w	1 625w
(**4**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_4PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Pink	66	44.5 (44.4)	4.1 (4.0)	1.5 (1.5)	1 960s	2 375w, 2 345w	1 650w
(**5**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_5PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Pink	60	45.0 (44.9)	4.3 (4.1)	1.6 (1.5)	1 960s	2 375w, 2 345w	1 660w
(**6**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_6PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Pink	63	45.5 (45.6)	4.2 (4.2)	1.4 (1.4)	1 970s	2 380w, 2 350w	1 660w
(**7**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$	Green	57	48.7 (49.0)	3.7 (3.4)	1.5 (1.4)	1 970s	2 355w, 2 335w	1 650w
(**8**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$	Green	57	49.8 (49.5)	3.7 (3.6)	1.5 (1.3)	1.970s	2 350w, 2 315w	1 640w
(**9**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$	Green	53	49.8 (49.9)	3.5 (3.7)	1.4 (1.3)	1 970s	2 350w, 2 320w	1 630w
(**10**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_4PPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$	Green	54	50.2 (50.4)	4.0 (3.9)	1.4 (1.3)	1 980s	2 355w, 2 330w	1 630w
(**11**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_5PPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$	Green	57	50.7 (51.0)	4.1 (4.0)	1.3 (1.3)	1 980s	2 350w, 2 330w	1 635w
(**12**) $[WI(CO)(NCMe)\{Ph_2P(CH_2)_6PPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$	Green	52	50.9 (51.4)	4.1 (4.1)	1.3 (1.3)	1 975s	2 345w, 2 300w	1 635w
(**13**) $[WI(CO)\{P(OMe)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Orange	53	39.7 (40.1)	3.8 (3.8)		1 975s		1 650w
(**14**) $[WI(CO)\{P(OEt)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Red	57	41.7 (42.0)	3.9 (4.2)		1 970s		1 675w
(**15**) $[WI(CO)\{P(OPr^i)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Red	58	43.7 (43.7)	4.6 (4.6)		1 965s		1 640w
(**16**) $[WI(CO)\{P(OBu^n)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$	Red	55	44.9 (45.3)	4.7 (5.0)		1 665s		1 635w

[a] Calculated values in parentheses. [b] Spectra recorded in $CHCl_3$ as thin films between NaCl plates; w = weak, m = medium, s = strong.

Table 2. Proton n.m.r. data* for the complexes $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$ and $[WI(CO)\{P(OR\ )_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$

Compd.	^1H (δ p.p.m.)
(**1**)	7.36 (br s, 20 H, aryl H), 3.3 (s, 6 H, MeC≡), 2.15 (br s, 3 H, NCMe), 1.3 (s, 2 H, CH_2)
(**2**)	7.69 (br s, 20 H, aryl H), 2.98 (s, 6 H, MeC≡), 1.99 (s, 3 H, NCMe), 1.83 (br m, 2 H, CH_2), 1.42 (br m, 2 H, CH_2)
(**3**)	7.44 (br s, 20 H, aryl H), 2.98 (s, 6 H, MeC≡), 1.99 (s, 3 H, NCMe), 1.73 (br m, 6 H, CH_2)
(**4**)	7.41 (br s, 20 H, aryl H), 2.64 (s, 6 H, MeC≡), 2.0 (s, 3 H, NCMe), 1.24 (br m, 8 H, CH_2)
(**5**)	7.4 (br s, 20 H, aryl H), 2.88 (s, 6 H, MeC≡), 2.01 (s, 3 H, NCMe), 0.96 (br m, 10 H, CH_2)
(**6**)	7.41 (br s, 20 H, aryl H), 2.67 (s, 6 H, MeC≡), 2.02 (s, 3 H, NCMe), 1.18 (br m, 12 H, CH_2)
(**7**)	7.41 (br s, 30 H, aryl H), 2.01 (s, 3 H, NCMe), 1.23 (s, 2 H, CH_2)
(**8**)	7.39 (br s, 30 H, aryl H), 2.01 (s, 3 H, NCMe), 1.48 (br m, 4 H, CH_2)
(**9**)	7.30 (br s, 30 H, aryl H), 2.0 (s, 3 H, NCMe), 1.2 (br m, 6 H, CH_2)
(**10**)	7.27 (br s, 30 H, aryl H), 2.0 (s, 3 H, NCMe), 1.19 (br m, 8 H, CH_2)
(**11**)	7.27 (br s, 30 H, aryl H), 2.14 (s, 3 H, NCMe), 0.88 (br m, 10 H, CH_2)
(**12**)	7.28 (br s, 30 H, aryl H), 2.01 (s, 3 H, NCMe), 0.93 (br m, 12 H, CH_2)
(**13**)	7.32 (br s, 20 H, aryl H), 3.69 (m, 9 H, OMe), 2.97 (s, 6 H, MeC≡), 0.93 (s, 2 H, CH_2)
(**14**)	7.26 (br s, 20 H, aryl H), 3.99 (m, 6 H, OCH_2CH_3), 2.37 (s, 6 H, MeC≡), 1.29 (m, 9 H, OCH_2CH_3), 0.94 (s, 2 H, CH_2)
(**15**)	7.26 (br s, 20 H, aryl H), 4.58 (m, 3 H, OCH), 2.3 (s, 6 H, MeC≡), 1.86 (s, 2 H, CH_2), 1.26 [d, J = 6 Hz, 18 H, $OCH(CH_3)_2$]
(**16**)	7.26 (br s, 20 H, aryl H), 3.9 (m, 6 H, OCH_2), 2.31 (s, 6 H, MeC≡), 1.83 (s, 2 H, CH_2), 1.5 (m, 12 H, $CH_2CH_2CH_3$), 0.92 (d, J = 4.8 Hz, 9 H, CH_2CH_3)

* Spectra recorded in $CDCl_3$ (+25 °C) and referenced to $SiMe_4$; d = doublet, m = multiplet, s = singlet.

