

Preliminary communication

The synthesis, structure and reactions of the novel cationic bisbut-2-yne complex $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$

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Abstract

The complex $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2]$ reacts with an equimolar amount of $\text{Na}[\text{BPh}_4]$ in acetonitrile at room temperature to give the cationic bisbut-2-yne complex $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ (**1**) by replacement of an iodide ligand by acetonitrile. The crystal structure of **1** has been determined and reveals a pseudo-octahedral geometry with the mid points of the two *cis*-but-2-yne ligands approximately coplanar with the sulphur atoms of the dithiocarbamate ligand. Carbon monoxide and acetonitrile occupy the axial sites. ¹³C NMR spectroscopy shows the two but-2-yne ligands in **1** donate a total of 6 electrons to the tungsten. Preliminary studies of the chemistry of **1** are also described.

The importance of cationic alkyne complexes of molybdenum(II) and tungsten(II) has been highlighted in recent years by the work of Green and co-workers on cationic alkyne complexes of the types $[\text{Mo}(\text{CO})(\eta^2\text{-RC}_2\text{R}')_2(\eta^5\text{-C}_5\text{H}_5 \text{ or } \text{-C}_9\text{H}_7)] [\text{BF}_4]$ [**1**], $[\text{Mo}(\text{CO})\text{L}(\eta^2\text{-RC}_2\text{R}')(\eta^5\text{-C}_5\text{H}_5 \text{ or } \text{-C}_9\text{H}_7)][\text{BF}_4]$ (L = monodentate phosphines) and $[\text{MoL}_2(\eta^2\text{-RC}_2\text{R}')(\eta^5\text{-C}_5\text{H}_5 \text{ or } \text{-C}_9\text{H}_7)][\text{BF}_4]$ (L = monodentate phosphines and phosphites) [**2**]. These complexes display a wide range of reaction especially with nucleophiles [**3**]. Although Lippard and co-workers [**4**] have described the synthesis of the cationic alkyne complexes $[\text{MI}(\text{CNR})_4(\eta^2\text{-RNHC}_2\text{-NHR})]\text{X}$ (M = Mo or W), by the reductive coupling of two isonitrile ligands, few other cationic alkyne complexes of molybdenum(II) and tungsten(II) have been reported. Recently we described the preparation of the versatile bisalkyne complexes $[\text{WI}_2(\text{CO})(\text{NCMe})(\eta^2\text{-RC}_2\text{R})_2]$ (R = Me or Ph) [**5**]. They react with, for example, an equimolar quantity of $[\text{S}_2\text{CX}]^-$ (X = NMe₂, NEt₂, NC₄H₈, NC₅H₁₀ and OEt) in CH₂Cl₂ at room temperature to eventually give the monoiodide-bisalkyne complexes $[\text{WI}(\text{CO})(\text{S}_2\text{CX})(\eta^2\text{-RC}_2\text{R})_2]$ [**6**]. We describe here the preparation

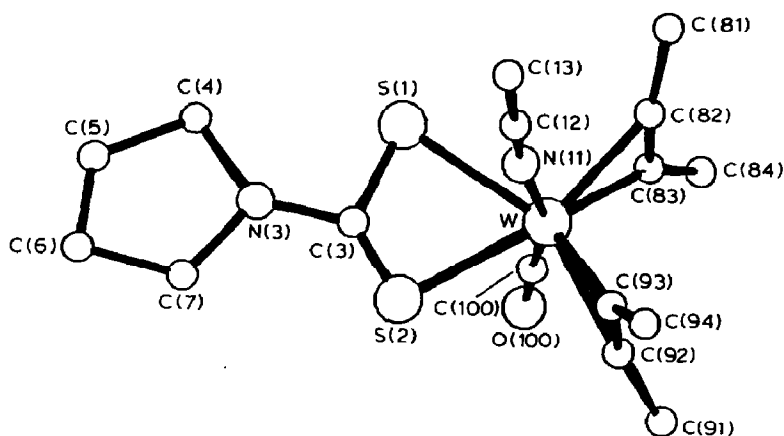


Fig. 1. The X-ray crystal structure of the cation $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2]^+$.

and structure of the first cationic bisalkyne complex of tungsten containing a dithiocarbamate ligand, $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ (**1**), and preliminary studies of its reactivity.

