Synthesis and Reactions of But-2-yne Complexes of Tungsten(II) containing Pyridine-2-thionate (SC_5H_4N): Crystal Structure of [W(CO)(NCMe)(SC_5H_4N)(η^2-$MeC_2Me)_2$][BPh_4]†

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The complex [WI_2(CO)(NCMe)(η^2-$MeC_2Me)_2$]·0.5CH_2Cl_2 reacted with an equimolar amount of K[SC_5H_4N] (SC_5H_4N = pyridine-2-thionate) to give [WI(CO)(SC_5H_4N)(η^2-$MeC_2Me)_2$] **1**. Two equivalents of K[SC_5H_4N] yielded the mono(but-2-yne) complex [W(CO)($SC_5H_4N)_2$(η^2-MeC_2Me)] **2**. Complex **1** reacted with a slight excess of Na[BPh_4] in acetonitrile to afford the cationic bis(but-2-yne) complex [W(CO)(NCMe)(SC_5H_4N)(η^2-$MeC_2Me)_2$][BPh_4] **3** which has been crystallographically characterised: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 19.806(21)$, $b = 13.498(13)$, $c = 15.289(13)$ Å, and $\beta = 117.4(1)°$. The structure was refined to $R = 0.064$ for 2102 reflections above background. The co-ordination geometry about the tungsten may be considered to be octahedral, with the nitrogen and sulfur atoms of the pyridine-2-thionate ligand and the two *cis* and parallel but-2-yne ligands occupying the equatorial sites with the carbonyl and acetonitrile ligands in the axial sites. The reaction chemistry of **3** with neutral mono- and bi-dentate donor ligands is discussed. The barrier to but-2-yne rotation of several of the complexes was investigated by variable-temperature ^1H NMR spectroscopy, and ^{13}C NMR spectroscopy was used to suggest the number of electrons donated by the but-2-yne ligands to the tungsten in these complexes.

A variety of alkyne complexes of molybdenum(II) and tungsten(II) containing bidentate anionic sulfur donor ligands such as dithiocarbamates have been described. For example, an early report[1] concerns the bis(diethyldithiocarbamate) molybdenum complexes [Mo(CO)($S_2CNEt_2)_2$(η^2-RC_2R')] ($R = R' =$ H, Ph or CO_2Me; R = H, R' = Me or Ph; R = Me, R' = Ph) prepared by treating the electrophilic reagent [Mo$(CO)_2$($S_2CNEt_2)_2$] with RC_2R'. More recently Templeton *et al.*[2] used [Mo$(CO)_3$($S_2CNEt_2)_2$] or [Mo(CO)($S_2CNEt_2)_2$(η^2-HC_2H)] as the organometallic reagent to react with RC_2R'. The dithiophosphinate complexes [Mo(CO)($S_2PPr^i{}_2)_2$(η^2-HC_2H)][3,4] and [Mo(CO)($S_2PPh_2)_2$(η^2-HC_2Ph)][5] have been described. The related tungsten complexes [W(CO)($S_2CNEt_2)_2$(η^2-RC_2R')] have been prepared by displacement of L = CO[6] or PPh_3[7] from [W$(CO)_2$L($S_2CNEt_2)_2$] by RC_2R'. The cyclooctyne complexes [M(CO)($S_2CNR_2)_2$(η^2-C_8H_{12})] (M = Mo or W, R = Me or Et) have also been described.[8] More recently Carlton and Davidson[9] reported the preparation of the mono(alkyne) complexes [W(CO)(L–L$')_2$(η^2-RC_2R')] [R = R' = Me; L–L' = S_2CNMe_2 or SC_5H_4N (pyridine-2-thionate); R = Ph, R' = Me, L–L' = S_2CNMe_2 or S_2PMe_2; R = R' = Ph, L–L' = S_2PMe_2] and the bis(diphenylacetylene) complex [W($SC_5H_4N)_2$(η^2-$PhC_2Ph)_2$]. The bis(but-2-yne) complexes [WBr(CO)(L–L)(η^2-$MeC_2Me)_2$][L–L = S_2CNMe_2, S_2PMe_2 or acac (acetylacetonate)] have also been reported by Davidson and Vasapollo.[10]

In 1988[11] we described the synthesis and molecular structures of the bis(alkyne) complexes [WI_2(CO)(NCMe)(η^2-$RC_2R)_2$] (R = Me or Ph). In 1990[12] we reported the reactions of [WI_2(CO)(NCMe)(η^2-$RC_2R)_2$] with an equimolar quantity of S_2CX^- [X = NMe_2, NEt_2, N($CH_2Ph)_2$, OEt, NC_4H_8 or NC_5H_{10}] to give [WI(CO)(S_2CX)(η^2-$RC_2R)_2$]. Two equivalents of S_2CX^- react with [WI_2(CO)(NCMe)(η^2-$RC_2R)_2$] to afford [W(CO)($S_2CX)_2$(η^2-RC_2R)] [R = Me, X = NMe_2, NEt_2, N($CH_2Ph)_2$, OEt, NC_4H_8, or NC_5H_{10}; R = Ph, X = NEt_2 or OEt]. Apart from Carlton and Davidson's[9] work describing the preparation and characterisation of [W(CO)($SC_5H_4N)_2$(η^2-MeC_2Me)] and [W($SC_5H_4N)_2$(η^2-$PhC_2Ph)_2$], no other alkyne complexes of tungsten(II) containing pyridine-2-thionate have been described. In this paper we describe the preparation and characterisation of a number of new neutral and cationic but-2-yne complexes of tungsten(II) containing pyridine-2-thionate as an attached ligand, including [W(CO)(NCMe)(SC_5H_4N)(η^2-$MeC_2Me)_2$][BPh_4] which was crystallographically characterised.

