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Cationic Bis(but-2-yne) Complexes of the Type $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$

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The compounds $[WI(CO)(S_2CX)(\eta^2\text{-}MeC_2Me)_2]$ (X = NC_4H_8, NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt) react with $Na[BPh_4]$ in acetonitrile at room temperature to give the new cationic bis(but-2-yne) complexes $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (1–5) in high yield. X-ray single-crystal studies were carried out on $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (1). The crystals are monoclinic, space group $P2_1/a$, $Z = 4$, in a unit cell of dimensions $a = 12.944$ (13) Å, $b = 26.671$ (25) Å, $c = 11.090$ (13) Å, and $\beta = 105.71$ (1)°. The structure was refined to $R = 0.085$ ($R_w = 0.087$) for 1989 independent reflections above background. The coordination geometry about the tungsten can be considered to be pseudooctahedral with the midpoints of the two *cis*-but-2-yne ligands in the same plane as the sulfur atoms of the dithiocarbamate ligand. Acetonitrile and carbon monoxide occupy the axial sites. Selected reactions of 1–5 with both monodentate (CO, $CNBu^t$, $P(OMe)_3$) and bidentate ($Ph_2P(CH_2)_nPPh_2$ (n = 1–6), $[Fe(\eta^5\text{-}C_5H_4\text{-}PPh_2)_2]$, 2,2′-bpy, 1,10-phen) ligands 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 suggest the number of electrons donated to the tungsten by the alkyne in selected compounds.

Introduction

The importance of coordinatively unsaturated alkyne complexes of molybdenum and tungsten has been known since the early report in 1963 of the zerovalent tris(alkyne) complex $[W(CO)(\eta^2\text{-hex-3-yne})_3]$[1] and has been highlighted by the extensive review by Templeton on Mo(II) and W(II) alkyne complexes published in 1989.[2] Cationic alkyne complexes have received particular attention, in particular by Green and co-workers. They described the synthesis[3] of the cationic bis(alkyne) compounds $[Mo(CO)(\eta^2\text{-}RC_2R')_2(\eta^5\text{-}C_5H_5 \text{ or } \text{-}C_9H_7)][BF_4]$ (R = R′ = Me, Ph; R = H, R′ = Me; R = H, R′ = Bu^t) and over the past 15 years have extensively investigated their chemistry with nucleophiles[4] to afford a wide range of novel organometallic compounds. Other cationic alkyne complexes of molybdenum(II) or tungsten(II) include those reported by Bergman and Watson ($[M(CO)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_5H_5)][PF_6]$ (M = Mo, W)),[5] Lippard and co-workers ($[MoI(CNR)_4(\eta^2\text{-}RNHC_2NHR)]I$),[6] Beck and co-workers ($[Mo(CO)L(\eta^2\text{-}RC_2R')(\eta^5\text{-}C_5H_5)][BF_4]$ (L = CO, $P(OPh)_3$, PEt_3, PPh_3; R = R′ = H, Me, Ph; R = H, R′ = Ph)),[7] and Templeton and co-workers ($[W(CO)(S_2CNEt_2)(dppe)(\eta^2\text{-}HOC_2CH_2Ph)][BF_4]$).[8] More recently we have described the synthesis of $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$[9a] and described its reactions with a wide range of donor ligands.[9b–e]

In 1988,[10] we described the preparation and X-ray crystal structures of the very versatile bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) and 2 years later the reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) with 1 equiv of S_2CX^- {X = NC_4H_8, NC_5H_{10}, NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt} to give the monoiodo complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$.[11] In this paper we describe the synthesis of the cationic bis(but-2-yne)tungsten compounds $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (X

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= NC_4H_8, NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt) and their reactions with both selected neutral mono- and bidentate donor ligands. The X-ray crystal structure of [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] is also described. A preliminary report of this work has been published.[12]

Experimental Section

General Procedures. All reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk-line techniques. Dichloromethane was dried over phosphorus pentoxide and purged with nitrogen before use. All materials used in this research were purchased from commercial sources. The compounds [WI(CO)(S_2CX)(η^2-MeC_2Me)$_2$] (X = NC_4H_8, NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt) were prepared by the literature method.[11]

Elemental analyses were determined by using a Carlo Erba MOD 1106 elemental analyzer (using helium as a carrier gas). Infrared spectra were recorded on a Perkin-Elmer 1430 ratio recording IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on either a Bruker AC 250-MHz CP/MAS or a Bruker WH 400-MHz NMR spectrometer and were referenced to tetramethylsilane.

Syntheses. [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (1). To [WI(CO)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$] (1.00 g, 1.68 mmol) dissolved in NCMe (40 cm^3) with continuous stirring under a stream of dry N_2 was added Na[BPh_4] (0.5749 g, 1.68 mmol). After the mixture was stirred for 10 h, the solvent was removed in vacuo. The crude product was then dissolved in the minimum amount of warm NCMe (30 °C) and the solution cooled to −18 °C for 4 h, which afforded X-ray-quality single crystals of [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (1), yield 1.18 g (85%).

Similar reactions of [WI(CO)(S_2CX)(η^2-MeC_2Me)$_2$] (where X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt) with Na[BPh_4] in NCMe afforded the analogous cationic bis(alkyne) complexes [W(CO)(NCMe)(S_2CX)(η^2-MeC_2Me)$_2$][BPh_4] (2–5).

[W(CO)$_2$($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (6). To [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (0.4 g, 0.484 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry N_2, CO (generated by the action of concentrated H_2SO_4 on HCO_2H) was vigorously bubbled through the solution. After 6 h the solution was filtered and the solvent volume reduced to 0.5 cm^3, in vacuo. Addition of diethyl ether to the stirred solution precipitated the cationic complex [W(CO)$_2$($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (6). Recrystallization from CH_2Cl_2/Et_2O afforded 0.33 g (83%) of analytically pure [W(CO)$_2$($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (6).

[W($CNBu^t$)$_2$($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (7). To [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (0.3952 g, 0.478 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry N_2 was added $CNBu^t$ (0.1 cm^3, 0.956 mmol). After it was stirred for 24 h, the solution was filtered and the solvent volume reduced to 2 cm^3 in vacuo. Dropwise addition of diethyl ether precipitated the yellow cationic bis(alkyne) complex [W($CNBu^t$)$_2$($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (7), which on recrystallization from CH_2Cl_2/Et_2O yielded 0.33 g (75%) of pure product.

[W(CO){P(OMe)$_3$}$_2$($S_2CNC_4H_8$)(η^2-MeC_2Me)][BPh_4] (8). To [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (0.4 g, 0.484 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry N_2 was added P(OMe)$_3$ (0.11 cm^3, 0.93 mmol). After it was stirred for 20 h, the solution was filtered and the solvent volume reduced to 1 cm^3 in vacuo. Dropwise addition of diethyl ether precipitated the blue cationic complex [W(CO){P(OMe)$_3$}$_2$($S_2CNC_4H_8$)(η^2-MeC_2Me)][BPh_4] (8), which on recrystallization from CH_2Cl_2/Et_2O yielded 0.27 g (58%) of pure product.

