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Some new but-2-yne phosphine complexes of tungsten(II)

Paul K. Baker* and Paul D. Jackson
Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW (UK)

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Abstract

Two equivalents of L (L = PPh_2Np (Np = napthyl) or *trans*-$Ph_2PCH{=}CHPPh_2$) or one equivalent of L L (L^L = *cis*-$Ph_2PCH{=}CHPPh_2$, R(+)-$Ph_2P\{CH(Me)CH_2\}PPh_2$ or $Me_2P(CH_2)_2PMe_2$) react with $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]\cdot 1/2CH_2Cl_2$ in CH_2Cl_2 at room temperature to give $[WI_2(CO)\{L_2$ or L^L$\}(\eta^2\text{-}MeC_2Me)]$ (**1**–**5**) in high yield. Reaction of $[WI_2(CO)\{$*cis*-$Ph_2PCH{=}CHPPh_2\}(\eta^2\text{-}MeC_2Me)]$ with an equimolar quantity of NaSR (R = Et or CH_2Ph) in CH_2Cl_2 at room temperature gave the thiolate complexes $[WI(SR)(CO)\{$*cis*-$Ph_2PCH{=}CHPPh_2\}(\eta^2\text{-}MeC_2Me)]$ (**6** and **7**). Treatment of $[WI_2(CO)(dmpe)(\eta^2\text{-}MeC_2Me)]$ (dmpe = $Me_2P(CH_2)_2PMe_2$) with an equimolar amount of $Ag[BF_4]$ in NCMe gave the cationic complex $[WI(CO)(NCMe)(dmpe)(\eta^2\text{-}MeC_2Me)][BF_4]$ (**8**) in high yield. The reactions of **8** with $OC(NH_2)_2$ and $SC(NH_2)_2$ are also described. The fluxionality of several of the complexes has been investigated by variable temperature ^1H NMR spectroscopy. ^{13}C NMR spectroscopy has been used to indicate the number of electrons donated to the tungsten in a number of these complexes.

Key words: Tungsten complexes; Alkyne complexes; Phosphine complexes

Introduction

The ability of alkyne ligands to donate two or four electrons to a transition-metal centre has been of considerable interest in recent years [1–5]. Alkynes attached to molybdenum or tungsten usually utilise both their filled pπ-orbitals and donate four electrons to the metal centre. An extensive review of four-electron alkyne complexes of molybdenum(II) and tungsten(II) was written by Templeton and published in 1989 [6].

In 1988 we described the preparation and molecular structures of the bis(alkyne) tungsten(II) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]\cdot 1/2CH_2Cl_2$ (R = Me or Ph) [7], both of which have four-electron donating alkyne ligands in order for them to obey the effective atomic number rule. We have investigated the reaction chemistry of these complexes with a wide range of both neutral [8–10] and anionic [11] donor ligands. In this paper we expand on some of our previous work and describe the reactions of the bis(but-2-yne) complex $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]\cdot 1/2CH_2Cl_2$ with some different phosphine ligands, and discuss the reaction chemistry of some of the products, including new types of reactions with thiolate ligands.

Experimental

All the reactions described in this paper were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques. The starting material used in this research, namely $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]\cdot 1/2CH_2Cl_2$, was prepared by the literature method [7]. All chemicals used were purchased from commercial sources. The solvents used were dried and distilled under dry nitrogen before use.

Elemental analyses (C, H and N) were determined by using a Carlo Erba elemental analyser MOD 1106 (using helium as the carrier gas). IR spectra were recorded on a Perkin Elmer 1430 IR spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker AC 250 MHz NMR spectrometer in Bangor, whilst ^{13}C NMR spectra were recorded on a Bruker WH 400 MHz NMR spectrometer at the University of Warwick. All ^1H and ^{13}C NMR spectra were calibrated against tetramethylsilane. ^{31}P NMR spectra were calibrated against 85% H_3PO_4.

$[WI_2(CO)(trans\text{-}Ph_2PCH{=}CHPPh_2)_2(\eta^2\text{-}MeC_2Me)]$ (2)

To $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]\cdot 1/2CH_2Cl_2$ (0.829 g, 1.262 mmol) dissolved in CH_2Cl_2 (25 cm^3) with continuous stirring under a stream of dry nitrogen

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*Author to whom correspondence should be addressed.

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was added *trans*-1,2-bis(diphenylphosphino)ethylene (1.0 g, 2.522 mmol). After 20 h the solvent was removed *in vacuo*. The crude product was washed with petroleum ether (40–60) which was syringed off and the solid remaining evacuated to dryness leaving a green solid [WI$_2$(CO)(*trans*-Ph$_2$PCH=CHPPh$_2$)$_2$(η^2-MeC$_2$Me)] (**2**), which was recrystallised from CH$_2$Cl$_2$. Yield of pure product = 1.51 g, 91%.