Equimolar quantities of $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2]$ and $\text{Na}[\text{BPh}_4]$ react in acetonitrile at room temperature to give the pale yellow cationic complex $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$ (**1**) in > 80% yield. Complex **1** is stable in the solid state when stored under nitrogen. It is soluble in acetonitrile (single crystals of **1** were grown for X-ray crystallography from a cooled (0°C) solution of complex **1** in acetonitrile) and CH_2Cl_2 , but insoluble in hydrocarbon solvents and diethyl ether. The infrared spectrum for **1** shows a strong single carbonyl band at $\nu(\text{CO})$ 2080 cm^{-1} , and a weak asymmetric doublet at 2325 and 2300 cm^{-1} due to coordinated acetonitrile. There is also a weak but-2-yne band at 1850 cm^{-1} , i.e. at a considerably lower wavenumber than that for free but-2-yne, and this suggests that there is considerable back donation of electron density from filled metal d -orbitals to empty π^* -orbitals on the but-2-yne. This is further reflected in the bending back of the methyl groups on the coordinated but-2-yne ligands (see Fig. 1).

Crystals of **1** were prepared as described above. $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2][\text{BPh}_4]$, $\text{C}_{40}\text{H}_{43}\text{BN}_2\text{OS}_2\text{W}$, $M = 826.1$, a $12.944(13)$, b $26.671(25)$, c $11.090(13)\text{ \AA}$, $\beta = 105.7(1)$, U 3685.8 \AA^3 , d_c 1.44 g cm^{-3} , d_m 1.45 g cm^{-3} , $F(000) = 1664$, $Z = 4$, λ 0.7107 \AA , $\mu = 33.5\text{ cm}^{-1}$, spacegroup $P2_1/a$. 1989 independent reflections above background ($I > 2\sigma(I)$) were measured on a Stoe Stadi 2 diffractometer. An empirical absorption correction was applied [7]. The structure was determined by the heavy atom method. The hydrogen atoms were included in calculated positions. The tungsten atom was refined anisotropically and all other atoms isotropically to a final R of 0.085 ($R_w = 0.087$). Calculations were carried out with the SHELX 76 program [8] and some in-house programs on the Amdahl 5870 at the University of Reading. Tables of atomic coordinates, bond lengths, and angles have been deposited at the Cambridge Crystallographic Data Centre. The structure consists of discrete units of $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2]^+$ cations and $[\text{BPh}_4]^-$ anions. The cation is shown in Fig. 1 together with the atomic numbering scheme. The environment of the tungsten atom can be regarded as

distorted octahedral with two *cis*-but-2-yne ligands occupying one site each. in the equatorial plane, the tungsten atom is bonded to the two sulphur atoms of the dithiocarbamate ligand. {W–S(1) 2.576(11), 2.505(10) Å}, with each sulphur atom *trans* to a *cis*-but-2-yne ligand {W–C(82) 2.13(4), W–C(83) 2.06(4) Å}. The axial sites are occupied by a carbonyl group {W–C(100) 1.92(3)} and an acetonitrile group {W–N(11) 2.10(2) Å}.

The geometric arrangement can be related to that of [W(CO)(S₂CNC₄H₈)(η²-MeC₂Me)₂] [6], in which the tungsten atom is similarly octahedral. But in that molecule, the carbonyl group is *trans* to one of the sulphur atoms, while the two alkynes are *trans* to the other sulphur atom and the iodide. Thus in both compounds, as is common in *d*⁴ systems, both alkyne moieties are parallel to the M–CO axis (Fig. 1), a configuration which optimises both the π-donor and π-acceptor roles of the alkyne ligand.

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 alkyne 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 the van der Waals' radii between the ions.

Alkynes have been shown by both (a) theoretical calculations [9] and (b) experimental studies [2,10] to be able to donate 2 or 4 electrons to a transition metal. The room temperature ¹³C NMR spectrum of 1* shows four alkyne contact