−35.71 p.p.m. (d, $^2J_{P-P}$ = 26.34 Hz) for (**7**), suggesting one isomer is present in solution. Since the *X*-ray crystal structure of $[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]$ has been determined [as shown in (*a*) in the Scheme][8] it is very likely that the iodide ligand will be substituted by an acetonitrile ligand *trans* to the carbon monoxide (carbon monoxide has a stronger *trans* effect than a phosphine ligand) to give the product as shown in (*b*) in the Scheme. A high-field ^{13}C n.m.r. spectrum of (**1**) (Table 3) shows J_{P-C} coupling on the alkyne contact carbons (δ = 221.0, J_{P-C} = 7.8 Hz) which conforms with the structure shown in (*b*) in the Scheme. Many unsuccessful attempts were made to grow crystals of compounds (**1**)—(**12**). However, satisfactory

Table 3. Carbon-13 n.m.r. data* (δ/p.p.m.) for the complexes $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$ and $[WI(CO)\{P(OR')_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$

Compd.	
(1)	221 (s, $C{\equiv}C$), 205.6 (s, $C{\equiv}O$), 132.4, 131.4, 130.3, 129.2 (m, Ph), 125.9 (s, $C{\equiv}N$), 20.4 (m, CH_2), 15.1 (s, ${\equiv}C\mathit{Me}$), 2.85 (s, $\mathit{Me}CN$)
(2)	223.4 (s, $C{\equiv}C$), 205.7 (s, $C{\equiv}O$), 134.6, 133.9, 132.1, 131.5, 128.5 (m, Ph), 124.6 (s, $C{\equiv}N$), 21.9 (m, CH_2), 15.2 (s, ${\equiv}C\mathit{Me}$), 3.6 (s, $\mathit{Me}CN$)
(3)	221.2 (s, $C{\equiv}C$), 204.9 (s, $C{\equiv}O$), 132.7, 130.5, 129.1, 128.4 (m, Ph), 116.6 (s, $C{\equiv}N$), 21.3 (m, CH_2), 15.2 (s, ${\equiv}C\mathit{Me}$), 3.1 (s, $\mathit{Me}CN$)
(4)	221.8 (s, $C{\equiv}C$), 205.2 (s, $C{\equiv}O$), 133.7, 132.9, 131.0, 129.8, 128.8 (m, Ph), 122.3 (s, $C{\equiv}N$), 23.1 (m, CH_2), 15.07 (s, ${\equiv}CMe$), 3.25 (s, $\mathit{Me}CN$)
(5)	220.8 (s, $C{\equiv}C$), 207.2 (s, $C{\equiv}O$), 132.8, 131.1, 129.8, 128.8 (m, Ph), 23.1 (m, CH_2), 20.53 (s, ${\equiv}C\mathit{Me}$), 2.9 (s, $\mathit{Me}CN$)
(6)	222.8 (s, $C{\equiv}C$), 204.1 (s, $C{\equiv}O$), 132.8, 130.9, 129.8, 128.8 (m, Ph), 122.3 (s, $C{\equiv}N$), 23.8 (m, CH_2), 20.92 (s, ${\equiv}C\mathit{Me}$), 3.12 (s, $\mathit{Me}CN$)
(7)	223.5 (s, $C{\equiv}C$), 201.4 (s, $C{\equiv}O$), 133.6, 131.6, 130.4, 128.9, 127.3 (m, Ph), 123.45 (s, $C{\equiv}N$), 24.4 (s, CH_2), 3.77 (s, $\mathit{Me}CN$)
(8)	223.5 (s, $C{\equiv}C$), 203.5 (s, $C{\equiv}O$), 133.1, 132.3, 129.9, 129.6, 129.2 (m, Ph), 123.5 ($C{\equiv}N$), 29.89 (m, CH_2), 3.3 (s, $\mathit{Me}CN$)
(9)	221.2 (s, $C{\equiv}C$), 205.9 (s, $C{\equiv}O$), 133.0, 132.2, 131.6, 129.2, 128.3 (m, Ph), 121.3 (s, $C{\equiv}N$), 24.4 (m, CH_2), 3.8 (s, $\mathit{Me}CN$)
(10)	218.9 (s, $C{\equiv}C$), 205.1 (s, $C{\equiv}O$), 138.0, 132.7, 131.6, 128.3 (m, Ph), 123.8 (s, $C{\equiv}N$), 29.6 (m, CH_2), 3.64 (s, $\mathit{Me}CN$)
(11)	218.6 (s, $C{\equiv}C$), 201.7 (s, $C{\equiv}O$), 132.7, 130.9, 129.9 (m, Ph), 122.8 (s, $C{\equiv}N$), 23.4 (m, CH_2), 3.2 (s, $\mathit{Me}CN$)
(12)	218.7 (s, $C{\equiv}C$), 205.5, (s, $C{\equiv}O$), 137.7, 131.0, 129.0, 128.3 (m, Ph), 125.7 (s, $C{\equiv}N$), 23.39 (m, CH_2), 3.12 (s, $\mathit{Me}CN$)
(13)	215.71 (s, $C{\equiv}C$), 207.3 (s, $C{\equiv}O$), 132.81, 131.31, 130.47, 128.52 (m, Ph), 54.38 (m, OMe), 21.83 (m, CH_2), 20.79 (s, ${\equiv}C\mathit{Me}$)
(14)	222.6 (s, $C{\equiv}C$), 211.29 (s, $C{\equiv}O$), 132.16, 130.99, 130.47, 129.17, 128.52 (m, Ph), 63.4 (m, OCH_2), 21.83 (m, CH_2), 20.79 (s, ${\equiv}C\mathit{Me}$), 15.72 ($CH_2\mathit{CH}_3$)
(15)	221.56 (s, $C{\equiv}C$), 216.17 (s, $C{\equiv}O$), 133.2, 132.81, 131.8, 129.56, 128.13 (m, Ph), 72.77 (d, OCH), 23.91 (s, CH_2), 22.09 (s, CH_3), 19.05 (s, ${\equiv}C\mathit{Me}$)
(16)	222.86 (s, $C{\equiv}C$), 205.77 (s, $C{\equiv}O$), 132.68, 131.12, 130.34, 129.17, 128.65 (m, Ph), 66.92 (d, $O\mathit{C}H_2CH_2$), 30.36 (d, $OCH_2\mathit{C}H_2CH_2$), 21.96 (s, CH_2), 20.95 (s, ${\equiv}C\mathit{Me}$), 18.84 (s, $OCH_2CH_2\mathit{C}H_2CH_3$), 13.51 (s, $OCH_2CH_2CH_2\mathit{C}H_3$)