[W(CO)($S_2CNC_4H_8$){$Ph_2P(CH_2)PPh_2$}(η^2-MeC_2Me)][BPh_4] (9). To [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (0.4 g, 0.484 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a steam of dry N_2 was added $Ph_2P(CH_2)PPh_2$ (0.186 g, 0.484 mmol). After it was stirred for 20 h, the solution was filtered and the solvent volume reduced to 2 cm^3 in vacuo. Dropwise addition of diethyl ether precipitated the red cationic complex [W(CO)($S_2CNC_4H_8$){$Ph_2P(CH_2)PPh_2$}(η^2-MeC_2Me)][BPh_4] (9), which on recrystallization from CH_2Cl_2/Et_2O yielded 0.41 g (75%) of pure product.

Similar reactions of [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] with equimolar quantities of $Ph_2P(CH_2)_nPPh_2$ (n = 2–6) or [Fe(η^5-$C_5H_4PPh_2$)$_2$] in CH_2Cl_2 afforded the analogous cationic complexes 10–15.

[W(CO)(bpy)($S_2CNC_4H_8$)(η^2-MeC_2Me)][BPh_4] (16). To [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (0.4 g, 0.484 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry N_2 was added bpy (0.0756 g, 0.484 mmol). After it was stirred for 20 h, the solution was filtered and the solvent volume reduced to 2 cm^3 in vacuo. Dropwise addition of diethyl ether precipitated the red cationic complex [W(CO)(bpy)($S_2CNC_4H_8$)(η^2-MeC_2Me)][BPh_4] (16), which on recrystallization from CH_2Cl_2/Et_2O yielded 0.39 g, 90% of pure product.

Similar reactions of [W(CO)(NCMe)(S_2CX)(η^2-MeC_2Me)$_2$][BPh_4] (where X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt) with equimolar quantities of bpy in CH_2Cl_2 afforded the analogous cationic complexes [W(CO)(S_2CX)(bpy)(η^2-MeC_2Me)][BPh_4] (18–21).

[W(CO)($S_2CNC_4H_8$)(1,10-phen)(η^2-MeC_2Me)][BPh_4] (17). To [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (0.4 g, 0.484 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry N_2 was added 1,10-phen (0.0872 g, 0.484 mmol). After it was stirred for 20 h, the solution was filtered and the solvent volume reduced to 3 cm^3 in vacuo. Adding 4 cm^3 of diethyl ether and cooling to −10 °C for 24 h afforded 0.38 g (87%) of the analytically pure complex [W(CO)($S_2CNC_4H_8$)(1,10-phen)(η^2-MeC_2Me)][BPh_4] (17).

Crystal Data. Crystals were prepared as described above: [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4], $WC_{40}H_{43}N_2OS_2B$, M_r = 826.1, a = 12.944 (13) Å, b = 26.671 (25) Å, c = 11.090 (13) Å, β = 105.7 (1)°, V = 3685.8 Å^3, d_c = 1.44 g cm^{-3}, d_m = 1.45 g cm^{-3}, $F(000)$ = 1664, Z = 4, λ = 0.7107 Å, μ = 33.5 cm^{-1}, space group $P2_1/a$. A crystal of size 0.02 × 0.03 × 0.035 mm was mounted to rotate around the a axis on a Stoe Stadi2 diffractometer. A total of 6349 independent reflections with $2\theta < 50°$ ($0 \le h \le 14$, $0 \le k \le 30$, $-11 \le l \le +11$) were collected using a variable-width ω scan of $(1.5 + 0.5 \sin \mu/\tan \theta)°$ and a scan speed of 0.0333° s^{-1}. No decay in intensity was observed for the standard reflections. The data were of poor quality due to a weakly diffracting crystal, and in subsequent calculations only 1952 independent reflections with $I > 2\sigma(I)$ were used. An empirical absorption correction was applied.[13] The position of the tungsten atom was located from the Patterson function, and the positions of the remaining atoms in the molecule were located from different Fourier maps. The hydrogen atoms were included in calculated positions. The tungsten atom was refined anisotropically and all other atoms were refined isotropically to a final R value of 0.085 (R_w = 0.087). Calculations were carried out using SHELX76[14] and some in-house programs on the Amdahl 5870 computer at the University of Reading. In the final cycle of refinement the maximum shift/error ratio was 0.085. In the final difference Fourier map the maximum and minimum peaks were 1.31 and −3.52 e Å^{-3}. Atomic coordinates for 1 are given in Table V and selected bond lengths and angles in Table VI. Additional bond lengths and angles, thermal parameters, and hydrogen atom positions have been deposited as supplementary material.

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Table I. Physical and Analytical[a] Data for the Complexes $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ and Derivatives

compd	color	yield, %	anal. found (calcd), % C	H	N
$[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**1**)	yellow	85	58.3 (58.1)	5.4 (5.2)	3.1 (3.4)
$[W(CO)(NCMe)(S_2CNMe_2)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**2**)	yellow	72	57.2 (57.0)	5.3 (5.2)	3.1 (3.5)
$[W(CO)(NCMe)(S_2CNEt_2)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**3**)	yellow	69	57.6 (58.0)	5.7 (5.5)	3.5 (3.4)
$[W(CO)(NCMe)\{S_2CN(CH_2Ph)_2\}(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**4**)	orange/yellow	73	62.5 (63.0)	4.9 (5.2)	2.4 (2.9)
$[W(CO)(NCMe)(S_2COEt)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**5**)	brown/orange	52	56.7 (56.9)	5.3 (5.0)	1.4 (1.7)
$[W(CO)_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**6**)	yellow	83	57.1 (57.6)	4.5 (5.0)	1.5 (1.7)
$[W(CNBu^t)_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**7**)	yellow	75	61.0 (61.1)	6.3 (5.7)	4.1 (4.5)
$[W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**8**)	blue	58	49.5 (49.1)	5.4 (5.4)	1.0 (1.4)
$[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**9**)	red	75	63.3 (63.5)	5.3 (5.1)	1.1 (1.3)
$[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**10**)	red	73	63.6 (63.7)	5.1 (5.2)	0.8 (1.2)
$[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**11**)	red	74	63.9 (64.1)	5.6 (5.3)	0.8 (1.2)
$[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_4PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**12**)	blue	78	64.4 (64.3)	5.7 (5.4)	0.8 (1.2)
$[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_5PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**13**)	blue	77	64.2 (64.6)	5.7 (5.5)	0.9 (1.2)
$[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_6PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**14**)	blue	81	65.2 (64.8)	5.9 (5.6)	0.9 (1.2)
$[W(CO)(S_2CNC_4H_8)\{[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]\}(\eta^2\text{-}MeC_2Me)\}][BPh_4]\cdot CH_2Cl_2$ (**15**)	brown	57	64.6 (64.3)	5.1 (4.8)	0.6 (0.7)
$[W(CO)(S_2CNC_4H_8)(2,2'\text{-}bpy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**16**)	red	90	59.7 (59.5)	4.8 (4.8)	4.6 (4.7)
$[W(CO)(S_2CNC_4H_8)(1,10\text{-}phen)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**17**)	red	87	59.9 (60.6)	4.8 (4.6)	2.8 (4.6)
$[W(CO)(S_2CNMe_2)(2,2'\text{-}bpy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**18**)	red	80	58.2 (58.6)	5.0 (4.7)	4.8 (4.9)
$[W(CO)(S_2CNEt_2)(2,2'\text{-}bpy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**19**)	red	81	59.0 (59.4)	4.7 (4.8)	3.7 (4.1)
$[W(CO)\{S_2CN(CH_2Ph)_2\}(2,2'\text{-}bpy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**20**)	red	77	62.9 (64.0)	4.2 (4.6)	2.8 (3.2)
$[W(CO)(S_2COEt)(2,2'\text{-}bpy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (**21**)	red	78	59.9 (60.6)	4.2 (4.6)	2.8 (3.2)

[a] Calculated values in parentheses.