Results and Discussion

Equimolar quantities of [WI_2(CO)(NCMe)(η^2-$MeC_2Me)_2$]·0.5CH_2Cl_2 and K[SC_5H_4N] react in CH_2Cl_2 at room temperature to give the new bis(but-2-yne) complex [WI(CO)(SC_5H_4N)(η^2-$MeC_2Me)_2$] **1** in good yield. Two equivalents of K[SC_5H_4N] react under the same conditions to afford the bis(pyridine-2-thionate) complex [W(CO)($SC_5H_4N)_2$(η^2-MeC_2Me)] **2**. Reaction of **1** with a slight excess of Na[BPh_4] in acetonitrile at room temperature gave the cationic iodide-displaced product [W(CO)(NCMe)(SC_5H_4N)(η^2-$MeC_2Me)_2$][BPh_4] **3** in good yield. Complex **3** reacts with 2 equivalents of PPh_3 in CH_2Cl_2 at room temperature to give [W(CO)($PPh_3)_2$(SC_5H_4N)(η^2-MeC_2Me)][BPh_4] **4**, or with 1 equivalent of L–L [L–L = 2,2'-bipyridine(bipy) 1,10-phenanthroline(phen), 4,7- and 5,6-dimethyl-1,10-phenanthroline (4,7- and 5,6-dmphen), $C_6H_{11}N{=}CHCH{=}NC_6H_{11}$, $S_2CP(C_6H_{11})_3$, $Ph_2P(CH_2)_nPPh_2$ (n = 1–6) or Fe(η^5-$C_5H_4PPh_2)_2$] in CH_2Cl_2 at room temperature to afford [W(CO)(L–L)(SC_5H_4N)(η^2-MeC_2Me)][BPh_4] **5**–**17** in high yield. All the complexes have been characterised by elemental analysis (C, H and N) (Table 1), infrared (Table 2), ^1H NMR (Table 3) and in selected

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Physical and analytical data * for but-2-yne complexes of tungsten(II) containing pyridine-2-thionate

Complex		Colour	Yield (%)	Analysis (%) C	H	N
1	$[WI(CO)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2]$	Green	70	29.8 (30.2)	2.9 (2.9)	2.4 (2.5)
2	$[W(CO)(SC_5H_4N)_2(\eta^2\text{-}MeC_2Me)]$	Green-brown	48	35.9 (37.0)	2.9 (2.9)	5.2 (5.8)
3	$[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$	Green	71	60.5 (60.8)	5.2 (5.0)	3.5 (3.5)
4	$[W(CO)(SC_5H_4N)(PPh_3)_2(\eta^2\text{-}MeC_2Me)][BPh_4]$	Brown	58	69.5 (68.9)	5.3 (5.0)	1.2 (1.2)
5	$[W(CO)(SC_5H_4N)(bipy)(\eta^2\text{-}MeC_2Me)][BPh_4]$	Deep red	93	62.4 (62.1)	4.8 (4.5)	4.6 (5.0)
6	$[W(CO)(SC_5H_4N)(phen)(\eta^2\text{-}MeC_2Me)][BPh_4]$	Red	63	62.9 (63.1)	4.7 (4.4)	4.6 (4.8)
7	$[W(CO)(SC_5H_4N)(4,7\text{-}dmphen)(\eta^2\text{-}MeC_2Me)][BPh_4]$	Brown-red	74	63.1 (63.8)	4.9 (4.7)	4.2 (4.7)
8	$[W(CO)(SC_5H_4N)(5,6\text{-}dmphen)(\eta^2\text{-}MeC_2Me)][BPh_4]$	Deep red	61	63.5 (63.8)	4.8 (4.7)	4.4 (4.7)
9	$[W(CO)(SC_5H_4N)(C_6H_{11}N{=}CHCH{=}NC_6H_{11})(\eta^2\text{-}MeC_2Me)][BPh_4]\cdot0.5\ CH_2Cl_2$	Red-brown	58	60.8 (60.8)	6.2 (5.8)	4.3 (4.4)
10	$[W(CO)(SC_5H_4N)\{S_2CP(C_6H_{11})_3\}(\eta^2\text{-}MeC_2Me)][BPh_4]$	Brown	51	60.5 (60.5)	6.9 (6.0)	1.3 (1.3)
11	$[W(CO)(SC_5H_4N)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)][BPh_4]$	Red	43	65.6 (65.6)	5.0 (4.9)	1.0 (1.3)
12	$[W(CO)(SC_5H_4N)\{Ph_2P(CH_2)_2PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$	Red-brown	63	65.7 (65.9)	5.2 (5.0)	1.3 (1.3)
13	$[W(CO)(SC_5H_4N)\{Ph_2P(CH_2)_3PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$	Green-brown	69	65.3 (66.1)	5.2 (5.1)	1.1 (1.3)
14	$[W(CO)(SC_5H_4N)\{Ph_2P(CH_2)_4PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$	Green-brown	69	66.9 (66.4)	5.4 (5.2)	1.1 (1.3)
15	$[W(CO)(SC_5H_4N)\{Ph_2P(CH_2)_5PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]\cdot0.5CH_2Cl_2$	Green-brown	59	64.8 (64.7)	5.5 (5.1)	1.1 (1.2)
16	$[W(CO)(SC_5H_4N)\{Ph_2P(CH_2)_6PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$	Green-brown	72	66.7 (66.9)	5.8 (5.4)	1.1 (1.2)
17	$[W(CO)(SC_5H_4N)\{Fe(\eta^5\text{-}C_5H_4PPh_2)_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$	Brown-orange	66	65.1 (65.4)	4.8 (4.7)	1.0 (1.1)

* Calculated values in parentheses.

Table 2 Infrared data* (cm^{-1}) for but-2-yne complexes of tungsten(II) containing pyridine-2-thionate

Complex	ν(C≡N)	ν(C≡O)	ν(C≡C)
1	—	2040s	1838vw
2	—	1906s	1694w
3	2326w 2298w	2070s	1875w
4	—	1945s	1682w
5	—	1934s	1712vw
6	—	1936s	1712vw
7	—	1934s	1706w
8	—	1932s	1707vw
9	—	1907w	1717vw
10	—	1906m	1700vw
11	—	1942m	1694vw
12	—	1940m	1687vw
13	—	1944m	1688vw
14	—	1943m	1700vw
15	—	1936m	1662vw
16	—	1937s	1662vw
17	—	1940s	1700vw

* Spectra recorded as thin films in $CHCl_3$ between NaCl plates; v = very, w = weak, m = medium, s = strong.

cases ^{13}C NMR spectroscopy (Table 4). The cationic complex $[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ **3** was also characterised by X-ray crystallography. The complexes $[W(CO)(C_6H_{11}N{=}CHCH{=}NC_6H_{11})(SC_5H_4N)(\eta^2\text{-}MeC_2Me)][BPh_4]\cdot0.5CH_2Cl_2$ **9** and $[W(CO)(SC_5H_4N)\{Ph_2P(CH_2)_5PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]\cdot0.5CH_2Cl_2$ **15** were confirmed as 0.5 CH_2Cl_2 solvates by repeated elemental analyses and ^1H NMR spectroscopy. The complexes are all soluble in polar chlorinated solvents such as $CHCl_3$ and CH_2Cl_2, with the bis(but-2-yne) complexes **1** and **3** being the most soluble. The neutral complexes **1**–**3** are all partially soluble in diethyl ether, whereas as expected the cationic complexes **4**–**17** are totally insoluble in this solvent. All the complexes are air-sensitive both in the solid state and in solution, however they can be stored under an inert atmosphere for prolonged periods.