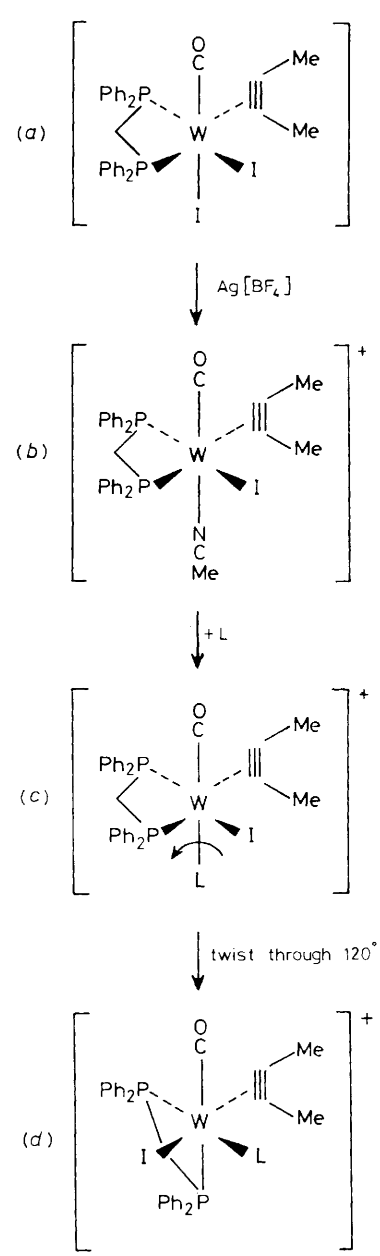
* Spectra recorded in $CDCl_3$ (+25 °C) and calibrated against $SiMe_4$; d = doublet, m = multiplet, s = singlet.

crystals of the tri-isopropyl phosphite-substituted compound, $[WI(CO)\{P(OPr^i)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]_{0.5}[OH]_{0.5}\cdot 0.5H_2O$ (**15**) were grown and the structure determined by *X*-ray crystallography (Figure) (see later).

The i.r. spectra of compound (**1**)—(**12**) all show a strong single carbonyl stretching band at *ca.* 1 970 cm^{-1} (Table 1), which are approximately 30 cm^{-1} higher than that of the neutral di-iodo complexes $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)]$.[8] This was expected since the complexes are cationic. The compounds (**1**)—(**12**) also show asymmetric doublets in the i.r. spectra at *ca.* 2 350 cm^{-1} which can be ascribed to the co-ordinated acetonitrile ligand. An increase in ν(CN) upon co-ordination of acetonitrile in these complexes can be attributed to a coupling of the C–N and N–metal stretching vibrations and to an increased C–N force constant. This also implies that the co-ordinated acetonitrile is functioning as a simple σ-donor ligand.[9] Reduction in the alkyne bond order is indicated by the weak ν($C{\equiv}C$) stretching band at *ca.* 1 650 cm^{-1} (considerably lower than the unco-ordinated alkyne). Donation from both filled perpendicular π orbitals of the alkyne and acceptance of metal d_π electron density to π* orbitals contribute to reduction in the alkyne bond order.

