C–S Bond Cleavage in Reactions of Thiolate Nucleophiles with Bridging Thioethers in Anionic Ditungsten(III) Complexes†

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The complexes $[PPh_4][Cl_3W(\mu\text{-}Cl)(\mu\text{-}SR_2)_2WCl_3]$ (R = Me, Et, or SR_2 = tetrahydrothiophene) react with thiolate anions SR'^- (R' = $C_6H_4Me\text{-}4$), *via* a nucleophilic displacement of the R group to yield the appropriate mixed thioether, RSR', and the dianion $[Cl_3W(\mu\text{-}SR_2)(\mu\text{-}SR)(\mu\text{-}Cl)WCl_3]^{2-}$. The structure of the complex $[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]\cdot 2CH_2Cl_2$ was determined by single-crystal X-ray diffraction, which shows that the anion possesses a confacial bioctahedral framework. A very short W–W interatomic distance [2.4418(6) Å] is indicative of a metal–metal triple bond. The unique combination of bridging ligands in this complex, all of which are *trans* to terminal chlorides, allows a comparison to be made between the $W\text{–}S_{thioether}$, $W\text{–}S_{thiolate}$ and W–Cl bond lengths. The configuration of the ethyl group on the μ-SEt group is axial with reference to the $\mu\text{-}SEt_2$ ligand. This geometry is retained upon dissolution in dichloromethane or acetonitrile for sufficient time to record the ^1H NMR spectra, but equilibration with the equatorial isomer occurs over a period of *ca.* 2 or 6 h respectively. A kinetic study of this process revealed that it is first order, with a forward rate constant of $1.32 \times 10^{-4}\ s^{-1}$. An absolute assignment of all the proton resonances for both isomers was achieved.

We recently described[1] the synthesis and characterization of three confacial bioctahedral complexes of tungsten(III) with thioether bridges $[Cl_3W(\mu\text{-}tht)_3WCl_3]$ **1** (tht = tetrahydrothiophene), $[Cl_3W(\mu\text{-}SEt_2)_3WCl_3]$ **2** and $[SMe_3][Cl_3W(\mu\text{-}SMe_2)_2(\mu\text{-}Cl)WCl_3]$ **3**. The relatively short W–S bond lengths observed in the structures of **2** and **3** are consistent with the observations of other workers[2–6] who have synthesized μ-thioether complexes of early transition metals, and support the idea that these are good bridging ligands for promoting metal–metal bonding.[1] In an attempt to synthesize binuclear tungsten complexes completely ligated by sulfur, we carried out reactions of **1** and **2** with thiolate anions. We were surprised to find that nucleophilic attack occurred at an α-carbon atom of a μ-thioether ligand, rather than at the metal centre to displace a chloride.[7] An example of such a reaction is given in equation (1).

$$[Cl_3W(\mu\text{-}SEt_2)_3WCl_3] + [PPh_4][SC_6H_4Me\text{-}4] \longrightarrow [PPh_4][Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}SEt)WCl_3] + EtSC_6H_4Me\text{-}4 \quad (1)$$

This type of reaction was also shown to be feasible between other anionic nucleophiles, X, and the neutral starting complexes **1** and **2**. Reactions with **1** result in tht ring opening, and the formation of anions of general formula $[Cl_3W(\mu\text{-}tht)_2\{\mu\text{-}S(CH_2)_4X\}WCl_3]^-$.

In this paper we report on an extension of this study of reactions between nucleophiles and bridging thioether ligands, in which we have examined the possibility of the anion of complex **3** undergoing dealkylation by reaction with thiolate. It was anticipated that the negative charge on this complex might inhibit nucleophilic attack, and lead to changes in reaction patterns. However, C–S bond cleavage was still observed and hence we extended the study to two new thioether complexes of the same structural type, namely $[PPh_4][Cl_3W(\mu\text{-}tht)_2(\mu\text{-}Cl)WCl_3]$ **4** and $[PPh_4][Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]$ **5**, whose syntheses we also report. These reactions have allowed the preparation of a series of novel binuclear complexes with three different bridging ligands. The X-ray crystal structure of one of these, $[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]$ **6**, has been determined, and a detailed analysis of the ^1H NMR spectrum of both possible configurational isomers involving the μ-SEt group, is reported.

Results

Synthesis of **4** *and* **5**.—The syntheses of complexes **4** and **5** were discovered when the conditions for the syntheses of **1** and **2** were varied outside the limits previously reported from our laboratory.[1] Both the nature of the sample of WCl_4 and the temperature of the reaction were found to be important in determining the distribution of products in the reduction of WCl_4 by sodium amalgam in the neat, parent thioether. When the sample of WCl_4 is prepared by the method of Schaefer King and McCarley[8] and is used immediately after preparation, the subsequent reduction with sodium amalgam at temperatures < 70 °C favours the formation of $Na[Cl_3W(\mu\text{-}tht)_2(\mu\text{-}Cl)WCl_3]$ and $Na[Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]$, rather than compounds **1** and **2**. Conversely, samples of WCl_4 which have been heated to remove volatile impurities lead to a product distribution favouring the neutral compounds **1** and **2**, as does the use of a reaction temperature higher than 70 °C. A second, minor product of the latter reaction has been isolated for the case of ethyl sulfide, namely $[SEt_3][Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]$ which is analogous to **3** reported earlier.[1] The sodium salts can be converted to the more soluble $[PPh_4]^+$ derivatives by reaction with $[PPh_4]Cl$ in dichloromethane. The $[PPh_4]^+$ derivative of the anion of **3** was prepared in a similar fashion, and is referred to as **3a**. The detailed preparations and characterizations are reported in the Experimental section.

Reactions of **3a**, **4** *and* **5** *with Thiolate Anions*.—Reactions between **3a**, **4** or **5** and $[PPh_4][SC_6H_4Me\text{-}4]$ were carried out in acetonitrile solution, in a 1:1.5 molar ratio at *ca.* 50 °C. The progress of the reactions was monitored by ^1H NMR spectroscopy, and after a period of *ca.* 4 h they were found to have