The complex $[WI(CO)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2]$ **1** is analogous to the bis(alkyne) complexes $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ [R = Me or Ph; X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt, NC_4H_8 or NC_5H_{10}], which was crystallographically characterised[12] in the case of X = NC_4H_8. The infrared spectrum of **1** shows a carbonyl band at 2040 cm^{-1} and a weak alkyne band at 1838 cm^{-1}, which as expected, is at considerably lower wavenumber compared with unco-ordinated but-2-yne. The room-temperature ^1H NMR spectrum shows four but-2-yne methyl resonances at δ 2.87, 2.91, 2.99 and 3.00 which suggests a structure similar to that of the crystallographically determined complex $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$[12] as shown, with the sulfur of the pyridine-2-thionate being *trans* to the carbonyl ligand. The *cis* and parallel but-2-yne ligands are opposite to an iodide and the nitrogen of the pyridine-2-thionate ligand respectively and hence the four methyl groups would be expected to exhibit different resonances in the ^1H NMR spectrum. The ^{13}C NMR spectrum (Table 4) shows the expected features in accordance with the structure illustrated. Alkyne contact-carbon resonances were observed at δ 162.46, 167.79, 177.98 and 183.69. According to Templeton and Ward's[13] correlation, these values suggest that the alkynes are

Table 3 Proton NMR data (δ, J in Hz)[a] for but-2-yne complexes of tungsten(II) containing pyridine-2-thionate

Complex	
1	7.56 (d, 1 H, NCH, J_{HH} = 0.99), 7.34 (t, 1 H, NCHCHC*H*, J_{HH} = 1.19), 6.91 (d, 1 H, SCC*H*, J_{HH} = 8.40), 6.67 (t, 1 H, NCHC*H*, J_{HH} = 3.63), 3.00, 2.99, 2.91, 2.87 (4s, 12H, MeC_2)
2	8.78 [dm, 1 H, NCH, J_{HH} = 5.42), 8.58 (dm, 1 H, NCH), 7.76–6.60 (m, 6 H, NCHCHC*H*, SCCH, NCHC*H*), 3.18 (s, 6 H, MeC_2)
3	7.80–6.60 (m, 20 H, Ph; 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCC*H*; 1 H, NCHC*H*), 3.03, 2.96, 2.84, 2.81 (4 s, 12 H, MeC_2), 2.11 (s, 3 H, NCMe)
4[b]	8.69 (d, 1 H, NC*H*, J_{HH} = 5.28), 7.84–6.81 (m, 50 H, Ph, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*), 3.06, 2.69 (2 s, 6 H, MeC_2)
5	7.83–6.50 (m, 28 H, Ph and bipy, 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCC*H*, 1 H, NCHC*H*), 3.40, 3.05 (2 s, 6 H, MeC_2)
6	10.20 (d, 2 H, NCH of phen, J_{HH} = 7.14), 8.97 (dd, 2 H, NCHC*H* of phen, J_{HH} = 1.25, 10.72), 8.80 (d, 2 H, NCHCHC*H* of phen, J_{HH} = 10.71), 7.95–6.45 (br m, 20 H, Ph, 2 H, phen, 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*), 3.47, 3.16 (2 s, 6 H, MeC_2)
7	9.94 (d, 2 H, NCH of phen, J_{HH} = 7.15), 9.64 (d, 2 H, NCHC*H* of phen, J_{HH} = 7.15), 8.05–6.70 (m, 20 H, Ph, 2 H, phen, 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCC*H*, 1 H, NCHC*H*), 3.46, 3.16 (2 s, 6 H, MeC_2), 2.83 (s, 6 H, CH_3)
8	9.94 (d, 2 H, NCH of phen, J_{HH} = 5.05), 9.27 (d, 2 H, NCHC*H* of phen, J_{HH} = 3.57), 8.63 (t, 2 H, NCHCHC*H* of phen, J_{HH} = 4.88), 8.02 (d, 1 H, NCH, J_{HH} = 9.69), 7.81 (d, 1 H, NCHCHC*H*, J_{HH} = 6.37), 7.65–6.69 (m, 20 H, Ph, 1 H, SCCH, 1 H, NCHC*H*), 3.44, 3.14 (2 s, 6 H, MeC_2), 2.70 (s, 6 H, CH_3)
9	9.15 (d, 1 H, NCH, J_{HH} = 5.10), 7.55–6.88 (m, 20 H, Ph, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*); 5.21 (s, 1 H, CH_2Cl_2), 4.25–4.1 (br m, 2 H, CH), 3.07, 2.70 (2 s, 6 H, MeC_2), 1.75–0.85 (br m, 22 H, C_6H_{11})
10	9.17 (d, 1 H, NCH, J_{HH} = 5.10), 8.73 (d, 1 H, NCHCHC*H*, J_{HH} = 3.57), 8.23 (d, 1 H, SCCH, J_{HH} = 7.15), 7.80 (br s, 1 H, NCHC*H*), 7.67–6.83 (m, 20 H, Ph), 3.09, 2.74 (2 s, 6 H, MeC_2), 1.87, 1.76, 1.43, 1.38, 1.34, 1.30 (6 br s, 33 H, C_6H_{11})
11[b]	9.09 (d, 1 H, NCH, J_{HH} = 2.78), 8.86 (dd, 1 H, NCHCHC*H*, J_{HH} = 1.35, 8.21), 8.64 (dd, 1 H, SCC*H*, J_{HH} = 1.25, 8.17), 8.52 (dd, 1 H, NCHC*H*, J_{HH} = 1.62, 8.11), 8.23–6.86 (br m, 40 H, Ph), 4.60 (br m, 2 H, PCH_2P), 3.51, 3.27 (2 s, 6 H, MeC_2)
12	7.81–7.34 (m, 40 H, Ph), 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*), 3.19 (m, 4 H, PCH_2), 2.77, 2.53 (2 s, 6 H, MeC_2)
13	7.79–6.79 (m, 40 H, Ph, 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*), 3.02, 2.68 (2 s, 6 H, MeC_2), 2.53 (m, 4 H, PCH_2), 2.19–2.13 (m, 2 H, PCH_2CH_2)
14	7.80–6.83 (m, 40 H, Ph, 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*), 3.07, 2.70 (2 s, 6 H, MeC_2), 2.01 (m, 4 H, PCH_2), 1.8 (m, 4 H, PCH_2CH_2)
15	7.83–6.80 (m, 40 H, Ph, 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*), 5.25 (s, 1 H, CH_2Cl_2), 3.07, 2.98 (2 s, 6 H, MeC_2), 2.63, 2.54 (2 br s, 4 H, PCH_2), 2.03 (br m, 4 H, PCH_2CH_2), 1.85 (br m, 2 H, $PCH_2CH_2CH_2$)
16	7.85–6.79 (m, 40 H, Ph, 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*), 3.09, 2.75 (2 s, 6 H, MeC_2), 2.58 (br m, 4 H, PCH_2), 2.26–1.79 (br m, 8 H, CH_2)
17	7.80–6.83 (m, 40 H, Ph, 1 H, NCH, 1 H, NCHCHC*H*, 1 H, SCCH, 1 H, NCHC*H*), 4.27 (s, 4 H, PPh_2CCH), 4.00 (s, 4 H, PPh_2CCHCH), 3.10, 2.75 (2 s, 6 H, MeC_2)

[a] Spectra recorded in $CDCl_3$ (+25 °C) referenced to $SiMe_4$. s = Singlet, d = doublet, t = triplet, m = multiplet, br = broad. [b] Spectrum recorded in CD_3CN.