The ^1H n.m.r. spectra of (**1**)—(**12**) all show the expected features for the structure illustrated in (*b*) in the Scheme. The room-temperature spectra of (**1**)—(**6**) all show a single resonance for the but-2-yne methyl protons which suggests that the alkyne is undergoing rapid propeller-like rotation. Attempts were made to determine the barrier to rotation of but-2-yne for (**1**)—(**6**) by variable-temperature ^1H n.m.r. spectroscopy using the Gutowsky–Holm equations.[10] However, at −60 °C the but-2-yne resonances were singlets and hence the barriers to rotation are lower than those of the di-iodo complex $[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]$ which has been measured ($\Delta G^\ddagger = 49.5$ kJ mol^{-1}).[8] The ^{13}C n.m.r. spectra are also consistent with the structure shown in (*b*) in the Scheme. Templeton and Ward[1] have shown how the ^{13}C n.m.r. chemical shifts of co-ordinated alkyne contact carbons and the number of electrons donated by the alkyne ligand are related. The complexes (**1**)—(**12**) show alkyne contact carbon chemical shifts above 200 p.p.m. (Table 3) which is in accord with the alkyne ligand donating four electrons to the tungsten in these compounds. Although it is difficult to distinguish between alkyne carbon chemical shifts and co-ordinated carbon monoxide resonances in these four-electron alkyne complexes, the high-field spectra of compounds (**1**) and (**15**), along with the crystal structure of (**15**), have enabled assignments to be made. The alkyne contact carbon resonances have twice the intensity of the carbon monoxide resonances. For compound (**1**) the alkyne contact carbon resonance is split into a doublet due to coupling to the *trans* phosphine ($\delta = 221.0$, $J_{P-C} = 7.8$ Hz). The high-field spectrum of compound (**15**) shows coupling between the co-ordinated carbon monoxide and a *trans* phosphine (δ 216.17, J_{P-C} 70 Hz). Evidence for the phosphine *trans* to the carbon monoxide comes from the crystal structure of (**15**), hence all alkyne contact carbons have been assigned to lower field of the co-ordinated carbon monoxide. Complexes (**1**)—(**12**) obey the effective atomic number rule if the alkyne donates four electrons to the tungsten.

Equimolar quantities of $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (**1**) and $P(OR')_3$ (R′ = Me, Et, Pr^i, or Bu^n) react at room temperature in CH_2Cl_2 to rapidly afford good yields of the substituted products $[WI(CO)\{P(OR')_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ [(**13**)—(**16**)]. These new, highly coloured complexes have been fully characterised by elemental analysis (C, H, and N) and i.r. spectroscopy (Table 1), and ^1H and ^{13}C n.m.r. spectroscopy (Tables 2 and 3). They are considerably more soluble in polar solvents than (**1**) and are stable for several days when stored under nitrogen. Previous studies on the related cationic cyclopentadienyl complex $[Mo(CO)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_5H_5)][BF_4]$ have suggested that reactions with phosphite and phosphine ligands can proceed by an associative mechanism.[4d] It is likely that reaction of $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ with $P(OR')_3$ will occur by an associative mechanism to give unstable two-electron alkyne intermediates $[WI(CO)(NCMe)\{P(OR')_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ which rapidly lose acetontrile to give the isolated four-electron alkyne compounds (**13**)—(**16**). Evidence to support this mechanism comes from some work by Templeton and co-workers.[11] They carried out kinetics studies on the substitution reactions of the



Scheme. Proposed structures for reaction of [WI$_2$(CO){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)] with Ag[BF$_4$] in NCMe to give [WI(CO)(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] (**1**), and reaction of (**1**) with L [L = P(OMe)$_3$, P(OEt)$_3$, P(OPr^i)$_3$, or P(OBu^n)$_3$]

molybdenum(II)–alkyne complexes [Mo(CO)(η^2-RC$_2$R)(S$_2$CNMe$_2$)$_2$] with P(OMe)$_3$, PEt$_3$, and CO, and their results suggested an associative substitution mechanism.

If the substitution of NCMe by P(OR′)$_3$ in (**1**) occurred with retention of configuration the complex shown in (*c*) in the Scheme would be formed. However, the structure of [WI(CO){P(OPr^i)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$]$_{0.5}$ [OH]$_{0.5}$·0.5[H$_2$O] (**15**) has been determined (see next section) and iodide shown to be *trans* to but-2-yne. It has been previously observed that alkyne ligands are stabilised by having halides *trans* to themselves.[12] The solid-state stereochemistry of (**15**) can be explained by a trigonal-twist rearrangement as shown in (*c*)—(*d*) in the Scheme. A high-field ^{13}C n.m.r. spectrum of (**15**) (Table 3) shows $J_{\mathrm{P-C}}$ coupling to the carbonyl ligand (δ = 216.17 p.p.m. $J_{\mathrm{P-C}}$ = 70 Hz) which is typical for a phosphine *trans* to a carbonyl in an octahedral complex.[13] This gives further evidence to support the trigonal-twist rearrangement in solution as illustrated in (*c*)—(*d*) in the Scheme.

