Nitrile exchange reactions of $[WI(CO)(NCMe)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$; X-ray crystal structures of $[WI(CO)(L)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ $\{L = NC^iPr, NC^tBu, NCCH_2Ph, 1,2\text{-}C_6H_4(NCCH_2)_2\}$

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Abstract

Equimolar quantities of $[WI(CO)(NCMe)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ and L $\{L = NCEt, NC^iPr, NC^tBu, NCPh, NCCH_2Ph, 1,2\text{-}C_6H_4(NCCH_2)_2, NCCH_2(C_4H_3S\text{-}3)\}$ react in CH_2Cl_2 at room temperature to give the nitrile exchanged products, $[WI(CO)L\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**1**–**7**). The complexes for L = NC^iPr (**2**), NC^tBu (**3**), $NCCH_2Ph$ (**5**), and 1,2-$C_6H_4(NCCH_2)_2$ (**6**) have all been crystallographically characterised. The geometry of all four complexes is *psuedo*-octahedral with the alkyne ligand occupying one site *trans*- to an iodo ligand, with the triisopropylphosphite ligand mutually *trans* and the carbonyl ligand *trans* to the nitrile group.
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1. Introduction

The ability of alkynes to act as four-electron donors to transition-metals, has been well documented, especially to complexes of molybdenum and tungsten [1–9]. Cationic alkyne complexes of molybdenum(II) and tungsten(II) have also been extensively studied [10–23].

In 1989 [24], we described the synthesis of the cationic complex containing bis(diphenylphosphino)methane (dppm) $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$, and its reactions with phosphites, $P(OR)_3$ to give $[WI(CO)\{P(OR)_3\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$, which for R = ^iPr was structurally characterised. In order to gain increased solubility of these complexes we decided to replace the dppm ligand with two phosphite ligands, and very recently [25] described the preparation and structural characterisation of the bis(triisopropyl)phosphite complex, $[WI(CO)(NCMe)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$. In this paper, we described the reactions of $[WI(CO)(NCMe)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ with a series of nitriles, L $\{L = NCEt, NC^iPr, NC^tBu, NCPh, NCCH_2Ph, 1,2\text{-}C_6H_4(NCCH_2)_2, NCCH_2(C_4H_3S\text{-}3)\}$ to give the acetonitrile replaced complexes, $[WI(CO)L\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$, which were structurally characterised for L = NC^iPr, NC^tBu, $NCCH_2Ph$ and 1,2-$C_6H_4(NCCH_2)_2$.

2. Results and discussion

Reaction of equimolar quantities of $[WI(CO)(NCMe)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ and L $\{L = NCEt, NC^iPr, NC^tBu, NCPh, NCCH_2Ph, 1,2\text{-}C_4H_6(NCCH_2)_2, NC(C_4H_3S\text{-}3)\}$ in CH_2Cl_2 at room temperature afforded the acetonitrile exchanged new complexes, $[WI(CO)L\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**1**–**7**) in excellent yield. All seven complexes were characterised by elemental analysis (C, H and N), IR

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Table 1
Physical and analytical data [a] for the complexes (**1–7**)

No	Complex	Colour	Yield (%)	Analysis (%)		
				C	H	N
(**1**)	[WI(CO)(NCEt){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$]	Pink	85	50.8 (50.7)	6.1 (6.2)	1.4 (1.2)
(**2**)	[WI(CO)(NC^{i}Pr){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$]	Red	78	51.2 (51.2)	6.3 (6.4)	1.3 (1.2)
(**3**)	[WI(CO)(NC^{t}Bu){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$]	Red	79	51.3 (51.5)	6.4 (6.4)	1.3 (1.2)
(**4**)	[WI(CO)(NCPh){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$]	Red	82	52.5 (52.7)	6.2 (6.0)	1.1 (1.1)
(**5**)	[WI(CO)(NCCH$_2$Ph){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$]	Red	82	53.7 (53.0)	6.4 (6.1)	1.6 (1.1)
(**6**)	[WI(CO){1,2-C$_6$H$_4$(NCCH$_2$)$_2$-*N*}{P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$]	Pink	85	53.1 (53.3)	6.0 (6.1)	2.1 (2.2)
(**7**)	[WI(CO){NCCH$_2$(C$_4$H$_3$S-3)}{P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$]	Pink	76	51.1 (50.9)	6.1 (5.9)	1.4 (1.1)

[a] Calculated values in parenthesis.

