

Novel cationic monobut-2-yne complexes of tungsten(II) containing dithiocarbamates and related ligands

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Abstract

Equimolar quantities of $[\text{W}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ ($\text{dppm} = \text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$) and MS_2CX ($\text{M} = \text{Na}$, $\text{X} = \text{NMe}_2$; $\text{M} = \text{Na}$, $\text{X} = \text{NEt}_2$; $\text{M} = [\text{NH}_4]$, $\text{X} = \text{NC}_4\text{H}_8$; $\text{M} = \text{Na}$, $\text{X} = \text{N}(\text{CH}_2\text{Ph})_2$; or $\text{M} = \text{K}$, $\text{X} = \text{OEt}$) react in CH_2Cl_2 at room temperature to eventually give the cationic monobut-2-yne complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$. The complex $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ can also be prepared by reacting equimolar quantities of $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$ with $[\text{NH}_4][\text{S}_2\text{CNC}_4\text{H}_8]$ in refluxing chloroform. Both these types of reaction involve the formation of the monodentate dithiocarbamate intermediates $[\text{WI}(\eta^1\text{-S}_2\text{CX})(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$. Reaction of $[\text{WI}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ and MS_2CX in a 2 : 1 molar ratio afforded a mixture of the cationic monobut-2-yne complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ and $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$. Variable temperature ^1H NMR studies carried out on $[\text{W}(\text{CO})(\text{S}_2\text{CNEt}_2)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ showed the complex to be fluxional. The barrier to but-2-yne rotation was calculated to be $49.7 \pm 1 \text{ kJ mol}^{-1}$. ^{13}C NMR studies show the but-2-yne ligand in $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ is donating four electrons to the tungsten in these compounds.

Introduction

Coordinatively unsaturated alkyne complexes of molybdenum(II) and tungsten(II) have been much studied over the past two decades [1]. In particular, the cationic alkyne complexes $[\text{Mo}(\text{CO})(\eta^2\text{-RC}_2\text{R}')_2(\eta^5\text{-C}_5\text{H}_5 \text{ or } \text{C}_9\text{H}_7)][\text{BF}_4]$ and their derivatives have generated an interesting range of new chemistry [2–10]. Although a wide range of neutral alkyne complexes of molybdenum(II) and tungsten(II) containing dithiocarbamates and related ligands have been described [11–16] very few cationic complexes of this type have been reported. One example is the cationic alkyne complex $[\text{W}(\text{CO})(\text{S}_2\text{CNEt}_2)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\eta^2\text{-MeOC}_2\text{CH}_2\text{Ph})][\text{BF}_4]$, which is

prepared by reacting the neutral ketyenyl product $[\text{W}(\text{CO})(\text{S}_2\text{CNEt}_2)\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\text{OCCH}_2\text{Ph})]$ with $[\text{Me}_3\text{O}][\text{BF}_4]$ [17].

We have recently described the synthesis of the cationic alkyne complexes $[\text{W}(\text{CO})(\text{NCMe})\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ ($n = 1-6$; $\text{R} = \text{Me}$ or Ph) [18]. These compounds are prepared by reacting the diiodide complexes $[\text{WI}_2(\text{CO})(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\eta^2\text{-RC}_2\text{R})]$ with an equimolar quantity of $\text{Ag}[\text{BF}_4]$ in acetonitrile. In this paper we describe the reactions of the cationic bis(diphenylphosphino)methane monobut-2-yne complex $[\text{W}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ with dithiocarbamates and related ligands.

Results and discussion

Reaction of the compound $[\text{W}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ with an equimolar quantity of $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$, $\text{NaS}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$, $[\text{NH}_4][\text{S}_2\text{CNC}_4\text{H}_8]$, $\text{NaS}_2\text{CN}(\text{CH}_2\text{Ph})_2$ and KS_2COEt eventually afforded the cationic complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ ($\text{X} = \text{NMe}_2$, NEt_2 , NC_4H_8 , $\text{N}(\text{CH}_2\text{Ph})_2$ and OEt) (1-5) in good yield. 1-5 were fully characterised by elemental analysis (C, H and N) (Table 1), IR (Table 1), ^1H and ^{13}C , NMR spectroscopy (Tables 2 and 3). The complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ are stable in the solid state when stored under nitrogen, however, they decompose when exposed to air in

Table 1

Physical, analytical and infrared^a data for the compounds $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$, $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ and $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$