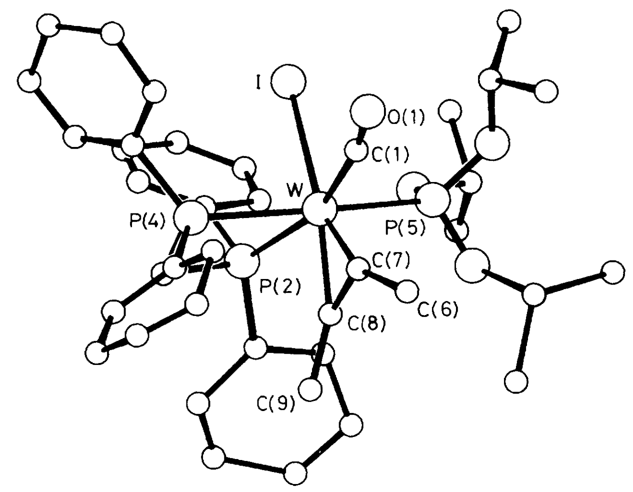


Figure. *X*-Ray crystal structure of [WI(CO){P(OPr^i)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)]$^+$ (**15**)

The crystal-structure determination confirms the conformation of the cation [WI(CO){P(OPr^i)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)]$^+$, but there is some doubt about the nature of the counter ions which appear to be a mixture of [BF$_4$]$^-$ and [OH]$^-$ (see later discussion). However, repeated elemental analyses and i.r. spectroscopy have confirmed that the bulk of the crystals that were not selected for *X*-ray analysis conformed with the formulation of the complex with tetrafluoroborate as the sole counter anion. The crystal selected for *X*-ray crystallography must have been formed from trace amounts of water reacting with the [BF$_4$]$^-$ ion to give HBF$_4$ leaving OH$^-$ as a co-existing counter ion.

The asymmetric unit contains two [WI(CO){P(OPr^i)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)]$^+$ cations, two [BF$_4$]$^-$ anions, each with half occupancy, and two oxygen atoms which together represent (OH$^-$ + H$_2$O).

The structures of the metal co-ordination spheres in the two cations (A and B) are similar within experimental error and cation A is shown in the Figure, together with the atomic numbering scheme.

The tungsten atom is bonded to an iodine atom [2.800(3), 2.796(3) Å in A and B respectively], a carbonyl group [2.05(4), 2.15(5) Å], two phosphorus atoms from a bidentate Ph$_2$P(CH$_2$)PPh$_2$ ligand [P(2) 2.581(9), 2.584(10); P(4) 2.573(10), 2.532(11) Å], one phosphorus from a P(OPr^i)$_3$ group [P(5) 2.526(9), 2.562(11) Å] and two carbons from the alkyne group [C(7), 2.08(3), 2.10(5), C(8) 1.92(5), 1.95(4) Å]. All these dimensions are similar to those found in previous complexes.[7,8] The geometry of the cation is best considered as distorted octahedral in which the methyl alkyne moiety occupies a site *trans* to iodine. The bidentate ligand phosphorus atoms P(2) and P(4) are *trans* to carbonyl and phosphite [P(5)] respectively.

The alkyne is *trans* to the iodine atom and lies in the equatorial plane defined also by the carbonyl group and P(2). Least-squares planes calculations show that atoms W(1), C(1), P(2), I(1), C(7), and C(8) are coplanar to within 0.20 Å. The other two carbon atoms [C(6), C(9)] of the methyl alkyne group remain close to this plane. This leads to some crowding in the equatorial plane and the C(1)–W–C(7) angles are only 66.7(16) in A, 67.7(17)° in B. The W–C(7) bond lengths are significantly greater than the W–C(8) bond lengths. These atoms are adjacent to P(2) with angles P(2)–W–C(8) 81.0(14) and 81.9(13)° respectively in A and B.

This crowding in the equatorial plane leads to variation in the C–C–C angles in the methyl alkyne group. Thus, C(6)–C(7)–C(8) [135(3) in A, 141(4)° in B] is much larger than C(7)–C(8)–C(9) [126(4) in A, 123(3)° in B].

There are no significant intramolecular contacts apart from O(2B) $\cdots$ O(2A) ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$) of 2.92(2) Å which presumably represents a hydrogen bond.

The i.r. spectra of compounds (**13**)—(**16**) show a single strong carbonyl band at slightly higher wavenumber than for the monoacetonitrile complex (**1**). This would be expected since phosphites are stronger π-acceptor ligands than acetonitrile. The phosphite complexes (**13**)—(**16**) show a weak $\nu(C{\equiv}C)$ band at *ca.* 1 650 cm^{-1}, similar to that of (**1**)—(**12**). Also, complexes (**1**)—(**12**) and the phosphite-substituted compounds (**13**)—(**16**) have a strong broad band at 1 016 cm^{-1} [ν(BF)] and a strong sharp band at 529 cm^{-1}.[14] This, together with repeated elemental analysis, confirms the formulation of the bulk materials (**1**)—(**16**) as tetrafluoroborate salts.

The ^1H n.m.r. spectra of (**13**)—(**16**) conform with the structure shown in the Figure. The room-temperature ^1H n.m.r. spectra of (**13**)—(**16**) all show a single resonance for the but-2-yne methyl protons, *i.e.* similar to complexes (**1**)—(**6**), which indicates rapid propeller-like rotation of the but-2-yne ligand in these complexes. The barrier to but-2-yne rotation of (**15**) (Figure) was measured by variable-temperature ^1H n.m.r. spectroscopy. Analysis of the spectrum[10] gave a value of $\Delta G^{\ddagger} = 56.9 \pm 0.5$ kJ mol^{-1} (T = 267 °C and $\Delta\nu$ = 18.5 Hz). This value is similar to other values determined for but-2-yne complexes of molybdenum(II) and tungsten(II)[4d,12,15] including the values for $[WI_2(CO)L_2(\eta^2\text{-}MeC_2Me)]$ described in a previous paper in this series.[8] The ^{13}C n.m.r. spectra of (**13**)—(**16**) again indicate that the but-2-yne is donating four electrons to the tungsten in these complexes. For example, complex (**15**) shows a carbonyl resonance *trans* to a phosphorus at δ = 216.17 p.p.m., J_{P-C} = 70 Hz, whereas the alkyne resonance is a singlet at lower field (δ = 221.56 p.p.m.), with twice the intensity of the carbonyl resonance.

