

Stepwise Activation of σ -Thienyl Ligands at Di-tungsten Centres

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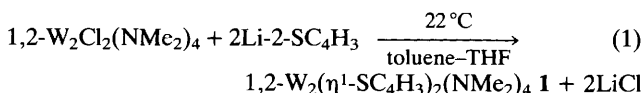
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The attachment of σ -2-thienyl and σ -2-benzothieryl ligands (but not σ -3-thiophenyl ligands) to W_2^{6+} containing centres leads to the stepwise opening of the five-membered ring to generate, in the presence of *tert*-butyl alcohol, a novel thiolato- μ -alkylidyne metallocycle in $W_2(OBu^t)_5(\mu-SC_4H_4)(\eta^1-2-SC_4H_3)$, which has been structurally characterized; the intermediate $W_2(OBu^t)_4(\mu-SC_4H_3)(\eta^1-2-SC_4H_3)$, which contains a bridging thiolato-vinylidene metallocycle has been characterized by NMR spectroscopy.

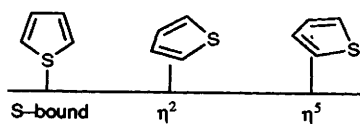
Hydrodesulfurization (HDS) of fossil fuels is the largest catalytic industrial process wherein sulfur is removed initially as hydrogen sulfide from sulfur-containing aromatic and other hydrocarbons over Co-Mo/Al₂O₃ catalysts.¹ This has led to many model studies of the reactions of thiophene and thiophene derivatives with both heterogeneous and homogeneous systems. Discussion has often focused on the initial binding mode of the thienyl group to the catalyst or metal centre.² Three modes of coordination are most commonly cited (Scheme 1). These three modes have been observed by spectroscopic studies on MoS₂ and sulfided Co-Mo/Al₂O₃ catalysts³ as well as single-crystal surfaces such as Ni(100),⁴ Pt(111),⁵ Cu(100),⁶ Cu(111),⁷ Mo(100),⁸ Mo(110),⁹ W(211),¹⁰ Ni(111)¹¹ and Re(0001).¹²

Recent work has shown that C-H activation may well precede carbon-sulfur bond cleavage as well as hydrogenation of the ring. The cobalt-molybdenum-sulfide catalyst will selectively bring about C-H/D exchange of the 2-5-thiophene ring positions at 200 °C, a temperature below which catalytic HDS proceeds.¹³ Recent mononuclear chemistry by Angelici,¹⁴ Jones¹⁵ and co-workers has focused on the potential of the σ -2-thienyl ligand as an entry point to ring-opening reactions. We describe here some of our observations of the activation of σ -thienyl ligands at di-tungsten centres supported by alkoxide ligands. These were prompted by our earlier work that revealed that related systems were capable of activating and cleaving C-X multiple bonds (X = O and N).¹⁶

The coordinatively unsaturated $W_2(OR)_6$ (R = Bu^t, Prⁱ and CH₂Bu^t)¹⁷ and $W_4(OCH_2R)_{12}$ compounds (R = Prⁱ and *c*-C₅H₉)¹⁸ failed to react with free thiophene, presumably because the alkoxide ligands are good π -buffers and sulfur is an extremely poor nucleophilic base when placed in this aromatic ring. Consequently, we introduced the thienyl ligand to the W_2^{6+} -containing centre by metathesis [eqn. (1)].[†]

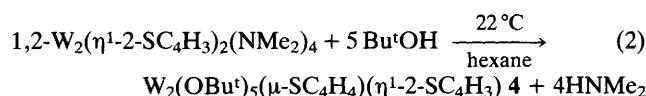


Compound **1** is an orange, hydrocarbon soluble and air-sensitive crystalline material that has been crystallographically characterized[§] and shown to be an ethane-like $W_2X_4Y_2$ compound.¹⁹ An ORTEP drawing of the molecule is given in Fig. 1. It is noteworthy that the sulfur atoms show no evidence of coordination to the W_2^{6+} centre ($W \cdots S = ca. 3.3 \text{ \AA}$). A related reaction involving Li-2-SC₈H₅ and 1,2- $W_2Cl_2(NMe_2)_4$ yields the related benzothieryl complex 1,2- $W_2(\eta^1-2-SC_8H_5)_2(NMe_2)_4$, **2**. Also a similar synthetic procedure involving Li-3-SC₄H₃ yields the complex 1,2- $W_2(\eta^1-3-SC_4H_3)_2(NMe_2)_4$, **3**. In solution, **1**, **2** and **3** exist in an equilibrium mixture of *anti*- and *gauche*-rotamers and show NMR spectroscopic properties similar to other 1,2- $M_2R_2(NMe_2)_4$ compounds.^{19b}



Scheme 1

Compound **1**, the η^1 -2-thienyl complex (Fig. 1) reacts with *tert*-butyl alcohol in hydrocarbon solvents (hexane or toluene) according to eqn. (2).