Table 4 Carbon-13 NMR data (δ, J in Hz)[a] for selected but-2-yne complexes of tungsten(II) containing pyridine-2-thionate

Complex	
1	209.83 (s, $C\equiv O$, J_{WC} = 40.24), 193.55 (s, NCS), 183.69, 177.98, 167.79, 162.46 (4 s, $C\equiv C$), 147.06 (s, NCH), 135.92 (s, NCH*C*H), 129.68 (s, SC*C*H), 117.60 (s, SCCH*C*H), 19.93, 18.22, 17.26, 15.49 (4 s, *Me*C_2)
3[b]	177.50 (s, NCS), 165.02, 164.54, 164.04, 163.56 (q, BC, J_{BC} = 49.11), 144.11 (s, NCH), 147.10, 142.00, 141.30, 139.61 (4 s, $C\equiv C$), 136.08, 125.90, 121.94 (3 s, BPh_4), 135.56 (NCH*C*H), 128.07 (s, SC*C*H), 127.54 (N*C*Me), 116.84 (s, SCCH*C*H), 21.43, 19.44, 18.77, 17.34 (4 s, *Me*C_2), 5.2 (s, NC*Me*)
4	225.40, 222.08 (2 s, $C\equiv C$), 215.60 (s, $C\equiv O$), 183.81 (s, NCS), 165.03, 164.54, 164.05, 163.56 (q, BC, J_{BC} = 49.37), 147.17 (s, NCH), 136.14, 125.82, 121.90 (3 s, BPh_4), 135.76 (s, NCH*C*H), 131.17–128.57 (m, Ph), 128.05 (s, SC*C*H), 117.25 (s, SCCH*C*H), 21.55, 18.58 (2 s, *Me*C_2)
5	230.80 (s, $C\equiv O$), 209.82, 208.96 (2 s, $C\equiv C$), 177.79 (s, NCS), 164.98, 164.49, 164.00, 163.51 (q, BC, J_{BC} = 49.30), 152.79, 152.47, 145.24, 141.70, 140.24, 140.08, 127.91, 127.41, 126.64, 124.56 (m, bipy), 148.45 (s, NCH), 136.10, 125.85, 121.98 (3 s, BPh_4), 134.85 (s, NCH*C*H), 128.04 (s, SC*C*H), 22.87, 18.39 (2 s, *Me*C_2)
6	230.20 (s, $C\equiv O$), 210.04, 209.79 (2 s, $C\equiv C$), 178.03 (s, NCS), 165.04, 164.54, 164.06, 163.56 (q, BC, J_{BC} = 49.51), 153.24, 149.54, 145.54, 141.74, 140.67, 140.02, 139.31, 130.96, 130.60, 127.91, 127.23, 126.44 (m, phen), 148.56 (s, NCH), 136.13, 125.89, 121.97 (3 s, BPh_4), 134.88 (s, NCH*C*H), 129.39–126.95 (m, Ph), 128.05 (s, SC*C*H), 117.14 (s, SCCH*C*H), 22.98, 18.63 (2 s, *Me*C_2)
10[b]	177.62 (s, NCS), 175.70 (s, CS_2), 164.96, 164.47, 163.98, 163.49 (q, BC, J_{BC} = 49.30), 143.68 (s, NCH), 136.16, 125.86, 122.03 (3 s, BPh_4), 134.89 (s, NCH*C*H), 128.48 (s, SC*C*H), 117.23 (s, SCCH*C*H), 37.22 (d, PCH, J_{PC} = 45.15), 29.87–25.17 (m, C_6H_{11}), 22.90, 18.40 (2 s, *Me*C_2)
11	226.50 (s, $C\equiv O$), 208.00, 206.50 (2 s, $C\equiv C$), 175.50 (s, NCS), 164.99, 164.51, 164.02, 163.52 (q, BC, J_{BC} = 49.28), 148.28 (s, NCH), 136.14, 125.78, 121.90 (3 s, BPh_4), 134.86 (s, NCH*C*H), 133.78–128.48 (m, Ph), 128.04 (s, SC*C*H), 117.12 (s, SCCH*C*H), 27.71 (t, PCH_2P, J_{PC} = 24.14), 20.72, 18.45 (2 s, *Me*C_2)
16[b]	170.40 (s, NCS), 165.00, 164.51, 164.02, 163.53 (q, BC, J_{BC} = 49.34), 146.78 (s, NCH), 136.14, 125.78, 121.88 (3 s, BPh_4), 134.84 (s, NCH*C*H), 132.83–128.46 (m, Ph), 128.01 (s, SC*C*H), 117.13 (s, SCCH*C*H), 30.53 (d, PCH_2, J_{PC} = 10.06), 29.84 (br s, PCH_2CH_2), 25.70 (br s, $PCH_2CH_2CH_2$), 23.57, 21.57 (2 s, *Me*C_2)
17[b]	175.80 (s, NCS), 164.99, 164.51, 164.01, 163.53 (q, BC, J_{BC} = 49.20), 148.2 (s, NCH), 136.11, 125.78, 121.87 (3 s, BPh_4), 134.86 (s, NCH*C*H), 129.33–128.03 (m, Ph), 117.11 (s, SCCH*C*H), 76.93 (d, PPh_2C, J_{PC} = 7.95), 73.89 (m, PPh_2CCH), 72.54 (s, PPh_2CCHCH), 22.88, 18.63 (2 s, *Me*C_2)

[a] Spectra recorded in CD_2Cl_2 (+25 °C) referenced to $SiMe_4$ on a Bruker WH 400 MHz NMR spectrometer. s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [b] The $C\equiv O$ and/or $C\equiv C$ resonances were not observed.

donating an average of three electrons each to the tungsten. This allows the complex to obey the effective atomic number rule.

Reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]\cdot 0.5CH_2Cl_2$ with 2 equivalents of $K[SC_5H_4N]$ in CH_2Cl_2 at room temperature affords the mono(but-2-yne) complex $[W(CO)(SC_5H_4N)_2(\eta^2\text{-}MeC_2Me)]$ **2** in modest yield. Complex **2** has very similar physical and spectroscopic properties to those of $[W(CO)(SC_5H_4N)_2(\eta^2\text{-}MeC_2Me)]$ previously described by

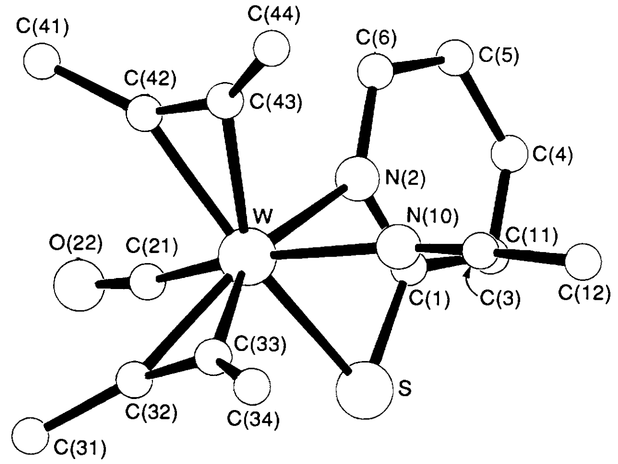
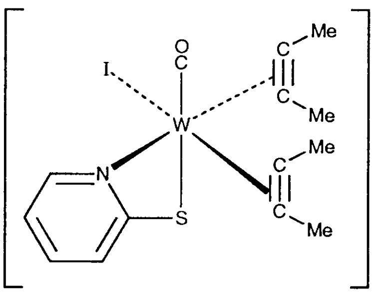


Fig. 1 Crystal structure of the cation $[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2]^+$ **3**, together with the atomic numbering scheme



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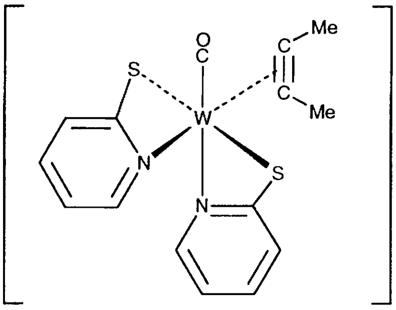

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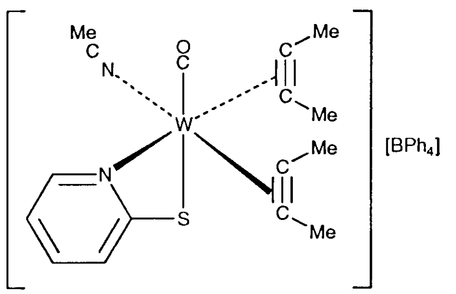
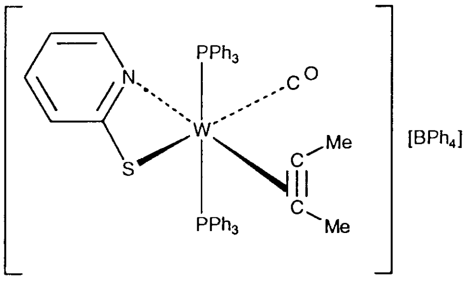


3



4

Carlton and Davidson.[9] Since the crystal structure of $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}HC_2H)]$ has been previously determined,[2] a possible structure of **2** will be similar with the carbonyl and but-2-yne ligands *cis* to each other as shown.

The cationic bis(but-2-yne) complex $[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ **3** must be formed *via* replacement of iodide by the neutral acetonitrile ligand. Complex **3** is related to the cationic bis(alkyne) molybdenum complexes $[Mo(CO)L(\eta^2\text{-}RC_2R')_2][BF_4]$ ($L = C_5H_5$ or C_9H_7; $R = R' =$ Me or Ph; $R =$ H, $R' =$ Me or Bu^t) reported by Bottrill and Green[14] in 1977 whereby the cyclopentadienyl or indenyl ligands are replaced by the acetonitrile and pyridine-2-thionate ligands in **3**. The colours of these complexes are similar. The infrared spectrum of **3** shows an asymmetric doublet at 2326 and 2298 cm^{-1} which can be ascribed to the ν(C≡N) of the co-ordinated acetonitrile. The increased ν(C≡N) when the acetonitrile is co-ordinated to the tungsten can be assigned to coupling of the C–N bond to the nitrogen–metal stretching vibrations and to an increased C–N force constant which in turn suggests that the co-ordinated acetonitrile is functioning as a pure σ donor.[15] The band at 2070 cm^{-1} is assigned to ν(C≡O) which is higher when compared with that of the neutral monoiodo compound $[WI(CO)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2]$ **1**. A weak band at about 1875 cm^{-1} is ascribed to ν(C≡C) of the co-ordinated but-2-yne ligands, and is in the expected range for this type of interaction.[16]

Single crystals of complex **3** suitable for X-ray crystallography were grown from a cooled CH_2Cl_2 solution and the molecular structure of the cation is shown in Fig. 1, together with the atomic numbering scheme. The structure contains discrete $[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2]^+$ cations and $[BPh_4]^-$ anions. The atomic coordinates and molecular dimensions in the co-ordination sphere are given in Tables 5 and 6. The tungsten atom can be considered to have a six-co-ordinate octahedral environment being bonded to the nitrogen and sulfur atoms [W-N 2.217(22), W-S 2.551(5) Å] of the pyridine-2-thionate ligand, two but-2-yne ligands [W-C 2.07(3), 2.02(2), 2.08(2), 2.05(2) Å], a carbonyl group [W-C 1.95(5) Å] and an acetonitrile [W-N 2.11(3) Å]. The dimensions in the structure are comparable with those in similar tungsten complexes. The acetonitrile and the carbonyl groups are mutually *trans* so that the two alkyne ligands and the pyridine-2-thionate ligand occupy the equatorial plane. Least-squares planes calculations show that the atoms W, S(1), N(2) together with the midpoints of the two C–C bonds are coplanar with a maximum deviation of 0.02 Å. The two MeC_2Me ligands are perpendicular to this plane intersecting at angles of 85.4 and 87.9°. This is a common feature amongst alkyne d^4 complexes of molybdenum(II) and tungsten(II) as it permits maximum overlap of both p_π-orbital systems of the co-ordinated alkyne and the available metal orbitals thereby optimising the π-donor and π-acceptor properties of bound alkynes. The tungsten to alkyne contact-carbon bond lengths are in the range[16] for three-electron donor alkynes. The bend-back angles β[17] are not equivalent [C(31)–C(32)–C(33) 34.6(8), C(32)–C(33)–C(34) 38.5(7), C(41)–C(42)–C(43) 36.4(7) and C(42)–C(43)–C(44) 32.9(8)°]. The molecular structure of the closely related pyrrolidine dithiocarbamate complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ has been previously described,[18] and has the same basic arrangement of ligands around the tungsten centre.