We are currently investigating the reactions of these cationic alkyne complexes (**1**)—(**16**), in particular with nucleophiles, in view of the diverse range of chemistry reported by Green[4e,f] for the reactions of the cationic cyclopentadienyl alkyne compounds $[Mo(CO)(\eta^2\text{-}RC_2R')_2(\eta^5\text{-}C_5H_5)][BF_4]$ and their phosphine and phosphite derivatives with nucleophiles.

Experimental

The synthesis, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using standard Schlenk-line techniques. The complexes $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)]$ (n = 1—4 and 6; R = Me) were prepared by the literature method[8] and $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)]$ (for n = 5, R = Me; for n = 1—6, R = Ph) were prepared in an analogous manner. All other chemicals were purchased from commercial sources. Dichloromethane was dried over P_2O_5 and distilled before use. Proton and ^{13}C n.m.r. spectra were recorded on a JEOL FX60 or Bruker AC 250 CPMAS n.m.r. spectrometer and calibrated against tetramethylsilane, ^{31}P N.m.r. spectra on a Bruker WH 400 n.m.r. spectrometer and calibrated against 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 1430 ratio recording spectrophotometer. Elemental analyses (C, H, and N) were performed on a Carlo Erba elemental analyser MOD 1106 (using helium as carrier gas) by Mr. E. Lewis of the Department of Chemistry, University College of North Wales, Bangor.

$[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$, (**1**).—To $[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]$ (0.5 g, 0.553 mmol) dissolved in NCMe (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added $Ag[BF_4]$ (0.1076 g, 0.553 mmol). After stirring for 20 h the solution was filtered to remove AgI. The solvent was then removed *in vacuo* and the crude product redissolved in CH_2Cl_2 and filtered again to remove the last traces of AgI. The solvent volume was then reduced *in vacuo* to 2 cm^3 and the purple cationic product $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (**1**) precipitated from the solution by dropwise addition of diethyl ether; yield of pure product = 0.55 g, 70%.

Similar reactions of $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)]$ (n = 2—6) with $Ag[BF_4]$ in NCMe afforded the analogous cationic products $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$, (**2**)—(**6**). (See Table 1 for colours and yields.)

$[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$, (**7**).—To $[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}PhC_2Ph)]$ (0.5 g, 0.486 mmol) dissolved in NCMe (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added $Ag[BF_4]$ (0.0946 g, 0.486 mmol). After stirring for 20 h the solution was filtered to remove AgI. The solvent was then removed *in vacuo* and the crude product redissolved in CH_2Cl_2 and filtered again to remove the last traces of AgI. The solvent volume was then reduced to 2.5 cm^3 *in vacuo* and the green cationic product $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$, (**7**) precipitated from solution by dropwise addition of diethyl ether; yield of pure product = 0.285 g, 57%.

Similar reactions of $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}PhC_2Ph)]$ (n = 2—6) with $Ag[BF_4]$ in NCMe yielded the analogous cationic products $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}PhC_2Ph)][BF_4]$ (**8**)—(**12**) (see Table 1 for colours and yields.)

$[WI(CO)\{P(OPr^i)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$, (**15**).—To $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (0.5 g, 0.552 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring under a stream of dry nitrogen, was added $P(OPr^i)_3$ (0.14 cm^3, 0.552 mmol). After stirring for 20 min the solvent was removed *in vacuo* yielding an orange-red oil which was stirred with diethyl ether (20 cm^3) for 20 min to wash away any unreacted $P(OPr^i)_3$. The diethyl ether was then syringed off and the crude product redissolved in CH_2Cl_2 and filtered. The solvent volume was then reduced to 4 cm^3 and diethyl ether (0.5 cm^3) was added. The solution was then cooled to −18 °C for 48 h which afforded analytically pure crystals of $[WI(CO)\{P(OPr^i)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (**15**); yield = 0.34 g, 58%.

Similar reactions of $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ with $P(OMe)_3$, $P(OEt)_3$, and $P(OBu^n)_3$ yielded analogous substituted products, (**13**), (**14**) and (**16**), (see Table 1 for colours and yields.)

Crystal-structure Determination for (**15**).—Crystals were prepared as described above.

Crystal data. $[WI(CO)\{P(OPr^i)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]_{0.5}[OH]_{0.5}\cdot 0.5H_2O$, $C_{39}H_{50.5}B_{0.5}F_2IP_3O_5W$, M = 1 046.2, monoclinic, space group $P2_1/n$, a = 19.494(18), b = 19.634(12), c = 25.063(15) Å, β = 101.3(1)°, U = 9 406.8 $Å^3$, D_c = 1.46 g cm^{-3}, $F(000)$ = 4 136, Z = 8, λ = 0.710 7 Å, μ = 34.1 cm^{-1}.

