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Reactions of the cationic but-2-yne complex $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ with bidentate nitrogen donor ligands

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Abstract

Reaction of the complex $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ with an equimolar quantity of NN {NN = 2,2′-bipyridyl, 1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, *N,N′*-cyclohexyldiazabutadiene, *N,N′*-^{t}butyldiazabutadiene or *N,N′-p*-methoxyphenyldiazabutadiene} at room temperature in CH_2Cl_2 smoothly affords good yields of the new dicationic mixed ligand complexes $[W(CO)(NN)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]I$ (**1–6**). The dicationic nature of these complexes was confirmed by reaction of $[W(CO)(2,2'\text{-bipy})\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]I$ with two equivalents of $Na[BPh_4]$ in acetonitrile to give the bis(tetraphenylborate) complex $[W(CO)(2,2'\text{-bipy})\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]_2$ (**7**). ^{13}C NMR spectroscopy indicates that the but-2-yne acts as a four-electron donor in these complexes.

Key words: Tungsten; But-2-yne

1. Introduction

Alkyne-containing complexes of molybdenum(II) and tungsten(II) have received considerable attention in the last 20 years and have recently been the subject of an extensive review article [1]. Although a wide range of monocationic alkyne complexes of molybdenum(II) and tungsten(II) have been reported [1–12], up to the time of the study described below very few dicationic alkyne complexes of this type had been described. Some recent examples described by Lippard and co-workers are $[Mo(CN^tBu)_5(\eta^2\text{-}^tBuHNC{\equiv}CNH^tBu)][BPh_4]_2$ [13] and $[Mo(CNR)_3(2,2'\text{-bipy})(\eta^2\text{-}RHNC{\equiv}CNHR)][PF_6]_2$ (R = Me or Et) [14].

In 1988 we reported the synthesis and structures of the coordinatively unsaturated bis(alkyne) complexes of tungsten(II), namely $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) [15]. These complexes have been shown to react with phosphorus donor ligands to give complexes of the type $[WI_2(CO)\{L_2 \text{ or } (LL)\}(\eta^2\text{-}RC_2R)]$ (R = Me or Ph; L = monodentate phosphine or phosphite; LL = bidentate phosphines) [16,17]. The phosphine-containing mono(alkyne) complexes $[WI_2(CO)\{L_2 \text{ or } (LL)\}(\eta^2\text{-}RC_2R)]$ (L = monodentate phosphine; LL = bidentate phosphines) are readily converted into the cationic species $[WI(CO)(NCMe)\{L_2 \text{ or } (LL)\}(\eta^2\text{-}RC_2R)][BF_4]$ *via* treatment with a stoichiometric quantity of $Ag[BF_4]$ in NCMe [18,19]. We have investigated the reactivity of these cationic alkyne containing complexes towards a variety of neutral and anionic donor ligands [20–24]. In this paper we report the reactions of the complex $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ with neutral bidentate nitrogen donor ligands to give dicationic mono(but-2-yne) complexes.

2. Results and discussion

The complex $[WI(CO)(NCMe)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ [19] reacts with a stoichiometric amount of NN {NN = 2,2′-bipyridyl, 1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, RNCHCHNR (where R = Cy, ^{t}Bu or *p*-$MeOC_6H_4$)} to give the mixed ligand complexes $[W(CO)(NN)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]I$ {dppm = $Ph_2P(CH_2)PPh_2$} (**1–6**) in good

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TABLE 1. Physical and analytical data for the compounds [W(CO)(NN)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I and [W(CO)(2,2′-bipy)(dppm)(η^2-MeC$_2$Me)][BPh$_4$]$_2$