Complex	Colour	Yield (%)	Analysis (Found (calcd.) (%))			$\nu(\text{CO}) (\text{cm}^{-1})^a$
			C	H	N	
$[\text{W}(\text{CO})(\text{S}_2\text{CNMe}_2)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ (1)	Red	42	44.3 (44.3)	3.9 (3.8)	1.3 (1.6)	1938 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{CNEt}_2)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ (2)	Red	44	45.4 (45.4)	4.4 (4.1)	1.4 (1.5)	1935 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ (3)	Red	43	45.8 (45.5)	4.1 (3.9)	1.4 (1.5)	1938 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ (4)	Red	41	52.8 (52.4)	4.3 (4.2)	1.3 (1.4)	1936 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{COEt})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]\text{I}$ (5)	Red	45	44.0 (44.1)	3.9 (3.7)	-	1940 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (6)	Red	95	63.4 (63.5)	5.0 (5.1)	1.2 (1.3)	1938 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{CNMe}_2)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (7)	Red	28	46.0 (46.2)	4.2 (4.2)	1.4 (1.6)	1938 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{CNEt}_2)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (8)	Red	27	46.9 (47.5)	4.4 (4.3)	1.2 (1.6)	1935 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (9)	Red	29	47.1 (47.6)	3.8 (4.1)	1.2 (1.6)	1938 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (10)	Red	22	52.9 (53.1)	3.8 (4.2)	1.2 (1.4)	1936 (s)
$[\text{W}(\text{CO})(\text{S}_2\text{COEt})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (11)	Red	26	46.5 (46.2)	3.9 (3.9)	-	1940 (s)

^a Spectra recorded in CHCl_3 as thin films between NaCl plates; s, strong.

Table 2

¹H NMR^a data for the complexes [W(CO)(S₂CX)(dppm)(η²-MeC₂Me)]I, [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)][BPh₄] and [W(CO)(S₂CX)(dppm)(η²-MeC₂Me)][BF₄]

Complex	¹ H NMR (δ) ppm
1	7.95–6.95 (bm, 20H, Ph–H); 4.6 (bm, 2H, PCH ₂ P); 3.05 (s, 3H, NMe); 2.95 (s, 6H, ≡CMe); 2.84 (s, 3H, NMe).
2	7.92–7.0 (bm, 20H, Ph–H); 4.58 (bm, 2H, PCH ₂ P); 3.46 (bm, 4H, NCH ₂); 2.91 (s, 6H, ≡CMe); 1.23 (bm, 6H, CH ₃).
3	7.9–6.95 (bm, 30H, Ph–H); 4.6 (bm, 2H, PCH ₂ P); 3.28 (bm, 4H, NCH ₂); 2.86 (s, 6H, ≡CMe); 1.95 (bm, 4H, CH ₂).
4	7.9–6.95 (bm, 30H, Ph–H); 4.38 (bm, 2H, PCH ₂ P); 4.04 (s, 4H, NCH ₂); 2.95 (s, 6H, ≡CMe).
5	7.92–6.95 (bm, 20H, Ph–H); 4.49 (bm, 2H, PCH ₂ P); 3.52 (q, 2H, OCH ₂ , J(H–H) = 7.2 Hz); 2.92 (s, 6H, ≡CMe); 1.28 (t, 3H, CH ₃ , J(H–H) = 7.2 Hz).
6	8.07–6.65 (bm, 40H, Ph–H); 4.62 (bm, 2H, PCH ₂ P); 3.33 (bm, 4H, NCH ₂); 2.86 (s, ≡CMe); 1.95 (bm, 4H, CH ₂).
7	7.95–6.95 (bm, 20H, Ph–H); 4.6 (bm, 2H, PCH ₂ P); 3.05 (s, 3H, NMe); 2.95 (s, 6H, ≡CMe); 2.84 (s, 3H, NMe).
8	7.92–7.0 (bm, 20H, Ph–H); 4.58 (bm, 2H, PCH ₂ P); 3.46 (bm, 4H, NCH ₂); 2.91 (s, 6H, ≡CMe); 1.23 (bm, 6H, CH ₃).
9	7.9–6.95 (bm, 20H, Ph–H); 4.62 (bm, 2H, PCH ₂ P); 2.88 (s, 6H, ≡CMe); 1.95 (bm, 4H, CH ₂).
10	8.0–6.89 (bm, 30H, Ph–H); 4.41 (bm, 2H, PCH ₂ P); 4.03 (s, 4H, NCH ₂); 2.95 (s, 6H, ≡CMe).
11	7.9–6.95 (bm, 20H, Ph–H); 4.6 (bm, 2H, PCH ₂ P); 3.52 (q, 2H, OCH ₂ , J(H–H) = 7.2 Hz); 2.92 (s, 6H, ≡CMe); 1.28 (t, 3H, Me, J(H–H) = 7.2 Hz).

^a Spectra recorded in CDCl₃ (+25 °C) referenced to SiMe₄; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bm, broad multiplet.

solution. **1–5** are soluble in CHCl₃ and CH₂Cl₂, but as expected are insoluble in hydrocarbon solvents and diethyl ether.