A crystal of approximate size 0.4 × 0.2 × 0.2 mm was set up to rotate about the a axis on a Stoe-Stadi 2 diffractometer and data were collected *via* variable-width ω scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 5 673 Independent reflections were

Table 4. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for complex (**15**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cation A							
W(1A)	6 447(1)	9 777(1)	2 426(1)	C(40A)	6 522(19)	9 471(19)	3 999(15)
I(1A)	5 262(1)	9 178(1)	2 706(1)	C(41A)	6 122(31)	10 052(28)	4 040(24)
C(1A)	5 954(21)	10 687(20)	2 495(15)	C(42A)	5 587(35)	9 925(34)	4 418(28)
O(1A)	5 615(15)	11 128(13)	2 564(11)	C(43A)	5 632(33)	9 371(34)	4 718(25)
P(2A)	7 018(4)	8 594(4)	2 621(3)	C(44A)	6 141(25)	8 905(22)	4 662(19)
C(3A)	7 514(18)	8 813(16)	3 295(14)	C(45A)	6 570(26)	8 919(24)	4 279(21)
P(4A)	7 045(5)	9 612(5)	3 429(4)	C(50A)	7 738(19)	10 248(18)	3 729(15)
P(5A)	5 833(5)	9 556(5)	1 457(4)	C(51A)	7 592(19)	10 918(18)	3 633(15)
C(6A)	7 178(19)	11 325(18)	2 126(15)	C(52A)	8 084(25)	11 461(23)	3 841(19)
C(7A)	6 985(16)	10 612(15)	2 204(12)	C(53A)	8 693(22)	11 168(20)	4 191(17)
C(8A)	7 355(24)	9 980(22)	2 275(18)	C(54A)	8 841(23)	10 449(21)	4 328(17)
C(9A)	8 107(22)	9 889(19)	2 290(16)	C(55A)	8 302(21)	10 017(19)	4 078(16)
C(20A)	7 663(14)	8 308(13)	2 210(11)	O(61A)	5 653(12)	8 775(11)	1 340(10)
C(21A)	7 491(16)	8 328(14)	1 636(13)	C(62A)	5 279(25)	8 475(22)	828(20)
C(22A)	7 970(24)	8 125(22)	1 367(18)	C(63A)	4 706(27)	8 032(25)	1 021(21)
C(23A)	8 579(23)	7 753(21)	1 599(18)	C(64A)	5 741(24)	8 169(23)	482(19)
C(24A)	8 770(20)	7 715(18)	2 219(16)	O(71A)	5 202(13)	9 953(11)	1 163(10)
C(25A)	8 412(15)	7 996(14)	2 577(12)	C(72A)	4 650(22)	10 339(21)	1 403(17)
C(30A)	6 593(20)	7 831(18)	2 758(17)	C(73A)	3 907(35)	9 879(32)	1 281(27)
C(31A)	6 618(21)	7 470(20)	3 238(17)	C(74A)	4 547(23)	11 019(21)	1 165(18)
C(32A)	6 199(20)	6 887(20)	3 270(16)	O(81A)	6 362(13)	9 646(12)	1 040(10)
C(33A)	5 811(28)	6 547(26)	2 809(23)	C(82A)	6 478(26)	10 259(26)	876(20)
C(34A)	5 818(22)	6 907(21)	2 377(18)	C(83A)	6 057(27)	10 457(25)	259(21)
C(35A)	6 255(17)	7 479(16)	2 328(13)	C(84A)	7 234(23)	10 364(22)	767(18)
Cation B							
W(1B)	3 528(1)	4 192(1)	2 346(1)	C(40B)	4 508(23)	4 575(22)	3 811(18)
I(1B)	4 809(1)	4 852(1)	2 388(1)	C(41B)	5 024(21)	4 222(19)	3 763(15)
C(1B)	4 130(24)	3 268(22)	2 389(18)	C(42B)	5 690(25)	4 301(23)	4 100(19)
O(1B)	4 524(13)	2 859(12)	2 448(10)	C(43B)	5 840(31)	4 925(29)	4 405(23)
P(2B)	3 054(5)	5 368(5)	2 561(4)	C(44B)	5 273(23)	5 358(21)	4 404(17)
C(3B)	3 114(18)	5 207(17)	3 300(14)	C(45B)	4 640(23)	5 241(22)	4 061(17)
P(4B)	3 685(5)	4 420(5)	3 358(4)	C(50B)	3 292(19)	3 754(18)	3 735(15)
P(5B)	3 389(5)	4 366(5)	1 317(4)	C(51B)	2 951(18)	3 984(16)	4 171(15)
C(6B)	2 698(24)	2 602(22)	2 186(18)	C(52B)	2 623(21)	3 494(21)	4 490(17)
C(7B)	2 946(18)	3 381(17)	2 316(14)	C(53B)	2 770(23)	2 840(22)	4 393(19)
C(8B)	2 496(24)	3 899(21)	2 358(18)	C(54B)	2 980(28)	2 661(25)	3 953(22)
C(9B)	1 785(25)	4 028(23)	2 465(19)	C(55B)	3 426(20)	3 111(20)	3 652(16)
C(20B)	2 152(16)	5 629(15)	2 340(13)	O(61B)	3 872(16)	3 976(14)	962(12)
C(21B)	1 964(22)	5 608(20)	1 765(18)	C(62B)	4 544(22)	3 602(22)	1 132(17)
C(22B)	1 190(21)	5 729(19)	1 477(16)	C(63B)	4 382(28)	2 884(26)	922(21)
C(23B)	800(24)	6 043(22)	1 834(20)	C(64B)	5 053(25)	3 961(23)	845(20)
C(24B)	1 105(22)	6 192(20)	2 469(17)	O(71B)	3 467(15)	5 136(14)	1 197(12)
C(25B)	1 686(18)	5 970(16)	2 693(14)	C(72B)	3 387(20)	5 386(19)	620(15)
C(30B)	3 594(12)	6 150(10)	2 586(12)	C(73B)	2 891(30)	5 906(28)	533(23)
C(31B)	3 534(12)	6 378(10)	2 051(12)	C(74B)	4 116(27)	5 730(24)	682(20)
C(32B)	3 828(12)	7 000(10)	1 947(12)	O(81B)	2 667(14)	4 217(13)	1 029(10)
C(33B)	4 182(12)	7 394(10)	2 377(12)	C(82B)	2 334(46)	3 455(43)	779(36)
C(34B)	4 242(12)	7 167(10)	2 912(12)	C(83B)	1 500(41)	3 482(36)	912(29)
C(35B)	3 949(12)	6 545(10)	3 016(12)	C(84B)	2 387(39)	3 541(38)	69(31)
O(1A)	5 198(12)	2 175(11)	4 444(10)	F(14)	2 246(22)	1 673(23)	109(15)
O(2B)	9 834(15)	2 261(13)	432(11)	B(2)	6 551(29)	2 566(27)	612(23)
B(1)	2 261(27)	1 335(26)	585(22)	F(24)	6 640(26)	3 229(21)	572(20)
F(11)	2 361(22)	671(20)	526(18)	F(23)	6 379(26)	2 442(24)	1 106(18)
F(12)	2 744(21)	1 586(20)	980(16)	F(22)	6 052(24)	2 335(24)	226(19)
F(13)	1 628(20)	1 482(20)	693(17)	F(21)	7 117(23)	2 219(24)	578(20)