A similar reaction of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$]·1/2CH$_2$Cl$_2$ with an equimolar amount of PPh$_2$Np in CH$_2$Cl$_2$ at room temperature for 72 h gave the analogous complex [WI$_2$(CO)(PPh$_2$Np)$_2$(η^2-MeC$_2$Me)] (**1**). (For physical and analytical data see Table 1).

[WI$_2$(CO)(cis-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (3)

To [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$]·1/2CH$_2$Cl$_2$ (1.0 g, 1.521 mmol) dissolved in CH$_2$Cl$_2$ (25 cm^3) with continuous stirring under dry nitrogen was added *cis*-1,2-bis(diphenylphosphino)ethylene (0.603 g, 1.521 mmol). After 20 h the solution was filtered. Removal of the solvent *in vacuo* afforded a green solid [WI$_2$(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (**3**), which was recrystallised from CH$_2$Cl$_2$. Yield of pure product = 1.02 g, 73%.

Similar reactions of [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$]·1/2CH$_2$Cl$_2$ with an equimolar quantity of L^L (L^L = R(+)-Ph$_2$P(CH(CH$_3$)CH$_2$)PPh$_2$ or Me$_2$P(CH$_2$)$_2$PMe$_2$) afforded the analogous neutral compounds [WI$_2$(CO)(L^L)(η^2-MeC$_2$Me)] (**4**, **5**). (For physical and analytical data see Table 1).

[WI(SEt)(CO)(cis-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (6)

To [WI$_2$(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (0.4 g, 0.437 mmol) dissolved in CH$_2$Cl$_2$ (25 cm^3) with continuous stirring under a stream of dry nitrogen was added NaSEt (0.037 g, 0.437 mmol). After 18 h the solution was filtered twice to remove the NaI. Removal of the solvent *in vacuo* afforded a green solid [WI(SEt)(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (**6**) which on recrystallisation from CH$_2$Cl$_2$/Et$_2$O by cooling to −25 °C for 12 h yielded 0.267 g, 72% of pure product.

A similar reaction of [WI$_2$(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] with an equimolar amount of NaSCH$_2$Ph afforded the analogous neutral complex [WI(SCH$_2$Ph)(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (**7**). (For physical and analytical data see Table 1.)

[WI(CO)(NCMe){Me$_2$P(CH$_2$)$_2$PMe$_2$}(η^2-MeC$_2$Me)][BF$_4$] (8)

To [WI$_2$(CO)(dmpe)(η^2-MeC$_2$Me)] (**5**) (1.0 g, 1.490 mmol) dissolved in NCMe (30 cm^3) with continuous stirring under a stream of dry nitrogen was added Ag[BF$_4$] (0.29 g, 1.490 mmol). After 20 h the solution was filtered to remove the AgI followed by removal of the solvent *in vacuo*. The crude product was then dissolved in CH$_2$Cl$_2$ (20 cm^3) and filtered again to remove the final traces of AgI. Reduction of the solvent volume *in vacuo* to 2 cm^3 followed by dropwise addition of diethyl ether precipitated the purple cationic complex [WI(CO)(NCMe)(dmpe)(η^2-MeC$_2$Me)][BF$_4$] (**8**) which on recrystallisation by cooling in a solution of NCMe at −25 °C for 12 h yielded 0.71 g, 71% of pure product.

[WI(CO){OC(NH$_2$)$_2$}(dmpe)(η^2-MeC$_2$Me)][BF$_4$] (9)

To [WI(CO)(NCMe)(dmpe)(η^2-MeC$_2$Me)][BF$_4$] (0.25 g, 0.373 mmol) dissolved in acetone (20 cm^3) with continuous stirring under a stream of dry nitrogen was added {OC(NH$_2$)$_2$} (0.022 g, 0.373 mmol). After 10 h the solvent was removed *in vacuo*. The crude product was dissolved in CH$_2$Cl$_2$ (20 cm^3) and filtered. Reduction of the solvent volume to 1 cm^3 *in vacuo* followed by dropwise addition of diethyl ether precipitated the brown cationic complex [WI(CO){OC(NH$_2$)$_2$}(dmpe)-

TABLE 1. Physical and analytical data[a] for the but-2-yne phosphine tungsten(II) complexes