Compound **4** is a red-purple, hydrocarbon soluble, air-sensitive, crystalline compound that has been characterized by X-ray crystallography[§] and shown thereby to contain the novel μ -alkylidyne thiolate heterocyclic ligand (Fig. 2). Five OBu^t ligands were identified by ¹H NMR spectroscopy and shown to be in the ratio 2 : 2 : 1 (consistent with the solid-state structure) and by use of COSY proton coupled 2D NMR the ¹H signals attributable to the η^1 -2-SC₄H₃ and μ -SC₄H₄ ligands can be distinguished. ¹³C NMR spectroscopy unequivocally allows the identification of the μ -alkylidyne carbon at $\delta 307$, which is typical for $W_2(\mu-CR)$ carbon atoms.²⁰

Reaction (2) was followed by NMR spectroscopy in [²H₆]benzene as solvent, which revealed the stepwise replacement of NMe₂ by OBu^t ligands and the formation of an intermediate that we formulate as a thiolato-vinylidene bridge complex $W_2(OBu^t)_4(\mu-SC_4H_3)(\eta^1-3-SC_4H_3)$ intermediate, **A**.

Evidence for the opening of one of the σ -thienyl ligands is readily apparent from the ¹H NMR spectrum which shows two sets of C₃H₃ signals of equal integral intensity in addition to four singlets of equal intensity for the four OBu^t ligands. The μ -vinylidene carbon appears at $\delta 287$. In reactions employing Bu^tOD, the formation of [²H₁]4 is seen where the alkylidyne

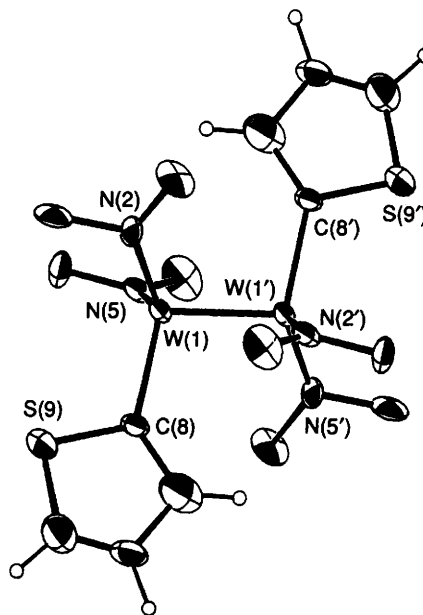


Fig. 1 An ORTEP drawing of $W_2(\eta^1-2-SC_4H_3)_2(NMe_2)_4$. Selected bond distances (Å) and angles (°) are as follows: W(1)–W(1') 2.290(5), W(1)–N(2) 1.966(1), W(1)–S(9) 3.285(13), W(1)–C(8) 2.138(15), W(1)–N(5) 1.914(14), S(9)–C(8) 1.737(17), W(1')–W(1)–N(2) 104.3(4), W(1')–W(1)–C(8) 100.0(4), W(1)–C(8)–S(9) 115.5(8)

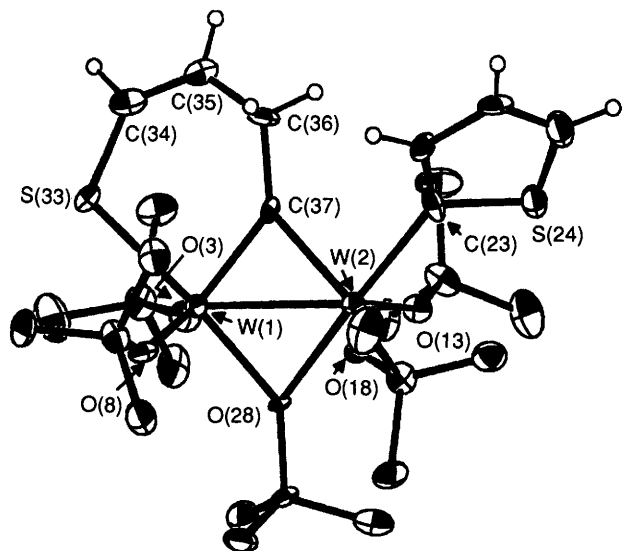
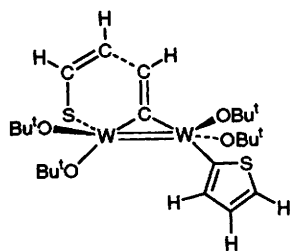


