

Preliminary Communication

Synthesis, molecular structure and reactions of the novel organometallic thioether ligand $[Wl_2(CO)\{(Me)S(CH_2)_2S(CH_2)_2SMe-S,S'\}(\eta^2-PhC_2Ph)]$

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Abstract

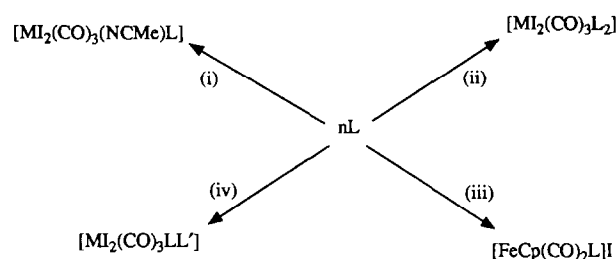
Reaction of $[Wl_2(CO)(NCMe)(\eta^2-PhC_2Ph)_2]$ with an equimolar quantity of $MeS(CH_2)_2S(CH_2)_2SMe$ in CH_2Cl_2 at room temperature gave the complex $[Wl_2(CO)\{(Me)S(CH_2)_2S(CH_2)_2SMe-S,S'\}(\eta^2-PhC_2Ph)]$ (**1**). The crystal structure of **1** shows the $MeS(CH_2)_2S(CH_2)_2SMe$ ligand attached to the tungsten via two adjacent sulphur atoms, leaving the third sulphur atom uncoordinated. Preliminary studies of the reactions of **1** are also described.

Keywords: Tungsten; Sulphur; Diphenylacetylene; Crystal structure

Transition-metal complexes containing thioether ligands play a central role as simple models of the molybdenum site of nitrogenase [1–8]. Nitrogenase can also reduce alkynes to alkenes, hence our interest in the study of tungsten(II) alkyne thioether complexes. Although several organotransition-metal phosphine complexes have been used as phosphine ligands to form bi- and multimetallic complex derivatives [9,10], hitherto, no organotransition-metal thioether complexes have been used in this way. In this communication, we describe the synthesis, molecular structure and some preliminary reactions of the novel monodentate thioether ligand alkyne complex $[Wl_2(CO)\{(Me)S(CH_2)_2S(CH_2)_2SMe-S,S'\}(\eta^2-PhC_2Ph)]$ functioning as a monodentate ligand.

Equimolar quantities of $[Wl_2(CO)(NCMe)(\eta^2-PhC_2Ph)_2]$ [11], and $MeS(CH_2)_2S(CH_2)_2SMe$ react in CH_2Cl_2 at room temperature, to give the acetonitrile and diphenylacetylene-displaced product $[Wl_2(CO)\{(Me)S(CH_2)_2S(CH_2)_2SMe-S,S'\}(\eta^2-PhC_2Ph)]$ in 85% yield. Complex **1** has been fully characterised by elemental analysis (C, H, N and S), infrared and ¹H NMR

spectroscopy [12]. Complex **1** is soluble in CH_2Cl_2 (single crystals of **1** suitable for X-ray crystallography were grown from a cooled solution ($-15^\circ C$) of CH_2Cl_2 /diethyl ether 85:15 ratio), chloroform and only sparingly soluble in diethyl ether. The infrared spectrum shows a broad strong carbonyl band at 1968 cm^{-1} , and a weak alkyne ($C\equiv C$) stretching band at 1651 cm^{-1} , as expected considerably lower than that of the free alkyne.



Scheme 1. $L = [Wl_2(CO)\{(Me)S(CH_2)_2S(CH_2)_2SMe-S,S'\}(\eta^2-PhC_2Ph)]$. All reactions were carried out in CH_2Cl_2 at room temperature. (i) Reaction of L with an equimolar quantity of $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W) for 8 hrs; (ii) Reaction of $2L$ with $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W) for 24 hrs; (iii) Reaction of L with $[MI_2(CO)_3(NCMe)L']$ ($M = Mo$ or W ; $L' = PPh_3$ or $AsPh_3$) for 2 hrs; (iv) Reaction of L with an equimolar quantity of $[FeI(CO)_2Cp]$ for 4 hrs.