Table II. Infrared Data[a] for the Complexes $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ and Derivatives

compd	$\nu(N{\equiv}C)$, cm^{-1}	$\nu(C{\equiv}O)$, cm^{-1}	$\nu(C{\equiv}C)$, cm^{-1}
1	2325 (m) 2300 (m)	2080 (s)	1850 (w)
2	2330 (m) 2295 (m)	2075 (s)	1820 (w)
3	2320 (m) 2275 (m)	2075 (s)	1830 (w)
4	2325 (m) 2280 (m)	2075 (s)	1825 (w)
5	2340 (m) 2295 (m)	2060 (s)	1835 (w)
6		2085 (s)	1845 (w)
7		2200 (s)[b]	1820 (w)
8		1958 (s)	1830 (w)
9		1938 (s)	
10		1932 (s)	
11		1925 (s)	
12		1920 (s)	
13		1920 (s)	
14		1922 (s)	
15		1935 (s)	
16		1935 (s)	
17		1937 (s)	
18		1932 (s)	
19		1930 (s)	
20		1933 (s)	
21		1930 (s)	

[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates. [b] $\nu(C{\equiv}N)$ stretching band.

Results and Discussion

Equimolar quantities of $[WI(CO)(S_2CX)(\eta^2\text{-}MeC_2Me)_2]$ (X = NC_4H_8, NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt) and Na[BPh$_4$] react in acetonitrile at room temperature to afford the cationic bis(but-2-yne) complexes $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (**1–5**) in high yield (eq 1).

$$[WI(CO)(S_2CX)(\eta^2\text{-}MeC_2Me)_2] + Na[BPh_4] \xrightarrow{NCMe} [W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4] + NaI\downarrow \quad (1)$$

All the complexes **1–5** have been characterized by elemental analysis (C, H, and N; Table I), IR (Table II), and ^1H and in selected cases ^{13}C NMR spectroscopy (Tables III and IV). The compounds **1–5** are soluble in CH_2Cl_2, $CHCl_3$, NCMe, and CH_3COCH_3 but are totally insoluble in diethyl ether and hydrocarbon solvents. Complexes **1–5** are all relatively stable in the solid state when stored under nitrogen, but they readily decompose when exposed to air in solution.

The infrared spectra for compounds **1–5** all show an asymmetric doublet around 2300 cm^{-1}, which can be ascribed to a coordinated acetonitrile ligand. The increased ν(CN) value when the acetonitrile is coordinated to the tungsten can be attributed to coupling of the C–N bond to the N–metal stretching vibrations and to an increased C–N force constant which suggests that the acetonitrile is acting as a pure σ-donor.[15] Each of the compounds **1–5** show, as expected, a strong single carbonyl band around 2080 cm^{-1}, which is slightly higher than for the neutral monoiodo compounds $[WI(CO)(S_2CX)(\eta^2\text{-}MeC_2Me)_2]$.[11]

Molecular Structure of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (1). The structure consists of discrete units of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]^+$ cations and $[BPh_4]^-$ anions. The cation is displayed in Figure 1 together with the atomic numbering scheme. The geometry is best described as a distorted octahedron, with the carbon monoxide (W–C(100) = 1.92 (3)) trans to the ligated acetonitrile (W–N(11) = 2.10 (2) Å). The two sulfur atoms of the pyrrolidine dithiocarbamate ligand (W–S(1) = 2.576 (11), 2.505 (10) Å) and the two *cis*-but-2-yne ligands (W–C(82) = 2.34 (3), W–C(83) = 2.04 (3), W–C(92) = 1.92 (4), W–C(93) = 2.22 (4) Å) occupy the four equatorial positions. It is not clear whether these distances are significantly different, given the poor quality of the data. The alkyne C≡C vectors are parallel to the W–(CO) axis. This is a common feature of d^4 alkyne complexes of Mo(II) and W(II), since it allows maximum overlap by both π-orbital systems on the coordinated alkyne and the available metal orbitals, which optimizes both π-donor and π-acceptor properties of the bound alkynes. The geometric arrangement can be related to that of $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$,[11] where the tungsten atom is also in an octahedral environment.

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[15] Ford, P. C.; Clarke, R. E. *Chem. Commun.* **1968**, 1109.

Table III. ^{1}H NMR Data[a] for the Complexes $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ and Derivatives

