

The synthesis and spectral properties of some new cationic mono(but-2-yne) bis(phosphine) complexes

$[W(CO)L_2(S_2CX)(\eta^2-MeC_2Me)][BPh_4]$ ($X = NC_4H_8, NMe_2, NEt_2, N(CH_2Ph)_2$ or OEt)

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Abstract

Reactions of the complex $[W(CO)(NCMe)(S_2CX)(\eta^2-MeC_2Me)][BPh_4]$ with two equivalents of L (for $X = NC_4H_8$; L = $PMe_3, PMe_2Ph, PMePh_2, PPh_3, PEtPh_2, PEt_2Ph, PEt_3, P^nPr_3, P^nBu_3, PCyPh_2, PCy_2Ph, P(CH_2CH=CH_2)Ph_2$ or $[Fe(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_5)]$) and for $X = NMe_2, NEt_2, N(CH_2Ph)_2$ and OEt; L = P^nBu_3) at room temperature in CH_2Cl_2 afford good yields of the new bis(phosphine) products $[W(CO)L_2(S_2CX)(\eta^2-MeC_2Me)][BPh_4]$ (1–17). ^{31}P NMR spectroscopy suggests that the two ligated phosphines are *trans* to each other in these compounds. ^{13}C NMR spectroscopy indicates the but-2-yne ligand is donating four electrons to the metal in 1–17. The barrier to but-2-yne rotation of $[W(CO)(PMe_3)_2(S_2CNC_4H_8)(\eta^2-MeC_2Me)][BPh_4]$ was calculated to be 66.9 ± 1 kJ mol $^{-1}$.

Introduction

Considerable interest has been paid to cationic alkyne complexes of molybdenum(II) and tungsten(II) in recent years. The cationic cyclopentadienyl or indenyl bis(alkyne) complexes $[Mo(CO)(\eta^2-RC_2R')_2(\eta^5-C_5H_5 \text{ or } C_9H_7)][BF_4]$ [1] have been shown to be useful precursors for a diverse range of chemistry [2–6]. To date there have been reports on a range of cationic alkyne complexes of molybdenum(II) and tungsten(II) containing ligated phosphines and phosphites, generally containing a coordinated cyclopentadienyl or indenyl moiety [7,8]. There have, however, been no reports of cationic alkyne bis(phosphine) complexes of molybdenum(II) and tungsten(II) containing a dithiocarbamate or related ligand.

In recent years we have been investigating the chemistry of the versatile bis(alkyne) precursors $[Wl_2(CO)(NCMe)(\eta^2-RC_2R)_2]$ [9]. These complexes react with one equivalent of dithiocarbamates or related ligands to give the bis(alkyne) complexes $[Wl(CO)(S_2CX)(\eta^2-RC_2R)_2]$ [10]. We have recently reported the synthesis and X-ray crystal structure of the cationic bis(alkyne) complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2-MeC_2Me)_2][BPh_4]$ [11], by treatment of $[Wl(CO)(S_2CNC_4H_8)(\eta^2-MeC_2Me)_2]$ with one molar equivalent of $Na[BPh_4]$ in acetonitrile. In this paper we

wish to describe the reactions of the cationic bis(alkyne) complexes $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CX})(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ with two equivalents of monodentate phosphines L (for $\text{X} = \text{NC}_4\text{H}_8$; $\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PPh}_3, \text{PEtPh}_2, \text{PEt}_2\text{Ph}, \text{PEt}_3, \text{P}^n\text{Pr}_3, \text{P}^n\text{Bu}_3, \text{PCyPh}_2, \text{PCy}_2\text{Ph}, \text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2$ or $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)]$ and for $\text{X} = \text{NMe}_2, \text{NEt}_2, \text{N}(\text{CH}_2\text{Ph})_2$ or OEt , $\text{L} = \text{P}^n\text{Bu}_3$) to afford the bis(phosphine) products $[\text{W}(\text{CO})\text{L}_2(\text{S}_2\text{CX})(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$.