	Complexes	Colour	Yield (%)	Analytical data (found(calc.) (%))
1	[W(CO)(2,2′-bipy)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I	Green	68	C: 46.9 (47.1) H: 3.5 (3.6) N: 2.7 (2.7)
2	[W(CO)(1,10-phen)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I	Green	62	C: 48.3 (48.3) H: 3.7 (3.5) N: 2.5 (2.7)
3	[W(CO)(5,6-Me$_2$-1,10-phen)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I	Green	64	C: 48.9 (49.3) H: 3.7 (3.8) N: 2.2 (2.6)
4	[W(CO)(CyNCHCHNCy)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I	Brown/green	58	C: 48.1 (48.7) H: 4.4 (4.8) N: 2.3 (2.6)
5	[W(CO)(^{t}BuNCHCHN^{t}Bu)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I	Brown/green	59	C: 46.0 (46.5) H: 4.7 (4.7) N: 2.3 (2.7)
6	[W(CO)(*p*-MeOPhNCHCHNPhOMe-*p*)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I	Brown	64	C: 49.1 (49.1) H: 3.9 (3.9) N: 2.5 (2.5)
7	[W(CO)(2,2′-bipy)(dppm)(η^2-MeC$_2$Me)][BPh$_4$]$_2$	Green	78	C: 72.5 (73.1) H: 5.3 (5.3) N: 1.7 (1.9)

yield. The complexes **1–6** have all been characterised by elemental analysis (C, H and N) (Table 1). IR, and ^{1}H, and in selected cases, ^{13}C NMR spectroscopy (Tables 2–4). The complexes **1–6** are all stable for prolonged periods when stored under nitrogen in the dark; however, they do slowly decompose when exposed to air in solution.

Complexes **1–6** are all soluble in chlorinated solvents and acetone, but, as expected, they are totally insoluble in hydrocarbon solvents and diethyl ether. Treatment of **1** with two equivalents of Na[BPh$_4$] in acetonitrile at room temperature resulted in exchange of the [BF$_4$]$^-$ and I$^-$ counterions to give the bis(tetraphenylborate) complex [W(CO)(2,2′-bipy)(dppm)(η^2-MeC$_2$Me)][BPh$_4$]$_2$ (**7**) in good yield. The preparation of complex **7** confirms the dicationic nature of **1–6**, and complex **7** was fully characterised by elemental analysis (C, H and N), IR, ^{1}H and ^{13}C NMR spectroscopy (Tables 1–4).

The IR spectra for complexes **1–6** all show a strong single carbonyl band at around 1940 cm^{-1}, and a broad strong band at 1020 cm^{-1} due to the tetrafluoroborate ligand (Table 1). The colour and carbonyl stretching

TABLE 2. Infrared data [a] for the complexes [W(CO)(NN)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I and [W(CO)(2,2′-bipy)(dppm)(η^2-MeC$_2$Me)][BPh$_4$]$_2$

Complex	ν(C≡O) (cm^{-1})	ν(BF) (cm^{-1})
1	1942 (s)	1016 (brs)
2	1940 (s)	1015 (brs)
3	1938 (s)	1016 (brs)
4	1940 (s)	1020 (brs)
5	1940 (s)	1020 (brs)
6	1943 (s)	1020 (brs)
7	1942 (s)	

[a] Spectra were recorded as thin films in CHCl$_3$ between NaCl plates; brs = broad strong, s = strong.

TABLE 3. ^{1}H NMR data [a] for the compounds [W(CO)(NN)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I and [W(CO)(2,2′-bipy)(dppm)(η^2-MEC$_2$-Me)][BPh$_4$]$_2$

Complex	^{1}H (δ) ppm
1	9.05 → 6.95 (brm, 28H, Ph-*H* and 2,2′-bipy-*H*); 4.38 (brm, 2H, PCH_2P); 2.5 (s, 6H, ≡C*Me*)
2	9.32 → 6.95 (brm, 28H, Ph-*H* and 1,10-phen); 4.52 (brm, 2H, PCH_2P); 2.65 (s, 6H, ≡C*Me*)
3	9.49 → 6.95 (brm, 26H, Ph-*H* and 1,10-phen-*H*); 4.28 (brm, 2H, PCH_2P); 2.84 (s, 3H, CH_3); 2.74 (s, 3H, CH_3); 2.53 (s, 6H, ≡C*Me*)
4	8.72 (s, 2H, C*H*=C*H*); 7.75 → 6.95 (brm, 20H, Ph-*H*); 4.62 (brm, 2H, PCH_2P); 3.15 (s, 6H, ≡C*Me*); 1.65 → 1.15 (brm, 22H, Cy-*H*)
5	9.05 (s, 2H, C*H*=C*H*); 7.85 → 6.95 (brm, 20H, Ph-*H*); 4.75 (brm, 2H, PCH_2P); 2.95 (s, 6H, ≡C*Me*); 2.2 (brs, 18H, CH_3)
6	8.85 (s, 2H, C*H*=C*H*); 7.95 → 6.85 (brm, 28H, Ph-*H*); 4.72 (brm, 2H, PCH_2P); 3.75 (brs, 6H, O*Me*); 2.95 (s, 6H, ≡C*Me*)
7	9.05 → 6.85 (brm, 68H, Ph-*H*, BPh$_4$-*H* and 2,2′-bipy-*H*); 4.38 (brm, 2H, PCH_2P); 2.48 (s, 6H, ≡C*Me*)