Fig. 2 An ORTEP drawing of $W_2(\mu\text{-SC}_4\text{H}_4)(\eta^1\text{-2-SC}_4\text{H}_3)(\text{OBu})_5$. Selected bond distances (Å) and angles ($^\circ$) are as follows: W(1)–W(2) 2.6633(6), W(1)–C(37) 1.979(9), W(1)–S(33) 2.4314(6), W(2)–C(37) 1.983(9), C(37)–C(36) 1.485(13), W(1)–O(28) 2.047(6), W(1)–O(8) 1.858(6), W(2)–C(23) 2.175(10), W(2)–O(28) 2.083(6), W(2)–O(18) 1.875(7), W(1)–C(37)–W(2) 84.5(4), W(1)–O(28)–W(2) 80.3(1), S(33)–W(1)–C(37) 86.5(1), S(33)–W(1)–O(28) 174.5(1)



bridged-complex contains one deuterium on the β -carbon to the alkyldiene carbon.

In bench-top reactions, the careful addition of 4 equiv. of Bu^tOH to **1** yields crude **5** which has been shown to be labile to reaction with an additional equivalent of Bu^tOH to yield **4**. The conversion of **5** to **4** represents the formal oxidative addition to the $(W=W)^{8+}$ centre to yield $(W-W)^{10+}$ by way of protonation of the β -carbon of the μ -vinylidene ligand which generates the μ -alkylidene and addition of Bu^tO^- to the metal centre. The details and order of this addition are not known but protonation of a μ -vinylidene ligand has ample precedent in organometallic chemistry.²¹

A related ring opening reaction and μ -alkylidene formation is observed when the σ -2-benzothienyl complex, **2**, is allowed to react with Bu^tOH (5 equiv.) but, in the related reaction involving the σ -3-thienyl complex, **3**, no ring opening is observed. The product is merely that of alcoholysis, namely $1,2\text{-W}_2(\eta^1\text{-3-SC}_4\text{H}_3)_2(\text{OBu}^t)_4$, **6**. It is interesting to speculate why compound **6** does not undergo ring opening to yield a μ -thiolato vinylidene containing complex analogous to **4**. We propose that this is because the C–S bond cleavage is facilitated by coordination of sulfur to a metal centre and this is much more readily achieved for the $\eta^1\text{-2-}$ relative to the $\eta^1\text{-3-}$ thienyl ligand.

In conclusion, we have shown that C–S bond cleavage is facilitated by metal–carbon σ -bond formation of the thio-phenyl ligand at the 2-position.

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Footnotes

† All operations were carried out under dry and deoxygenated N_2 atmospheres and solvents. Satisfactory elemental analyses have been obtained except for **5** which, being a reactive intermediate, has not been isolated in a pure form.

§ Crystal data for **1** at -170°C : $a = 16.405(4)$, $b = 16.486(4)$, $c = 8.757(2)$ Å, $\alpha = 104.87(1)^\circ$, $\beta = 103.90(1)^\circ$, $\gamma = 88.79(1)^\circ$, $Z = 4$, $D_c = 2.12$ g cm^{-3} and space group $P\bar{1}$. Of 8825 reflections collected ($\text{Mo-K}\alpha$, $6 < 2\theta < 45^\circ$), 5820 were unique and the 5177 reflections having $F > 3\sigma(F)$ were used in the refinement. Final residuals are $R(F) = 0.0518$ and $R_w(F) = 0.0525$. All atoms other than H atoms were refined anisotropically. A refinement of the occupancies for positions that could be either carbon or sulfur gave preferred orientation with occupancies ranging from 74–86%. The labelling in the figures is for the preferred orientations, however, it should be kept in mind that the distances and angles for the rings are less reliable because of this disorder.

For **4** at -165°C : $a = 15.231(2)$, $b = 12.733(2)$, $c = 18.516(3)$ Å, $\beta = 112.52(1)^\circ$, $D_c = 1.803$ g cm^{-3} , $Z = 4$ and space group $P2_1/n$. Of the 7344 reflections collected, 4350 were unique and the 3884 with $F > 3\sigma(F)$ were used in the full refinement. Final residuals are $R(F) = 0.0366$ and $R_w(F) = 0.0351$. All atoms other than H atoms were refined anisotropically.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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