Table 2
Infrared spectral data [a] for the complexes (**1–7**)

Complex	v(N≡C) (cm^{-1})	v(C≡O) (cm^{-1})	v(C≡C) (cm^{-1})	v(B–C) (cm^{-1})
(**1**)	2285(w)	1966(s)	1579(w)	1099(s,sh)
(**2**)	2282(w)	1968(s)	1580(m)	1099(s)
(**3**)	2276(w)	1968(s)	1579(m)	1099(s)
(**4**)	2264(w)	1969(s)	1579(m)	1099(s)
(**5**)	2252(w)	1968(s)	1579(m)	1099(s)
(**6**)	2400, 2251(w)	1968(s)	1579(m)	1099(s)
(**7**)	2281(w)	1968(s)	1579(m)	1099(s)

[a] Run as thin films in chloroform between NaCl plates; s, strong; m, medium; w, weak intensity; sh, sharp band.

Table 3
Proton NMR data [a] for complexes (**1–7**)

Complex	^{1}H (δ) ppm
(**1**)	7.51 (brs, 10H, B*Ph*$_4$); 7.14–6.91 (m, 10H, B*Ph*$_4$); 4.57–4.47 (m, 6H, (CH$_3$)$_2$C*H*O); 3.16–3.06 (m, 2H, C*H*$_2$CN); 2.97 (m, 6H, C*H*$_3$C$_2$C*H*$_3$); 2.39–2.22 (m, 3H, C*H*$_3$CH$_2$CN); 1.28–1.21 (m, 36H, (C*H*$_3$)$_2$CHO)
(**2**)	7.45–7.36 (m, 10H, B*Ph*$_4$); 7.10–6.90 (m, 10H, B*Ph*$_4$); 4.52–4.48 (m, 6H, (CH$_3$)$_2$C*H*O); 3.09 (m, 1H, (CH$_3$)$_2$C*H*CN); 2.94 (m, 6H, C*H*$_3$C$_2$C*H*$_3$); 1.43 (dd, 6H, (C*H*$_3$)$_2$CHCN, J = 2.8, 7.1 Hz); 1.27–1.18 (m, 36H, (C*H*$_3$)$_2$CHO)
(**3**)	7.48–7.40 (m, 10H, B*Ph*$_4$); 7.13–6.94 (m, 10H, B*Ph*$_4$); 4.55–4.50 (m, 6H, (CH$_3$)$_2$C*H*O); 2.99 (t, 6H, C*H*$_3$C$_2$C*H*$_3$)$_3$); 1.60 (s, 9H, (C*H*$_3$)$_3$CCN);1.32–1.22 (m, 36H, (C*H*$_3$)$_2$CHO)
(**4**)	7.90–7.70 (m, 5H, *Ph*CN); 7.55–7.45 (m, 10H, B*Ph*$_4$); 7.15–6.95 (m, 10H, B*Ph*$_4$); 4.65–4.50 (m, 6H, (CH$_3$)$_2$C*H*O); 3.10 (s, 6H, C*H*$_3$C$_2$C*H*$_3$); 1.35–1.15 (m, 36H, (C*H*$_3$)$_2$CHO)
(**5**)	7.60–7.50 (m, 10H, B*Ph*$_4$); 7.45–7.30 (m, 5H, *Ph*CH$_2$CN); 7.10–6.90 (m, 10H, B*Ph*$_4$); 4.55–4.45 (m, 6H, (CH$_3$)$_2$C*H*O); 3.75 (s, 2H, PhC*H*$_2$CN); 3.00 (s, 6H, C*H*$_3$C$_2$C*H*$_3$); 1.25–1.15 (m, 36H, (C*H*$_3$)$_2$CHO)
(**6**)	7.53 (brs, 10H, B*Ph*$_4$); 7.40–7.33 (m, 4H, 1,2-*Ph*(CH$_2$CN)); 7.27–6.87 (m, 10H, B*Ph*$_4$); 4.56–4.45 (m, 6H, (CH$_3$)$_2$C*H*O); 3.32 (s, 2H, C*H*$_2$CN-uncoord); 2.99 (m, 6H, C*H*$_3$C$_2$C*H*$_3$); 2.75 (s, 2H, C*H*$_2$CN-coord); 1.26–1.11 (m, 36H, (C*H*$_3$)$_2$CHO)
(**7**)	7.54 (br s, 10H, B*Ph*$_4$); 7.40–7.30 (m, 3H, C$_4$H$_3$S); 7.14–6.90 (m, 10H, B*Ph*$_4$); 4.59–4.46 (m, 6H, (CH$_3$)$_2$C*H*O); 3.51 (s, 2H, C*H*$_2$CN); 2.99 (s, 6H, C*H*$_3$C$_2$C*H*$_3$); 1.28–1.17 (m, 36H, (C*H*$_3$)$_2$CHO); (where C$_4$H$_3$S–3-CH$_2$CN=thiophene-3–acetonitrile)

[a] Spectra recorded in CDCl$_3$ at +25 °C, referenced to SiMe$_4$; s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; dd, doublet of doublets.

spectroscopy and ^{1}H-, ^{11}B{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy (Tables 1–4). Complex **7** was also characterised by ^{13}C{^{1}H}-NMR spectroscopy (Table 5). The seven cationic complexes **1–7** were all stable in air for up to one hour and could be stored under nitrogen at −17 °C for up to 2 months with no obvious deterioration. Solutions of **1–7** showed decomposition within 24 h on exposure to air, but could be kept at −17 °C for up to 2 months under a nitrogen atmosphere. The cations **1–7** are very soluble in acetone, acetonitrile, dichloromethane and chloroform, and insoluble in diethyl ether and hydrocarbon solvents, which was expected as the complexes are salts.