compd	δ, ppm
1	7.45–6.85 (m, 20 H, Ph *H*); 3.92 (t, 2 H, NCH_2, J_{H-H} = 6.24 Hz);3.61 (t, 2 H, NCH_2, 6.27 Hz); 3.02, 2.98, 2.94, 2.85 (4 s, 12 H, ≡C*Me*); 2.07 (s, 3 H, NC*Me*); 1.99 (bm, 4 H, CH_2)
2	7.45–6.87 (m, 20 H, Ph *H*); 3.15 (s, 3 H, N*Me*); 3.11 (s, 3 H, N*Me*); 3.08, 2.88, 2.82 (3 s, 12 H, ≡C*Me*); 1.98 (s, 3 H, NC*Me*)
3	7.43–6.86 (m, 20 H, Ph *H*); 3.82 (bm, 2 H, NCH_2); 3.38 (bm, 2 H, NCH_2); 3.05, 2.92, 2.86, 2.72 (4 s, 12 H, ≡C*Me*); 1.99 (s, 3 H, NC*Me*); 1.35 (bm, 6 H, CH_3)
4	7.85–6.85 (m, 30 H, Ph *H*); 5.01 (s, 2 H, NCH_2); 4.63 (s, 2 H, NCH_2); 2.95 (s, 6 H, ≡C*Me*); 2.87 (s, 6 H, ≡C*Me*); 2.01 (s, 3 H, NC*Me*)
5	7.57–6.85 (m, 20 H, Ph *H*); 4.65 (q, 2 H, OCH_2, J_{H-H} = 7.12 Hz); 2.99 (d, 3 H, ≡C*Me*, J_{H-H} = 0.97 Hz); 2.84 (d, 3 H, ≡C*Me*, J_{H-H} = 0.97 Hz); 2.82 (d, 3 H, ≡C*Me*, J_{H-H} = 0.73 Hz); 2.72 (d, 3 H, ≡C*Me*, J_{H-H} = 0.74 Hz); 2.0 (s, 3 H, NC*Me*); 1.49 (t, 3 H, CH_3, J_{H-H} = 7.12 Hz)
6	7.6–6.92 (m, 20 H, Ph *H*); 3.32 (t, 4 H, NCH_2, J_{H-H} = 6.4 Hz); 2.88 (s, 12 H, ≡CMe); 2.01 (t, 4 H, CH_2, J_{H-H} = 6.3 Hz)
7	7.49–6.85 (m, 20 H, Ph *H*); 3.43 (t, 4 H, NCH_2, J_{H-H} = 6.25 Hz); 2.88 (s, 12 H, ≡C*Me*); 1.85 (qt, 4 H, NCH_2, J_{H-H} = 3.2 Hz); 1.65 (s, 18 H, CH_3)
8	7.45–6.8 (m, 20 H, Ph *H*); 3.85 (t, 18 H, OCH_3, J_{P-H} = 12.5 Hz); 3.48 (bm, 4 H, NCH_2); 2.98 (s, 3 H, ≡C*Me*); 2.71 (s, 3 H, ≡C*Me*); 1.95 (bm, 4 H, CH_2)
9	7.35–6.85 (bm, 40 H, Ph *H*); 4.62 (bm, 2 H, PCH_2P); 3.45 (m, 4 H, NCH_2); 2.9 (s, 6 H, ≡C*Me*); 1.85 (bm, 4 H, CH_2)
10	7.5–6.85 (bm, 40 H, Ph *H*); 3.40 (m, 4 H, NCH_2); 2.7 (s, 6 H, ≡C*Me*); 1.93 (m, 4 H, *C*H_2); 1.75 (m, 4 H, *C*H_2)
11	7.85–6.85 (bm, 40 H, Ph *H*); 3.2 (m, 4 H, NCH_2); 2.68 (s, 6 H, ≡C*Me*); 2.10 (m, 4 H, PCH_2); 1.89 (bm, 4 H, CH_2); 1.6 (bm, 2 H, CH_2)
12[b]	7.75–6.8 (bm, 40 H, Ph *H*); 3.25 (m, 4 H, NCH_2); 2.65 (s, 6 H, ≡C*Me*); 2.15 (m, 4 H, PCH_2); 1.85 (m, 4 H, CH_2); 1.64 (bm, 4 H, CH_2)
13[b]	7.85–6.85 (bm, 40 H, Ph *H*); 2.85 (m, 4 H, NCH_2); 2.65 (s, 6 H, ≡C*Me*); 1.95 (m, 4 H, CH_2); 1.75 (m, 4 H, PCH_2); 1.35 (bm, 6 H, CH_2)
14[b]	7.85–6.8 (bm, 40 H, Ph *H*); 2.86 (m, 4 H, NCH_2); 2.68 (s, 6 H, ≡C*Me*); 1.85 (m, 4 H, CH_2); 1.68 (m, 4 H, PCH_2); 1.35 (bm, 8 H, CH_2)
15	7.85–6.75 (bm, 40 H, Ph *H*); 5.27 (s, 2 H, CH_2Cl$_2$); 4.65–3.95 (s, 8 H, Cp *H*); 3.05 (m, 4 H, NCH_2); 2.63 (s, 6 H, ≡C*Me*); 1.89 (m, 4 H, CH_2)
16	8.75–7.25 (bm, 28 H, Ph *H* and 2,2′-bpy *H*); 3.65 (m, 4 H, NCH_2); 3.42 (s, 6 H, ≡C*Me*); 2.25 (m, 4 H, CH_2)
17	8.8–6.8 (bm, 28 H, Ph *H* + 1,10-phen *H*); 3.95 (m, 4 H, NCH_2); 3.45 (s, 6 H, ≡C*Me*); 2.15 (m, 4 H, CH_2)
18	9.45–6.81 (bm, 28 H, Ph *H* and 2,2′-bpy *H*); 3.42 (s, 6 H, ≡C*Me*); 3.15 (s, 3 H, NCH_3); 3.08 (s, 3 H, NCH_3)
19	9.45–6.75 (bm, 28 H, Ph *H* and 2,2′-bpy *H*); 3.65 (bm, 4 H, NCH_2); 3.45 (s, 6 H, ≡C*Me*); 1.23 (bm, 6 H, CH_3)
20	9.46–6.75 (bm, 38 H, Ph *H* and 2,2′-bpy *H*); 5.23 (s, 2 H, NCH_2); 4.92 (s, 2 H, NCH_2); 3.55 (s, 6 H, ≡C*Me*)
21	9.47–6.75 (bm, 28 H, Ph *H* and 2,2′-bpy *H*); 4.73 (q, 2 H, OCH_2, J_{H-H} = 7.32 Hz); 3.48 (s, 6 H, ≡C*Me*); 1.52 (t, 3 H, CH_3, J_{H-H} = 7.32 Hz)

[a] Spectra recorded in CDCl$_3$ (+25 °C) and referenced to SiMe$_4$. Abbreviations: s = singlet; m = multiplet; t = triplet; q = quartet; qt = quintet. [b] Recorded in CD$_2$Cl$_2$ on a Bruker WH 400-MHz NMR spectrometer (University of Warwick).

Table IV. Selected ^{13}C NMR Data[a] for the Complexes $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ and Derivatives