Complex	Colour	Yield (%)	Analysis (%)		
			C	H	N
[WI$_2$(CO)(PPh$_2$Np)$_2$(η^2-MeC$_2$Me)] (**1**)	yellow–green	68	51.7(51.4)	3.9(3.5)	
[WI$_2$(CO)(*trans*-Ph$_2$PCH=CHPPh$_2$)$_2$(η^2-MeC$_2$Me)] (**2**)	green	91	51.7(52.2)	3.8(3.8)	
[WI$_2$(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (**3**)	green	73	40.6(40.6)	3.2(3.1)	
[WI$_2$(CO){R(+)-Ph$_2$P{CH(CH$_3$)CH$_2$}PPh$_2$}(η^2-MeC$_2$Me)] (**4**)	green	77	40.7(41.2)	3.5(3.5)	
[WI$_2$(CO){Me$_2$P(CH$_2$)$_2$PMe$_2$}(η^2-MeC$_2$Me)] (**5**)	dark green	92	21.0(19.7)	3.5(3.3)	
[WI(SEt)(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (**6**)	green	72	46.2(46.6)	4.3(3.9)	
[WI(SCH$_2$Ph)(CO)(*cis*-Ph$_2$PCH=CHPPh$_2$)(η^2-MeC$_2$Me)] (**7**)	brown	44	49.4(48.8)	4.0(3.8)	
[WI(CO)(NCMe)(dmpe)(η^2-MeC$_2$Me)][BF$_4$] (**8**)	purple	71	23.5(23.3)	3.9(3.8)	1.2(2.1)
[WI(CO){OC(NH$_2$)$_2$}(dmpe)(η^2-MeC$_2$Me)][BF$_4$] (**9**)	brown	39	21.9(20.9)	4.0(3.8)	3.7(4.1)
[WI(CO){SC(NH$_2$)$_2$}(dmpe)(η^2-MeC$_2$Me)][BF$_4$] (**10**)	pink	42	21.1(20.4)	3.8(3.7)	3.9(4.0)

[a] Calculated values in parentheses.

(η^2-MeC$_2$Me)] [BF$_4$] (**9**) which was recrystallised from acetone/Et$_2$O. Yield of pure product = 0.10 g, 39%.

A similar reaction of [WI(CO)(NCMe)(dmpe)(η^2-MeC$_2$Me)][BF$_4$] with an equimolar amount of SC(NH$_2$)$_2$ afforded the analogous cationic complex [WI(CO){SC(NH$_2$)$_2$}(dmpe)(η^2-MeC$_2$Me)][BF$_4$] (**10**). (For physical and analytical data see Table 1.)

Results and discussion

Reaction of the bis(but-2-yne) complex [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$]·1/2CH$_2$Cl$_2$ with either two equivalents of L (L = PPh$_2$Np (Np = napthyl) or *trans*-Ph$_2$PCH=CHPPh$_2$) or one equivalent of the bidentate ligands L^L (L^L = *cis*-Ph$_2$PCH=CHPPh$_2$, R(+)-Ph$_2$P{CH(CH$_3$)CH$_2$}PPh$_2$ or Me$_2$P(CH$_2$)$_2$PMe$_2$) gives high yields of the new di-iodo mono(but-2-yne) complexes [WI$_2$(CO){L$_2$ or L^L}(η^2-MeC$_2$Me)] (**1–5**). All the new complexes have been characterised by elemental analysis (C, H and N) (Table 1), IR spectroscopy (Table 2), ^{1}H NMR spectroscopy (Table 3) and in selected cases ^{13}C NMR spectroscopy (Table 4) and ^{31}P NMR spectroscopy (Table 5). Complexes **1–5** are reasonably air-stable in the solid state but decompose when exposed to air in solution. They are soluble in chlorinated solvents but only sparingly soluble in diethyl ether and hydrocarbon solvents. All the complexes show a strong carbonyl band in their IR spectra between 1933 and 1962 cm^{-1} (Table 2). The weak alkyne stretching bands lie between 1650 and 1708 cm^{-1} which is at considerably lower wavenumber compared with the uncoordinated alkyne ligands. This is expected as there is considerable backdonation of electron density from the filled metal orbitals to the empty π^*-orbitals on the alkyne ligand upon coordination to the metal. The ^{31}P NMR spectrum of complex **2** (Table 5) shows two singlets of equal intensity at $\delta = -5.16$ and -11.86 ppm. The resonance furthest downfield corresponds to the coordinated phosphorus atoms. Since there are only two resonances one can postulate that as in related octahedral alkyne complexes of molybdenum(II) and tungsten(II) with two phosphine ligands, they are oriented *trans* to each other. The other resonance at $\delta = -11.86$ ppm corresponds to the uncoordinated phosphorus atoms. The ^{31}P NMR spectral data suggest the most likely structure for **2** to be as shown in Fig. 1. It should be noted that the molecular structure of the related molybdenum(II) complex [MoBr$_2$(CO)(PEt$_3$)$_2$(η^2-PhC$_2$H)] has been determined crystallographically [12] and has the structure with *trans*-phosphines as shown in Fig. 1.