Complexes **1–5** show no ν(BF) (ν(BF) = 1020 brs) [19] in their infrared spectra, and this together with elemental analysis confirms the compounds **1–5** have an iodide as the counter ion. The infrared spectra of **1–5** also show a single carbonyl band at ~1935 cm⁻¹. The X-ray crystal structure of the *N*-pyrrolidene dithiocarbamate tetrafluoroborate complex [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)][BF₄] was determined by Harman and Hursthouse [20], and has the geometry shown in Fig. 1. The tetrafluoroborate complex [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂-Me)][BF₄] was prepared by reacting the bis (but-2-yne) complex [W(CO)-(NCMe)(S₂CNC₄H₈)(η²-MeC₂Me)₂][BF₄] with an equimolar quantity of dppm in CH₂Cl₂ at room temperature [20]. The physical and spectroscopic properties of the cationic complex [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)]I (**3**) are identical to those of [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)][BF₄] except for spectroscopic differences due to the counter anions. Hence it is very likely that the structures of **1–5** are the same as [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)][BF₄] [20], which is shown in Fig. 1.

The ¹H NMR spectra of **1–5** showed the expected resonances for the structure shown in Fig. 1. Variable temperature ¹H NMR studies were carried out on the

Table 3

¹³C NMR data ^a for the complexes [W(CO)(S₂CX)(dppm)(η²-MeC₂Me)]⁺, [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)][BPh₄]⁻ and [W(CO)(S₂CX)(dppm)(η²-MeC₂Me)][BF₄]⁻

Complex	¹³ C NMR (δ) ppm
2	223.31 (s, C≡C); 207.48 (s, C≡O); 194.46 (s, CS ₂); 133.22–128.6 (m, Ph–C); 46.98 (s, NCH ₂); 45.06 (s, NCH ₂); 32.0 (t, PCH ₂ P, <i>J</i> (P–C) = 25 Hz); 19.58 (s, ≡CMe); 12.6 (s, CH ₃); 11.91 (s, CH ₃).
3	223.8 (s, C≡C); 206.7 (s, C≡O); 202.5 (s, CS ₂); 133.15–126.49 (m, Ph–C); 50.96 (s, NCH ₂); 49.8 (s, NCH ₂); 30.43 (t, PCH ₂ P, <i>J</i> (P–C) = 26.1 Hz); 24.89 (s, CH ₂); 24.72 (s, CH ₂); 19.6 (s, ≡CMe).
6	223.72 (s, C≡C); 206.5 (s, C≡O); 202.3 (s, CS ₂); 165.42, 164.94, 164.16, 163.38 (q, B–C, <i>J</i> (B–C) = 49.5 Hz); 136.2, 125.8, 121.9 (3s, BPh ₄ –C); 136.1–125.9 (m, Ph–C); 50.96 (s, NCH ₂); 49.9 (s, NCH ₂); 30.43 (t, PCH ₂ P, <i>J</i> (P–C) = 26.1 Hz); 24.8 (s, CH ₂); 24.4 (s, CH ₂); 19.61 (s, ≡CMe).
7	222.09 (s, C≡C); 207.58 (s, C≡O); 196.42 (s, CS ₂); 133.09–126.89 (m, Ph–C); 40.72 (s, NCH ₃); 30.17 (s, NCH ₃); 30.83 (t, PCH ₂ P, <i>J</i> (P–C) = 30.1 Hz); 19.6 (s, ≡CMe).
8	223.31 (s, C≡C); 207.48 (s, C≡O); 197.5 (s, CS ₂); 133.22–128.6 (m, Ph–C); 46.47 (s, NCH ₂); 45.07 (s, NCH ₂); 32.0 (t, PCH ₂ P, <i>J</i> (P–C) = 25 Hz); 19.57 (s, ≡CMe); 12.61 (s, CH ₃); 11.91 (s, CH ₃).
9	223.8 (s, C≡C); 206.6 (s, C≡O); 203.0 (s, CS ₂); 133.15–126.49 (m, Ph–C); 50.95 (s, NCH ₂); 49.8 (s, NCH ₂); 30.43 (t, PCH ₂ P, <i>J</i> (P–C) = 26.1 Hz); 24.87 (s, CH ₂); 24.72 (s, CH ₂); 19.60 (s, ≡CMe).
10	224.24 (s, C≡C); 210.8 (s, C≡O); 198.2 (s, CS ₂); 134.64–128.09 (m, Ph–C); 52.7 (s, NCH ₂); 51.36 (s, NCH ₂); 31.06 (t, PCH ₂ P, <i>J</i> (P–C) = 28.4 Hz); 21.09 (s, ≡CMe).