The room-temperature ^1H NMR spectrum of complex **3** (Table 3) shows four singlets at δ 2.81, 2.84, 2.96 and 3.03 which

Table 5 Atomic coordinates (× 10^4) with estimated standard deviations in parentheses for complex **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1423(0)	2501(2)	2731(1)	C(52)	4653(16)	2644(26)	3044(20)
C(21)	2123(18)	3172(43)	2358(22)	C(53)	4297(20)	2741(33)	3652(25)
O(22)	2317(20)	3701(25)	1907(17)	C(54)	4579(21)	3314(25)	4386(25)
S	2642(4)	2641(8)	4355(5)	C(55)	5217(21)	3845(25)	4594(21)
C(1)	2184(15)	3683(16)	4432(17)	C(56)	5590(17)	3645(19)	4025(19)
N(2)	1526(11)	3822(16)	3647(14)	C(61)	5254(14)	2435(26)	1469(16)
C(3)	2441(21)	4383(24)	5209(22)	C(62)	4545(14)	2872(17)	901(17)
C(4)	2011(19)	5100(24)	5125(27)	C(63)	4115(15)	2640(30)	−100(19)
C(5)	1362(18)	5295(17)	4353(24)	C(64)	4355(19)	1975(27)	−574(23)
C(6)	1099(15)	4651(20)	3580(21)	C(65)	5058(17)	1512(23)	−18(24)
N(10)	1024(13)	1899(17)	3678(16)	C(66)	5439(15)	1671(16)	956(16)
C(11)	850(14)	1462(18)	4201(18)	C(71)	6344(17)	3561(19)	2533(16)
C(12)	681(17)	896(22)	4892(20)	C(72)	6968(15)	3360(17)	2416(18)
C(31)	2294(17)	1348(24)	1521(20)	C(73)	7408(16)	4070(19)	2268(18)
C(32)	1838(12)	1489(18)	2082(15)	C(74)	7151(22)	5044(29)	2147(20)
C(33)	1454(13)	1034(16)	2491(14)	C(75)	6477(19)	5278(20)	2203(19)
C(34)	1178(15)	37(21)	2592(17)	C(76)	6089(17)	4502(18)	2388(15)
C(41)	463(19)	3794(22)	588(21)	C(81)	6272(15)	1792(20)	3275(20)
C(42)	600(16)	3126(19)	1438(17)	C(82)	6980(14)	1933(16)	4134(17)
C(43)	277(12)	2719(14)	1905(15)	C(83)	7345(17)	1148(20)	4773(21)
C(44)	−463(16)	2258(16)	1849(20)	C(84)	7042(19)	198(17)	4615(21)
B	5769(16)	2717(12)	2603(21)	C(85)	6390(18)	41(23)	3800(22)
C(51)	5307(16)	3004(17)	3218(17)	C(86)	6029(15)	796(24)	3184(19)

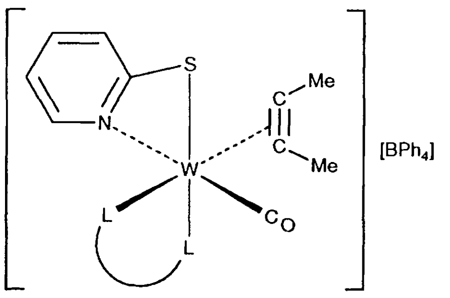
Table 6 Molecular dimensions (lengths in Å, angles in °) in the co-ordination sphere of complex **3**

W–C(21)	1.948(46)	W–C(32)	2.068(26)
W–S	2.551(5)	W–C(33)	2.021(22)
W–N(2)	2.217(22)	W–C(42)	2.077(21)
W–N(10)	2.107(29)	W–C(43)	2.049(20)
C(21)–W–S	76.6(8)	C(32)–W–C(33)	38.1(10)
C(21)–W–N(2)	86.6(16)	C(21)–W–C(42)	83.4(13)
S–W–N(2)	63.6(5)	S–W–C(42)	150.8(7)
C(21)–W–N(10)	157.5(9)	N(2)–W–C(42)	94.5(8)
S–W–N(10)	81.2(5)	N(10)–W–C(42)	115.6(11)
N(2)–W–N(10)	80.3(9)	C(32)–W–C(42)	97.0(9)
C(21)–W–C(32)	70.9(17)	C(33)–W–C(42)	107.5(8)
S–W–C(32)	96.3(5)	C(21)–W–C(43)	119.2(12)
N(2)–W–C(32)	153.2(8)	S–W–C(43)	150.8(7)
N(10)–W–C(32)	115.6(9)	N(2)–W–C(43)	91.6(7)
C(21)–W–C(33)	108.5(18)	N(10)–W–C(43)	79.6(9)
S–W–C(33)	98.9(5)	C(32)–W–C(43)	111.8(8)
N(2)–W–C(33)	154.3(8)	C(33)–W–C(43)	98.4(8)
N(10)–W–C(33)	78.4(10)	C(42)–W–C(43)	36.2(12)

may suggest the presence of an asymmetric isomer as shown which was the crystallographically found geometry for $[WI(CO)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2]$.[12] However, since the solid-state structure for **3** is asymmetric (Fig. 1) it may be that in this case the solid- and solution-state structures are the same. The ^{13}C NMR spectrum (Table 4) shows four different methyl groups of the but-2-yne ligands at δ 17.34, 18.77, 19.44 and 21.43. The spectrum also showed a quartet at δ 164 (J_{BC} = 49.11 Hz) which confirms the presence of the $[BPh_4]^-$ counter ion. The ^{11}B NMR spectrum has a sharp singlet at δ −6.92 which also indicates the presence of $[BPh_4]^-$ and compares favourably with those for other complexes with $[BPh_4]^-$ counter ions.[18] The ^{13}C NMR spectrum has alkyne contact-carbon resonances at δ 139.61, 141.30, 142.00 and 147.10, in accord[13] with the two but-2-yne ligands donating a total of six electrons to the tungsten.