[a] Spectra recorded in CDCl$_3$ (+25°C) referenced to SiMe$_4$; br = broad, m = multiplet, s = singlet.

TABLE 4. ^{13}C NMR data [a] for the complexes [W(CO)(NN)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I and [W(CO)(2,2′-bipy)(dppm)(η^2-MeC$_2$-Me)][BPh$_4$]$_2$

Complex	^{13}C (δ) ppm
1	220.32 (bs, $C{\equiv}C$); 217.95 (s, $C{\equiv}O$); 154.69 → 125.9 (brm, Ph–C and 2,2′-bipy-C); 30.29 (t, PCH$_2$P, J(P–C) = 13.82 Hz); 22.35 (s, ≡CMe)
3	218.9 (s, $C{\equiv}C$); 207.6 (s, $C{\equiv}$O); 156.96 → 125.68 (brm, Ph–C and 1,10-phen-C); 28.3 (t, PCH$_2$P, J(P–C) = 14.2 Hz); 23.9 (s, CH$_3$); 22.94 (s, CH$_3$); 19.86 (s, ≡Me)
4	221.7 (s, $C{\equiv}C$); 143.45 (N=C); 133.42 → 128.32 (brm, Ph–C); 33.81 → 24.3 (brm, PCH$_2$P, Cy–CH$_2$); 22.03 (s, ≡CMe)
7	220.30 (brs, $C{\equiv}C$); 217.95 (s, $C{\equiv}$O); 165.38, 164.60, 163,81, 163.04 (q, B–C, J(B–C) = 49.5 Hz); 136.21, 125.68 121.78 (3s, BPh$_4$–C); 154.69 → 125.9 (brm, Ph–C and 2,2′-bipy-C); 30.29 (t, PCH$_2$P, J(P–C) = 13.81 Hz); 22.35 (s, ≡CMe)

[a] Spectra recorded in CDCl$_3$ (+25°C) referenced to SiMe$_4$; br = broad, m = multiplet, q = quartet, s = singlet, t = triplet.

bands of **1** and **7** are as expected, identical. The carbonyl resonances for **1–7** are all shifted compared to the starting material [WI(CO)(NCMe)(dppm)(η^2-MeC$_2$Me)][BF$_4$] which has ν(CO) = 1960 cm^{-1} (in CHCl$_3$) [19].

The most likely coordination geometry about the tungsten centre is shown in Fig. 1; in this the carbonyl and but-2-yne ligands are *cis* to each other, as was observed in the structures of related complexes [1,16,17,19,20]. The geometries of the monocationic complexes [WI(CO)L(dppm)(η^2-MeC$_2$Me)]X {L = P(O^{i}Pr)$_3$ (X = BF$_4^-$) [19] and SC(NH$_2$)$_2$ (X = ClO$_4^-$) [20]} have been crystallographically determined, and have the structure shown in Fig. 1, in which the iodide and L are replaced by the bidentate NN donor ligand. Many attempts to grow suitable single crystals for X-ray crystallography of **1–7** were unsuccessful.

The ^{1}H NMR spectra of all the complexes **1–7** all show the expected features for the structure shown in Fig. 1. They also all show a single but-2-yne methyl resonance in their ^{1}H NMR spectra at room temperature which indicates the but-2-yne ligand is undergoing rapid propeller-like rotation at room temperature which is in accord with other workers' results for mono(but-2-yne) complexes of molybdenum(II) and tungsten(II) [1,7,25,26]. Similarly ^{13}C NMR spectra also have the expected features for the geometry shown in Fig. 1. The ^{13}C NMR spectrum of **7** clearly confirms the incorporation of [BPh$_4$]$^-$ counteranions, which shows the characteristic BC quartet at 164.2 (J(BC) = 49.5 Hz) ppm. Templeton and Ward [27] have correlated the number of electrons donated by the alkyne and the ^{13}C NMR chemical shift. The values observed for complexes **1**, **3**, **4** and **7** at 220.32, 218.90, 221.70 and 220.30 ppm, respectively, are in accord with the but-2-yne ligand utilising both of its filled pπ-orbitals and donating four-electrons to the tungsten in these complexes. If the but-2-yne donates four-electrons to the tungsten in **1–7** then they obey the effective atomic number rule.