^a Spectra recorded in CDCl₃ (+25 °C) referenced to Me₄Si; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

diethyldithiocarbamate complex [W(CO)(S₂CNEt₂)(dppm)(η²-MeC₂Me)][BF₄]⁻ (2), since at room temperature a single resonance was observed for the but-2-yne methyl groups, which would not be expected for the static structure shown in Fig. 1. On

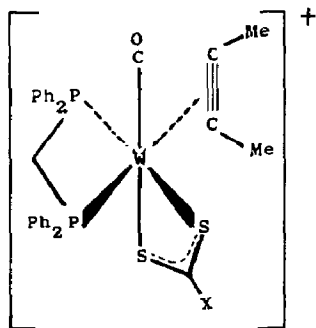
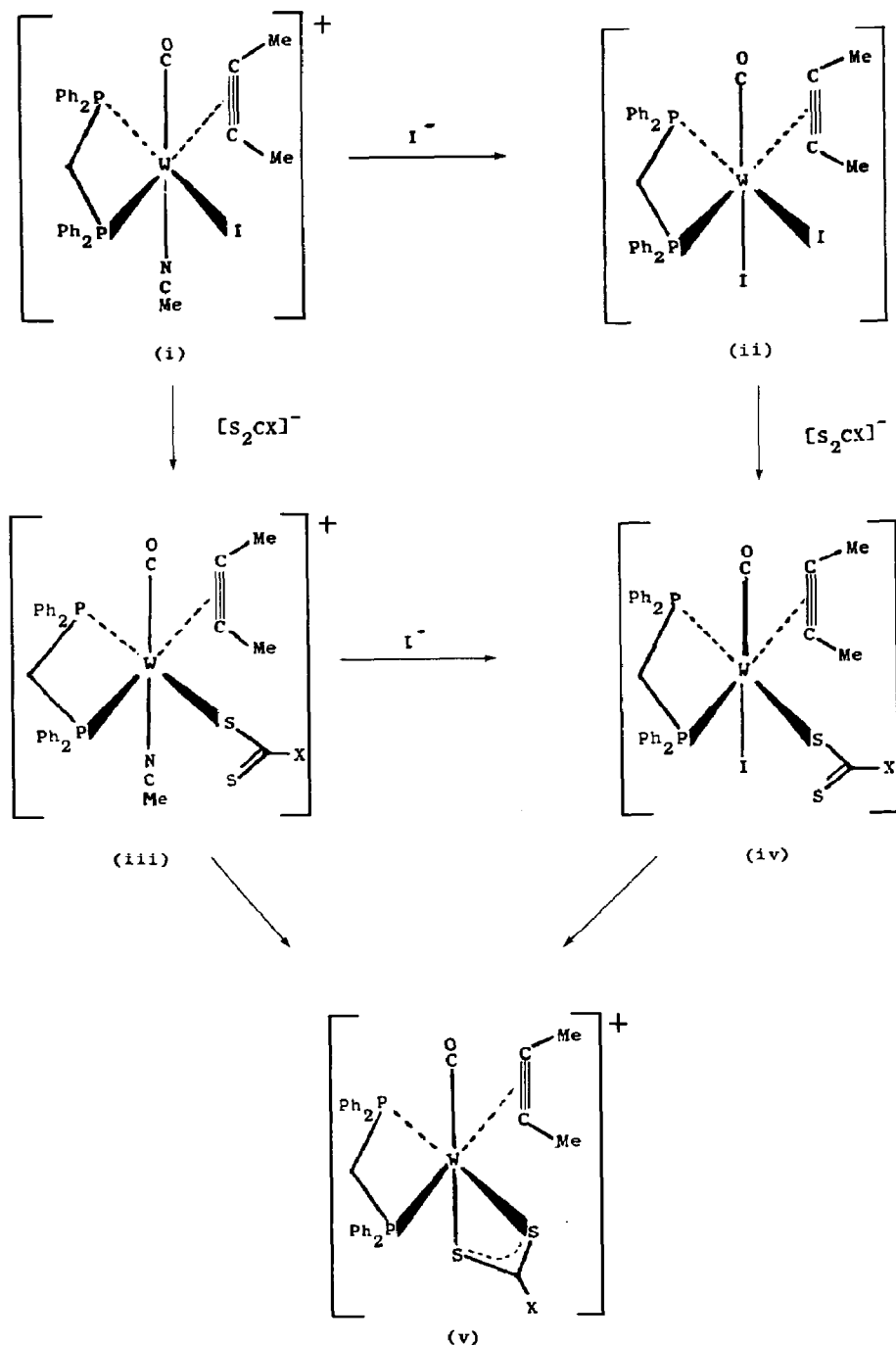


Fig. 1. Proposed structure for the cationic complexes [W(CO)(S₂CX)(dppm)(η²-MeC₂Me)]⁺.