Results and discussion

The complexes $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CX})(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ react with two equivalents of L ($\text{X} = \text{NC}_4\text{H}_8$; $\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PPh}_3, \text{PEtPh}_2, \text{PEt}_2\text{Ph}, \text{PEt}_3, \text{P}^n\text{Pr}_3, \text{P}^n\text{Bu}_3, \text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2, \text{PCyPh}_2, \text{PCy}_2\text{Ph}$ or $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)]$; $\text{X} = \text{NMe}_2, \text{NEt}_2, \text{N}(\text{CH}_2\text{Ph})_2$ and OEt ; $\text{L} = \text{P}^n\text{Bu}_3$) in CH_2Cl_2 at room temperature to give the new acetonitrile/mono(but-2-yne) displaced products $[\text{W}(\text{CO})\text{L}_2(\text{S}_2\text{CX})(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (1–17) in good yield. Compounds 1–17 are all stable in the solid state when stored under nitrogen for prolonged periods, however, they slowly decompose when exposed to air in solution. The complexes are all very soluble in $\text{CH}_2\text{Cl}_2, \text{CHCl}_3, \text{NCMe}, \text{OC}(\text{CH}_3)_2$, but are totally insoluble in hydrocarbon solvents and Et_2O . The new complexes 1–17 have been fully characterised by microanalysis (C, H and N) (Table 1), IR, ^1H , and in selected cases ^{13}C and ^{31}P NMR spectroscopy (Tables 2–5).

The IR spectra of 1–17 all show a strong single carbonyl band around 1930 cm^{-1} (Table 2). A weak band was also observed in the region of 1830 cm^{-1} and has been assigned to the $\nu(\text{C}\equiv\text{C})$ of the coordinated but-2-yne. These observed values are at considerably lower wavenumber than for free alkynes which is indicative of considerable interaction between both sets of alkyne $p\pi$ orbitals and the orbitals available on the metal.

The ^{31}P NMR spectra of compounds 2, 5–9 show a single phosphorus resonance with tungsten satellites. This single phosphorus resonance, for example in 2 2.51 ppm (s, $J(\text{W}-\text{P}) = 125.09\text{ Hz}$), is indicative of the two phosphines being in the same environment and thus *trans* to each other. This leads to the postulation of the geometry illustrated in Fig. 1. The ligated carbon monoxide and but-2-yne ligands are *cis* to each other, as expected on theoretical grounds, and mutually *trans* to one sulphur of the coordinated dithiocarbamate ligand. This is similar to the X-ray crystallographically found geometry of the complex $[\text{MoBr}_2(\text{CO})(\text{PEt}_3)_2(\eta^2\text{-PhC}_2\text{H})]$ reported by Templeton and co-workers [12], shown in Fig. 2, where the two bromide ligands have been replaced by the chelating dithiocarbamate or xanthate ligand.

The room temperature ^1H NMR spectra of compounds 1–17 all show the expected features corresponding to the proposed geometry shown in Fig. 1. The but-2-yne methyl resonances all appeared as doublets; which is indicative of the but-2-yne not undergoing rapid propeller-like rotation with respect to the NMR time scale. Variable temperature ^1H NMR studies were undertaken to see if the but-2-yne propeller-like rotation could be observed. The only complex that could be induced to show the propeller-like fluxional process was compound 1. On heating to 302 K the doublet methyl resonance coalesced which on further heating to 315 K gave a singlet, illustrated in Fig. 3. Using the Gutowsky–Holm equation ($\Delta G_{7c}^\ddagger = -RT_c \ln(\pi \Delta\nu h / \sqrt{2} K_B T_c)$) [13,14] the barrier to but-2-yne rotation was calculated to be $66.9 \pm 1\text{ kJ mol}^{-1}$. Heating of the other compounds to 323 K in CDCl_3 didn't

Table 1

Physical and analytical data for the compounds $[\text{W}(\text{CO})\text{L}_2(\text{S}_2\text{CX})(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$