Likewise, for complex **1** a single resonance at $\delta = -1.71$ ppm indicates that the two phosphine ligands are coordinated *trans* to one another. The ^{31}P NMR spectrum for the bidentate phosphine (*cis*-Ph$_2$PCH=CHPPh$_2$) complex **3** shows two doublets at 26.63 and 11.97 ppm (J(P–P) = 34.92 Hz). Tungsten satellites are also evident (J(W–P) = 122.21 Hz). From this spectral information, the structure for the complex is as proposed in Fig. 2. This structure is similar to the X-ray crystallographically determined geometry for the complex [WI$_2$(CO){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)] [9] which is also green and has a carbonyl stretching band at 1938 cm^{-1} (cf. **3** has ν(CO) = 1934 cm^{-1}). It is likely that complexes **4** and **5** also adopt the geometry proposed in Fig. 2 in view of their similar colours and spectral properties to the crystallographically characterised complex.

The room temperature ^{1}H NMR spectra (Table 3) for the complexes **1–5** show the expected features for the proposed structures shown in Figs. 1 and 2. It is interesting to note that complex **2** shows a singlet at room temperature for the but-2-yne methyl protons. This indicates that at room temperature the alkyne is rotating rapidly with respect to the NMR timescale.

TABLE 2. IR data^a for the but-2-yne phosphine complexes of tungsten(II)

Complex	ν(C≡N) (cm^{-1})	ν(C≡O) (cm^{-1})	ν(C=O) (cm^{-1})	ν(C≡C) (cm^{-1})	ν(C=S) (cm^{-1})	ν(BF) (cm^{-1})
1		1948(s)				
2		1933(s)		1650(w)		
3		1934(s)		1655(w)		
4		1962(s)		1669(w)		
5		1952(brs)		1708(w)		
6		1934(s)		1721(m)		
7		1959(s)		1650(w)		
8	2317(w) 2286(w)	1939(s)		1700(w)		1061(brs)
9		1960(brm)	1675(m)			1067(brs)
10		1931(brs)			1626(s)	1066(brs)

^{a}Spectra recorded in CHCl$_3$ as thin films between NaCl plates; w = weak; m = medium; s = strong; br = broad.

TABLE 3. ^{1}H NMR data[a] for the but-2-yne phosphine complexes of tungsten(II)

Complex	^{1}H NMR data (δ (ppm))
1	8.44–7.31 (m, 34H, Ph-*H*), 3.09, 3.01 (2s, 6H, *Me*C$_2$)
2	7.58–7.07 (m, 40H, Ph-*H*), 6.73 (vt, 4H, =C*H*P, *J*(P–H) = 15.3 Hz), 2.12 (s, 6H, *Me*C$_2$)
3	8.60–6.85 (m, 20H, Ph-*H*), 5.51 (s, 2H, PC*H*), 3.06, 2.92, (2s, 6H, *Me*C$_2$)
4	8.42–6.76 (brm, 20H, Ph-*H*), 4.05 (brm, 1H, PC*H*), 3.30 (brm, 2H, PC*H*$_2$), 3.03, 2.75 (2s, 6H, *Me*C$_2$), 1.33 (brm, 3H, CHC*H*$_3$)
5[b]	3.17, 3.01 (2s, 6H, *Me*C$_2$), 2.26 (brd, 4H, PC*H*$_2$, *J*(P–H) = 8.6 Hz), 2.03 (d, 3H, PC*H*$_3$, *J*(P–H) = 9.6 Hz), 1.92 (d, 3H, P*Me*$_3$, *J*(P–H) = 11.1 Hz), 1.78 (d, 3H, P*Me*$_3$, *J*(P–H) = 11.69 Hz), 1.09 (m, 3H, PC*H*$_3$)
6	8.86–6.83 (m, 20H, Ph-*H*), 4.23 (dd, 2H, PC*H*, *J*(P–H) = 2.5, 5.7 Hz), 3.02, 2.95 (2s, 6H, *Me*C$_2$), 1.33 (m, 2H, SC*H*$_2$), 0.93 (t, 3H, C*H*$_3$, *J*(H–H) = 6.84 Hz)
7	8.57–6.83 (brm, 25H, Ph-*H*), 4.90 (d, 1H, PC*H*, *J*(P–H) = 13.1 Hz), 4.60 (d, 1H, PC*H*, *J*(P–H) = 12.62 Hz), 3.61 (s, 2H, SC*H*$_2$Ph), 2.7, 2.6 (2s, 6H, *Me*C$_2$)
8	3.17, 3.09 (2s, 6H, *Me*C$_2$), 2.29 (brd, 4H, PC*H*$_2$, *J*(P–H) = 9.8 Hz), 2.16 (d, 3H, PC*H*$_3$, *J*(P–H) = 8.71 Hz), 2.05 (d, 3H, PC*H*$_3$, *J*(P–H) = 10.9 Hz), 2.01 (s, 3H, NC*Me*), 1.83 (d, 3H, PC*H*$_3$, *J*(P–H) = 12.0 Hz), 0.83 (m, 3H, PC*H*$_3$)
9[c]	6.80 (brs, 4H, N*H*$_2$), 3.19 (s, 6H, *Me*C$_2$), 2.55 (brd, 4H, PC*H*$_2$, *J*(P–H) = 6.4 Hz), 2.37 (d, 3H, PC*H*$_3$, *J*(P–H) = 9.2 Hz), 2.05 (d, 3H, PC*H*$_3$, *J*(P–H) = 10.7 Hz), 1.85 (d, 3H, PC*H*$_3$, *J*(P–H) = 8.8 Hz), 1.24 (m, 3H, PC*H*$_3$)
10[c]	6.89 (brs, 4H, N*H*$_2$), 3.36, 3.23 (2s, 6H, *Me*C$_2$), 2.45 (brd, 4H, PC*H*$_2$, *J*(P–H) = 9.6 Hz), 2.26 (d, 3H, PC*H*$_3$, *J*(P–H) = 8.9 Hz), 2.07 (d, 3H, PC*H*$_3$, *J*(P–H) = 10.6 Hz), 1.83 (d, 3H, PC*H*$_3$, *J*(P–H) = 10.6 Hz), 1.22 (m, 3H, PC*H*$_3$)