The IR spectra of **1–7** all show a strong carbonyl stretching band between 1966 and 1969 cm^{-1}, a weak or medium intensity alkyne stretch at 1579 or 1580 cm^{-1}, and a strong v(B–C) band characteristic of the [BPh$_4$]$^-$ anion at 1099 cm^{-1}. These data are comparable to that of the acetonitrile cation precursor, [WI(CO)-(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$], which was expected as in complexes **1–7**, only the substituent on the nitrile ligand is different, with the coordination geometry about the tungsten centre retained. For complexes **1–7**, the IR spectra show considerable differences in the v(C≡N) band only. The wavenumber of the weak nitrile stretching frequencies decrease from 2285 to 2252 cm^{-1} over the series **1–5**, R = Et, ^{i}Pr, ^{t}Bu, Ph and PhCH$_2$, respectively. This difference is due to an

increase in chain length and size of the R substituent. Complex **6** shows two distinct nitrile stretches due to the uncoordinated nitrile (2400 cm^{-1}) and the coordinated nitrile (2251 cm^{-1}) of the 1,2-C$_6$H$_4$(NCCH$_2$)$_2$ ligand. The thiophene-3-acetonitrile ligand of **7** shows a weak nitrile v(C≡N) band at 2281 cm^{-1}.

The ^{1}H-NMR spectra of complexes **1–7** show signals in the expected regions, based on their cationic precursor and the crystal structures obtained for complexes

Table 4
Boron and phosphorus NMR data [a,b] for complexes (1–7)

	$^{11}B\{^1H\}$ (δ) ppm [a]	$^{31}P\{^1H\}$ (δ) ppm [b]
(1)	−6.85(s)	101.78 (s, $J_{W–P}$ = 218.5 Hz)
(2)	−6.92(s)	101.44 (s, $J_{W–P}$ = 218.2 Hz)
(3)	−6.92(s)	101.19 (s, $J_{W–P}$ = 218.4 Hz)
(4)	−6.85(s)	101.13 (s, $J_{W–P}$ = 217.6 Hz)
(5)	−6.85(s)	101.47 (s, $J_{W–P}$ = 217.2 Hz)
(6)	−6.85(s)	101.31 (s, $J_{W–P}$ = 216.7 Hz)
(7)	−6.84(s)	101.48 (s, $J_{W–P}$ = 217.5 Hz)

[a] Spectra recorded in $CDCl_3$ at +25 °C, referenced to $BF_3 \cdot OEt_2$.
[b] Spectra recorded in $CDCl_3$ at +25 °C, referenced to 85% H_3PO_4; s = singlet.

2, 3, 5 and 6 (Figs. 1–4) (see later in the paper). Variable temperature ^1H-NMR studies were attempted for 2, 3 and 5, with only 2 showing successful separation of the 2-butyne singlet (298 K) into a doublet. The barrier to 2-butyne rotation for 2 is calculated [26,27] to be $\Delta G^{\neq}$ = 49 kJ mol^{-1} with T_c = 228 K and Δv = 12.8 Hz, which is typical of other complexes of this type [25]. The $^{11}B\{^1H\}$-NMR spectra of 1–7 all show a singlet between −6.92 and −6.84 ppm, which confirms the presence of the tetraphenylborate counter ion. For all seven cations, the $^{31}P\{^1H\}$-NMR spectra showed a singlet resonance attributable to the two *trans*-triisopropylphosphite ligands, between +101.78 and +101.13 ppm, with tungsten–phosphite coupling ($J_{W–P}$) between 218.5 and 216.7 Hz. There is no apparent trend in chemical shift and increasing size of the nitrile ligand, because the change of nitrile substituent does not appear to significantly affect the metal–nitrile bond, hence other bonds such as W–P should also be largely unaffected. The $^{13}C\{^1H\}$-NMR spectrum of complex 7 showed the expected features, with the alkyne contact carbon resonance at δ = 217.68 ppm, which is indicative of the 2-butyne ligand behaving as a four-electron donor towards the tungsten centre [28] and enables complex 7 to obey the 18 electron rule.