compd	δ, ppm
1	207.41 (s, *C*≡O); 193.09 (s, *C*S$_2$); 183.4, 174.9, 173.8, 162.89 (4 s, *C*≡*C*); 165.44, 164.65, 163.89, 163.11 (q, B–*C*, J_{B-C} = 49.5 Hz); 136.17, 125.82, 121.88 (3 s, Ph *C*); 126.81 (s, N*C*Me); 50.58 (s, N*C*H$_2$); 50.33 (s, N*C*H$_2$); 24.93 (s, *C*H$_2$); 24.60 (s, *C*H$_2$); 19.16, 19.13, 18.3, 17.05 (4 s, ≡C*Me*); 4.05 (s, NC*Me*)
2	209.92 (s, *C*≡O); 195.4 (s, *C*S$_2$); 183.5, 178.89, 174.2 (3 s, *C*≡*C*); 165.43, 164.65, 163.87, 163.08 (q, B–*C*, J_{B-C} = 49.5 Hz); 136.2, 125.8, 121.89 (3 s, Ph *C*); 126.6 (s, N*C*Me); 39.44 (s, N*Me*); 39.22 (s, N*Me*); 20.50, 18.78, 17.12 (3 s, ≡C*Me*); 3.36 (s, NC*Me*)
6	238.13 (s, *C*≡O); 182.53 (s, *C*≡*C*); 165.13, 164.34, 163.55, 162.79 (q, B–*C*, J_{B-C} = 49.5 Hz); 136.33, 125.32, 121.42 (m, Ph *C*); 50.46 (s, N*C*H$_2$); 24.9 (s, *C*H$_2$); 18.83 (s, ≡C*Me*)
7	195.57 (s, *C*S$_2$); 169.71 (s, *C*≡*C*); 165.4, 164.6, 163.8, 163.05 (q, B–*C*, J_{B-C} = 49.5 Hz); 136.25, 125.35, 121.42 (3 s, Ph-*C*); 59.3 (s, *C*NCH$_3$); 50.96 (s, N*C*H$_2$); 30.53 (*C*NCH$_3$); 24.99 (s, *C*H$_2$); 18.61 (s, ≡C*Me*)
9	223.74 (s, *C*≡*C*); 206.5 (s, *C*≡O); 202.3 (s, *C*S$_2$); 165.42, 164.84, 163.85, 163.07 (q, B–*C*, J_{B-C} = 49.5); 136.3–125.7 (m, Ph *C*); 50.96 (s, N*C*H$_2$); 49.9 (s, N*C*H$_2$); 30.43 (t, P*C*H$_2$P, J_{P-C} = 13.1 Hz); 24.8 (s, *C*H$_2$); 24.4 (s, *C*H$_2$); 19.6 (s, ≡C*Me*)
10	220.7 (s, *C*≡*C*); 208.7 (s, *C*≡O); 203.5 (s, *C*S$_2$); 165.42, 164.3, 163.84, 163.06 (q, B–*C*, J_{B-C} = 49.5 Hz); 136.22, 125.8, 121.9 (3 s, BPh$_4$ *C*); 136.3–125.9 (m, Ph *C*); 50.5 (N*C*H$_2$); 49.6 (s, N*C*H$_2$); 28.84 (d, P*C*H$_2$, J_{P-C} = 13 Hz); 28.29 (d, P*C*H$_2$, J_{P-C} = 12.8 Hz); 24.61 (s, *C*H$_2$); 24.35 (s, *C*H$_2$); 19.76 (s, ≡C*Me*)
11	219.9 (s, *C*≡*C*); 207.6 (s, *C*≡O); 203.1 (s, *C*S$_2$); 165.4, 164.28; 163.82, 163.03 (q, B–*C*, J_{B-C} = 49.5 Hz); 136.3, 125.8, 121.7 (3 s, BPh$_4$ *C*); 137.08–124.5 (m, Ph *C*); 50.4 (s, N*C*H$_2$); 49.3 (s, N*C*H$_2$); 29.6 (m, P*C*H$_2$, *C*H$_2$); 24.61 (s, *C*H$_2$); 24.16 (s, *C*H$_2$); 19.99 (s, ≡C*Me*)
13[b]	225.72 (s, *C*≡*C*); 212.42 (s, *C*≡O); 198.16 (s, *C*S$_2$); 165.03, 164.54, 164.05, 163.56 (q, B–*C*, J_{B-C} = 49.5 Hz); 136.18, 125.79, 121.89 (3 s, BPh$_4$ *C*); 133.49–127.6 (m, Ph *C*); 50.17 (s, N*C*H$_2$); 49.46 (s, N*C*H$_2$); 32.47–28.99 and 24.82–21.9 (m, P*C*H$_2$ and *C*H$_2$); 21.30 (s, ≡C*Me*)
14	225.85 (s, *C*≡*C*); 212.42 (s, *C*≡O); 198.30 (s, *C*S$_2$); 165.03, 164.54, 164.04, 163.55 (q, B–*C*, J_{B-C} = 49.5 Hz); 136.17, 125.77, 121.88 (3 s, BPh$_4$ *C*); 134.29–127.32 (m, Ph *C*); 50.13 (s, N*C*H$_2$); 49.4 (s, N*C*H$_2$); 30.53–21.29 (m, *C*H$_2$ and ≡C*Me*)
16	218.9 (s, *C*≡*C*); 209.9 (s, *C*≡O); 203.3 (s, *C*S$_2$); 165.36, 164.58, 163.80, 163.02 (q, B–*C*, J_{B-C} = 49.5 Hz); 153.14, 153.0, 151.2, 148.42, 141.72, 140.13, 127.4, 126.2, 125.1, 124.5 (m, bpy *C*); 136.21, 125.77, 122.0 (3 s, BPh$_4$ *C*); 51.87 (s, N*C*H$_2$); 50.5 (s, N*C*H$_2$); 24.93 (s, *C*H$_2$); 24.77 (s, *C*H$_2$); 22.3 (s, ≡C*Me*)

[a] Spectra recorded in CDCl$_3$ (+25 °C) and referenced to SiMe$_4$. Abbreviations: s = singlet; m = multiplet; q = quartet. [b] Recorded in CD$_2$Cl$_2$ on a Bruker WH 400-MHz NMR spectrometer (University of Warwick).

However, in that compound the carbonyl group is trans to one of the sulfur atoms of the pyrrolidine dithiocarbamate ligand and the two *cis*-but-2-yne ligands are trans to the other sulfur atom and the iodide.

The tungsten to alkyne contact carbon bond lengths are in the expected range[2] for "three-electron"-donor alkynes. The bend-back angles β[16] of the coordinated but-2-yne ligands are not all equivalent but are within the expected range[2] (β: C(81)–C(82)–C(83) = 32.5°; C(82)–C(83)–C(84) = 48.8°; C(91)–C(92)–C(93) = 43.9°, C(92)–C(93)–C(94) = 32.3°). The equatorial plane containing atoms W, S(1), S(2), CM(8), and CM(9) (CM(8) and CM(9) are the midpoints of the two central but-2-yne bonds) is planar with a maximum deviation of 0.08 Å. The remaining dimensions are as expected, given the large standard deviations obtained from a weakly diffracting crystal. There are no intermolecular distances less than the sum of van der Waals radii between the ions.

^{1}H and ^{13}C NMR Spectroscopic Studies of $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (1–5). The ^{1}H NMR spectrum for **1** shows four but-2-yne methyl singlets at room temperature, which suggests the presence of the asymmetric isomer at room temperature as shown in Figure 2, which is also the geometry displayed by [WI(CO)-

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(16) Davies, B. W.; Payne, N. C. *Inorg. Chem.* **1974**, *13*, 1848.