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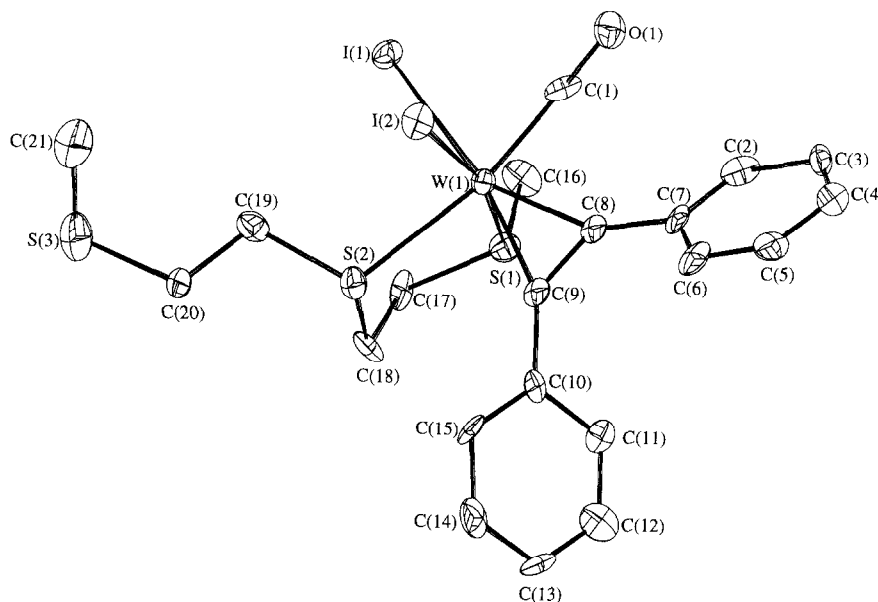


Fig. 1. The X-ray crystal structure of $[\text{W}_2(\text{CO})\{(\text{Me})\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{SMe-S,S'}\}(\eta^2\text{-PhC}_2\text{Ph})]$ (**1**), showing the atom numbering scheme. Selected bond lengths are: W1–C8 2.031(10), W1–C9 2.021(10), W1–S1 2.470(3), W1–S2 2.574(3), W1–C1 1.931(10), W1–I1 2.848(2), W1–I2 2.785(2), C(8)–C(9) 1.319(12) Å.

The crystal structure [13] of **1** shows a distorted octahedral structure with *cis*-iodoligands, the diphenylacetylene and the coordinated thioether–sulphur atom forming the equatorial plane. The central bound sulphur of the thioether and carbon monoxide occupy the axial sites. As is common in d^4 systems [11], the diphenylacetylene is parallel to the W–CO axis (Fig. 1). This configuration optimises both the π -acceptor and σ -donor properties of the alkyne.

The chemistry of complex **1** is extensive. For example, equimolar amounts of $[\text{FeI}(\text{CO})_2\text{Cp}]$ and **1** react in CH_2Cl_2 at room temperature to give the novel bimetallic complex $[\text{Cp}(\text{OC})_2\text{Fe}(\text{S}(\text{Me})(\text{CH}_2)_2\text{S}(\text{CH}_2)_2(\text{Me})\text{S-S,S',S''})\text{W}_2(\text{CO})(\eta^2\text{-PhC}_2\text{Ph})]$ (**2**) which was fully characterised [19]. Scheme 1 also illustrates the reactions of **1** as a monodentate thioether ligand with organomolybdenum(II) and tungsten(II) complexes.