It is somewhat surprising that the acetonitrite ligand is apparently completely displaced by NCR which are very similar ligands, from a reaction with equimolar amounts of complex and L in CH_2Cl_2 at r.t. However, no acetonitrile remained from ^1H-NMR measurements on complexes 1–7, and the elemental analysis data was very close to agreed values for the NCR complexes, and

the crystal structures (see Section 3) of four of the complexes all have the appropriate NCR attached to the tungsten. It may be the ability of the alkyne ligand to convert from a 'four-electron-donor' [28] to a 'two-electron-donor' to incorporate another ligand in an associative substitution reaction, which enables this type of alkyne complex to strongly favour ligand substitution reactions with a wide range of donor ligands [7–9].

Four of the complexes, 2, 3, 5 and 6 have been structurally characterised by X-ray crystallography. Suitable single crystals were grown from dichloromethane–diethyl ether solutions (4:10 cm^3) cooled to −17 °C for between 1 and 5 days. The molecular structures of each complex 2, 3, 5 and 6 consist of a discrete cation, [WI(CO)(NCR){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)]$^+$, and the tetraphenylborate anion, [BPh$_4$]$^-$. The structures of 2 (NC^{i}Pr), 3 (NC^{t}Bu), 5 (NCCH$_2$Ph) and 6 (1,2-C$_6$H$_4$(NCCH$_2$)$_2$} are shown in Figs. 1–4, respectively. The crystal data and structural refinement for 2, 3, 5 and 6 are given in Table 6, and bond lengths and angles are given in Table 7. The structures of the four nitrile-exchange complexes 2, 3, 5 and 6 can be compared with their acetonitrile precursor [25]. In each case, only the nitrile substituent is different, with the same atoms coordinated to the metal centre. The structures of the cations of complexes 2, 3, 5 and 6 are best described as *pseudo*-octahedral, with the 2-butyne occupying one coordination site *trans* to the iodine, the two triisopropylphosphite ligands are mutually *trans* and the nitrile ligand is *trans* to the carbonyl group. As is apparent from Table 7 the molecular dimensions in the coordination spheres are very similar in all four compounds. Indeed the angles in the coordination spheres differ on average only by 2–3°. The W–P bond lengths for all five complexes are very similar, [2.503(3) and 2.504(3) Å for [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] [25]; 2.526(3) and 2.524(4) Å for 2; 2.520(3) and 2.529(3) Å for 3; 2.517(4) and 2.524(3) Å for 5; 2.529(6) and 2.544(7) Å for 6]. The bond lengths between the tungsten and the remaining iodine are also similar for all five complexes, [W–I = 2.790(3) Å for [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] [25], 2.823(3) Å for 2, 2.814(3) Å for 3, 2.819(4) Å for 5 and 2.819(4) Å for 6]. Thus, there is no apparent trend in the change in length of W–I or W–P bonds with increasing size of the nitrile

Table 5
Carbon NMR data [a] for complex 7

$^{13}C\{^1H\}$ (δ) ppm

(7) 228.61 (s, $C\equiv O$); 217.68 (s, $C\equiv C$); 165.52, 164.74, 163.17 (4 × s, BC); 136.32, 125.62, 121.71 (3 × s, $C=C$, BPh_4); 130.48 (s, CN); 128.36, 127.34, 124.49, 123.13 (4 × s C$_4$H$_3$S–thiophene); 72.21 (m, (CH$_3$)$_2$$C$HO); 24.03 (d, (CH$_3$)$_2$CHO, J = 12.0 Hz); 21.92 (s, CH$_3$C$_2$$CH_3$); 19.27 (s, CH$_2$CN)