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

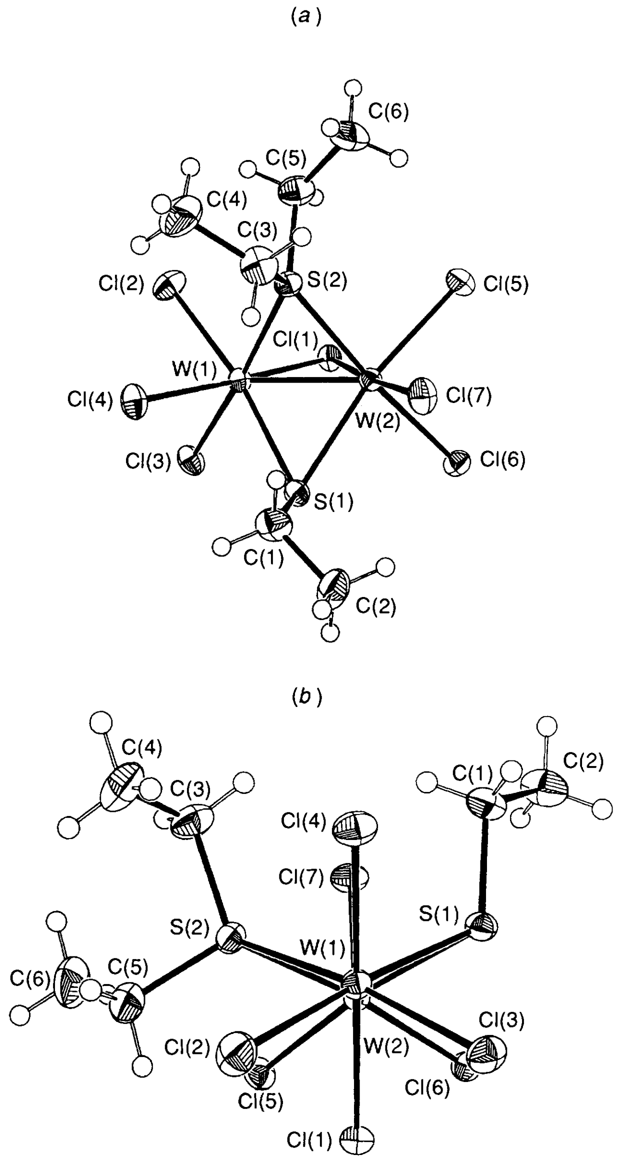


Fig. 1 Structure of the anion of **6**, showing the numbering scheme, (*a*) side view, and (*b*) as viewed down the W–W vector

consumed 1 mol equivalent of thiolate. This is considerably slower than corresponding reactions between thiolate anion and the neutral complexes **1** and **2**, as anticipated. The observed reactions are shown in equations (2)–(4).

Upon completion of the reactions as monitored by NMR spectroscopy, the solutions were evaporated to dryness under vacuum to prevent any further reaction with the excess thiolate. The residues were extracted with diethyl ether to remove the organic sulfides, then with propan-2-ol to extract the residual phosphonium thiolate. The identity of the organic sulfides produced in reactions (2) and (4) was established by GC–MS and ^{1}H NMR spectroscopy. The tungsten-containing products were characterized spectroscopically and by their elemental analyses, and in the case of **6**, by an X-ray crystal-structure determination of the dichloromethane solvate.

Table 1 Selected bond distances (Å) and angles (°) for compound **6**

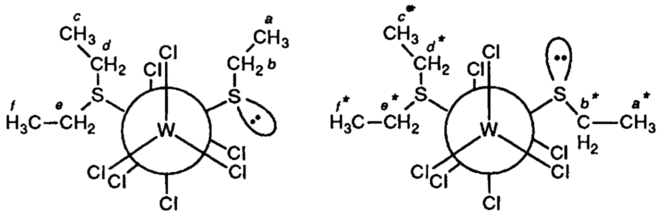
W(1)–S(2)	2.354(2)	W(2)–Cl(1)	2.502(2)
W(1)–Cl(4)	2.396(2)	W(2)–Cl(6)	2.426(2)
W(1)–S(1)	2.401(2)	W(2)–Cl(5)	2.430(2)
W(1)–Cl(3)	2.438(2)	S(1)–C(1)	1.823(10)
W(1)–W(2)	2.4418(6)	S(2)–C(5)	1.804(10)
W(1)–Cl(2)	2.453(2)	S(2)–C(3)	1.806(8)
W(1)–Cl(1)	2.478(2)	C(1)–C(2)	1.51(1)
W(2)–S(2)	2.365(2)	C(3)–C(4)	1.52(1)
W(2)–Cl(7)	2.394(2)	C(5)–C(6)	1.51(1)
W(2)–S(1)	2.413(2)		
S(2)–W(1)–Cl(4)	90.28(7)	S(2)–W(2)–W(1)	58.62(5)
S(2)–W(1)–S(1)	102.49(7)	Cl(7)–W(2)–S(1)	88.96(8)
S(2)–W(1)–Cl(3)	172.86(8)	Cl(7)–W(2)–Cl(6)	95.07(7)
S(2)–W(1)–W(2)	59.05(5)	Cl(7)–W(2)–Cl(5)	91.13(8)
S(2)–W(1)–Cl(2)	89.90(7)	Cl(7)–W(2)–W(1)	122.68(5)
S(2)–W(1)–Cl(1)	92.64(7)	S(1)–W(2)–Cl(6)	83.39(7)
Cl(4)–W(1)–S(1)	87.76(7)	S(1)–W(2)–Cl(5)	170.51(5)
Cl(4)–W(1)–Cl(3)	92.92(7)	S(1)–W(2)–W(1)	59.29(5)
Cl(4)–W(1)–W(2)	124.02(5)	Cl(6)–W(2)–Cl(5)	87.16(7)
Cl(4)–W(1)–Cl(2)	89.60(8)	Cl(6)–W(2)–W(1)	123.08(5)
Cl(4)–W(1)–Cl(1)	174.77(7)	Cl(5)–W(2)–W(1)	127.72(6)
S(1)–W(1)–Cl(3)	84.03(7)	W(1)–Cl(1)–W(2)	58.7(1)
S(1)–W(1)–W(2)	59.75(5)	C(1)–S(1)–W(1)	115.8(3)
S(1)–W(1)–Cl(2)	170.26(7)	C(1)–S(1)–W(2)	114.5(3)
S(1)–W(1)–Cl(1)	95.84(7)	W(1)–S(1)–W(2)	60.96(6)
Cl(3)–W(1)–W(2)	123.49(5)	C(5)–S(5)–C(3)	103.4(4)
Cl(3)–W(1)–Cl(2)	86.75(7)	C(5)–S(2)–W(1)	119.8(3)
Cl(3)–W(1)–Cl(1)	83.70(7)	C(5)–S(2)–W(2)	119.8(3)
W(2)–W(1)–Cl(2)	128.86(6)	C(3)–S(2)–W(1)	123.4(3)
W(2)–W(1)–Cl(1)	61.20(5)	C(3)–S(2)–W(2)	124.9(3)
Cl(2)–W(1)–Cl(1)	86.23(7)	W(1)–S(2)–W(2)	62.33(5)
S(2)–W(2)–Cl(7)	87.98(7)	C(2)–C(1)–S(1)	109.1(6)
S(2)–W(2)–S(1)	101.84(7)	C(4)–C(3)–S(2)	112.7(7)
S(2)–W(2)–Cl(6)	174.03(8)	C(6)–C(5)–S(2)	114.2(7)
S(2)–W(2)–Cl(5)	87.65(7)		