cooling to 254 K the but-2-yne resonance broadened, until, on further cooling gave a doublet for the two different but-2-yne methyl groups, with the splitting $\Delta\nu = 155$ Hz. Using the equation, $\Delta G_{T_c}^\ddagger = -RT_c \ln(\pi\Delta\nu h/\sqrt{2} K_B T_c)$ [21,22], the barrier to but-2-yne rotation of **2** was calculated to be 49.7 ± 1 kJ mol⁻¹. This agrees closely with the barrier to but-2-yne rotation of the tetrafluoroborate complex [W(CO)-(S₂CNC₄H₈)(dppm)(η^2 -MeC₂Me)][BF₄] which was calculated to be 49.9 kJ mol⁻¹ [20]. As expected these values are the same within the experimental error of the measurements, since the electronic and steric effects of the two dithiocarbamate ligands are very similar. It should be noted that the dimethyldithiocarbamate complex [W(CO)(S₂CNMe₂)(dppm)(η^2 -MeC₂Me)]I (**1**) shows a single resonance for the but-2-yne methyl groups down to 218 K. The ¹³C NMR spectra of **1–5** also show the expected features for the structure shown in Fig. 1. Templeton and Ward [23] have suggested how the alkyne contact carbon resonances can indicate how many electrons are being donated by an alkyne to a transition-metal. In complexes **1–5** the but-2-yne contact carbon chemical shifts occur above 200 ppm which suggests that the but-2-yne is utilizing both of its filled *p* π -orbitals and donating 4-electrons to the metal. This is supported by the fact that the complexes [W(CO)(S₂CX)(dppm)(η^2 -MeC₂Me)]I (**1–5**) obey the effective atomic number rule if the but-2-yne is donating four-electrons to the metal.

As stated earlier it was surprising that **1–5** have an iodide as the counter anion rather than tetrafluoroborate. The crude reaction products formed from reaction of [WI(CO)(NCMe)(dppm)(η^2 -MeC₂Me)][BF₄] with an equimolar amount of [NH₄][S₂CNC₄H₈] gave an infrared spectrum which showed carbonyl bands at 1938 cm⁻¹ (strongest band) due to [W(CO)(S₂CNC₄H₈)(dppm)(η^2 -MeC₂Me)]I (**3**), a medium shoulder at 1940 and a weak band at 1905 cm⁻¹. The band at 1940 cm⁻¹ can be ascribed to the previously reported neutral green diiodide compound [WI₂(CO)(dppm)(η^2 -MeC₂Me)] [24] and the band at 1905 cm⁻¹ is likely to be due to the monodentate coordinated dithiocarbamate compound [WI(η^1 -S₂CNC₄H₈)(CO)(dppm)(η^2 -MeC₂Me)]. The proposed mechanism for the reaction of equimolar quantities of [WI(CO)(NCMe)(dppm)(η^2 -MeC₂Me)][BF₄] and [NH₄][S₂CNC₄H₈] is given in Scheme 1. The initial step in the mechanism is likely to be displacement of iodide by the anionic dithiocarbamate ligand to give the monodentate dithiocarbamate intermediate (iii), which liberates sodium iodide, which can give either [WI₂(CO)(dppm)(η^2 -MeC₂Me)] (ν (CO) = 1940 cm⁻¹) (ii) or the monodentate coordinated dithiocarbamate compound [WI(η^1 -S₂CNC₄H₈)(CO)(dppm)(η^2 -MeC₂Me)] (iv) by attack of iodide on [WI(CO)(NCMe)(dppm)(η^2 -MeC₂Me)]-[BF₄] (i) or [W(η^1 -S₂CNC₄H₈)(CO)(NCMe)(dppm)(η^2 -MeC₂Me)]⁺ (iii). The monodentate coordinated dithiocarbamate intermediates [W(η^1 -S₂CNC₄H₈)(CO)(NCMe)(dppm)(η^2 -MeC₂Me)]⁺ (iii) and [WI(η^1 -S₂CNC₄H₈)(CO)(dppm)(η^2 -MeC₂Me)] (iv) can give the finally isolated product [W(CO)(S₂CNC₄H₈)(dppm)(η^2 -MeC₂Me)]I (Scheme 1 (v) by displacement of either acetonitrile or iodide from (iii) or (iv), respectively).