[a] Spectrum recorded in $CDCl_3$ at +25 °C, referenced to SiMe$_4$; s, singlet; d, doublet; m, multiplet.
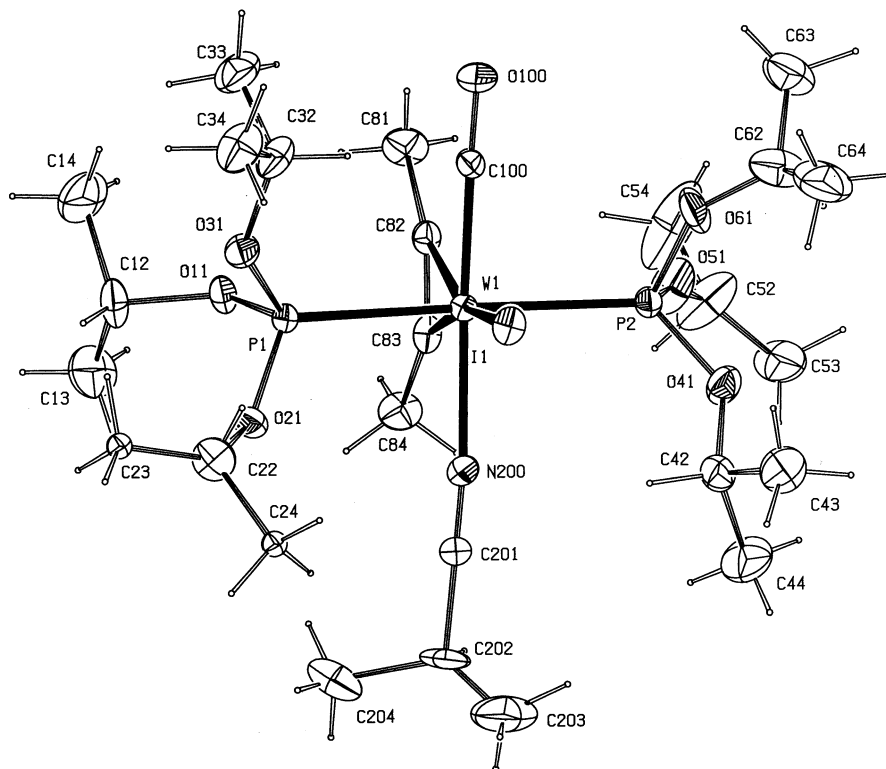
Fig. 1. The structure of the cation, [WI(CO)(NC^{i}Pr){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)]$^+$, **2** with ellipsoids shown at 15% probability.
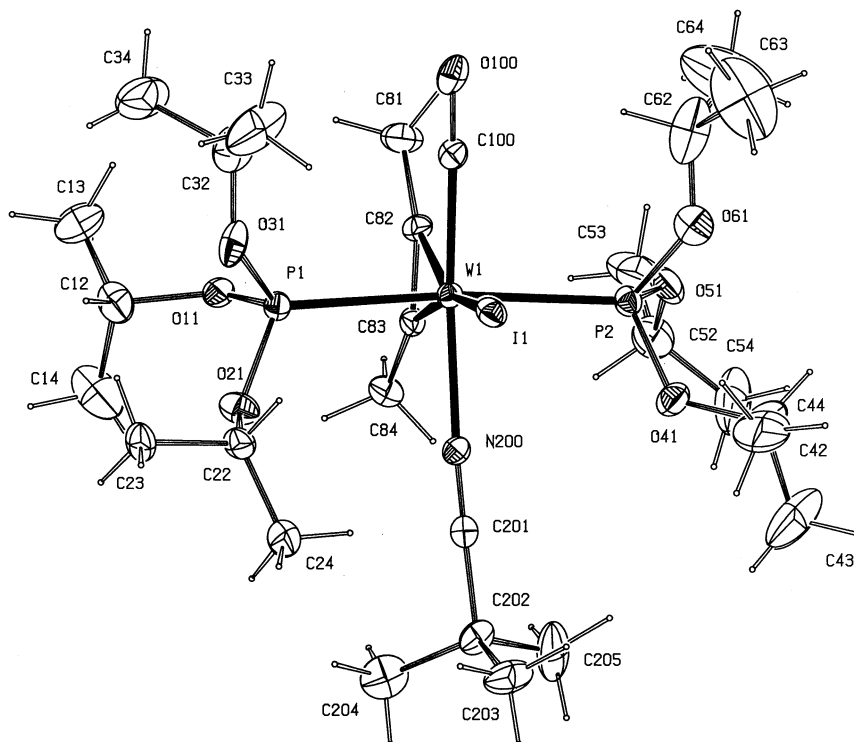
Fig. 2. The structure of the cation, [WI(CO)(NC^{t}Bu){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)]$^+$, **3** with ellipsoids shown at 15% probability.
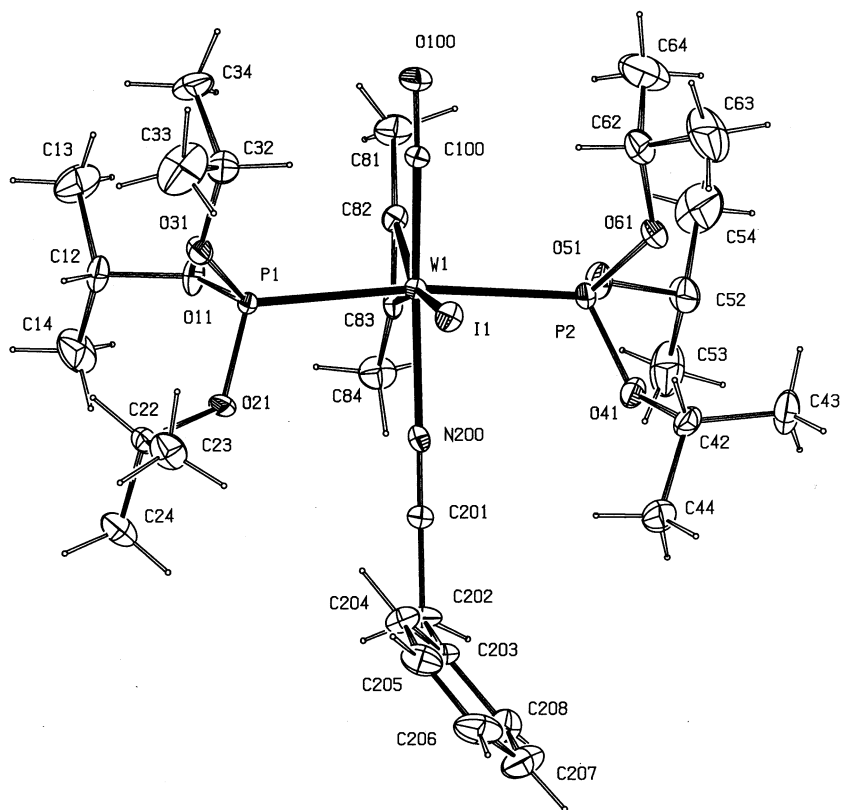
Fig. 3. The structure of the cation, $[WI(CO)(NCCH_2Ph)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)]^+$, **5** with ellipsoids shown at 15% probability.
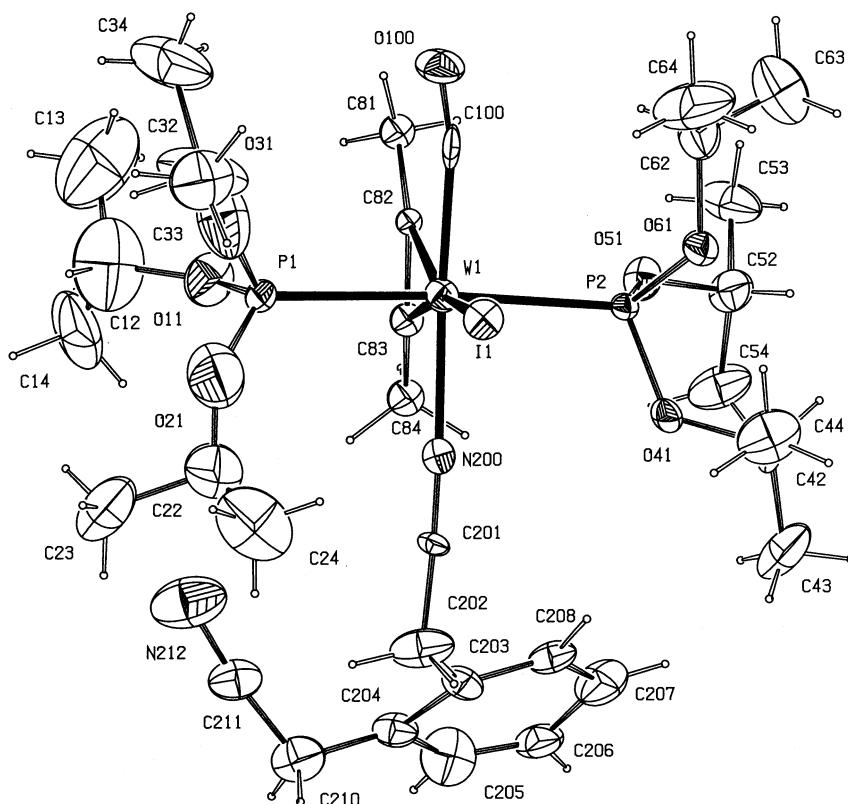
Fig. 4. The structure of the cation $[WI(CO)\{1,2\text{-}C_6H_4(NCCH_2)_2\text{-}N\}(\eta^2\text{-}MeC_2Me)]^+$, **6** with ellipsoids shown at 15% probability.