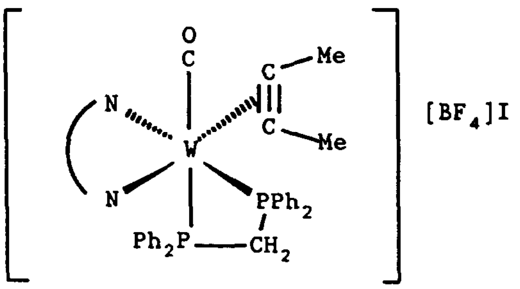

Fig. 1. Proposed structure for the dicationic mono(but-2-yne) complexes [W(CO)(NN)(dppm)(η^2-MeC$_2$Me)][BF$_4$]I (**1–6**).

3. Experimental details

The synthesis and purification of the new compounds were carried out under dry nitrogen by use of standard Schlenk line techniques. The compounds [WI(CO)(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] [19] and N,N'-cyclohexyldiazabutadiene, N,N'-^{t}butyldiazabutadiene and N,N'-p-methoxyphenyldiazabutadiene [28] were prepared by the published methods. All other chemicals were obtained commercially and used without further purification, except for solvents, which were dried and distilled before use.

Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental Analyser MOD 1106 (using helium as the carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1430 ratio recording infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer, with tetramethylsilane as the internal standard.

3.1. [W(CO)(2,2′-bipy){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$]I (1)

Bipy (0.0862 g, 0.552 mmol) was added to a stirred solution of [WI(CO)(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$] (0.5 g, 0.552 mmol) in CH$_2$Cl$_2$ (15 cm^3) under a stream of dry nitrogen. After 6 days stirring the solution was filtered and the volume reduced to 2 cm^3 *in vacuo*. Dropwise addition of diethyl ether precipitated the green dicationic complex [W(CO)(2,2′-bipy){Ph$_2$P(CH$_2$)PPh$_2$}(η^2-MeC$_2$Me)][BF$_4$]I (**1**), which on recrystallisation from CH$_2$Cl$_2$/Et$_2$O yielded analytically pure **1** (0.38 g, 68%).

Similar reactions of [WI(CO)(NCMe){$Ph_2P(CH_2)PPh_2$}(η^2-MeC_2Me)][BF_4] with an equimolar quantity of NN (NN = 1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, *N,N'*-cyclohexyldiazabutadiene, *N,N'*-^{t}butyldiazabutadiene or *N,N'-p*-methoxyphenyldiazabutadiene) in CH_2Cl_2 at room temperature afforded the analogous complexes [W(CO)(NN){$Ph_2P(CH_2)PPh_2$}(η^2-MeC_2Me)][BF_4]I (**2**–**6**) (see Table 1 for physical and analytical data).

3.2. *[W(CO)(2,2'-bipy){$Ph_2P(CH_2)PPh_2$}(η^2-MeC_2Me)][BPh_4]$_2$ (7)*

Na[BPh_4] (0.1677 g, 0.49 mmol) was added to a solution of [W(CO)(2,2'-bipy){$Ph_2P(CH_2)PPh_2$}(η^2-MeC_2Me)][BF_4]I (0.25 g, 0.245 mmol) in NCMe (20 cm^3) with stirring under a stream of dry nitrogen. After 17 h stirring the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and the solution filtered to remove NaI and Na[BF_4] and reduced to a volume of 2 cm^3 *in vacuo*. Dropwise addition of diethyl ether precipitated the green dicationic complex [W(CO)(2,2'-bipy){$Ph_2P(CH_2)PPh_2$}(η^2-MeC_2Me)][BPh_4]$_2$ (**7**), which on recrystallisation from CH_2Cl_2/Et_2O afforded analytically pure **7** (0.26 g, 72%) (see Table 1 for physical and analytical data).

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