X-Ray Crystal Structure of $[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]\cdot 2CH_2Cl_2$.—The anion of **6** is shown in Fig. 1(*a*) in a conventional orientation which shows the $W(\mu\text{-}L)_3W$ geometry, and in Fig. 1(*b*) as viewed along the W–W vector. The expected confacial bioctahedral structure is confirmed, and the dealkylation of one of the SEt_2 ligands of the parent anion is established. The anion is, to our knowledge, the first strictly confacial bioctahedral complex to be studied crystallographically which possesses three different bridging ligands. One related structure has been reported,[9] namely $[(\eta^5\text{-}C_5Me_4Et)Cl_2Ta(\mu\text{-}\sigma\text{-}N,\eta^2\text{-}C,N\text{-}NCHMe)(\mu\text{-}Cl)(\mu\text{-}H)TaCl_2(\eta^5\text{-}C_5Me_4Et)]$, which contains H, Cl and N as the bridging ligands. An additional feature of interest in the structure of **6** is that, since the bridges are all *trans* to terminal chlorides, the structure offers a rare example in which direct comparisons can be made

$$\underset{\textbf{3a}}{[PPh_4][Cl_3W(\mu\text{-}SMe_2)_2(\mu\text{-}Cl)WCl_3]} + [PPh_4][SC_6H_4Me\text{-}4] \longrightarrow \underset{\textbf{7}}{[PPh_4]_2[Cl_3W(\mu\text{-}SMe_2)(\mu\text{-}SMe)(\mu\text{-}Cl)WCl_3]} + MeSC_6H_4Me\text{-}4 \qquad (2)$$

$$\underset{\textbf{4}}{[PPh_4][Cl_3W(\mu\text{-}tht)_2(\mu\text{-}Cl)WCl_3]} + [PPh_4][SC_6H_4Me\text{-}4] \longrightarrow \underset{\textbf{8}}{[PPh_4]_2[Cl_3W(\mu\text{-}tht)\{\mu\text{-}S(CH_2)_4SC_6H_4Me\text{-}4\}(\mu\text{-}Cl)WCl_3]} \qquad (3)$$

$$\underset{\textbf{5}}{[PPh_4][Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]} + [PPh_4][SC_6H_4Me\text{-}4] \longrightarrow \underset{\textbf{6}}{[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]} + EtSC_6H_4Me\text{-}4 \qquad (4)$$



(axial) (equatorial)

Fig. 2 Newman projection diagrams of the axial and equatorial isomers of the anion of **6** showing the labelling used in discussion of the spectral assignments

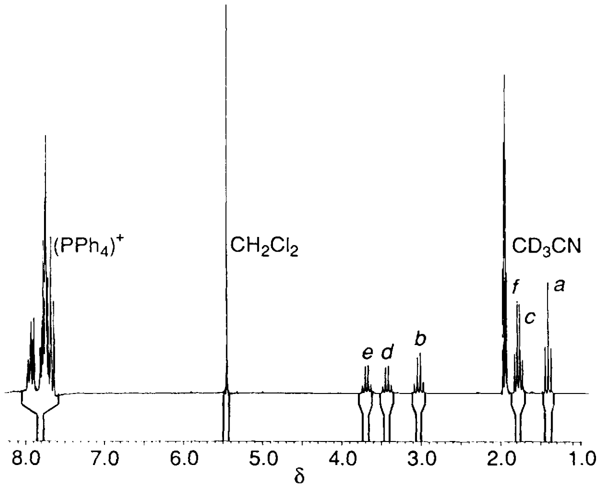


Fig. 3 Proton NMR spectrum (CD_3CN solution) of pure, crystalline, $[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]\cdot 2CH_2Cl_2$ **6**

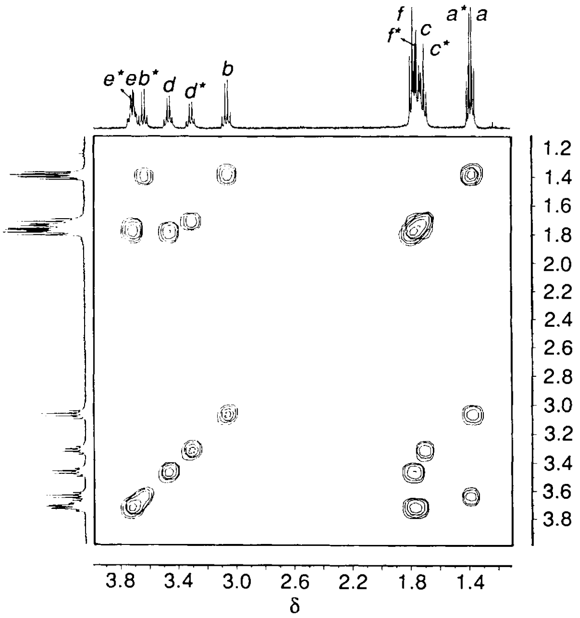
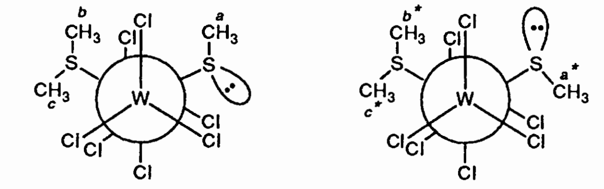


Fig. 4 COSY ^1H NMR spectrum of a mixture of the axial and equatorial isomers of $[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]\cdot 2CH_2Cl_2$ **6**, with assignments based on labels in Fig. 2

between metal–μ-$S_{thiolate}$, metal–μ-$S_{thioether}$ and metal–μ-Cl bond lengths. It can be seen (Table 1) that the shortest bonds are those between the W and the S of the bridging thioether, while the longest bonds involve the μ-Cl atom. It is noteworthy that the thiolate possesses weaker interactions with the metal than does the thioether ligand, based on these bond distances. The angles subtended at the bridging atoms are all much smaller than the 70.5° angle expected for an undistorted confacial bioctahedron, and are indicative of strong metal–metal interactions.[10] The W–W distance [2.4418(6) Å] is shorter than those observed in either **2** [2.4990(9) Å] or **3** [2.4752(8) Å].[1] A key feature of this structure, which is clearly shown in Fig. 1, is the orientation of the Et group of the μ-SEt, which is axial with reference to the μ-SEt_2 ligand. This stereochemistry is retained upon dissolution in certain organic solvents, a fact which has been exploited to provide unique and unambiguous information on the assignment of the ^1H NMR spectra of this and the related equatorial isomer. It also allows some possible insight into the steric influence on the course of the original nucleophilic displacement of S from the α-carbon atom of a μ-SEt_2 ligand.