Table 6
Crystal data and structure refinement for **2**, **3**, **5**, **6**

Compound	**2**	**3**	**5**	**6**
Empirical formula	$C_{51}H_{75}BINO_7PW$	$C_{53}H_{77}INO_7P_2W$	$C_{63}H_{82}BIN_2O_7P_2W$	$C_{58}H_{76}BIN_2O_7P_2W$
Formula weight	1197.6	1212.85	1362.81	1296.71
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Unit cell dimensions				
a (Å)	9.638(12)	16.329(18)	9.249(12)	9.401(12)
b (Å)	16.224(18)	18.88(2)	36.63(4)	23.77(3)
c (Å)	19.82(2)	19.46(2)	20.00(2)	28.75(4)
α (°)	108.95(1)	(90)	(90)	(90)
β (°)	90.55(1)	96.57(1)	91.91(1)	98.46(1)
γ (°)	101.93(1)	(90)	(90)	(90)
V (Å^3)	2859	5959	6771	6353
Z	2	4	4	4
D_{calc} (mg m^{-3})	1.391	1.352	1.337	1.356
Absorption coefficient (mm^{-1})	2.661	2.554	2.257	2.401
Reflections collected/unique (R_{int})	8169/8169	17 242/9964/0.0226	19 416/11 548/0.0377	10 232/8074/0.0986
Data/restraints/parameters	8169/0/572	9964/0/604	11 548/0/659	8074/13/623
Final R indices [$I > 2\sigma(I)$] R_1	0.0595	0.0550	0.0712	0.1337
wR_2	0.1735	0.1479	0.1312	0.2833
R indices (all data) R_1	0.1003	0.1010	0.1247	0.1667
wR_2	0.2039	0.1758	0.1424	0.2949
Largest difference peak and hole (e Å^{-3})	1.863, -1.423	3.073, -1.427	1.716, -1.438	1.863, -1.421