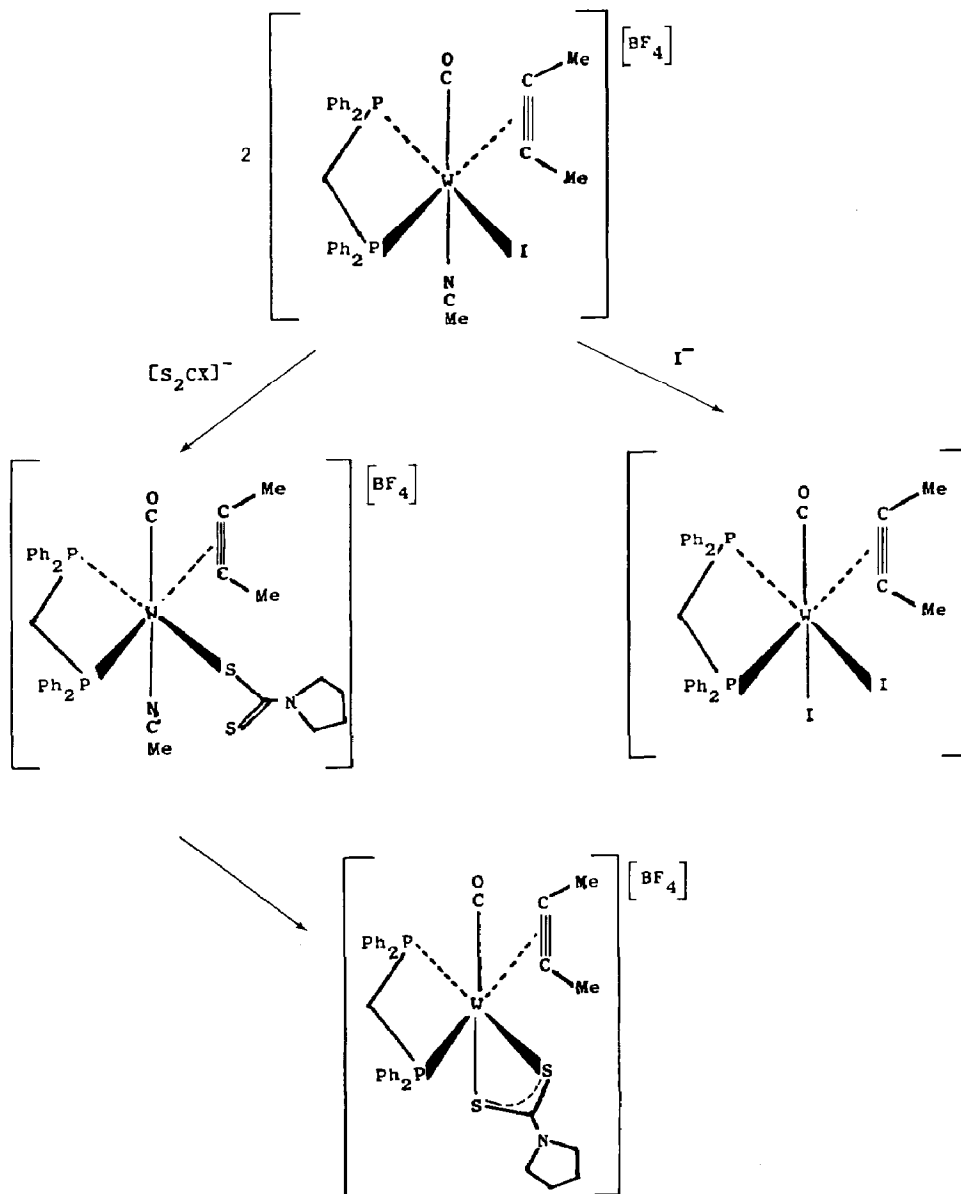
Evidence to support this mechanism comes from reaction of [WI₂(CO)(dppm)(η^2 -MeC₂Me)] with one equivalent of [NH₄][S₂CNC₄H₈] in chloroform at room temperature after 1 h the infrared spectrum showed carbonyl bands at 1940 (m, sh), 1938 (s) and 1905 (w) cm⁻¹ which can be assigned to unreacted starting material [WI₂(CO)(dppm)(η^2 -MeC₂Me)] [24], [W(CO)(S₂CNC₄H₈)(dppm)(η^2 -MeC₂Me)]I (**3**) and [WI(η^1 -S₂CNC₄H₈)(CO)(dppm)(η^2 -MeC₂Me)] respectively. It should be noted



Scheme 1. The proposed reaction pathway for reacting equimolar quantities of $[WI(CO)(NCMe)(dppm)(\eta^2-MeC_2Me)][BF_4]$ and $[S_2CX]^-$ in CH_2Cl_2 at room temperature.

that reaction of $[WI(CO)(NCMe)(dppm)(\eta^2-MeC_2Me)][BF_4]$ with an equimolar quantity of PhS^- to give $[WI(SPh)(CO)(dppm)(\eta^2-MeC_2Me)]$, which is a red/brown solid and has $\nu(CO) = 1897\text{ cm}^{-1}$ [25], ie similar to the proposed $[WI(\eta^1-$

$S_2CNC_4H_8)(CO)(dppm)(\eta^2-MeC_2Me)]$ ($\nu(CO) = 1905\text{ cm}^{-1}$). The reaction of $[WI_2(CO)(dppm)(\eta^2-MeC_2Me)]$ with an equimolar amount of $[NH_4][S_2CNC_4H_8]$ in refluxing chloroform after 24 h gave a deep red solution, which following purification gave the cationic complex $[W(CO)(S_2CNC_4H_8)(dppm)(\eta^2-MeC_2Me)]I$ (3). The complex prepared by this method was fully characterised by elemental analysis, infrared, 1H and ^{13}C NMR spectroscopy (see Experimental section). Hence, the reaction of $[WI_2(CO)(dppm)(\eta^2-MeC_2Me)]$ with one equivalent of $[NH_4][S_2CNC_4H_8]$ in $CHCl_3$ very likely proceeds via the pathway shown in Scheme 1 (ii) \rightarrow (iv) \rightarrow (v). Unsuccessful attempts were made to exchange I^- for BF_4^- , by reacting



Scheme 2. Reaction of $[WI(CO)(NCMe)(dppm)(\eta^2-MeC_2Me)][BF_4]$ and $[S_2CX]^-$ in a 2:1 molar ratio.