Compound	Colour	Yield (%)	Analysis (Found (calcd.) (%))		
			C	H	N
$[\text{W}(\text{CO})(\text{PMe}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (1)	Blue	75	54.3 (54.4)	5.9 (5.9)	1.5 (1.6)
$[\text{W}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (2)	Blue	74	59.2 (59.6)	5.6 (5.6)	1.0 (1.3)
$[\text{W}(\text{CO})(\text{PMePh}_2)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (3)	Blue	73	63.0 (63.6)	5.2 (5.3)	0.9 (1.2)
$[\text{W}(\text{CO})(\text{PPh}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4] \cdot \text{CH}_2\text{Cl}_2$ (4)	Blue	77	63.8 (63.6)	5.0 (5.0)	0.8 (1.0)
$[\text{W}(\text{CO})(\text{PEtPh}_2)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (5)	Blue	69	64.4 (64.2)	5.1 (5.0)	0.8 (1.2)
$[\text{W}(\text{CO})(\text{PET}_2\text{Ph})_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (6)	Blue	71	60.6 (61.0)	6.2 (6.1)	0.9 (1.3)
$[\text{W}(\text{CO})(\text{PET}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (7)	Blue	84	57.3 (57.1)	6.9 (6.7)	1.6 (1.4)
$[\text{W}(\text{CO})(\text{P}^n\text{Pr}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (8)	Blue	83	59.5 (59.4)	7.5 (7.3)	1.2 (1.3)
$[\text{W}(\text{CO})(\text{P}^n\text{Bu}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (9)	Blue	78	61.3 (61.3)	7.8 (7.8)	1.2 (1.2)
$[\text{W}(\text{CO})(\text{P}^n\text{Bu}_3)_2(\text{S}_2\text{CNMe}_2)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (10)	Blue	68	60.3 (60.6)	7.7 (7.8)	0.9 (1.3)
$[\text{W}(\text{CO})(\text{P}^n\text{Bu}_3)_2(\text{S}_2\text{CNEt}_2)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (11)	Blue	72	61.2 (61.2)	7.8 (8.0)	0.9 (1.2)
$[\text{W}(\text{CO})(\text{P}^n\text{Bu}_3)_2(\text{S}_2\text{CN}(\text{CH}_2\text{Ph})_2)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (12)	Blue	71	64.9 (64.7)	7.3 (7.7)	0.8 (1.1)
$[\text{W}(\text{CO})(\text{P}^n\text{Bu}_3)_2(\text{S}_2\text{COEt})(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (13)	Blue	73	60.0 (60.5)	7.3 (7.7)	- -
$[\text{W}(\text{CO})(\text{PCyPh}_2)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (14)	Blue	72	65.0 (65.8)	6.0 (6.0)	1.1 (1.1)
$[\text{W}(\text{CO})(\text{PCy}_2\text{Ph})_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (15)	Blue	64	65.6 (65.7)	7.1 (6.9)	0.8 (1.1)
$[\text{W}(\text{CO})\{\text{P}(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ph}_2\}_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (16)	Blue	72	65.2 (64.9)	5.6 (5.4)	1.0 (1.2)
$[\text{W}(\text{CO})\{\{\text{FeC}_5\text{H}_4\text{PPh}_2(\eta^2\text{-C}_5\text{H}_5)\}_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4] \cdot \text{CH}_2\text{Cl}_2$ (17)	Brown	59	60.7 (61.0)	4.9 (4.8)	0.7 (0.9)

cause any change in the observed spectra. Using the Gutowsky-Holm equation [13,14], ($T_c > 323$ and $\Delta\nu$ obtained from the spectra) the barriers to but-2-yne rotation are likely to be in excess of 70 kJ mol^{-1} . We reported a series of but-2-yne rotational barriers for the complexes $[\text{WI}_2(\text{CO})\text{L}_2(\eta^2\text{-MeC}_2\text{Me})]$ ($\text{L} = \text{PMe}_3$, PMe_2Ph , PMePh_2 , PPh_3 , PEtPh_2 , PEt_2Ph , PEt_3 and P^nBu_3) [15]. The bis(trimethylphosphine) complex $[\text{WI}_2(\text{CO})(\text{PMe}_3)_2(\eta^2\text{-MeC}_2\text{Me})]$ had a barrier some 24 kJ mol^{-1} less than compound 1. These observations show that subtle changes in steric and electronic properties within a complex can have substantial effects on fluxional processes.

The ^{13}C NMR spectra of compounds 1–3, 5–9, 14 and 16 all show the expected features in accordance with the structure proposed in Fig. 1. The alkyne contact

Table 2

IR data ^a for the compounds $[\text{W}(\text{CO})\text{L}_2(\text{S}_2\text{CX})(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$

Compound	$\nu(\text{C}\equiv\text{O}) \text{ cm}^{-1}$	$\nu(\text{C}\equiv\text{C}) \text{ cm}^{-1}$
1	1935 (s)	1820 (w)
2	1938 (s)	1825 (w)
3	1936 (s)	1830 (w)
4	1938 (s)	1820 (w)
5	1928 (s)	1822 (w)
6	1925 (s)	1822 (w)
7	1925 (s)	1825 (w)
8	1930 (s)	1825 (w)
9	1925 (s)	1820 (w)
10	1930 (s)	1825 (w)
11	1930 (s)	1820 (w)
12	1931 (s)	1825 (w)
13	1928 (s)	1830 (w)
14	1920 (s)	1825 (w)
15	1918 (s)	1820 (w)
16	1935 (s)	1820 (w)
17	1925 (s)	1825 (w)

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

carbon resonances were observed above 200 ppm, which is indicative of the ligated but-2-yne utilising both sets of $p\pi$ orbitals to donate four-electrons [16] to the tungsten, thus, allowing complexes 1–17 to obey the effective atomic number rule. A quartet around 164 ppm ($J(\text{B}-\text{C}) = 49.5$ Hz) is indicative of the $[\text{BPh}_4]^-$ counter anion. A ^{11}B NMR spectrum of **8** shows a strong single resonance at -7.14 ppm which is again indicative of the $[\text{BPh}_4]^-$ counter anion.