Assignment of the ^1H *NMR Spectrum of* **6**.—The crystal structure of **6** shows that the configuration of the S atom of the bridging thiolate ligand [S(1)] puts the ethyl group into an axial position with respect to the μ-thioether ligand, with the S(1)–C(1) bond lying almost parallel to the vertical plane which contains the W(1), W(2), Cl(1), Cl(4) and Cl(7) atoms. It can be seen that there should be three different sets of ^1H NMR signals due to the ethyl groups in this structure. Inversion at S(1) would give the equatorial isomer, which would be predicted to display a further three sets of ethyl resonances. This is shown schematically in Fig. 2, with each set of H atoms labelled for referencing to the actual spectra. The spectrum of the crystalline sample used in the X-ray study was measured immediately after dissolution in CD_3CN and is shown in Fig. 3, with the signals assigned according to the following arguments. The signals due to the phosphonium cation are in the expected range δ 8.0–7.61. There are three sets of resonances due to ethyl groups as expected for the single, axial isomer. The two-dimensional correlation (COSY) spectrum (*cf.* Fig. 4) shows that the triplet at δ 1.422 is correlated with the quartet at δ 3.037, and the two overlapping triplets at δ 1.772 and 1.802 are correlated with the quartets at δ 3.440 and 3.697 respectively. To distinguish the SEt from the SEt_2 resonances, reference is made to the spectrum of the analogous anion, $[Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}SEt)WCl_3]^-$, in which we found previously[7] that the triplets due to the methyl component of the ethyl resonances were divided into two groups. The unique triplet was centred at δ 1.40, while the other four were at δ 1.70, 1.71, 1.74 and 1.76. The quartets due to the methylene protons were less useful as a diagnostic tool. Even though the quartet shown by selective decoupling to be due to the SEt ligand was still at highest field, it overlaps with one of the quartets due to the μ-SEt_2 ligands. In the spectrum of **6**, the triplet at highest field, δ 1.422, can now be assigned to the thiolate ligand (the protons labelled *a* in Fig. 2). The triplets at δ 1.772 and 1.802 are thus associated with the methyl groups of diethyl sulfide, while the *b* methylene resonances are at δ 3.037. By examining Fig. 2 it can be seen that the methylene protons likely to be least sensitive to changing from the axial to the equatorial isomer would be *e*/*e**. Comparing the spectrum of the pure axial isomer (Fig. 3) with that of the mixture (Fig. 4, see below), the CH_2 resonances which are virtually unchanged are those at lowest field, δ 3.697. This quartet is thus assigned to the *e* protons, and the triplet at δ 1.802 to the *f* protons. This leaves the assignment of the *c* and *d* protons to the triplet at δ 1.772 and the quartet at δ 3.440 respectively.

These assignments are compatible with the trends expected as a result of deshielding effects of the bridging Cl ligand. Such a through-space deshielding effect by chloride has been observed previously in the ^1H NMR spectra of 2-chloroadamantane.[11,12] The *e* protons, which were assigned to the quartet at lowest field (*i.e.* δ 3.697) would be most affected by the deshielding influence of Cl(1). The *b* and *d* protons in the axial isomer would be more difficult to differentiate on this basis, but as shown in Fig. 1(*b*) the *b* set are furthest away from Cl(1), and would be expected to be at highest field, as assigned. Also, they would obviously be



(axial) (equatorial)

Fig. 5 Newman projection diagrams of the axial and equatorial isomers of the anion of **7**, $[Cl_3W(u\text{-}SMe_2)(u\text{-}SMe)(u\text{-}Cl)WCl_3]^{2-}$, with the labelling scheme used in NMR spectral assignments

the most sensitive to a change in configuration at S(1) (see below).

The ^1H NMR spectrum of the solution of **6** in CD_2Cl_2 was remeasured after standing for 1, 3 and 6 h, and during this time it was found that the second, equatorial, isomer was formed. The equilibration between structures was essentially complete at the 3 h point. A COSY spectrum of this solution after standing for 24 h is presented in Fig. 4. The resonances for the equatorial isomer were assigned using the correlations derived from the COSY spectrum, and by analogy with the axial isomer, with labels as shown in Fig. 2. It will first be noted that the ratio of isomers is approximately 1:0.84 in favour of the axial. The most dramatic change in the spectra is the low field of the *b** as compared with *b* resonances. This supports the arguments presented above relating to the deshielding effect of μ-Cl on the methylene resonances of the neighbouring SEt groups. As shown in Fig. 2, this is precisely the trend which would be expected, since the CH_2 group of the SEt ligand is now approximately the same distance from the u-Cl as the *e* protons are. The *a** protons remain largely unaffected, as expected on the basis of this argument.

Assignment of the ^1H *NMR Spectrum of* $[PPh_4]_2[Cl_3W(\mu\text{-}SMe_2)(\mu\text{-}SMe)(u\text{-}Cl)WCl_3]$ **7**.—The methyl resonances in the spectrum of this compound show that two isomers are present in the original synthesis, and upon crystallization from acetone only one (presumably again the axial) form is present. These isomers are shown, with labels for the methyl groups, in Fig. 5. Redissolving in CD_3CN gives a spectrum with resonances at δ 3.28, 3.05 and 2.63. By extension of the above argument for the ethyl case, the lowest field resonance should be due to the *c* protons, with the *a* protons at highest field, at δ 2.63. The equatorial isomer shows resonances at δ 3.287 (*c**), 3.14 (*a**) and 2.93 (*b**) respectively.

Interconversion between the Axial and Equatorial Isomers.—This process was subjected to a kinetic study, using ^1H NMR spectroscopy. A solution of the axial isomer was made up in CD_2Cl_2 using crystals of **6**. The solution was frozen in a liquid nitrogen bath, then the tube was immediately flame-sealed, under vacuum. Data acquisition was commenced immediately after warming to 25 °C, and the interconversion process was followed by using the intensities of two well separated quartets due to the different isomers. The process was complete within 2 h, but the final equilibrium concentrations were measured after 24 h. The isomerization process, as represented by equation (5), was found to be rigorously first order, with no evidence for decomposition in this solvent, over the 24 h period.

$$\text{axial} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{equatorial} \qquad (5)$$

The rate constants were found to be: $k_1 = 1.32 \times 10^{-4}\ s^{-1}$; $k_{-1} = 1.57 \times 10^{-4}\ s^{-1}$; the equilibrium constant at 25 °C is 0.84 and ΔG for the conversion of the axial to the equatorial isomer is $+432\ J\ mol^{-1}$.