$[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})\text{I}]$ with $\text{Na}[\text{BF}_4]$ in methanol, however, reaction of $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})\text{I}]$ with $\text{Na}[\text{BPh}_4]$ in NCMe gave the anion exchanged product $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (6), which was fully characterised by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy (see Tables 1–3).

Further evidence to support the mechanism given in Scheme 1 was obtained by reacting the cationic complex $[\text{WI}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ with $\text{NaS}_2\text{CNMe}_2 \cdot 2\text{H}_2\text{O}$, $\text{NaS}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$, $[\text{NH}_4][\text{S}_2\text{CNC}_4\text{H}_8]$, $\text{NaS}_2\text{CN}(\text{CH}_2\text{Ph})_2$ and KS_2COEt in CH_2Cl_2 at room temperature in a 2 : 1 molar ratio. The reactions of two equivalents of $[\text{WI}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ with one equivalent of $[\text{S}_2\text{CX}]^-$ in CH_2Cl_2 at room temperature after 24 h gave a red/brown solution. Column chromatography separated two products from each of the five reactions which were in roughly equal proportions. The first material eluted from the columns was the neutral green diiodide complex $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$, which was previously prepared by reacting the bisalkyne complex $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2]$ with an equimolar quantity of dppm [24]. The $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$ complexes which were isolated from the reaction of $[\text{WI}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ with $[\text{S}_2\text{CX}]^-$ in a 2 : 1 molar ratio were fully characterised (see experimental) and had identical properties to the previously reported complex $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$ [24]. The second products obtained from the columns were the cationic complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (7–11). These complexes were confirmed as the tetrafluoroborate salts by elemental analysis (Table 1) and infrared spectroscopy (Table 2), where a strong band for $\nu(\text{BF})$ around 1016 cm^{-1} was observed [19]. The ^1H and ^{13}C NMR spectra for 7–11 were, as expected, the same as those obtained for 1–5. This evidence suggests that after initial attack by the dithiocarbamate or xanthate on $[\text{WI}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ afforded $[\text{W}(\text{CO})(\text{NCMe})(\eta^1\text{-S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ and I^- . The liberated I^- can attack some unreacted $[\text{WI}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ to afford the observed complex $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$. This allows chelation of the dithiocarbamate by displacement of NCMe to give the observed products $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (7–11). No evidence was obtained when the reactions were followed by infrared spectroscopy for the formation of the neutral monodentate dithiocarbamate complexes $[\text{WI}(\text{CO})(\eta^1\text{-S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$. The proposed mechanism for the reaction of $[\text{WI}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ and $[\text{S}_2\text{CX}]^-$ in a 2 : 1 molar ratio is given in Scheme 2.

Experimental

All reactions described in this paper were carried out under an atmosphere of nitrogen using standard Schlenk line techniques. The compound $[\text{WI}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ was prepared by the literature method [18]. All chemicals were purchased from commercial sources. Elemental analyses for carbon, hydrogen and nitrogen were determined using a Carlo Erba Elemental analyser MOD 1106 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin Elmer 1430 ratio recording infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC250 CP/MAS NMR spectrometer (all spectra were calibrated relative to tetramethylsilane).

[W(CO)(S₂CNMe₂)(dppm)(η²-MeC₂Me)]I (1)

To [W(CO)(NCMe)(dppm)(η²-MeC₂Me)][BF₄] (0.5 g, 0.552 mmol) dissolved in CH₂Cl₂ (20 cm³) with continuous stirring under a stream of nitrogen was added Na[S₂CNMe₂] · 2H₂O (0.0989 g, 0.552 mmol). After stirring for 20 h the solution was filtered to remove Na[BF₄] and the solvent volume was reduced to 2 cm³ in vacuo. Dropwise addition of diethyl ether precipitated the red cationic complex [W(CO)(S₂CNMe₂)(dppm)(η²-MeC₂Me)]I (1), which on recrystallisation from CH₂Cl₂/Et₂O yielded 0.21 g, 42% of pure product.

Similar reactions of [W(CO)(NCMe)(dppm)(η²-MeC₂Me)][BF₄] with an equimolar quantity of Na[S₂CNEt₂] · 3H₂O, [NH₄][S₂CNC₄H₈], Na[S₂CN-(CH₂Ph)₂] and K[S₂COEt] in CH₂Cl₂ at room temperature gave the analogous cationic complexes [W(CO)(S₂CX)(dppm)(η²-MeC₂Me)]I (2–5) (see Table 1 for colour and yields).