measured with a 2θ maximum of 40°, of which 3 987 with $I > 2\sigma(I)$ were used in subsequent refinement. An empirical absorption correction[2] was applied.[16a] The structure was determined by statistical methods.

All atoms in the cation were easily located. However, the expected $[BF_4]^-$ anions were hard to find. These were refined as rigid groups and with an occupancy of 1 their thermal parameters *U*, converged to *ca.* 0.25 Å^2 and the *R* value 0.0815. When these atoms were given an occupancy of 0.5 the *R* value dropped significantly to 0.0800 and the thermal parameters became a more reasonable 0.12 Å^2. It seems likely from this evidence that the $[BF_4]^-$ anions have an occupancy of 0.5 and that the charge must be balanced *via* loss of a proton from one or other of the two water molecules in the asymmetric unit. It is possible that one of these represents a distinct OH^- anion and the other a water molecule, but more likely that there is some disorder and both peaks represent 50% water and 50% hydroxide anion.

Table 5. Molecular dimensions [distances (Å) and angles (°)] in the co-ordination spheres of complex (**15**)

	Cation A	Cation B
W–I	2.800(3)	2.796(3)
W–C(1)	2.05(4)	2.15(5)
W–P(2)	2.581(9)	2.584(10)
W–P(4)	2.573(10)	2.532(11)
W–P(5)	2.526(9)	2.562(11)
W–C(7)	2.08(2)	2.10(5)
W–C(8)	1.92(5)	1.95(4)
I–W–C(1)	85.5(13)	85.1(13)
I–W–P(2)	85.4(2)	86.0(2)
C(1)–W–P(2)	163.7(12)	163.1(12)
I–W–P(4)	86.6(3)	87.1(3)
C(1)–W–P(4)	99.1(11)	98.1(12)
P(2)–W–P(4)	66.8(3)	67.1(3)
I–W–P(5)	84.8(3)	83.9(2)
C(1)–W–P(5)	95.1(11)	96.5(13)
P(2)–W–P(5)	97.6(3)	96.8(3)
P(4)–W–P(5)	162.8(3)	162.1(3)
I–W–C(7)	151.9(9)	152.8(11)
C(1)–W–C(7)	66.7(16)	67.7(17)
P(2)–W–C(7)	122.6(9)	120.7(8)
P(4)–W–C(7)	101.9(9)	98.0(11)
P(5)–W–C(7)	92.7(9)	97.1(11)
I–W–C(8)	166.5(14)	167.9(13)
C(1)–W–C(8)	107.5(19)	106.5(18)
P(2)–W–C(8)	81.0(14)	81.9(13)
P(4)–W–C(8)	87.8(14)	87.9(13)
P(5)–W–C(8)	97.3(14)	97.9(13)
C(7)–W–C(8)	41.6(17)	39.1(17)

Apart from this local difficulty, the refinement proceeded successfully with W, I, and P refined anisotropically and C, O, B, and F isotropically, to an *R* value of 0.080. One of the benzene rings, 3B, was refined as a rigid group. Hydrogen atoms were not included. The structure was given a weighting scheme in the form $w = 1/[\sigma_2(F) + 0.003F^2]$. Calculations were carried out using SHELX 76[16b] and some of our own programs on the Amdahl V7 at the University of Reading. Positional parameters are given in Table 4 and molecular dimensions in the co-ordination spheres are compared in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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