Discussion

The dealkylation of bridging thioethers in the monoanionic complexes **3a**, **4** and **5** can be effected by reaction with thiolate anion. The ^1H NMR spectrum of the initial reaction product in the SEt_2 case (**5**) shows that both the axial and equatorial isomers are present, in the thermodynamically determined 1:0.84 ratio in favour of the axial. Although, as discussed above, interconversion between these two isomers of **6** occurs in solution, crystallization from dichloromethane–hexane solution yields only the axial species. The preferential formation of the axial isomer might also have been predicted on the basis of the steric factors involved in the synthesis, since access by the nucleophile to the α-carbon atoms of the SEt_2 ligands would be easier from the Cl side (*cf.* Fig. 2). However, as the kinetic study in CD_2Cl_2 showed, there is a slight thermodynamic preference for the axial over the equatorial isomer, and the equilibrium between them is achieved over a relatively short time period (*ca.* 2 h). The interconversion process was too slow at room temperature to study by NMR line-broadening techniques, and attempts to do so at 60 °C in $CDCl_2CDCl_2$ resulted in decomposition, with production of free SEt_2. By comparison with previous work in our laboratory,[13,14] the (implied) high value of the activation energy for inversion at S(1) may be due to the acute W–S–W angle associated with the strong W–W bonding. For the more weakly bonded W^V–W^V complex, $[Cl_2OW(u\text{-}Cl)(u\text{-}SBu^i)_2WOCl_2]^-$, for inversion at sulfur the free energy of activation was found to be 75 ± 5 kJ mol^{-1}, resulting in a coalescence temperature of 363 ± 5 K. The equatorial–equatorial isomer, on which a crystal structure determination was performed, interconverted with the equatorial–axial isomer so quickly that solutions always displayed both sets of resonances. This complex had a W–W bond length of 2.854(2) Å, and W–S–W angles of *ca.* 72°.[13] A W^{IV}–W^{IV} complex, $[W_2Cl_4(u\text{-}SBu^i)_2(u\text{-}S)(SMe_2)_2]$ with similar structural features except for a stronger metal–metal interaction,[14] was shown to exist as only one isomer over the accessible temperature range.

Experimental

General Procedures and Techniques.—All manipulations were carried out using standard glove-box and double-manifold vacuum-line techniques under an atmosphere of dry nitrogen. Solvents were dried and degassed by standard procedures, as described previously.[1] Elemental analyses were performed by the University of Calgary Department of Chemistry Analytical Services Laboratory. Routine ^1H NMR spectra were recorded on a Bruker ACE-200 spectrometer; the ACE-200 was also to record the data for two-dimensional COSY spectra, and the data were then transferred to a Bruker Aspect-2000 data station for computation and plotting. UV/VIS spectra were measured in the range 200–800 nm using a Varian 219 spectrophotometer.

Preparation of Complexes of the Ditungsten(III) *Anions* $[Cl_3W(u\text{-}SR_2)_2(\mu\text{-}Cl)WCl_3]$.—(*a*) $Na[Cl_3W(u\text{-}SEt_2)_2(u\text{-}Cl)WCl_3]$. Freshly prepared WCl_4 (4 g, 0.01228 mol), Na/Hg (0.4%, 73 g) and SEt_2 (50 cm^3) were placed in a Schlenk vessel and stirred at 60–70 °C for *ca.* 40 min. The slurry became orange-brown, and on standing an orange-brown solid settled out. The supernatant liquid was removed, and the residual solid was washed with diethyl ether, then extracted with CH_2Cl_2 several times to remove any $[Cl_3W(\mu\text{-}SEt_2)_3WCl_3]$ which is a minor reaction product under these conditions. The remaining CH_2Cl_2-insoluble solid was then extracted with dry acetonitrile (3 × 100 cm^3) and the resulting orange solution was then pumped to dryness. The orange solid so produced was washed with CH_2Cl_2, and redissolved in acetonitrile. After filtration of this solution to remove any insoluble contaminants, the removal of solvent gave rise to the pure product. Yield of $Na[Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]$, 3.17 g, 63% (Found: C, 11.15; H, 2.20. Calc. for $C_4H_{20}Cl_7NaS_2W_2$: C, 11.75; H, 2.45%). ^1H