[a] Spectra recorded in $\mathrm{CDCl_3}$ (+25 °C) referenced to $\mathrm{SiMe_4}$. [b] Spectrum recorded in NCMe-d_3. [c] Spectra recorded in acetone-d_6; s = singlet, d = doublet, vt = virtual triplet, m = multiplet, br = broad.

TABLE 4. ^{13}C NMR data[a] for the but-2-yne phosphine complexes of tungsten(II)

Complex	^{13}C NMR data (δ (ppm))
1	218.90 (s, *C*≡O), 208.23, 207.50 (2s, *C*≡*C*), 135.47–125.99 (m, Ph-*C*), 19.72, 17.99 (2s, *Me*C$_2$)
2	224.40 (s, *C*≡*C*), 222.25 (s, *C*≡O), 142.65 (t, PCH (coord.), *J*(P–C) = 23.7 Hz), 134.49–127.66 (m, Ph-*C* and PCH (uncoord.)), 23.09 (s, *Me*C$_2$)
3	218.05, 218.34 (2s, *C*≡*C*), 202.02 (s, *C*≡O), 150.60, 150.42, 150.25, 150.04 (dd, PCH, *J*(P–C) = 21.3, 35.4 Hz), 148.92, 148.70, 148.49, 148.28 (dd, PCH, *J*(P–C) = 22.11, 44.3 Hz), 136.9 (d, Ph-*C*P, *J*(P–C) = 45.2 Hz), 135.52 (d, Ph-*C*P, *J*(P–C) = 52.8 Hz), 134.65 (d, Ph-*C*P, *J*(P–C) = 30.2 Hz), 130.94 (d, Ph-*C*P, *J*(P–C) = 36.9 Hz), 134.11–127.44 (md, Ph-*C*), 22.04, 20.15 (2br, s, *Me*C$_2$)
8	223.66 (d, *C*≡*C*), *J*(P–C) = 3.94 Hz), 223.49 (d, *C*≡*C*, *J*(P–C) = 4.1 Hz), 214.80 (brs, *C*≡O), 128.39 (s, NCMe), 31.60–11.73 (md, *Me*$_3$PCH$_2$ and *Me*C$_2$), 4.02, (s, NC*Me*)

[a] Spectra recorded in $\mathrm{CD_2Cl_2}$ (+25 °C) referenced to $\mathrm{SiMe_4}$ on a Bruker WH 400 MHz; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