Acknowledgements

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References and notes

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- [12] Selected data for complex **1**. Anal.: ($\text{C}_{21}\text{H}_{24}\text{OS}_3\text{W}_2$) requires C, 30.5%; H, 2.9%; S, 11.6%. Found: C, 30.6%; H, 2.9%; S, 11.0%. IR (CH_2Cl_2) $\nu(\text{C}=\text{O}) = 1968$ (s) cm^{-1} ; $\nu(\text{C}=\text{C}) = 1651$ (w) cm^{-1} . ^1H NMR (25°C, CDCl_3) 7.3–7.5 (brm, 10H, Ph-H); 3.2 [bm, 4H, CH_2SCH_2 (coord.)]; 3.1 [s, 3H, CH_3 (coord.)]; 2.6 [m, 2H, CH_2SCH_3 (coord.)]; 2.35 (m, 2H, CH_2SCH_3 (uncoord.)); 2.2 [s, 3H, CH_3 (uncoord.)] ppm (referenced to SiMe_4).
- [13] Single-crystal X-ray studies of (**1**). Crystal data for $\text{C}_{21}\text{H}_{24}\text{OS}_3\text{W}_2$. $M_r = 826.23$, monoclinic, $a = 8.458(2)$, $b = 13.494(12)$, $c = 22.03(3)$ Å, $\beta = 99.48(8)$, (by least-squares analysis of 50 reflections), $U = 2480(4)$ Å³, space group $\text{P}2_1/c$ (No. 14), $Z = 4$, $D_c = 2.213$ g cm^{-3} , $F(000) = 1544$, $\mu = 7.412$ mm⁻¹, $T = 120$ K, crystal size $0.11 \times 0.11 \times 0.21$ mm³ (approx.). Data were collected on a Delft Instrument FAST TV area detector [14] at the window of a rotating anode generator, with a molybdenum target ($\lambda\text{Mo-K}\alpha = 0.71069$ Å). 6633 reflections collected ($2.44 < \theta < 22.76^\circ$), index ranges $-6 < h < 8$; $-10 < k < 14$; $-23 < l < 22$, producing 2830 unique data ($R_{\text{int}} = 0.067$ after absorption correction, DIFABS) [15]. The structure was solved by heavy atom methods (SHELX-S [16]) and then subjected to full-matrix least squares refinement based on F_o^2 (SHELXL-93 [17]). The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$. Final wR_2 and R_1 values are 0.0743 and 0.0602 respectively, for all data and 249 parameters ($\rho_{\text{max}}, \rho_{\text{min}}$

- 1.208, $-0.742 \text{ e}\text{\AA}^{-3}$). Corresponding wR_2 and R_1 values for 1946 data with $F_0 > 4\sigma(F_0)$ are 0.0684 and 0.0349 respectively. Diagrams were drawn with SNOOP1 [18]. Sources of scattering factor data are given in Ref. [17]. Full tables of bond lengths and angles, anisotropic displacement parameters of non-hydrogen atoms, hydrogen atom parameters, and tables of structure factors have been deposited at the Cambridge Crystallographic Data Centre.
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- [19] Selected data for complex **2**. Anal.: ($\text{C}_{28}\text{H}_{29}\text{OS}_3\text{FeWl}_3$) requires C, 29.8%; H, 2.6%; S, 8.5%. Found: C, 29.6%; H, 2.8%; S, 9.1%. IR (CH_2Cl_2) $\nu(\text{C}=\text{O}) = 1960$ (s), 1998 (s), 2045 (s) cm^{-1} ; $\nu(\text{C}=\text{C}) = 1667$ (w) cm^{-1} . ^1H NMR (25°C, CDCl_3) 7.3–7.5 (brm, 10H, Ph-H); 5.1 (s, 5H, Cp-H); 3.4 (bm, 4H, CH_2SCH_2); 3.2 (bm, 2H, CH_2SCH_3); 3.1 (bm, 3H, SCH_3); 2.8 (bm, 5H, CH_2SCH_3) ppm (referenced to SiMe_4).