Table 2 Fractional atomic coordinates for the non-hydrogen atoms of compound **6**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W(1)	0.211 49(3)	0.310 54(3)	0.712 80(1)
W(2)	0.170 20(3)	0.251 69(3)	0.808 17(1)
S(1)	0.192 8(2)	0.111 7(2)	0.747 2(1)
S(2)	0.048 8(2)	0.445 8(2)	0.752 9(1)
Cl(1)	0.366 6(2)	0.289 6(2)	0.784 6(1)
Cl(2)	0.252 6(2)	0.496 1(2)	0.666 3(1)
Cl(3)	0.392 3(2)	0.189 6(2)	0.670 6(1)
Cl(4)	0.073 2(2)	0.337 1(2)	0.637 5(1)
Cl(5)	0.166 9(2)	0.361 9(2)	0.880 6(1)
Cl(6)	0.303 9(2)	0.064 6(2)	0.869 7(1)
Cl(7)	−0.018 6(2)	0.223 1(2)	0.835 5(1)
Cl(8)	0.596 5(2)	−0.164 1(2)	0.749 9(1)
Cl(9)	0.689 9(2)	−0.011 4(3)	0.800 8(1)
Cl(10A)	0.603 2(17)	0.436 0(17)	0.635 6(7)
Cl(10B)	0.636 8(18)	0.404 7(16)	0.640 0(7)
Cl(11A)	0.690 3(6)	0.311 2(8)	0.744 4(3)
Cl(11B)	0.611 7(8)	0.427 0(11)	0.750 3(3)
P(1)	0.207 5(2)	0.118 2(2)	0.500 6(1)
P(2)	0.249 5(2)	0.672 7(2)	0.985 7(1)
C(1)	0.048 7(7)	0.097 2(8)	0.727 4(4)
C(2)	0.036 3(8)	0.017 2(8)	0.763 6(4)
C(3)	−0.112 7(7)	0.490 8(8)	0.731 9(4)
C(4)	−0.154 3(8)	0.598 6(9)	0.682 5(4)
C(5)	0.059 7(7)	0.587 9(8)	0.765 2(4)
C(6)	−0.032 0(9)	0.647 9(9)	0.804 1(4)
C(7)	0.558 6(8)	−0.039 8(9)	0.783 3(4)
C(8)	0.566 4(9)	0.370 1(9)	0.700 0(4)
C(11)	0.057 4(6)	0.225 1(7)	0.509 1(3)
C(12)	−0.016 6(7)	0.188 7(7)	0.548 1(3)
C(13)	−0.133 4(7)	0.270 7(8)	0.553 2(4)
C(14)	−0.176 5(7)	0.387 8(8)	0.518 9(4)
C(15)	−0.103 7(8)	0.422 8(7)	0.479 9(4)
C(16)	0.012 7(7)	0.342 7(7)	0.475 3(3)
C(21)	0.206 6(6)	0.062 5(7)	0.439 7(3)
C(22)	0.311 8(7)	0.031 5(8)	0.428 5(4)
C(23)	0.314 0(8)	0.075 7(8)	0.381 7(4)
C(24)	0.211 4(8)	0.025 2(8)	0.345 2(4)
C(25)	0.106 3(8)	0.068 7(8)	0.355 9(3)
C(26)	0.103 9(7)	0.113 0(7)	0.403 0(3)
C(31)	0.246 3(6)	−0.012 3(7)	0.557 3(3)
C(32)	0.213 5(7)	−0.113 3(7)	0.552 0(3)
C(33)	0.230 0(7)	−0.210 1(7)	0.597 0(3)
C(34)	0.276 8(7)	−0.204 5(7)	0.646 4(3)
C(35)	0.310 1(8)	−0.104 8(8)	0.650 7(4)
C(36)	0.294 5(7)	0.008 9(7)	0.606 7(3)
C(41)	0.314 4(7)	0.198 9(7)	0.495 6(3)
C(42)	0.320 2(7)	0.261 1(7)	0.536 1(3)
C(43)	0.404 1(8)	0.322 6(7)	0.533 1(4)
C(44)	0.475 8(7)	0.324 9(8)	0.489 6(4)
C(45)	0.466 4(7)	0.268 3(8)	0.448 4(4)
C(46)	0.386 9(7)	0.203 7(7)	0.451 0(3)
C(51)	0.250 0(7)	0.525 9(7)	1.023 8(3)
C(52)	0.328 7(7)	0.462 7(8)	1.070 2(4)
C(53)	0.324 0(8)	0.349 8(8)	1.098 6(4)
C(54)	0.246 5(8)	0.299 1(8)	1.080 9(4)
C(55)	0.170 5(8)	0.360 5(8)	1.034 5(4)
C(56)	0.170 4(8)	0.475 2(8)	1.005 9(3)
C(61)	0.306 3(7)	0.659 1(7)	0.920 1(3)
C(62)	0.339 7(7)	0.546 5(7)	0.903 0(3)
C(63)	0.378 7(8)	0.540 8(8)	0.850 8(4)
C(64)	0.383 9(8)	0.647 0(9)	0.815 5(4)
C(65)	0.350 2(7)	0.758 9(8)	0.832 3(4)
C(66)	0.312 4(7)	0.765 3(7)	0.884 3(4)
C(71)	0.341 5(7)	0.727 2(7)	1.023 9(3)
C(72)	0.313 6(7)	0.740 1(7)	1.076 0(3)
C(73)	0.383 7(8)	0.781 0(8)	1.106 3(4)
C(74)	0.481 8(8)	0.810 2(8)	1.082 4(4)
C(75)	0.509 5(8)	0.798 1(8)	1.030 2(4)
C(76)	0.440 8(7)	0.755 6(8)	1.000 7(4)
C(81)	0.091 4(7)	0.779 4(7)	0.978 2(3)
C(82)	0.038 1(7)	0.856 6(8)	0.929 0(3)
C(83)	−0.083 2(8)	0.940 1(9)	0.926 4(4)
C(84)	−0.149 7(7)	0.947 6(8)	0.971 9(4)
C(85)	−0.095 5(7)	0.869 8(8)	1.021 1(4)
C(86)	0.023 1(7)	0.785 8(8)	1.023 9(3)

NMR $[(\mathrm{CD_3})_2\mathrm{CO}]$: δ 3.92 (q, 4 H), 3.47 (q, 4 H), 1.86 (t, 6 H) and 1.80 (t, 6 H).

(*b*) $[\mathrm{PPh_4}][\mathrm{Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3}]$ **5**. The complex $\mathrm{Na[Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]}$ (1.99 g, 0.002 44 mol) and $[\mathrm{PPh_4}]\mathrm{Cl}$ (1.01 g, 0.002 70 mol) were loaded into a Schlenk tube with $\mathrm{CH_2Cl_2}$ (50 $\mathrm{cm^3}$). An orange solution was quickly produced, and after stirring for 2 h the residual NaCl was filtered off, and the filtrate evaporated to dryness. The solid was then extracted with propan-2-ol (2 × 60 $\mathrm{cm^3}$) in an ultrasonic bath, which dissolves any unreacted $[\mathrm{PPh_4}]\mathrm{Cl}$, and then with diethyl ether (3 × 60 $\mathrm{cm^3}$). The solid was then pumped for 24 h giving an analytically pure sample of the target compound **5**. Yield: 2.52 g, 91% (Found: C, 33.90; H, 3.45. Calc. for $\mathrm{C_{32}H_{40}Cl_7PS_2W_2}$: C, 33.85; H, 3.45%). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 8.0–7.6 (m, 20 H), 3.91 (q, 4 H), 3.48 (q, 4 H), 1.81 (t, 6 H) and 1.76 (t, 6 H). UV/VIS spectrum (MeCN): λ/nm ($\varepsilon/\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) 526 (320), 400 (7500) and 317 (3970).

(*c*) $\mathrm{Na[Cl_3W(\mu\text{-}tht)_2(\mu\text{-}Cl)WCl_3]}$. This complex was prepared in an exactly analogous way to its $\mathrm{SEt_2}$ analogue as described in (*a*) above, and its identity was confirmed as follows (Found: C, 11.45; H, 2.00. Calc. for $\mathrm{C_8H_{16}Cl_7NaS_2W_2}$: C, 11.80; H, 1.85%). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 3.99 (m, 4 H), 3.41 (m, 4 H) and 2.43 (m, 8 H).

(*d*) $[\mathrm{PPh_4}][\mathrm{Cl_3W(u\text{-}tht)_2(\mu\text{-}Cl)WCl_3}]$ **4**. This complex was obtained in high yield from the sodium salt by reaction with $[\mathrm{PPh_4}]\mathrm{Cl}$ as in (*b*) above (Found: C, 33.85; H, 3.20. Calc. for $\mathrm{C_{32}H_{36}Cl_7PS_2W_2}$: C, 33.85; H, 3.20%). UV/VIS spectrum (MeCN): λ/nm ($\varepsilon/\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) 526 (480), 400 (7900) and 319 (4000).