Variable-temperature ^{1}H NMR spectra were obtained for complexes **3**–**5**. The barriers to but-2-yne rotation were calculated for these complexes using the Gutowsky–Holm equation [13, 14] (Table 6). Complex **5** showed no coalescence point even at 353 K with the two but-2-yne methyl resonances still remaining as singlets. This indicates that the barrier to alkyne rotation is >74 kJ mol^{-1}. This value together with the value of 74.0 kJ mol^{-1} for complex **3** is significantly higher than previous values for similar phosphine complexes [9]. For example, the crystallographically characterised complex $[\mathrm{WI_2(CO)(dppm)}(\eta^2\text{-}\mathrm{MeC_2Me})]$ (dppm = $\mathrm{Ph_2P(CH_2)PPh_2}$) has a calculated barrier to but-2-yne rotation of 49.5 kJ mol^{-1}. When comparing this complex with $[\mathrm{WI_2(CO)(dmpe)}(\eta^2\text{-}\mathrm{MeC^2Me})]$ (**5**) the smaller methyl groups in the dmpe ligand donate more electron density to the metal centre than the phenyl groups in the dppm ligand. Thus, more electron density is available

TABLE 5. ^{31}P NMR data[a] for the but-2-yne phosphine complexes of tungsten(II)

Complex	^{31}P NMR data (δ (ppm))
1	-1.71
2	-5.16, -11.86 (2s)
3	26.63, 11.97 (2s, J(W–P) = 122.2 Hz; J(P–P) = 34.9 Hz)

[a] Spectra recorded on $CDCl_3$ and referenced to H_3PO_4 (85%).

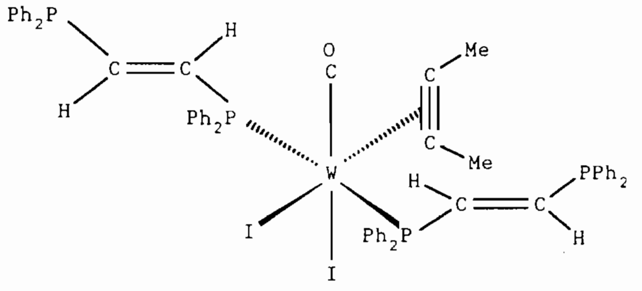

Fig. 1. Proposed structure for $[WI_2(CO)($*trans*-$Ph_2PCH{=}CHPPh_2)_2(\eta^2$-$MeC_2Me)]$ (**2**).

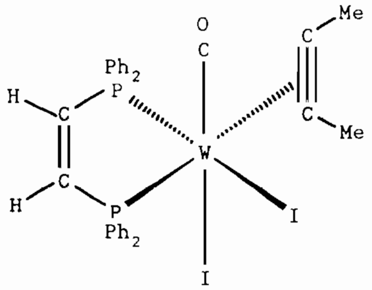

Fig. 2. Proposed structure for $[WI_2(CO)($*cis*-$Ph_2PCH{=}CHPPh_2)(\eta^2$-$MeC_2Me)]$ (**3**).

TABLE 6. Barriers to but-2-yne rotation of selected but-2-yne phosphine complexes of tungsten(II)

Complex	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^{\#}$ (kJ mol^{-1})
3	353	36.88	74.0
4	318	71.48	64.6
5	> 353	41.38	> 74
8	> 353	18.58	> 76

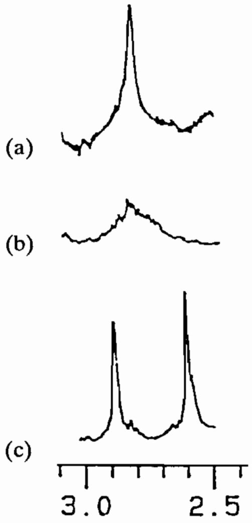

Fig. 3. The but-2-yne methyl resonances at (a) 353 K, (b) 318 K and (c) 298 K for the complex $[WI_2(CO)\{R(+)$-$Ph_2P\{CH(CH_3)CH_2\}PPh_2\}(\eta^2$-$MeC_2Me)]$ (**4**).

for synergic bonding to the alkyne ligand thereby hindering rotation. The other factor that must be considered is of a steric nature. There is an extra CH_2 group present in the dmpe ligand and this may increase hindrance to alkyne rotation. However, the value obtained for the barrier to but-2-yne rotation for compound **4** of 64.6 kJ mol^{-1} does coincide with the values in the literature [6]. The but-2-yne methyl resonances at 353, 318 and 298 K for $[WI_2(CO)\{R(+)$-$Ph_2P\{CH(CH_3)$-$CH_2\}PPh_2\}(\eta^2$-$MeC_2Me)]$ (**4**) are shown in Fig. 3. It is interesting that the value for **4** is at least 10 kJ mol^{-1} lower than the more electron-rich and smaller dmpe ligand, $Me_2P(CH_2)_2PMe_2$ of compound **5**. Hence, one can tentatively suggest from the above evidence that electronic effects are predominant in this system.