It is interesting to note that treatment of $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ with one equivalent of PPh_3 in CH_2Cl_2 at room temperature gave a roughly equal mixture of $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ and the 2:1 product $[\text{W}(\text{CO})(\text{PPh}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ with no evidence for the formation of the most likely 1:1 product $[\text{W}(\text{CO})(\text{PPh}_3)(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ when the reaction was followed by infrared spectroscopy.

Experimental

All the reactions described were carried out under dry nitrogen using standard Schlenk line techniques. The complexes $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CX})(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ were all prepared by the method in ref. 11, described for $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$. All other chemicals were purchased from commercial sources and used without further purification. IR spectra were recorded as CHCl_3 films between NaCl plates on a Perkin Elmer 1430 ratio recording IR spectrophotometer. ^1H , ^{13}C , and ^{11}B NMR spectra were recorded on either a Bruker AC 250 NMR spectrometer or a Bruker WH 400 MHz spectrometer and calibrated against tetramethylsilane. ^{31}P NMR spectra were recorded on a Bruker WH 400 MHz spectrometer at the University of Warwick and calibrated against 85% H_3PO_4 . Microanalysis (C, H and N) were determined on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas).

Table 3

¹H NMR data ^a for the compounds [W(CO)L₂(S₂CX)(η²-MeC₂Me)][BPh₄]