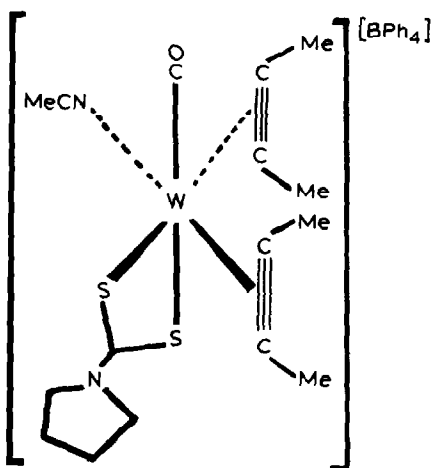
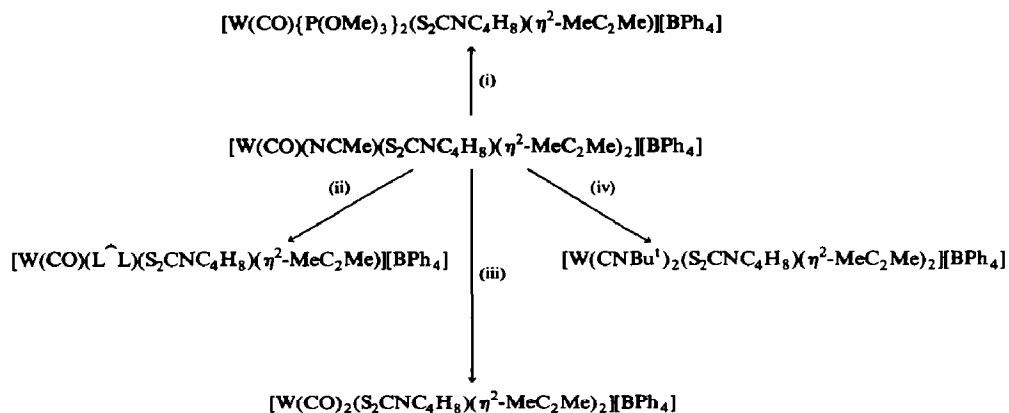


Fig. 2. The proposed geometry of [W(CO)(NCMe)(S₂CNC₄H₈)(η²-MeC₂Me)₂][BPh₄] in solution.

* Selected data for compound 1: Analysis: C₄₀H₃₇N₂BOS₂W requires C, 58.1; H, 5.2; N, 3.4. Found: C, 58.3; H, 5.4; N, 3.1. IR (CHCl₃) ν(CN) 2325 and 2300 w cm⁻¹; ν(CO) 2080 s cm⁻¹; ν(C≡C) 1850 w cm⁻¹. ¹H NMR (25 °C, CD₂Cl₂) 7.45–6.85 (m, 20H, Ph–H); 3.92 (t, 2H, NCH₂, J(H–H) = 6.24 Hz); 3.61 (t, 2H, NCH₂, 6.27 Hz); 3.02, 2.98, 2.94, 2.85 (4 × s, 12H, ≡CMe); 2.07 (s, 3H, NCMe); 1.99 (bm, 4H, CH₂). ¹³C NMR (25 °C, CD₂Cl₂) 207.41 (s, C≡O); 193.09 (s, CS₂); 183.40, 174.90, 173.80, 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, NCMe); 50.58 (s, NCH₂); 50.33 (s, NCH₂); 24.93 (s, CH₂); 24.60 (s, CH₂); 19.16, 19.13, 18.30, 17.05 (4 × s, ≡CMe); 4.05 (s, NCMe).



Scheme 1. Reaction conditions: (i) $2\text{P}(\text{OMe})_3$ in CH_2Cl_2 at room temperature for 24 h; (ii) $\widehat{\text{L}}\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1-6$) or 2,2'-bipyridine in CH_2Cl_2 at room temperature for 24 h; (iii) bubbling CO (generated in situ from $\text{H}_2\text{SO}_4/\text{HCO}_2\text{H}$) through a CH_2Cl_2 solution for 12 h; (iv) 2CNBu^1 in CH_2Cl_2 at room temperature for 24 h.

carbon resonances between 183.40 and 162.89 ppm suggesting [11] that the but-2-yne ligands are donating a total of 6 electrons to the tungsten in **1**. Both the ^1H and ^{13}C NMR spectra for **1** are more complex than would be expected for the symmetrical solid state structure shown in Fig. 1. At room temperature the ^1H NMR spectrum of **1** shows four resonances due to the but-2-yne methyl groups, and hence it is very likely that **1** has the asymmetric structure in solution with the two *cis*-but-2-yne ligands *trans* to acetonitrile and a sulphur of the dithiocarbamate with carbon monoxide and the other sulphur atom of the bidentate ligand in the axial positions, as shown in Fig. 2. This geometry was also observed for the solid state structure of $[\text{W}(\text{CO})(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})_2]$ [6].

The reactions of **1** are very diverse; some reactions with neutral donor ligands are shown in Scheme 1. For example, **1** reacts with two equivalents of $\text{P}(\text{OMe})_3$ in CH_2Cl_2 at room temperature to give the deep blue 4-electron monobut-2-yne coordinated complex $[\text{W}(\text{CO})\{\text{P}(\text{OMe})_3\}_2(\text{S}_2\text{CNC}_4\text{H}_8)(\eta^2\text{-MeC}_2\text{Me})][\text{BPh}_4]$. We are currently investigating the chemistry of **1** and its derivatives, and in particular their reactions with nucleophiles.

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