(*e*) $[\mathrm{PPh_4}][\mathrm{Cl_3W(\mu\text{-}SMe_2)_2(\mu\text{-}Cl)WCl_3}]$ **3a**. This complex was made from the trimethylsulfonium salt of the same anion, the synthesis of which was reported earlier.[1] The salt $[\mathrm{SMe_3}][\mathrm{Cl_3W(u\text{-}SMe_2)_2(u\text{-}Cl)WCl_3}]$ (3.0 g, 0.0035 mol) and $[\mathrm{PPh_4}]\mathrm{Cl}$ (2.0 g, 0.00533 mol) were weighed into a Schlenk tube and $\mathrm{CH_2Cl_2}$ (100 $\mathrm{cm^3}$) was introduced. The mixture was stirred for 12 h, then filtered. The filtrate was pumped to dryness, and the solid was extracted with propan-2-ol (2 × 100 $\mathrm{cm^3}$) in an ultrasonic bath, then with diethyl ether (3 × 60 $\mathrm{cm^3}$). The solid (3.56 g, 94%) was pumped to dryness, then recrystallized from acetone giving crystals of the acetone solvate, $[\mathrm{PPh_4}][\mathrm{Cl_3W(\mu\text{-}SMe_2)_2(\mu\text{-}Cl)WCl_3}]\cdot(\mathrm{CH_3})_2\mathrm{CO}$. Yield: 3.60 g, 90% (Found: C, 32.90; H, 3.20. Calc. for $\mathrm{C_{31}H_{38}Cl_7OPS_2W_2}$: C, 32.75; H, 3.35%). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 8.0–7.6 (m, 20 H), 3.46 (s, 6 H), 3.06 (s, 6 H) and 2.09 [s, 6 H, $(\mathrm{C}H_3)_2\mathrm{CO}$]. UV/VIS spectrum (MeCN): λ/nm ($\varepsilon/\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) 526 (360), 394 (8880) and 318 (4060).

(*f*) *Alternative route to the anion* $[\mathrm{Cl_3W(u\text{-}SEt_2)_2(u\text{-}Cl)WCl_3}]^-$. As a footnote to these preparative procedures, it should be observed that upon careful work-up, the reactions reported in ref. 1 can yield other complexes as minor products. For example, $[\mathrm{SEt_3}][\mathrm{Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3}]$ **9**, was discovered as a by-product in the preparation of the neutral complex $[\mathrm{Cl_3W(\mu\text{-}SEt_2)_3WCl_3}]$ **2**. It could be used to prepare the $[\mathrm{PPh_4}]^+$ salt of the same anion, **5**, by a procedure analogous to that described for **3a** in (*e*) above. Complex **9** was first isolated as follows; $\mathrm{WCl_4}$, prepared by the method of Schaefer King and McCarley,[8] was heated in a sealed evacuated tube at 225 °C for a period of 24 h to remove any traces of higher tungsten chlorides. This $\mathrm{WCl_4}$ (9.7 g, 0.0297 mol) was loaded into a Schlenk flask with Na/Hg (0.4%, 172 g) and $\mathrm{SEt_2}$ (100 $\mathrm{cm^3}$). The mixture was heated to reflux at atmospheric pressure with vigorous stirring for 40 min, then cooled to room temperature. The red solution was decanted from the residual solids which were then washed with diethyl ether (3 × 100 cm^3) and extracted with portions of CH_2Cl_2 until the extractant solvent was almost colourless. The combined CH_2Cl_2 extracts were then pumped to remove solvent, leaving a tarry residue. This material was extracted with portions of acetone (in total *ca.* 50 cm^3) leaving **2** as the major component of the solid residue. The acetone solution was found to contain largely the ionic product **9**, which was obtained by first precipitating traces of **2** with diethyl ether (20 cm^3), pumping to dryness and recrystallizing the residue from thf (30 cm^3). The total yield of $[SEt_3][Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]$ **9** was 1.3 g, 9.6% (Found: C, 18.45; H, 3.85. Calc. for $C_{14}H_{35}Cl_7S_3W_2$: C, 18.45; H, 3.85%). ^1H NMR (CD_3CN): δ 3.90 (q, 4 H), 3.49 (q, 4 H), 3.20 (q, 6 H), 1.83 (t, 6 H), 1.77 (t, 6 H) and 1.39 (t, 9 H). The preferred synthetic method for obtaining the anion $[Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]^-$ is clearly *via* the sodium salt as in (*a*), since this optimises the yield as compared with that of the neutral complex **2**.

Reactions of $[PPh_4][Cl_3W(\mu\text{-}SR_2)_2(\mu\text{-}Cl)WCl_3]$ *with* $[PPh_4][SC_6H_4Me\text{-}4]$.—(*a*) *Preparation of* $[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]\cdot 2CH_2Cl_2$ **6**. The compounds $[PPh_4][Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}Cl)WCl_3]$ **5** (1.00 g, 0.884 mmol) and $[PPh_4][SC_6H_4Me\text{-}4]$ (0.63 g, 1.37 mmol) were loaded into a Schlenk tube fitted with a rubber septum, and degassed MeCN (60 cm^3) was added *via* a transfer tube. The solution was stirred, and maintained at 50 °C until ^1H NMR testing of extracted samples revealed that the original complex **5** had all been consumed. The reaction was normally found to be complete within 4 h. (The test samples were removed using a syringe, and then placed in an NMR tube. The solvent was removed under vacuum, and the solids redissolved in CD_3CN.) After completion of the reaction, the solution was evaporated to dryness under vacuum, and the residual solids extracted with diethyl ether to remove the $EtSC_6H_4Me\text{-}4$ [^1H NMR (CD_3CN): δ 7.27–7.10 (m, 4 H, C_6H_4), 2.91 (q, 2 H, CH_3CH_2), 2.30 (s, 3 H, $C_6H_4CH_3$) and 1.24 (t, 3 H, CH_3CH_2)]. The remaining solid was then extracted with propan-2-ol to remove excess thiolate salt, washed with diethyl ether, and dried under vacuum. Yield of $[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]$, 1.23 g, 96%. The ^1H NMR spectrum of this material revealed that it is a mixture of two isomers, which differ in the configuration of the μ-thiolato sulfur atom (see Results section). Recrystallization from CH_2Cl_2–hexanes yielded well formed crystals, almost cubic in shape. Several successive crops of crystals (which had identical form and ^1H NMR spectra) were obtained over a period of a month. Analyses and ^1H NMR studies confirmed the identity of these crystals as a dichloromethane solvate, **6** (Found: C, 41.45, H, 3.55. Calc. for $C_{56}H_{59}Cl_{11}P_2S_2W_2$: C, 41.60; H, 3.70%). The ^1H NMR spectrum of **6**, which is a single configurational isomer, is discussed in the Results section.