Compound	¹ H (δ ppm)
1	7.4–6.8 (m, 20H, Ph-H); 3.65 (t, 2H, NCH ₂ , J(H-H) = 6.98 Hz); 3.49 (t, 2H, NCH ₂ , J(H-H) = 6.21 Hz); 3.15 (s, 3H, ≡CMe); 3.12 (s, 3H, ≡CMe); 1.95 (m, 4H, CH ₂); 1.1 (t, 9H, CH ₃ , J(P-H) = 4.14 Hz).
2	7.45–6.8 (m, 30H, Ph-H); 3.18 (bs, 4H, NCH ₂); 2.81 (s, 3H, ≡CMe); 2.63 (s, 3H, ≡CMe); 1.8 (bs, 4H, CH ₂); 1.6 (t, 3H, CH ₃); 1.4 (t, 3H, CH ₃).
3	7.5–6.75 (m, 40H, Ph-H); 3.05 (bs, 2H, NCH ₂); 2.95 (bs, 2H, NCH ₂); 2.8 (s, 3H, ≡CMe); 2.55 (s, 3H, ≡CMe); 1.89 (t, 6H, CH ₃); 1.65 (m, 4H, CH ₂).
4	7.9–6.85 (m, 50H, Ph-H); 5.3 (s, 2H, CH ₂ Cl ₂); 2.95 (bm, 4H, NCH ₂); 2.72 (s, 3H, ≡CMe); 2.61 (s, 3H, ≡CMe); 2.0 (bm, 4H, CH ₂).
5	7.7–6.85 (m, 40H, Ph-H); 2.98 (bm, 4H, NCH ₂); 2.82 (s, 3H, ≡CMe); 2.71 (s, 3H, ≡CMe); 2.15 (bm, 4H, CH ₂); 1.65 (m, 4H, CH ₂); 0.85 (m, 6H, CH ₃).
6	7.6–6.85 (m, 30H, Ph-H); 3.0 (bm, 4H, NCH ₂); 2.95 (s, 3H, ≡CMe); 2.78 (s, 3H, ≡CMe); 1.98 (m, 2H, CH ₂); 1.75 (m, 4H, CH ₂); 1.45 (m, 2H, CH ₂); 0.85 (m, 12H, CH ₃).
7	7.45–6.85 (m, 20H, Ph-H); 3.65 (t, 2H, NCH ₂ , J(H-H) = 6.73 Hz); 3.45 (t, 2H, NCH ₂ , J(H-H) = 6.72 Hz); 3.18 (s, 3H, ≡CMe); 3.03 (s, 3H, ≡CMe); 1.95 (m, 4H, CH ₂); 1.55 (m, 6H, CH ₂); 0.95 (m, 18H, CH ₃).
8	7.45–6.8 (m, 20H, Ph-H); 3.68 (t, 2H, NCH ₂ , J(H-H) = 6.72 Hz); 3.48 (t, 2H, NCH ₂ , J(H-H) = 6.63 Hz); 3.17 (s, 3H, ≡CMe); 3.05 (s, 3H, ≡CMe); 1.95 (m, 4H, CH ₂); 1.49–1.35 (bm, 24H, CH ₂); 0.95 (t, 18H, CH ₃ , J(H-H) = 6.72 Hz).
9	7.48–6.79 (m, 20H, Ph-H); 3.65 (t, 2H, NCH ₂ , J(H-H) = 6.46 Hz); 3.48 (t, 2H, NCH ₂ , J(H-H) = 6.46 Hz); 3.19 (s, 3H, ≡CMe); 3.05 (s, 3H, ≡CMe); 1.92 (m, 4H, CH ₂); 1.55–1.19 (bm, 36H, CH ₂); 0.95 (t, 18H, CH ₃ , J(H-H) = 6.98 Hz).
10	7.48–6.8 (m, 20H, Ph-H); 3.25 (s, 3H, NCH ₃); 3.09 (s, 3H, NCH ₃); 2.98 (s, 3H, ≡CMe); 2.81 (s, 3H, ≡CMe); 1.35 (bm, 36H, CH ₂); 0.95 (t, 18H, CH ₃ , J(H-H) = 6.98 Hz).
11	7.48–6.8 (m, 20H, Ph-H); 3.65 (q, 2H, NCH ₂); 3.46 (q, 2H, NCH ₂); 3.18 (s, 3H, ≡CMe); 3.07 (s, 3H, ≡CMe); 1.38 (bm, 36H, CH ₂); 1.14 (m, 6H, CH ₃); 0.95 (t, 18H, CH ₃ , J(H-H) = 6.97 Hz).
12	7.48–6.8 (m, 30H, Ph-H); 3.48 (s, 4H, NCH ₂); 3.26 (s, 3H, ≡CMe); 3.09 (s, 3H, ≡CMe); 1.39 (bm, 36H, CH ₂); 0.95 (t, 18H, CH ₃ , J(H-H) = 6.97 Hz).
13	7.45–6.8 (m, 20H, Ph-H); 3.62 (q, 2H, OCH ₂ , J(H-H) = 7 Hz); 3.14 (s, 3H, ≡CMe); 3.01 (s, 3H, ≡CMe); 1.36 (bm, 39H, CH ₂ + CH ₃); 0.97 (t, 3H, CH ₃ , J(H-H) = 6.98 Hz).
14	7.85–6.85 (m, 40H, Ph-H); 3.25 (m, 4H, NCH ₂); 2.95 (s, 3H, ≡CMe); 2.87 (s, 3H, ≡CMe); 1.85 (m, 4H, CH ₂); 1.25 (m, 22H, Cy-H).
15	7.85–6.89 (m, 30H, Ph-H); 3.30 (m, 4H, NCH ₂); 2.98 (s, 3H, ≡CMe); 2.85 (s, 3H, ≡CMe); 1.92 (m, 4H, CH ₂); 1.35 (m, 44H, Cy-H).
16	7.9–6.8 (m, 40H, Ph-H); 5.16 (m, 4H, CH ₂); 4.70 (m, 4H, NCH ₂); 3.54 (m, 2H, CH); 3.0 (bs, 4H, NCH ₂); 2.78 (s, 3H, ≡CMe); 2.72 (s, 3H, ≡CMe); 1.99 (m, 4H, CH ₂).
17	7.85–6.8 (m, 40H, Ph-H); 5.3 (s, 2H, CH ₂ Cl ₂); 4.35, 4.05, 3.85 (3s, 18H, C ₅ H ₅ and C ₅ H ₅ PPh ₂); 3.41 (m, 4H, NCH ₂); 2.75 (s, 3H, ≡CMe); 2.5 (s, 3H, ≡CMe); 2.04 (m, 4H, CH ₂).