Table V. Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
W(1)	1633 (1)	1157 (0)	280 (1)
C(100)	1424 (26)	717 (11)	−1129 (32)
O(100)	1295 (22)	541 (9)	−2106 (28)
S(1)	2944 (8)	460 (3)	1323 (9)
S(2)	3511 (7)	1311 (3)	129 (8)
C(3)	3860 (31)	815 (13)	872 (34)
N(3)	4898 (18)	638 (7)	1274 (19)
C(4)	5266 (32)	184 (13)	2046 (36)
C(5)	6536 (44)	283 (19)	2170 (49)
C(6)	6830 (38)	574 (16)	1321 (45)
C(7)	5846 (21)	905 (9)	866 (24)
N(11)	2277 (17)	1552 (8)	2021 (21)
C(12)	2595 (29)	1710 (13)	2939 (37)
C(13)	2945 (33)	1945 (14)	4143 (36)
C(81)	177 (26)	982 (11)	2384 (32)
C(82)	301 (22)	931 (9)	1252 (27)
C(83)	190 (24)	818 (10)	139 (29)
C(84)	−784 (31)	525 (12)	−926 (31)
C(91)	1460 (42)	2356 (19)	271 (46)
C(92)	1294 (29)	1835 (13)	−259 (37)
C(93)	881 (29)	1644 (12)	−1339 (36)
C(94)	299 (36)	1697 (16)	−2652 (39)
B(11)	6404 (33)	1528 (15)	5989 (38)
C(41)	5935 (14)	1941 (6)	4948 (16)
C(42)	5641 (14)	1802 (6)	3688 (16)
C(43)	5108 (14)	2143 (6)	2777 (16)
C(44)	4869 (14)	2622 (6)	3125 (16)
C(45)	5162 (14)	2761 (6)	4385 (16)
C(46)	5695 (14)	2402 (6)	5296 (16)
C(31)	7237 (14)	1131 (7)	5558 (19)
C(32)	7868 (14)	1331 (7)	4837 (19)
C(33)	8678 (14)	1042 (7)	4573 (19)
C(34)	8857 (14)	553 (7)	5030 (19)
C(35)	8225 (14)	353 (7)	5751 (19)
C(36)	7415 (14)	642 (7)	6015 (19)
C(21)	7114 (16)	1741 (8)	7255 (17)
C(22)	7746 (16)	2166 (8)	7271 (17)
C(23)	8465 (16)	2321 (8)	8387 (17)
C(24)	8555 (16)	2050 (8)	9487 (17)
C(25)	7924 (16)	1624 (8)	9470 (17)
C(26)	7204 (16)	1470 (8)	8354 (17)
C(51)	5321 (15)	1209 (9)	6051 (22)
C(52)	4744 (15)	1400 (9)	6845 (22)
C(53)	3714 (15)	1221 (9)	6763 (22)
C(54)	3261 (15)	852 (9)	5888 (22)
C(55)	3838 (15)	662 (9)	5094 (22)
C(56)	4868 (15)	840 (9)	5176 (22)

Table VI. Bond Distances (Å) and Angles (deg) in the Tungsten Coordination Sphere

W(1)–S(1)	2.570 (9)	W(1)–C(82)	2.34 (3)
W(1)–S(2)	2.516 (9)	W(1)–C(83)	2.04 (3)
W(1)–C(100)	1.91 (3)	W(1)–C(92)	1.92 (4)
W(1)–N(11)	2.16 (2)	W(1)–C(93)	2.22 (4)
C(100)–W(1)–S(1)	81.7 (9)	C(82)–W(1)–C(83)	31.9 (9)
C(100)–W(1)–S(2)	88.4 (10)	C(100)–W(1)–C(92)	110.7 (14)
S(1)–W(1)–S(2)	67.4 (3)	S(1)–W(1)–C(92)	152.8 (11)
C(100)–W(1)–N(11)	164.7 (11)	S(2)–W(1)–C(92)	88.2 (10)
S(1)–W(1)–N(11)	84.4 (5)	N(11)–W(1)–C(92)	79.6 (12)
S(2)–W(1)–N(11)	80.4 (6)	C(82)–W(1)–C(92)	104.5 (12)
C(100)–W(1)–C(82)	105.1 (11)	C(83)–W(1)–C(92)	105.4 (13)
S(1)–W(1)–C(82)	94.9 (6)	C(100)–W(1)–C(93)	76.3 (13)
S(2)–W(1)–C(82)	156.4 (6)	S(1)–W(1)–C(93)	151.6 (9)
N(11)–W(1)–C(82)	82.4 (8)	S(2)–W(1)–C(93)	94.0 (9)
C(100)–W(1)–C(83)	75.1 (13)	N(11)–W(1)–C(93)	114.6 (10)
S(1)–W(1)–C(83)	101.2 (7)	C(82)–W(1)–C(93)	107.9 (11)
S(2)–W(1)–C(83)	161.4 (8)	C(83)–W(1)–C(93)	90.3 (12)
N(11)–W(1)–C(83)	114.1 (10)	C(92)–W(1)–C(93)	35.1 (12)

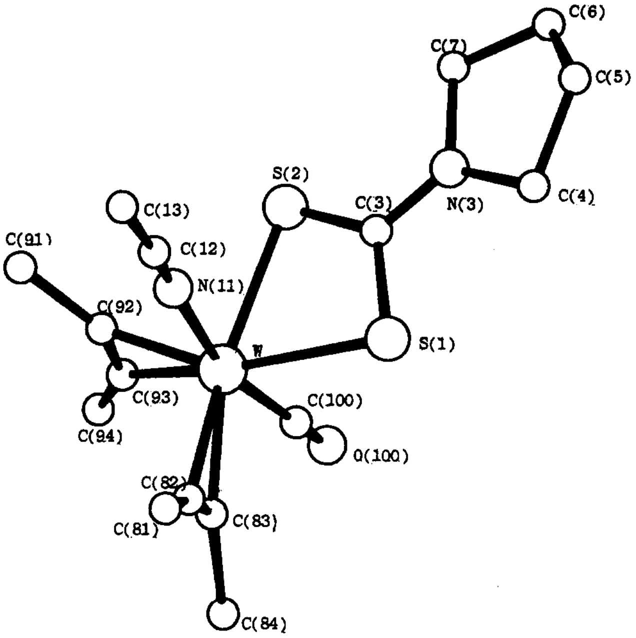

Figure 1. Molecular structure of the cation of **1**, [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$]. Ellipsoids are shown at 50% probability.

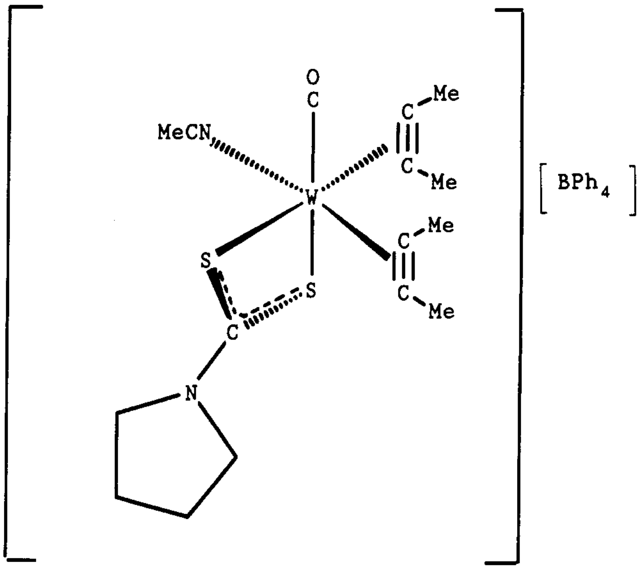

Figure 2. Proposed solution-state geometry for **1**.

($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$].[11] It should also be noted that complex **5** shows four but-2-yne methyl resonances.

The ^{13}C NMR spectra for **1** and **2** show the expected features in solution for fluxional complexes in solution. The alkyne contact carbon resonances at 183.4, 174.9, 173.8, and 162.89 ppm (C≡C) for **1** suggest[17] the two but-2-yne ligands are donating a total of six electrons to the metal, which would allow **1**–**5** to obey the effective atomic number rule. The quartet around 164 ppm (J_{B-C} = 49.5 Hz) for complexes **1**–**5** confirms the presence of the $[BPh_4]^-$ counteranion.