Table 7
Molecular dimensions in the coordination spheres (Å, °)

	2	**3**	**5**	**6**
Bond lengths				
W(1)–C(100)	1.984(13)	2.008(10)	1.968(11)	2.04(3)
W(1)–C(83)	1.992(11)	1.998(9)	2.008(11)	2.18(2)
W(1)–C(82)	2.038(11)	2.019(9)	2.014(11)	1.93(2)
W(1)–N(200)	2.197(12)	2.180(7)	2.189(9)	2.184(19)
W(1)–P(2)	2.526(3)	2.529(3)	2.517(4)	2.529(6)
W(1)–P(1)	2.528(4)	2.520(3)	2.524(3)	2.544(7)
W(1)–I(1)	2.823(3)	2.814(3)	2.819(4)	2.819(4)
Bond angles				
C(100)–W(1)–C(83)	110.8(6)	110.9(4)	108.9(5)	107.2(10)
C(100)–W(1)–C(82)	72.6(5)	72.3(4)	72.2(4)	67.3(10)
C(83)–W(1)–C(82)	38.2(5)	38.6(4)	36.7(4)	40.1(8)
C(100)–W(1)–N(200)	169.0(4)	168.2(3)	168.1(4)	171.9(9)
C(83)–W(1)–N(200)	80.3(5)	80.9(3)	82.9(4)	80.8(8)
C(82)–W(1)–N(200)	118.4(5)	119.4(4)	119.6(4)	120.8(7)
C(100)–W(1)–P(2)	87.0(3)	91.8(3)	93.3(3)	91.0(6)
C(83)–W(1)–P(2)	96.5(3)	98.2(2)	91.7(3)	93.9(7)
C(82)–W(1)–P(2)	96.1(3)	98.0(3)	93.4(3)	98.1(6)
N(200)–W(1)–P(2)	91.9(3)	85.7(2)	86.0(2)	87.5(5)
C(100)–W(1)–P(1)	92.9(3)	91.9(3)	92.6(3)	91.6(7)
C(83)–W(1)–P(1)	91.9(3)	89.8(2)	92.5(3)	91.7(7)
C(82)–W(1)–P(1)	92.4(3)	92.5(3)	94.7(3)	89.1(6)
N(200)–W(1)–P(1)	86.4(3)	88.7(2)	86.9(2)	89.0(5)
P(2)–W(1)–P(1)	171.1(1)	169.5(1)	171.1(1)	172.9(2)
C(100)–W(1)–I(1)	84.6(4)	84.6(3)	85.7(1)	88.2(8)
C(83)–W(1)–I(1)	164.5(4)	164.1(3)	165.3(4)	164.6(6)
C(82)–W(1)–I(I)	157.0(4)	156.8(3)	157.9(3)	155.0(6)
N(200)–W(1)–I(1)	84.3(3)	83.7(2)	82.4(3)	83.8(6)
P(2)–W(1)–I(1)	85.8(1)	84.5(1)	87.0(1)	86.3(1)
P(1)–W(1)–I(1)	85.3(1)	86.0(1)	86.9(1)	87.1(2)

substituent. The bond lengths between tungsten and the nitrogen of the nitrile (W–N) for all five complexes, [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] [25], **2**, **3**, **5** and **6** show no observable trend, [2.181(7) Å [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$], 2.197(12) Å for **2**, 2.180(7) Å for **3**, 2.189(9) Å for **5** and 2.184(19) Å for **6**]. The W–C distances are similarly equivalent.

The internal bond angles between the two triisopropylphosphite ligands and the tungsten atom for complexes **2**, **3**, **5** and **6**, [171.10(9), 169.46(8), 171.15(9) and 172.9(2)°, respectively] are comparable to that of [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] [25], [172.27(7)°]. The deviation of 3° between **3** and its precursor, [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$-Me)][BPh$_4$] [25] is probably due to the size of the *tert*-butyl group, which causes the two phosphites to move away from the bulky nitrile ligand and serves to reduce the P–W–P angle. Similarly, on consideration of the W–N≡C bond angle for the five complexes, [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$], **2**, **3**, **5** and **6**, [170.7(7), 171.6(11), 174.5(7), 178.8(9) and 176.7(18)°, respectively], there is an observed trend. As the steric bulk of the nitrile increases, the angle between the nitrile and tungsten also increases, with the anomalous value for **5** possibly due to the accommodation of the second nitrile functionality into the coordination sphere with the minimum steric hindrance.