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

Table 4

¹³C NMR data ^a for the compounds [W(CO)L₂(S₂CNC₄H₈)(η²-MeC₂Me)][BPh₄]

Compound	¹³ C (δ ppm)
1	224.67 (s, C≡C); 221.14 (s, C≡C); 212.5 (s, C=O); 199.94 (s, CS ₂); 165.4, 164.62, 163.83, 163.05 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.29, 125.44, 121.57 (3s, BPh ₄ -C); 50.78 (s, NCH ₂); 50.42 (s, NCH ₂); 24.69 (s, CH ₂); 24.49 (s, CH ₂); 21.61 (s, ≡CMe); 20.94 (s, ≡CMe); 15.47 (t, PMe, <i>J</i> (P-C) = 15.63 Hz).
2	212.82 (s, C=O); 199.14 (s, CS ₂); 165.44, 164.66, 163.87, 163.09, (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.33, 125.43, 121.54 (3s, BPh ₄ -C); 134.34–127.95 (m, Ph-C); 50.31 (s, NCH ₂); 49.79 (s, NCH ₂); 24.54 (s, CH ₂); 24.30 (s, CH ₂); 21.11 (s, ≡CMe); 20.87 (s, ≡CMe); 15.55 (t, PMe, <i>J</i> (P-C) = 15.4 Hz); 13.31 (t, PMe, <i>J</i> (P-C) = 16.33 Hz).
3	224.69 (s, C≡C); 197.64 (s, CS ₂); 165.37, 164.58, 163.81, 163.02 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.23, 125.36, 121.42 (3s, BPh ₄ -C); 132.54–127.82 (m, Ph-C); 49.98 (s, NCH ₂); 49.45 (s, NCH ₂); 24.34 (s, CH ₂); 24.12 (s, CH ₂); 21.12 (s, ≡CMe); 20.06 (s, ≡CMe); 14.49 (t, PMe, <i>J</i> (P-C) = 16.2 Hz).
5	225.3 (s, C≡C); 222.37 (s, C≡C); 212.17 (s, C=O); 198.1 (s, CS ₂); 164.96, 164.47, 163.98, 163.49 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.24, 125.38, 121.41 (3s, BPh ₄ -C); 135.2–127.8 (m, Ph-C); 49.92 (s, NCH ₂); 49.26 (s, NCH ₂); 24.35 (s, CH ₂); 24.11 (s, CH ₂); 22.06 (t, PCH ₂ , <i>J</i> (P-C) = 13.8 Hz); 21.6 (s, ≡CMe); 21.14 (s, ≡CMe); 7.9 (s, CH ₃).
6	225.9 (s, C≡C); 221.6 (s, C≡C); 211.94 (s, C=O); 198.7 (s, CS ₂); 165.51, 164.72, 163.93, 163.15 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.37, 125.4, 121.5 (3s, BPh ₄ -C); 134.72–127.68 (m, Ph-C); 49.94 (s, NCH ₂); 49.44 (s, NCH ₂); 24.48 (s, CH ₂); 24.24 (s, CH ₂); 21.59 (s, ≡CMe); 21.10 (s, ≡CMe); 18.13 (t, PCH ₂ , <i>J</i> (P-C) = 12.18 Hz); 17.09 (t, PCH ₂ , <i>J</i> (P-C) = 14.07 Hz); 7.67 (s, CH ₃); 7.18 (s, CH ₃).
7	226.23 (s, C≡C); 221.07 (s, C≡C); 213.04 (s, C=O); 198.04 (s, CS ₂); 164.46, 164.67, 163.88, 163.1 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.31, 125.42, 121.51 (3s, BPh ₄ -C); 50.71 (s, NCH ₂); 50.37 (s, NCH ₂); 24.65 (s, CH ₂); 24.46 (s, CH ₂); 21.97 (s, ≡CMe); 21.52 (s, ≡CMe); 17.20 (t, PCH ₂ , <i>J</i> (P-C) = 13 Hz); 7.54 (s, CH ₃).
8	226.25 (s, C≡C); 221.02 (s, C≡C); 212.74 (s, C=O); 198.30 (s, CS ₂); 165.49, 164.71, 163.91, 163.12 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.32, 125.39, 121.48 (3s, BPh ₄ -C); 50.8 (s, NCH ₂); 50.41 (s, NCH ₂); 27.13 (t, PCH ₂ , <i>J</i> (P-C) = 12.8 Hz); 24.72 (s, CH ₂); 24.56 (s, CH ₂); 21.76 (s, ≡CMe); 21.40 (s, ≡CMe); 17.06 (s, CH ₂); 15.5 (s, CH ₃).
9	226.29 (s, C≡C); 220.75 (s, C≡C); 212.62 (s, C=O); 198.25 (s, CS ₂); 165.49, 164.71, 163.92, 163.14 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.33, 125.42, 121.49 (3s, BPh ₄ -C); 50.41 (s, NCH ₂); 50.19 (s, NCH ₂); 27.14–23.79 (m, PCH ₂ , CH ₂); 21.74 (s, ≡CMe); 21.41 (s, ≡CMe); 13.64 (s, CH ₃).
14 ^b	227.5 (s, C≡C); 221.6 (s, C≡C); 210.2 (s, C=O); 198.2 (s, CS ₂); 164.96, 164.46, 163.96, 163.47 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.34, 125.42, 121.5 (3s, BPh ₄ -C); 138.04–126.7 (m, Ph-C); 50.13 (s, NCH ₂); 49.67 (s, NCH ₂); 29.85–24.18 (m, CH ₂); 21.33 (s, ≡CMe); 21.19 (s, ≡CMe).
16	224.63 (s, C≡C); 222.78 (s, C≡C); 212.75 (s, C=O); 197.88 (s, CS ₂); 165.5, 164.72, 163.94, 163.16 (q, B-C, <i>J</i> (B-C) = 49.5 Hz); 136.34, 125.46, 121.51 (3s, BPh ₄ -C); 134.72–127.09 (m, Ph, C=C); 50.2 (s, NCH ₂); 49.55 (s, NCH ₂); 33.72 (t, PCH ₂ , <i>J</i> (P-C) = 12.6 Hz); 24.51 (s, CH ₂); 24.25 (s, CH ₂); 21.87 (s, ≡CMe); 21.28 (s, ≡CMe).