Reactions of complex **3** with 2 equivalents of PPh_3 in CH_2Cl_2 at room temperature afforded the brown acetonitrile and but-2-yne-displaced product $[W(CO)(SC_5H_4N)(PPh_3)_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ **4**. The infrared spectrum shows an intense single carbonyl stretching band at 1945 cm^{-1} and a weak band at 1682 cm^{-1} which is assigned to the ν(C≡C) stretching band. The ^{31}P NMR spectrum ($CDCl_3$, 25 °C) shows a single resonance at δ 21.07 with tungsten satellites (J_{WP} = 103.33 Hz). The single phosphorus resonance indicates that the two monodentate ligated phosphines are *trans* to one another. The most likely structure is shown with the two phosphine ligands occupying the axial sites and the pyridine-2-thionate and the but-2-yne and carbonyl ligands in the equatorial plane. This structure is similar to the X-ray crystallographically determined geometry of the complex $[MoBr_2(CO)(PEt_3)_2(\eta^2\text{-}PhC_2H)]$ reported by Templeton and co-workers,[19] *i.e.* with *trans*-PEt_3 ligands. The room-temperature ^1H NMR spectrum of **4** (Table 3) shows the expected features for the proposed structure. The but-2-yne methyl resonances occur as singlets at δ 2.69 and 3.06. Variable-temperature ^1H NMR studies were carried out in order to calculate the barrier to but-2-yne rotation. The two singlets observed at room temperature coalesced at 353 K. Using the Gutowsky–Holm equation $[\Delta G^{\ddagger}{}_{T_c} = -RT_c \ln(\pi\Delta\nu h/2^{\frac{1}{2}}k_BT_c)]$[20,21] the free energy for activation was calculated to be $\Delta G^{\ddagger}{}_{T_c}$ = 73.8 kJ mol^{-1}. It is interesting that the barrier to but-2-yne rotation of the related complex $[WI_2(CO)(PPh_3)_2(\eta^2\text{-}MeC_2Me)]$[22] was calculated to be 50.4 kJ mol^{-1}. The considerably higher barrier to rotation for **4** may be due to the greater steric bulk of the pyridine-2-thionate ligand compared with two iodo ligands in the periphery of the molecule. The ^{13}C NMR spectrum (Table 4) also showed the expected features for the proposed structure with the broad alkyne contact-carbon resonances being observed at δ 225.4 and 222.08 which indicates[13] that but-2-yne is donating four electrons to the tungsten. The quartet present at δ 164 confirmed the presence of the $[BPh_4]^-$ counter ion.

Reaction of complex **3** with an equimolar amount of the bidentate ligands L–L [L–L = bipy, phen, 4,7- or 5,6-dmphen, $C_6H_{11}N{=}CHCH{=}NC_6H_{11}$, $S_2CP(C_6H_{11})_3$, $Ph_2P(CH_2)_nPPh_2$ (*n* = 1–6) or $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$] affords good yields of the mono(but-2-yne) products $[W(CO)(SC_5H_4N)(L\text{–}L)(\eta^2\text{-}MeC_2Me)][BPh_4]$ **5**–**17**. The co-ordination geometry for **5**–**17** would be expected to be similar to that crystallographically determined for $[W(CO)(S_2CNC_4H_8)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)][BF_4]$.[23] Hence, the most likely structure for complexes **5**–**17** is as shown. The ^{31}P NMR spectrum ($CDCl_3$, 25 °C) of **11** was obtained and showed resonances at δ −1.72, −2.16 (d, J_{PP} = 40.51) and −21.15, −21.61 (d, J_{PP} = 40.51 Hz), which conforms with this structure. The room-temperature ^1H NMR spectra for these complexes (Table 3) all exhibit the expected features for this geometry. Variable-temperature ^1H NMR



5–17

Table 7 Calculated[20,21] barriers to but-2-yne rotation of selected complexes*

Complex	T_c/K	$\Delta\nu$/Hz	$\Delta G^\ddagger_{T_c}$/kJ mol^{-1}
4	353	39.30	73.80
5	343	85.75	69.40
6	326	50.02	67.28
9	353	92.90	71.27
10	343	71.46	69.92
11	331	60.67	67.83
12	318	64.31	64.90
13	343	64.31	70.22
14	353	53.60	72.89
15	353	42.88	73.68
16	>353	78.61	>72.00
17	348	92.90	70.22

* Spectra recorded in CD_3CN.

studies were carried out for complexes **5**, **6** and **9**–**17**. All gave two resonances at room temperature, however these collapsed to a singlet upon warming, with the exception of those of $[W(CO)(SC_5H_4N)\{Ph_2P(CH_2)_6PPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ **16**. The barriers to but-2-yne rotation ($\Delta G^\ddagger_{T_c}$) were calculated using the Gutowsky–Holm[20,21] equation (Table 7). They are all approximately 25 kJ mol^{-1} higher than for the bis(phosphine) complexes $[WI_2(CO)L_2(\eta^2\text{-}MeC_2Me)]$[L = monodentate phosphine, $L_2 = Ph_2P(CH_2)_nPPh_2$ (n = 1–6) or $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$] previously described.[22] This is almost certainly due to the increased steric crowding induced by the pyridine-2-thionate ligand. It should also be noted that there is generally a small increase in the barrier to rotation on going from n = 1 to 6 for the bidentate phosphine complexes $[W(CO)(SC_5H_4N)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ **11**–**16** with the exception of n = 1 to 2 where there is a slight decrease in energy. This is in contrast to the values for but-2-yne rotation of the closely related pyrrolidine dithiocarbamate complexes $[W(CO)(S_2CNC_4H_8)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}MeC_2Me)][BPh_4]$ (n = 1–3)[18] which show a linear increase in $\Delta G^\ddagger_{T_c}$ versus n. The values for $\Delta G^\ddagger_{T_c}$ are also considerably lower than for the analogous pyridine-2-thionate complexes (Table 7) which indicates that steric crowding is greater with this ligand compared with the smaller pyrrolidine dithiocarbamate complexes.[18]

The ^{13}C NMR spectra (Table 4) of selected complexes also show the expected features for the proposed structure. The alkyne contact-carbon resonances were found to be above δ 200. For example, complex **6** shows two resonances at δ 210.04 and 209.79 indicating[13] that the but-2-yne ligand is donating four electrons to the metal centre and thus allowing the complex to obey the effective atomic number rule.

Experimental

The syntheses, purifications and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using standard Schlenk-line techniques. The bis(but-2-yne) starting material $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]\cdot0.5CH_2Cl_2$ was prepared according to the literature method.[11] The potassium salt of pyridine-2-thione was prepared by the reaction of KOH with 1 equivalent of the thione in methanol. Concentration of the solution afforded a yellow solid which was washed with diethyl ether and dried in a vacuum oven. All other chemicals used were obtained from commercial sources and used without further purification. Dichloromethane was dried and distilled before use.