The ^{13}C NMR spectra for these complexes (Table 4) all show, as expected, alkyne contact-carbon shifts above 200 ppm with the exception of complexes **4** and **5** which failed to give interpretable spectra due to decomposition whilst accumulating data. For example, the complex $[WI_2(CO)(PPh_2Np)_2(\eta^2$-$MeC_2Me)]$ (**1**) shows two resonances at $\delta = 208.23$ and 207.50 ppm. It can therefore be deduced that the alkyne is using both its filled pπ-orbitals and so donating four electrons to the tungsten, which is in accord with the correlation of Templeton and Ward [15] of the alkyne contact carbon ^{13}C chemical shift and the number of electrons donated to the metal.

Reaction of complex **3** with either one equivalent of NaSEt or $NaSCH_2Ph$ in CH_2Cl_2 at room temperature afforded modest yields of the complexes $[WI(SR)(CO)($*cis*-$Ph_2PCH{=}CHPPh_2)(\eta^2$-$MeC_2Me)]$ (**6** and **7**). These new complexes have been fully characterised by elemental analysis (C, H and N) (Table 1), IR spectroscopy (Table 2) and ^{1}H NMR spectroscopy (Table 3). They are soluble in chlorinated solvents, NCMe and CH_3COCH_3, slightly soluble in diethyl ether and insoluble in hydrocarbon solvents. The complexes are stable in the solid state when stored under dry nitrogen but slowly decompose in solution on exposure to air. It is likely that the geometry of **6** and **7** is similar to the X-ray crystallographically determined complex $[WI_2(CO)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)]$ (**9**) (Fig. 2) with the anionic sulfur donor ligand replacing either iodide ligand as shown in Fig. 2. The IR spectra (Table 2) of compounds **6** and **7** both show strong, single carbonyl bands at 1934 and 1959 cm^{-1}, respectively. The ^1H NMR spectra for these complexes (Table 3) show the expected features for the geometry proposed in Fig. 2 with the alkyne methyl resonances appearing as two singlets thereby suggesting that the alkyne ligand is not undergoing propellor-like rotation at room temperature. It should be noted that reaction of **3** with an equimolar quantity of NaSPh and $NaS(CH_2)_3CH_3$ failed to yield any pure products. Also, reaction of **3** with two equivalents of NaSEt, $NaS(CH_2)_3CH_3$, NaSPh or $NaSCH_2Ph$ failed to give the desired products $[W(SR)_2(CO)(\textit{cis}\text{-}Ph_2PCH{=}CHPPh_2)(\eta^2\text{-}MeC_2Me)]$ in a pure state.

Reaction of $[WI_2(CO)\{Me_2P(CH_2)_2PMe_2\}(\eta^2\text{-}MeC_2Me)]$ (**5**) with one equivalent of $Ag[BF_4]$ in acetonitrile at room temperature affords the new, purple cationic complex $[WI(CO)(NCMe)(dmpe)(\eta^2\text{-}MeC_2Me)][BF_4]$ (**8**) in good yield. The highly coloured nature of this compound is similar to that observed for other cationic four-electron alkyne complexes such as $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (n = 1–6) [16]. Complex **8** has been fully characterised in the usual manner and is soluble in chlorinated solvents, NCMe and CH_3COCH_3 but insoluble in diethyl ether and hydrocarbon solvents. It can be stored under dry nitrogen for considerable lengths of time but decomposes when exposed to air in solution. The IR spectrum (Table 2) shows a strong carbonyl band at 1939 cm^{-1} which is 20 cm^{-1} lower than in the neutral di-iodo complex $[WI_2(CO)(dmpe)(\eta^2\text{-}MeC_2Me)]$ (**7**). This is unusual in that previous examples cited in the literature [16] show an increase in carbonyl stretching frequency for the related cation. Also present, is an asymmetric doublet at around 2300 cm^{-1} which can be attributed to the coordinated acetonitrile ligand. The increase in ν(CN) upon coordination of the acetonitrile is due to the coupling of the C–N and N–metal stretching vibrations and an increased C–N force constant. This also suggests that the acetonitrile ligand is functioning as a simple σ-donor ligand [17]. The weak band at 1700 cm^{-1} is assigned to the alkyne $\nu(C{\equiv}C)$ stretching frequency.