Reactions of [W(CO)(NCMe)($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (1) with CO, CNBu^t, and P(OMe)$_3$. Reaction of **1** with carbon monoxide gave the acetonitrile-replaced compound [W(CO)$_2$($S_2CNC_4H_8$)(η^2-MeC_2Me)$_2$][BPh_4] (**6**) in 83% yield. Compound **6** shows a single carbonyl band (ν(C≡O) = 2085 cm^{-1}) in the IR spectrum, which suggests the *trans*-dicarbonyl structure shown in Figure 3. The ^1H and ^{13}C NMR spectra for **6** support the structure shown in Figure 3. The ^1H NMR spectrum shows a single but-2-yne methyl resonance at δ

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[17] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

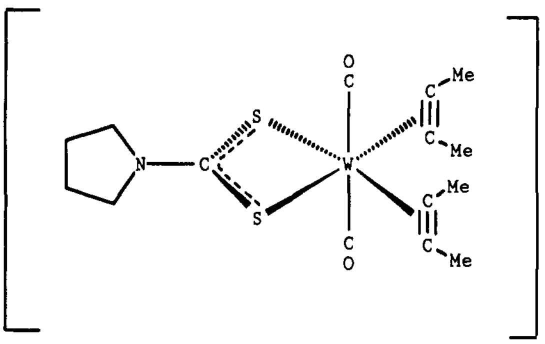

Figure 3. Proposed structure for $[W(CO)_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (6).

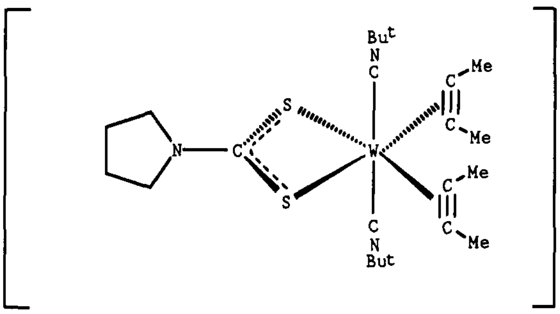

Figure 4. Proposed structure for $[W(CNBu^t)_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (7).

2.88 ppm, and the ^{13}C NMR spectrum shows a single alkyne contact carbon resonance at δ 182.53 ppm. The ^{13}C NMR alkyne contact carbon resonance at δ 182.53 ppm also indicates[17] that the two but-2-yne ligands are donating a total of six electrons to the tungsten in this complex.

Several unsuccessful attempts were made to obtain the 1:1 adducts of 1 with $CNBu^t$ and $P(OMe)_3$. For example, reaction of 1 with an equimolar quantity of $P(OMe)_3$ in CH_2Cl_2 at room temperature showed two $\nu(C{\equiv}O)$ bands at 2080 and 1958 cm^{-1} in the IR spectrum due to 1 and $[W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (8). After 2 h the two carbonyl bands became equally intense and the spectrum did not alter over the following 6 h, suggesting the reaction had gone to completion.

A 2-equiv amount of both $CNBu^t$ and $P(OMe)_3$ reacts with 1 in CH_2Cl_2 at room temperature to afford $[W(CNBu^t)_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (7) and $[W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (8), respectively. Complexes 6–8 have all been characterized by elemental analysis (Table I), IR (Table II), and ^1H and, for 6 and 7, ^{13}C NMR spectroscopy (Tables III and IV). It is interesting to note that reaction of 1 with 2 equiv of $CNBu^t$ gave the product $[W(CNBu^t)_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ via displacement of acetonitrile and carbon monoxide ligands, which is in contrast to reaction with 2 $P(OMe)_3$, which gives the product $[W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)][BPh_4]$ by displacement of acetonitrile and a but-2-yne group. The ^1H NMR spectrum for 7 shows a broad triplet (due to second-order effects) for the NCH_2 protons of the pyrrolidine ring, a single but-2-yne methyl resonance at δ 2.88 ppm, and a quintet at δ 1.85 (J_{H-H} = 3.2 Hz) for the other protons (CH_2) in the pyrrolidine ring. These results suggest the most likely structure for 7 is the symmetric structure shown in Figure 4 with trans-$CNBu^t$ groups. The ^{13}C NMR spectrum shows the expected features for the symmetrical structure displayed in Figure 4. The single alkyne contact carbon resonance at δ 169.71 suggests[17] both the but-2-yne ligands are donating a total of six electrons to the metal, which allows 7 to obey the effective atomic number rule. Reactions of 1 with 3 equiv of $CNBu^t$ in refluxing CH_2Cl_2 gave only 7 and unreacted $CNBu^t$.

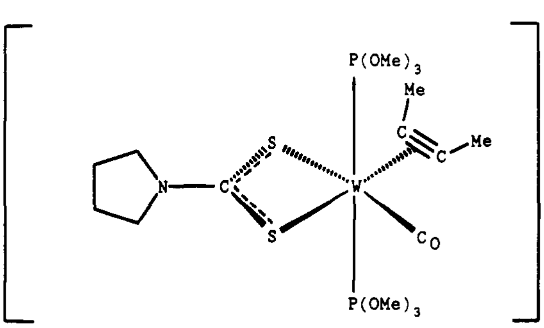

Figure 5. Proposed structure for $[W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (8).

The blue complex $[W(CO)\{P(OMe)_3\}_2(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)][BPh_4]$ has, as expected, one carbonyl band in the IR spectrum at 1958 cm^{-1}. It also shows a but-2-yne stretching band at $\nu(C{\equiv}C)$ 1830 cm^{-1} (i.e. lower than that of "free" but-2-yne, due to back-donation of electron density from filled metal orbitals into empty π^* orbitals on the but-2-yne ligand). The simple triplet ^1H NMR spectrum of 8 for the methyl groups of the two $P(OMe)_3$ ligands suggests a trans-phosphite structure as shown in Figure 5. Templeton and co-workers[18] have shown by X-ray crystallography that the bis(phosphine) complex $[MoBr_2(CO)(PEt_3)_2(\eta^2\text{-}PhC_2H)]$ has a trans-phosphine structure, and the steric bulk of the $P(OMe)_3$ ligands suggests the structure shown in Figure 5.

Reactions of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (1) with 1 Equiv of Neutral Bidentate Ligands. Reaction of equimolar quantities of 1 with $L\frown L$ ($L\frown L$ = $Ph_2P(CH_2)_nPPh_2$ (n = 1–6), $[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$, 2,2′-bpy, 1,10-phen) gave reasonable yields of the highly colored acetonitrile- and but-2-yne-displaced products $[W(CO)(S_2CNC_4H_8)(L\frown L)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (9–17). The reaction of 2,2′-bpy with an equimolar amount of $[W(CO)(NCMe)(S_2CX)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt) gave the new complexes $[W(CO)(S_2CX)(2,2'\text{-}bpy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ (18–21). The complexes 9–21 were characterized by elemental analyses (C, H, and N; Table I), infrared spectroscopy (Table II), ^1H NMR (Table III), and in selected cases ^{13}C NMR spectroscopy (Table IV). The compound $[W(CO)(S_2CNC_4H_8)\{[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]\}(\eta^2\text{-}MeC_2Me)][BPh_4]\cdot CH_2Cl_2$ (15) was confirmed as a CH_2Cl_2 solvate by repeated elemental analysis and ^1H NMR spectroscopy. Compound 11 has also been studied by variable-temperature ^1H NMR spectroscopy. The compounds 9–21 are all soluble in CH_2Cl_2, NCMe, and $OC(Me)_2$ but insoluble in Et_2O and hydrocarbon solvents. The complexes are stable in the solid state when stored under nitrogen for prolonged periods of time; however, they slowly decompose when exposed to air in solution. It should be noted that we have previously reported the synthesis of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$[19] and described its reactions with $L\frown L$ ($L\frown L$ = $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2), $Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, 2,2′-bpy, 1,10-phen, 5,6-Me_2-1,10-phen, S_2CPCy_3) to give $[W(CO)(S_2CNC_4H_8)(L\frown L)(\eta^2\text{-}$

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(18) Winston, P. B.; Burgmayer, S. J. N.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1986**, *5*, 1707.