(*b*) *Preparation of* $[PPh_4]_2[Cl_3W(\mu\text{-}SMe_2)(\mu\text{-}SMe)(\mu\text{-}Cl)WCl_3]$ **7**. This compound was prepared from the reaction between $[PPh_4][Cl_3W(\mu\text{-}SMe_2)_2(\mu\text{-}Cl)WCl_3]$ **3a** and $[PPh_4][SC_6H_4Me]$ in CH_3CN solution using the same procedure, and on the same scale, as described for **6**. The yield was >90%. The organic sulfide by-product, $MeSC_6H_4Me\text{-}4$, was identified by a GC–MS study (M^+ 138), and by its ^1H NMR spectrum ($CDCl_3$): δ 7.23–7.06 (m, 4 H, C_6H_4), 2.47 (s, 3 H, SCH_3) and 2.32 (s, 3 H, $C_6H_4CH_3$). The solid product, after washing with propan-2-ol and diethyl ether, was characterized as $[PPh_4][Cl_3W(\mu\text{-}SMe_2)(\mu\text{-}SMe)(\mu\text{-}Cl)WCl_3]$ (Found: C, 42.85; H, 3.25. Calc. for $C_{51}H_{49}Cl_7P_2S_2W_2$: C, 43.65; H, 3.50%). The ^1H NMR spectrum in CD_3CN solution, which confirmed the identity of the product, and showed the existence of two isomers, is discussed in the Results section.

(*c*) *Preparation of* $[PPh_4]_2[Cl_3W(\mu\text{-}tht)\{\mu\text{-}S(CH_2)_4\text{-}SC_6H_4Me\text{-}4\}(\mu\text{-}Cl)WCl_3]$ **8**. This compound was prepared in almost 100% yield from the reaction between $[PPh_4][Cl_3W(\mu\text{-}tht)_2(\mu\text{-}Cl)WCl_3]$ **4** and $[PPh_4][SC_6H_4Me]$ using the same procedures as described for **6** and **7**, with the omission of the step of isolating a thioether (Found: C, 49.05; H, 4.10. Calc. for $C_{67}H_{71}Cl_7P_2S_3W_2$: C, 48.75; H, 4.35%). ^1H NMR (CD_3CN): δ 8.07–7.61 (m), 7.35–7.09 (quasi q), 3.76 (m), 3.44–3.30 (m), 2.96–2.84 (2 overlapping triplets), 2.48–2.30 (m), 2.28 (s) and 1.91–1.58 (m). A COSY ^1H NMR spectrum confirmed that this complicated spectrum was compatible with the proposed structure, which has two configurational isomers based on the geometry of the bridging thiolate ligand.

X-Ray Crystal Structure of Compound **6**.—*Crystal data*. $[PPh_4]_2(Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]\cdot 2CH_2Cl_2$ **6**, $C_{56}H_{59}Cl_{11}P_2S_2W_2$, $M = 1615.85$, triclinic, space group $P\bar{1}$, $a = 11.566(3)$, $b = 11.736(4)$, $c = 25.113(4)$ Å, $\alpha = 78.23(2)$, $\beta = 89.05(2)$, $\gamma = 69.18(2)^\circ$, $U = 3113.2$ Å^3, $Z = 2$, $D_c = 1.724$ g cm^{-3}, $F(000) = 1584$ and $\mu(\text{Mo-K}\alpha) = 41.1$ cm^{-1}.

A fragment of dimensions 0.50 × 0.40 × 0.38 mm was cut from a dark orange, rectangular block-shaped crystal, and mounted on a glass fibre using epoxy resin, with which it was also coated. It was subsequently mounted on an Enraf-Nonius CAD4 diffractometer. Accurate cell dimensions and a crystal orientation matrix were determined by a least-squares refinement of 25 reflections with θ in the range 10–15°. Intensity data were collected using Mo-Kα radiation, at 165 K by the ω–2θ scan method, with variable scan speed (1.54–6.67° min^{-1}), scan width [(1.00 + 0.35 tanθ)°], in the range $2 < \theta < 24^\circ$ and h 0 to 13, k −13 to 13, and l −28 to 28. Three reflections were monitored every two hours of exposure time and showed insignificant variations. The intensities of 10 463 reflections were measured, of which 8407 had $I > 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0.04\ (S - B)]^2$, with S = scan count, and B = time averaged background count extended 25% on either side. Data were corrected for Lorentz, polarization and absorption effects (DIFABS[15]). Correction coefficients were in the range 0.870–1.266.

The structure was solved by direct methods. Refinement of the structure was done by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic thermal parameters for the non-hydrogen atoms. At an intermediate stage of the refinement, a difference map revealed most of the hydrogen atoms and these were included in subsequent steps in idealized positions, and a fixed, overall isotropic thermal parameters. The two Cl atoms [Cl(10), Cl(11)] of one CH_2Cl_2 solvent molecule are disordered, and partially occupy two pairs of sites. The disordered H atoms of this CH_2Cl_2 solvent molecule were ignored. Refinement converged with $R = 0.035$, and $R' = 0.042$. In the refinement cycles, weights derived from the counting statistics were used. Scattering factors were taken from Cromer and Mann,[16] and allowance was made for anomalous dispersion.[17] A difference map calculated at the end of the refinement showed no chemically significant features. All computer programs used in this study were part of the XTAL2.6 system,[18] and Fig. 1 was plotted using ORTEP II.[19]

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

Kinetic Study of the Conversion of the Axial to the Equatorial Isomer of $[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]^{2-}$.—Pure crystalline $[PPh_4]_2[Cl_3W(\mu\text{-}SEt_2)(\mu\text{-}SEt)(\mu\text{-}Cl)WCl_3]\cdot 2CH_2Cl_2$ **6** (13.0 mg) was loaded into an NMR tube in a glove-box, and CD_2Cl_2 (0.75 cm^3) added. The solution was immediately removed from the glove-box, frozen in liquid nitrogen, then evacuated and sealed. The acquisition of NMR data was commenced immediately the solution reached 25 °C. The concentrations of each of the isomers were determined indirectly using the ratio of integration between the two well squared quartets of each isomer, and the multiplets due to the protons of the $[PPh_4]^+$ cation. The isomerization of the axial to the equatorial isomer reached equilibrium in *ca.* 2 h, but the values at 24 h were taken as the final equilibium concentrations. The rate constants, as defined in reaction (5), which were determined from these data are: $k_1 = 1.32 \times 10^{-4}$ s^{-1}; $k_{-1} = 1.572 \times 10^{-4}$ s^{-1}. The equilibrium constant $K = 0.84$, for the ratio [equatorial]/[axial] and ΔG for the reaction is 432 J mol^{-1}. Thus the axial isomer is marginally more stable than the equatorial isomer in this system. The linear correlation coefficient for the plot of $\ln[(R - R_\infty)/(R_0 - R_\infty) \times 10^4]$ *vs.* t was 0.990 where R is defined as the ratio of the average intensity of two quartets due to the axial isomer, to the intensity of the multiplets due to the $[PPh_4]^+$ ion.

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