The ^1H NMR spectrum of **8** (Table 3) shows the expected features for the structure proposed in Fig. 4 which is related to the crystallographically characterised complex $[WI(CO)\{P(O^iPr)_3\}\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ previously described [16]. The dmpe ligand in **8** is in place of the dppm ligand and the acetonitrile replacing the triisopropylphosphite ligand in the coordination sphere as shown in Fig. 4. The

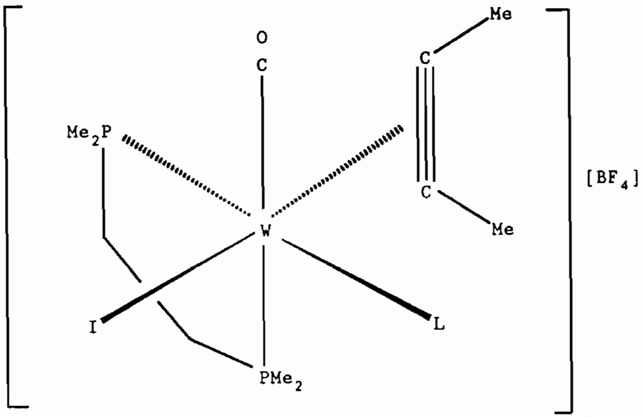

Fig. 4. Proposed structure for $[WI(CO)L(dmpe)(\eta^2\text{-}MeC_2Me)][BF_4]$ (L = NCMe (**8**), $OC(NH_2)_2$ (**9**), $SC(NH_2)_2$ (**10**)).

but-2-yne methyl resonances occur as two singlets at room temperature which implies that the alkyne ligand is not undergoing rapid propellor-like rotation. Variable-temperature ^1H NMR studies revealed that the energy barrier to alkyne rotation was > 76 kJ mol^{-1} with the two methyl singlets still observed at 353 K. This behaviour is analogous to that of the neutral complex $[WI_2(CO)(dmpe)(\eta^2\text{-}MeC_2Me)]$ (**5**) which was found to be in excess of 74 kJ mol^{-1}. The ^{13}C NMR spectrum (Table 4) also conformed with the postulated structure showing alkyne contact-carbon resonances at 223.66 and 223.49 ppm. These values are consistent with the correlation of Templeton and Ward [15] for four-electron alkynes and also allow the complex to obey the effective atomic number rule. The ^{11}B NMR spectrum of **8** confirmed the presence of the $[BF_4]^-$ counterion showing a sharp singlet at $\delta = -1.48$ ppm. This value agrees with those cited in the literature for other $[BF_4]^-$ salts.

The complex $[WI(CO)(NCMe)(dmpe)(\eta^2\text{-}MeC_2Me)][BF_4]$ (**8**) reacts with an equimolar quantity of L (L = $OC(NH_2)_2$ or $SC(NH_2)_2$) to afford reasonable yields of the new complexes $[WI(CO)L(dmpe)(\eta^2\text{-}MeC_2Me)][BF_4]$ (**9** and **10**). Both of the complexes have been fully characterised by elemental analysis (C, H and N) (Table 1), IR spectroscopy (Table 2) and ^1H NMR spectroscopy (Table 3). As expected, the complexes are soluble in CH_2Cl_2, $CHCl_3$, NCMe and CH_3COCH_3 but completely insoluble in diethyl ether and hydrocarbon solvents. Complexes **9** and **10** are stable in the solid state when stored under nitrogen but decompose when exposed to air in solution. The reaction of **8** with these oxygen and sulfur donor ligands is likely to occur via an associative mechanism. This involves initial formation of an unstable two-electron donor alkyne intermediate $[WI(CO)(NCMe)L(dmpe)(\eta^2\text{-}MeC_2Me)][BF_4]$ which rapidly converts back to a four-electron donor and expels the coordinated acetonitrile, thus affording the complexes **9** and **10**. Evidence to support this mechanism arises from work carried out by Templeton and co-workers [18]. Kinetic studies on the substitution reactions of $[Mo(CO)(S_2CNMe_2)_2(\eta^2\text{-}RC_2R')]$ with L (L = CO, PEt_3, $P(OMe)_3$ or RC_2R') suggested an associative mechanism which supports the associative mechanism proposed for the formation of compounds **9** and **10**.

The geometry of these compounds is thought to be similar to that of $[WI(CO)\{SC(NH_2)_2\}(dppm)(\eta^2\text{-}MeC_2Me)][ClO_4]$ [19] which has been crystallographically characterised with the alkyne being *trans* to the iodide. This has the same disposition of ligands around the metal centre as proposed for complex **8** and the crystallographically characterised complex $[WI(CO)\{P(O^iPr)_3\}(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ [16]. The coordinated oxygen or sulfur donor ligand and carbonyl ligand lie *cis* to one another and each *trans* to one end of the bidentate phosphine ligand in the equatorial plane. The IR spectra (Table 2) of compounds **9** and **10** both show strong carbonyl stretching bands at 1960 and 1931 cm^{-1}, respectively. A strong band due to $\nu(BF)$ is present around 1060 cm^{-1}. The ^1H NMR spectra (Table 3) of these complexes show the expected features for the proposed structure shown in Fig. 4.

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