Proton and ^{13}C NMR spectra were recorded on either a Bruker AC 250/CP/MAS (University of Wales, Bangor) or a Bruker WH 400 spectrometer (University of Warwick) and calibrated against tetramethylsilane, ^{31}P NMR spectra on a Bruker AC 250/CP/MAS spectrometer and calibrated against 85% H_3PO_4 and ^{11}B NMR spectra on a Bruker AC 250 CP/MAS spectrometer and calibrated against $BF_3\cdot OEt_2$. All infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. Elemental analyses (C, H and N) were determined using a Carlo Erba MOD 1106 Elemental Analyser (using helium as the carrier gas).

$[WI(CO)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2]$ **1**.—To $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]\cdot0.5CH_2Cl_2$ (1.0 g, 1.521 mmol) dissolved in CH_2Cl_2 (20 cm^3) with continuous stirring under a stream of dry nitrogen was added $K[SC_5H_4N]$ (0.227 g, 1.521 mmol). After 18 h the solution was filtered to remove the KI. Removal of the solvent *in vacuo* afforded a green solid $[WI(CO)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2]$ **1** which on recrystallisation from CH_2Cl_2–Et_2O at −25 °C for 12 h yielded 0.59 g of pure product. In a similar reaction 2 equivalents of $K[SC_5H_4N]$ gave the green-brown complex $[W(CO)(SC_5H_4N)_2(\eta^2\text{-}MeC_2Me)]$ **2**. For physical and analytical data see Table 1.

$[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ **3**.—To $[WI(CO)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2]$ (1.0 g, 1.79 mmol) dissolved in NCMe (30 cm^3) with continuous stirring under a stream of dry nitrogen was added $Na[BPh_4]$ (0.676 g, 1.97 mmol). After 20 h the solvent was removed *in vacuo*. The crude product was dissolved in CH_2Cl_2 (20 cm^3) and filtered twice to remove the NaI. Removal of the solvent *in vacuo* afforded a green solid $[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ **3**. Yield of pure product = 1.01 g. A sample was recrystallised from CH_2Cl_2 at −25 °C for 12 h affording suitable single crystals for X-ray crystallography.

$[W(CO)(SC_5H_4N)(PPh_3)_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ **4**.—To $[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (0.26 g, 0.329 mmol) dissolved in CH_2Cl_2 (20 cm^3) with continuous stirring under a stream of dry nitrogen was added PPh_3 (0.173 g, 0.658 mmol). After 24 h the solution was filtered twice and the solvent removed *in vacuo*. The crude product was washed with diethyl ether which was syringed off and the solid remaining evacuated to dryness leaving a brown solid $[W(CO)(SC_5H_4N)(PPh_3)_2(\eta^2\text{-}MeC_2Me)][BPh_4]$ **4** which was recrystallised from CH_2Cl_2–Et_2O. Yield of pure product = 0.18 g.

$[W(CO)(SC_5H_4N)(bipy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ **5**.—To $[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (0.3 g, 0.380 mmol) dissolved in CH_2Cl_2 (20 cm^3) with continuous stirring under a stream of dry nitrogen was added 2,2′-bipyridine (0.06 g, 0.380 mmol). After 20 h the solution was filtered and the solvent volume reduced to 2 cm^3 *in vacuo*. Dropwise addition of diethyl ether precipitated the deep red cationic complex $[W(CO)(SC_5H_4N)(bipy)(\eta^2\text{-}MeC_2Me)][BPh_4]$ **5** which on recrystallisation from CH_2Cl_2–Et_2O at −25 °C for 12 h gave 0.3 g pure product. Similar reactions with an equimolar amount of L–L [phen, 4,7- or 5,6-dmphen, $C_6H_{11}N{=}CHCH{=}NC_6H_{11}$ or $S_2CP(C_6H_{11})_3$] afforded the analogous cationic compounds $[W(CO)(SC_5H_4N)(L\text{–}L)(\eta^2\text{-}MeC_2Me)][BPh_4]$ **6**–**10**.

$[W(CO)(SC_5H_4N)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)][BPh_4]$ **11**.—To $[W(CO)(NCMe)(SC_5H_4N)(\eta^2\text{-}MeC_2Me)_2][BPh_4]$ (0.3 g, 0.380 mmol) dissolved in CH_2Cl_2 (20 cm^3) with continuous stirring under a stream of dry nitrogen was added $Ph_2PCH_2PPh_2$ (0.146 g, 0.380 mmol). After 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 $[W(CO)(SC_5H_4N)(Ph_2PCH_2PPh_2)(\eta^2\text{-}MeC_2Me)][BPh_4]$ **11** which on recrystallisation from CH_2Cl_2–Et_2O at −25 °C for 12 h yielded 0.135 g of pure product. Similar reactions with an equimolar amount of L–L $[Ph_2P(CH_2)_nPPh_2$ (n = 2–6) or $Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$ afforded the analogous cationic compounds $[W(CO)(SC_5H_4N)(L\text{-}L)(\eta^2\text{-}MeC_2Me)][BPh_4]$ **12**–**17**.

Crystallography for Complex 3.—Crystals of complex **3** were prepared as described above.

Crystal data. $C_{40}H_{39}BN_2OSW$, $M = 790.481$, $F(000) = (1584)$, monoclinic, space group $P2_1/n$, $a = 19.806(21)$, $b = 13.498(13)$, $c = 15.289(13)$ Å, $\beta = 117.4(1)°$, $U = 3629.0$ Å^3, $D_m = 1.44$ g cm^{-3}, $Z = 4$, $D_c = 1.42$ g cm^{-3}, $\lambda = 0.7107$ Å, $\mu = 34.5$ cm^{-1}.

A crystal of approximate size 0.30 × 0.30 × 0.30 mm was set up to rotate about the a axis on a Stoe Stadi2 diffractometer and data were collected *via* variable-width ω scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. 4437 Independent reflections were measured with a 2θ maximum of 50°, of which 2102 with $I > 2\sigma(I)$ were used in subsequent refinement. No deterioration in the crystal was observed during the data collection. An empirical absorption correction was applied.[24] The structure was determined by the heavy-atom method. Non-hydrogen atoms in the cation were refined anisotropically. Hydrogen atoms were included in calculated positions and refined isotropically. Methyl hydrogen atoms on MeC_2Me however could not be refined successfully and were not included. Data were weighted $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R value was 0.064 (R' = 0.068). Calculations were carried out using SHELX 76[25] together with some of our own programs on the Amdahl 5870 computer at the University of Reading. In the final cycles of refinement, no shift/error ratio was greater than 0.1σ. In the final Fourier difference map the maximum and minimum peaks were 2.32 and −0.82 e Å^{-3}. Atomic coordinates are given in Table 5, dimensions of the metal co-ordination sphere in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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