^a Spectra recorded in CDCl₃ (+25 °C) referenced to SiMe₄. s = singlet, q = quartet, t = triplet, m = multiplet. ^b Recorded on a Bruker WH 400 MHz.

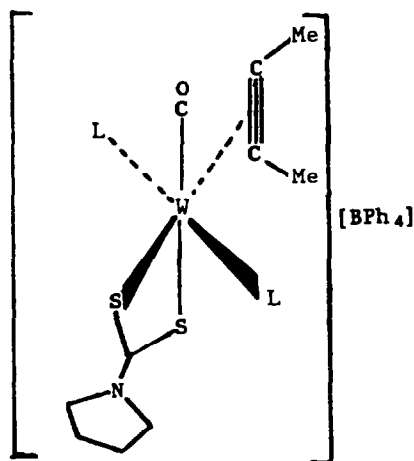
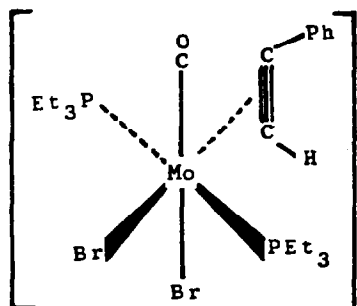
Table 5

³¹P NMR data ^a for the compounds [W(CO)L₂(S₂CNC₄H₈)(η²-MeC₂Me)][BPh₄]

Compound	³¹ P (δ ppm)
2	2.51 (<i>J</i> (W-P) = 125.09 Hz)
5	16.17 (<i>J</i> (W-P) = 128.87 Hz)
6	10.23 (<i>J</i> (W-P) = 126.22 Hz)
7	9.36 (<i>J</i> (W-P) = 125.12 Hz)
8	11.63 (<i>J</i> (W-P) = 128.73 Hz)
9	-10.49 (<i>J</i> (W-P) = 129.91 Hz)

^a Spectra recorded in CDCl₃ and referenced to H₃PO₄ (85%).*[W(CO)(PMe₃)₂(S₂CNC₄H₈)(η²-MeC₂Me)][BPh₄] (1)*

A solution of [W(CO)(NCMe)(S₂CNC₄H₈)(η²-MeC₂Me)][BPh₄] (0.8 g, 0.968 mmol) in CH₂Cl₂ (15 cm³) contained in a Schlenk tube was frozen in a liquid N₂ bath, then evacuated. PMe₃ (0.1473 g, 1.936 mmol) was distilled into the Schlenk tube by direct pyrolysis of [{AgI(PMe₃)₄] (0.5892 g) at 200 °C *in vacuo*. After completion of pyrolysis the reaction Schlenk was opened to N₂ and allowed to

Fig. 1. Proposed molecular geometry for the complexes [W(CO)L₂(S₂CNC₄H₈)(η²-MeC₂Me)][BPh₄] (2, 5–9).Fig. 2. The crystallographically found geometry for [MoBr₂(CO)(PEt₃)₂(η²-PhC₂H)] [12].