Reaction of [W(CO)(dppm)(η²-MeC₂Me)] with [NH₄][S₂CNC₄H₈] in refluxing chloroform to give [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)]I.

To [W(CO)(dppm)(η²-MeC₂Me)] (1.00 g, 1.106 mmol), dissolved in CHCl₃ (30 cm³) with continuous stirring under a stream of nitrogen was added [NH₄][S₂CNC₄H₈] (0.1817 g, 1.106 mmol). The solution was heated to reflux for 24 hr, after which time the solution was cooled and filtered to remove [NH₄]⁺I⁻. The solvent volume was reduced to 2 cm³ and the red cationic complex [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)]I was precipitated by the dropwise addition of diethyl ether. The crude product was redissolved in CH₂Cl₂ (20 cm³), filtered and the solvent volume reduced to 2 cm³ in vacuo. Addition of diethyl ether and cooling yielded analytically pure red crystals of [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)]I, 0.76 g, 75%. Analysis. Found: C, 44.9; H, 3.8; N, 1.3. C₃₅H₃₆INOP₂S₂W calc: C, 45.5; H, 3.9; N, 1.5%. IR, ν(C≡O) 1938 cm⁻¹. ¹H NMR (CDCl₃, +25 °C): δ 7.9–6.95 (bm, 20H, Ph-H); 4.61 (bm, 2H, PCH₂P); 3.29 (bm, 4H, NCH₂); 2.87 (s, 6H, ≡CMe); 1.95 (bm, 4H, CH₂).

[W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)][BPh₄] (6)

To [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)]I (0.25 g, 0.271 mmol) dissolved in NCMe (15 cm³) with continuous stirring under a stream of nitrogen was added Na[BPh₄] (0.0926 g, 0.271 mmol). After stirring for 20 h the solvent was removed in vacuo. The crude product was dissolved in CH₂Cl₂ (20 cm³) and filtered to remove NaI. The solvent volume was reduced to 1 cm³ in vacuo, dropwise addition of diethyl ether precipitated the red cationic complex [W(CO)(S₂CNC₄H₈)(dppm)(η²-MeC₂Me)][BPh₄] (6), which after recrystallisation from CH₂Cl₂/Et₂O yielded 0.29 g, 95% of pure product. (See Tables 1–3 for physical and analytical data).

[W(CO)(S₂CNMe₂)(dppm)(η²-MeC₂Me)][BF₄] (7)

To [W(CO)(NCMe)(dppm)(η²-MeC₂Me)][BF₄] (1.00 g, 1.04 mmol) dissolved in CH₂Cl₂ (20 cm³) with continuous stirring under a stream of nitrogen was added Na[S₂CNMe₂] · 2H₂O (0.0959 g, 0.552 mmol). After stirring for 20 hr the solvent was removed in vacuo. The crude product was dissolved in CHCl₃ (10 cm³) and transferred to a silica chromatography column. Elution of the column with CHCl₃ afforded a green band, which after filtration and recrystallisation from CH₂Cl₂/Et₂O yielded 0.26 g, 27% of analytically pure green crystals of [W(CO)(dppm)(η²-MeC₂Me)]. Analysis. Found: C, 40.4; H, 3.3. C₃₀H₂₈I₂OP₂W

calc: C, 39.9; H, 3.1%. IR $\nu(\text{C}\equiv\text{O})$ 1940s cm^{-1} . ^1H NMR (CDCl_3 , +25°C): δ 7.8–7.1 (bm, 20H, Ph-H); 4.72 (bm, 2H, PCH_2P); 2.99 (s, 6H, $\equiv\text{CMe}$). The top 5 cm of the silica was removed from the column, and transferred to a nitrogen filled filtration unit. NCMe (50 cm^3) was washed through the silica into a Schlenk tube. The solvent was removed in vacuo and the red solid was redissolved in CH_2Cl_2 (20 cm^3) and filtered. The solvent volume was reduced to 2 cm^3 in vacuo and dropwise addition of diethyl ether precipitated the red cationic complex $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (**6**), which on recrystallisation from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ yielded 0.26 g, 28% of pure product.

Similar reactions of two equivalents of $[\text{W}(\text{CO})(\text{NCMe})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ with one equivalent of $\text{Na}[\text{S}_2\text{CNET}_2]$, $[\text{NH}_4][\text{S}_2\text{CNC}_4\text{H}_8]$, $\text{Na}[\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2]$ and $\text{K}[\text{S}_2\text{COEt}]$ in CH_2Cl_2 afforded the neutral green diiodide complex $[\text{WI}_2(\text{CO})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})]$ and the analogous cationic complexes $[\text{W}(\text{CO})(\text{S}_2\text{CX})(\text{dppm})(\eta^2\text{-MeC}_2\text{Me})][\text{BF}_4]$ (**8–11**). (See Table 1 for physical and analytical data).

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