(19) Baker, P. K.; Flower, K. R.; Harman, M. E.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 3169.

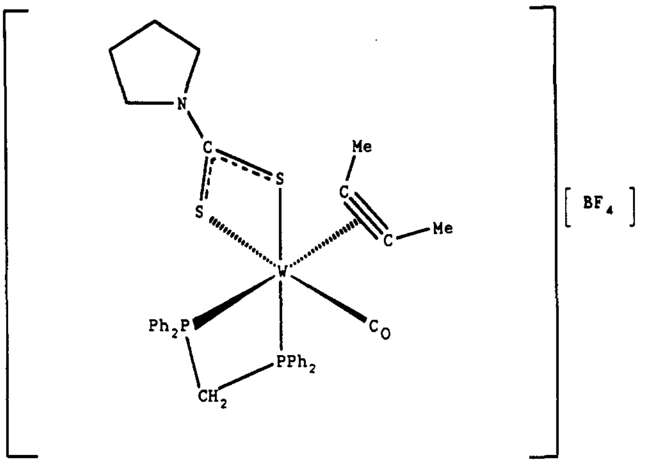

Figure 6. Structure for $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)PPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$.

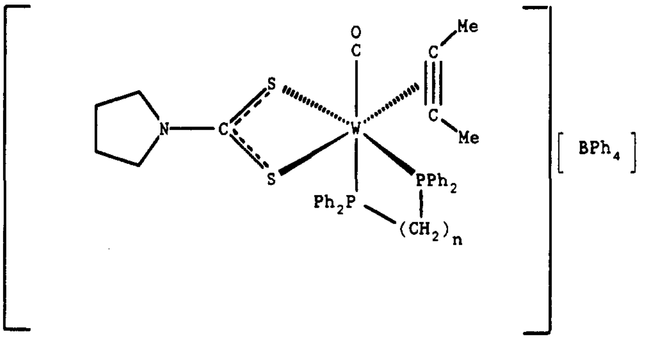

Figure 7. Proposed structure for the complexes $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (n = 4–6; 12–14).

$MeC_2Me)][BF_4]$. The $[BF_4]^-$ complex is very much less stable compared to the $[BPh_4]^-$ compound **1** described herein; however, the X-ray crystal structure of the dppm compound $[W(CO)(S_2CNC_4H_8)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ was determined and has the geometry shown in Figure 6. Hence, the geometries of **9–11** and **15–21** are likely to be similar; however, it is interesting to note that the color of $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (n = 1–3; **9–11**) is red whereas for n = 4–6 (complexes **12–14**) the color is blue. It may be that the sterically more crowded (n = 4–6) complexes undergo a trigonal-twist rearrangement to give the geometry shown in Figure 7. The ^1H NMR spectra for **9–21** all show the expected features for the geometries proposed in Figures 6 and 7. The but-2-yne methyl resonances for compounds **9-11** and **16–21** all show a single methyl group resonance which suggests the coordinated but-2-yne is undergoing rapid propeller-like rotation at room temperature. Varible-temperature ^1H NMR spectroscopy was carried out on complex **11**, and the barrier to but-2-yne rotation was calculated using the Gutowsky–Holm equation.[20] The free energy ($\Delta G^{\ddagger}$) was calculated to be 62.8 kJ mol^{-1} (±1.0 kJ mol^{-1}) ($\Delta\nu$ = 27.5 Hz, T_c = 298 K). The barriers to but-2-yne rotation of the tetrafluoroborate compounds $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)][BF_4]$ (n = 1, 2) have been previously calculated[19] to be 49.9 (n = 1) and 55.6 (n = 2) kJ mol^{-1}. A graph of the calculated barrier to but-2-yne rotation versus the number of CH_2 groups is shown in Figure 8. The barrier to rotation increases in a linear manner with increasing "n". This might be expected from steric effects, since the addition of extra methylene groups will increase steric constraints for rotation of the but-2-yne ligand.

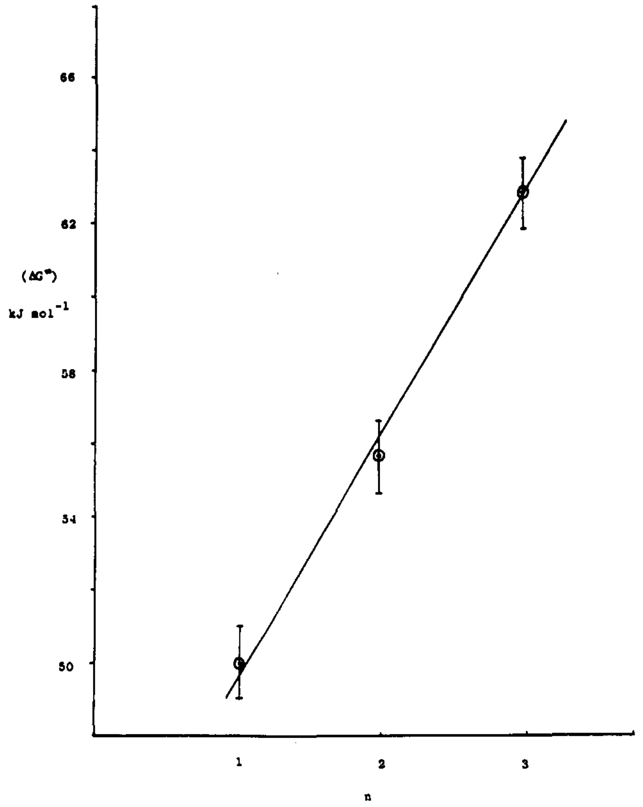

Figure 8. Graph of calculated barriers to but-2-yne rotation versus the number of CH_2 groups in the coordinated bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1–3) for the cations $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)]^+$.

The ^{13}C NMR spectra for complexes **9–21** show alkyne contact carbon resonances above 200 ppm, which indicate[17] the coordinated but-2-yne is donating four electrons to the tungsten in these compounds.

Acknowledgment. We thank the SERC for support; we also thank Dr. O. W. Howarth (University of Warwick) for recording several ^1H and ^{13}C NMR spectra for us.

Supplementary Material Available: Tables of additional bond lengths and angles, anisotropic thermal parameters, and positional parameters for the hydrogen atoms in **1** (7 pages). Ordering information is given on any current masthead page.

OM920393D

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[20] (a) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228. (b) Allerhand, A.; Gutowsky, H. S.; Jones, J.; Meinzer, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 3185.