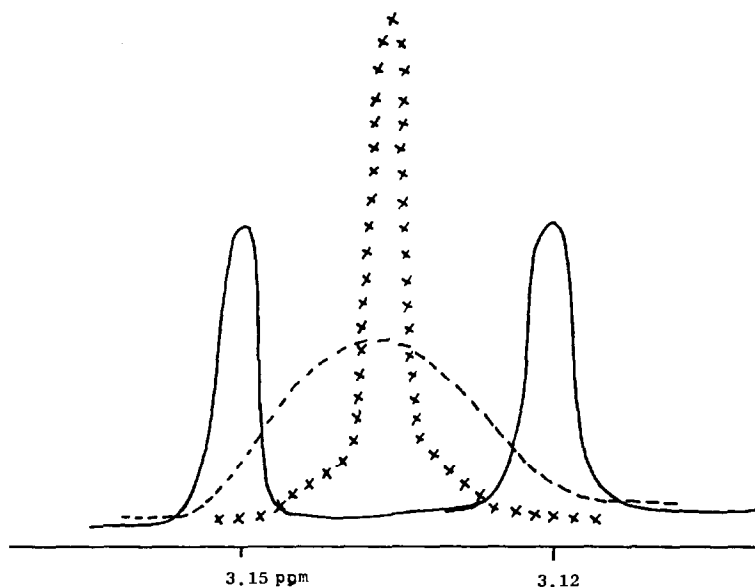


Fig. 3. A diagrammatical representation of the but-2-yne methyl resonances for $[\text{W}(\text{CO})(\text{PMe}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ at three temperatures; — = 265 K, - - - - = 302 K, $\times \times \times \times \times \times \times = 315$ K; $T_c = 302$ K, $\Delta\nu = 7.5$ Hz, $\Delta G^\ddagger = 66.9$ kJ mol $^{-1}$.

warm up to room temperature. After the reaction had been stirring for 20 h the solution was filtered and the solvent volume reduced to 2 cm 3 *in vacuo*. Dropwise addition of Et $_2$ O precipitated the blue cationic complex $[\text{W}(\text{CO})(\text{PMe}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (1) which on recrystallisation from CH $_2$ Cl $_2$ -Et $_2$ O yielded 0.64 g (75%) of pure product.

$[\text{W}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (2)

To $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ (0.4 g, 0.484 mmol) dissolved in CH $_2$ Cl $_2$ (15 cm 3) with continuous stirring under a stream of dry N $_2$ was added PMe $_2$ Ph (0.137 cm 3 , 0.968 mmol). After stirring for 20 h the solution was filtered and the solvent volume reduced to 2 cm 3 *in vacuo*. Dropwise addition of Et $_2$ O precipitated the blue cationic complex $[\text{W}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (2) which on recrystallisation from CH $_2$ Cl $_2$ -Et $_2$ O yielded 0.36 g (74%) of pure product.

Similar reactions of $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ with two equivalents of PMePh $_2$, PPh $_3$, PEtPh $_2$, PEt $_2$ Ph, PEt $_3$, P n Pr $_3$, PCyPh $_2$, PCy $_2$ Ph, PPh $_2$ (CH $_2$ CH=CH $_2$) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\eta^5\text{-C}_5\text{H}_5)]$ in CH $_2$ Cl $_2$ afforded the analogous cationic compounds $[\text{W}(\text{CO})\text{L}_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$ (3-8 and 14-17).

$[\text{W}(\text{CO})(\text{P}^n\text{Bu}_3)_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ (9)

To $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ (0.4 g, 0.484 mmol) dissolved in CH $_2$ Cl $_2$ (15 cm 3) with continuous stirring under a stream of dry N $_2$ was added P n Bu $_3$ (0.241 cm 3 , 0.968 mmol). After stirring for 20 h the solution was filtered and the solvent volume reduced to 2 cm 3 *in vacuo*. Dropwise addition of

Et₂O precipitated the blue cationic complex [W(CO)(PⁿBu₃)₂(S₂CNC₄H₈)(η²-MeC₂Me)][BPh₄] (**9**) which on recrystallisation from CH₂Cl₂-Et₂O yielded 0.43 g (78%) of pure product.

Similar reactions of [W(CO)(NCMe)(S₂CX)(η²-MeC₂Me)₂][BPh₄] (where X = NMe₂, NEt₂, N(CH₂Ph)₂ or OEt) with two equivalents of PⁿBu₃ in CH₂Cl₂ afforded the analogous cationic complexes [W(CO)(PⁿBu₃)₂(S₂CX)(η²-MeC₂Me)]-[BPh₄] (**10**-**13**).

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