In conclusion, we have prepared and characterised a series of new cationic nitrile complexes of tungsten(II) of the type, [WI(CO)L{P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$]

(L = nitrile), and due to success in growing suitable single crystals of four of these complexes, we have been able to compare the structure of four of the complexes, for L = NC^{i}Pr, NC^{t}Bu, NCCH$_2$Ph and 1,2-C$_6$H$_4$(NCCH$_2$)$_2$.

3. Experimental

3.1. General remarks

All the reactions described in this paper were carried out using standard vacuum/Schlenk line techniques. The starting material, namely the cationic tungsten(II) complex, [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)]-[BPh$_4$], was prepared by reacting equimolar quantities of [WI$_2$(CO){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)] and Na[BPh$_4$] in MeCN as previously described [25]. Diethyl ether was dried over sodium wire before use, and CH$_2$Cl$_2$ was dried over calcium hydride before use. All chemicals used were purchased from commercial sources.

Elemental analyses (C, H and N) were determined by a Carlo Erba Elemental Analyser MOD 1108 (using helium as the carrier gas). IR spectra were recorded as thin CHCl$_3$ films between NaCl plates. ^{1}H-, ^{13}C{^{1}H}-, ^{31}P{^{1}H}- and ^{11}B{^{1}H}-NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were referenced to SiMe$_4$, ^{31}P{^{1}H}-NMR spectra were referenced to 85% H$_3$PO$_4$ and ^{11}B{^{1}H}-NMR spectra were referenced to BF$_3$·OEt$_2$.

3.2. Synthesis of [WI(CO)(NC^{t}Bu){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] (3)

To a stirred solution of [WI(CO)(NCMe){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] (0.03 g, 0.43 mmol) in CH$_2$Cl$_2$ (30 cm^3), 2,2′-dimethylpropionitrile (^{t}BuCN), 0.048 cm^3, 0.36 g, 0.43 mmol) was added and the solution stirred for 20 h. The resultant pinkish–red solution was filtered over celite, the solvent volume reduced in vacuo to a minimum volume (4 cm^3), layered with Et$_2$O (10 cm^3) and cooled to −17 °C. After 5 days, red single crystals of the product, [WI(CO)-(NC^{t}Bu){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] (3) were obtained, which were suitable for X-ray crystallography, yield of pure product = 0.413 g, 79%.

Complexes [WI(CO)(NCR){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$-Me)][BPh$_4$] {R = Et (1), ^{i}Pr (2), Ph (4) and PhCH$_2$ (5)}, [WI(CO){1,2-C$_6$H$_4$(CH$_2$CN)$_2$-N}{P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] (6) and [WI(CO){NCCH$_2$(C$_4$H$_3$S-3)}{P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] (7) were all prepared in a similar manner. Three complexes, [WI(CO)(NC^{i}Pr){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] (2), [WI(CO)(NCCH$_2$Ph){P(O^{i}Pr)$_3$}$_2$(η^2-MeC$_2$Me)][BPh$_4$] (5) and [WI(CO){1,2-C$_6$H$_4$(CH$_2$CN)$_2$-N}{P(O^{i}Pr)$_3$}$_2$-

(η^2-MeC$_2$Me)][BPh$_4$] (6), have also been characterised by X-ray crystallography from suitable single crystals grown from CH$_2$Cl$_2$–Et$_2$O solutions (4:10 cm^3) cooled to −17 °C for between 24 and 72 h.

3.3. X-ray crystallography–crystal structure determinations

The structures of 2, 3, 5 and 6 were determined by single crystal X-ray diffraction techniques. Cell data and refinement details are given in Table 6. Crystal data were collected with Mo–K$_\alpha$ radiation using the MAR-research Image Plate System. The crystals were positioned at 70 mm from the Image Plate. One hundred frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [29]. The structures were solved using direct methods with the SHELX-86 program [30] and contain discrete cations and BPh$_4^-$ anions. In 5 there was an additional discrete solvent NCH$_2$Ph ligand in the asymmetric unit. In all four structures the non-hydrogen atoms were refined with anisotropic thermal parameters. The only exception being in 6 where the data were poor due to misshapen spots. In this structure the alkyne group was refined isotropically. In the four structures, the hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Empirical absorption corrections were carried out using the DIFABS program [31]. The structures were refined on F^2 using SHELXL [32].

4. Supplementary material

Crystallographic data for the structural analysis not included in this paper, have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 168580–168583 for compounds 2, 3, 5 and 6, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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