

*Journal of Organometallic Chemistry*, 437 (1992) 191–199  
Elsevier Sequoia S.A., Lausanne  
JOM 22665

## Static and dynamic structures of pentacarbonyl-chromium(0) and -tungsten(0) complexes of dithioether ligands

### I. Symmetrical dithioether complexes and X-ray crystal structure of $[\text{W}(\text{CO})_5(\text{}^t\text{BuSCH}_2\text{S}^t\text{Bu})]$ \*

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(Received January 16, 1992)

#### Abstract

The complexes  $[\text{M}(\text{CO})_5(\text{RSCH}_2\text{SR})]$  ( $\text{M} = \text{Cr}$ ,  $\text{R} = \text{Et}$ ,  $^i\text{Pr}$ ,  $^t\text{Bu}$ ;  $\text{M} = \text{W}$ ,  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $^i\text{Pr}$ ,  $^t\text{Bu}$ ) were synthesised. Total bandshape NMR analysis was used to measure energies of inversion of the coordinated S atom in the tungsten complexes.  $\Delta G^\ddagger$  (298.15 K) values were in the range 34–42  $\text{kJ mol}^{-1}$ . An X-ray structure of  $[\text{W}(\text{CO})_5(\text{}^t\text{BuSCH}_2\text{S}^t\text{Bu})]$  was obtained.

#### Introduction

Transition metal pentacarbonyl complexes of thioether ligands have been the subject of our attention for a number of years [1]. In particular we have reported on the static and dynamic structures of Group VI metal pentacarbonyl complexes of acyclic thio-, seleno- and selenothio-ethers [2–5].

These complexes exhibit a combination of dynamic processes in solution, namely pyramidal inversion of the coordinated chalcogen atom and, at higher temperatures, 1,3-metallotropic shifts of the  $\text{M}(\text{CO})_5$  moiety. Our previous studies

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\* Dedicated to Professor Alwyn G. Davies in recognition of his distinguished contributions to organometallic chemistry.

were confined to complexes with dithia-, diselena- and thiaselena-pentane ligands, namely  $[M(CO)_5L]$  ( $L = MeECH_2E'Me$ ,  $E = E' = S, Se$  or  $E = S, E' = Se$ ) [2–4] and to complexes with linear polysulphur ligands, namely  $[M(CO)_5)_mL]$  ( $L = MeS(CH_2S)_nMe$ ,  $m = 1, n = 2; m = 2, n = 2, 3$ ) [5]. Thus, in all previous instances the inverting S atoms were part of methylthio groups. The aim of the present work was to investigate how the pyramidal inversion and metallotropic shift fluxions are affected by the nature of the group attached to sulphur. Accordingly, we have prepared the following Group VI metal complexes  $[M(CO)_5(RSCH_2SR)]$  ( $M = Cr, R = Et, ^iPr, ^tBu$ ;  $M = W, R = Me, Et, ^iPr, ^tBu$ ) where the influence of different alkyl R groups can be assessed. In this paper, we discuss the effect on the low temperature inversions of the coordinated S atoms.

## Experimental

### General

All preparations involving air-sensitive materials were performed under dry, oxygen-free nitrogen, by standard Schlenk techniques [6]. Benzene, tetrahydrofuran, hexane, light petroleum, and dichloromethane were freshly distilled under nitrogen.

Melting points of the solid complexes were recorded on a digital Gallenkamp apparatus and are uncorrected. Elemental analyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlesex. Infrared spectra of the complexes in chloroform solution were recorded on a Perkin-Elmer Model 881 spectrometer using matched  $CaF_2$  solution cells.

$^1H$  and  $^{13}C\{^1H\}$  NMR spectra were recorded on a Bruker AM250 spectrometer operating at 250.13 and 62.90 MHz, respectively. All  $^1H$  and  $^{13}C$  shifts are quoted relative to internal  $Me_4Si$ . All samples were measured as  $CDCl_3$  solutions at ambient temperatures and as  $CD_2Cl_2/C_6D_5CD_3$  solutions at low temperatures. Temperatures were measured with a Comark digital thermometer, and are considered accurate to  $\pm 1^\circ C$ . Bandshape analyses were carried out with the authors' version of the standard DNMR3 program [7].

Table 1

$^1H$  and  $^{13}C\{^1H\}$  NMR shifts <sup>a</sup> of the ligands  $RSCH_2SR$

Ligand	-SCH <sub>2</sub> S-		-SCH <sub>3</sub> -SCH <sub>2</sub> CH <sub>3</sub> -SCH(CH <sub>3</sub> ) <sub>2</sub> -SC(CH <sub>3</sub> ) <sub>3</sub>		-SCH <sub>2</sub> CH <sub>3</sub> -SCH(CH <sub>3</sub> ) <sub>2</sub> -SC(CH <sub>3</sub> ) <sub>3</sub>	
	<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H	<sup>13</sup> C
MeSCH <sub>2</sub> SMe	3.62(s)		2.15(s)		-	-
EtSCH <sub>2</sub> SEt	3.65(s)	34.48	2.65(q)	24.70	1.25(t)	14.19
<sup>i</sup> PrSCH <sub>2</sub> S <sup>i</sup> Pr	3.64(s)	32.57	3.1(sp)	34.09	1.23(d)	22.94
<sup>t</sup> BuSCH <sub>2</sub> S <sup>t</sup> Bu	3.67(s)	27.98	-	43.54	1.34(s)	30.91

<sup>a</sup> Relative to int.  $Me_4Si$ . Ligands diluted in  $CDCl_3$ . s, singlet; d, 1:1 doublet; t, 1:2:1 triplet; q, 1:3:3:1 quartet; sp, binomial septet.

### Synthesis of ligands

All the symmetrical dithioethers  $\text{RSCH}_2\text{SR}$  ( $\text{R} = \text{Me}, \text{Et}, {}^i\text{Pr}, {}^t\text{Bu}$ ) were synthesised by phase transfer catalysis in a similar manner [8,9]. The preparation of  ${}^i\text{PrSCH}_2\text{S}^i\text{Pr}$  is described below as a representative example.

Distilled water ( $230 \text{ cm}^3$ ), dichloromethane ( $200 \text{ cm}^3$ ), isopropyl thiol,  ${}^i\text{PrSH}$ , ( $20.0 \text{ g}$ ), sodium hydroxide ( $15.0 \text{ g}$ ) and 10–12 drops of phase transfer catalyst Adogen 464 (Aldrich Chemical Company Ltd.,) were combined and stirred vigorously at room temperature in a stoppered  $1 \text{ dm}^3$  conical flask for 3 days. The organic layer was separated, washed with water ( $3 \times 100 \text{ cm}^3$ ), and dried over magnesium sulphate. After filtering, the solvent was removed under vacuum to give a colourless oil which was vacuum distilled. B.p.  $110\text{--}115^\circ\text{C}$  (15 Torr). Yield 60%. All ligands were characterized by  ${}^1\text{H}$  and  ${}^{13}\text{C}$  NMR (Table 1).

### Synthesis of complexes

The general method of preparation [10–13] is described below.

Metal hexacarbonyl ( $2.7 \text{ mmol}$ ) was placed in a cylindrical glass vessel containing a Hanovia 125 W ultraviolet lamp enclosed in a water-cooled quartz jacket, under dry nitrogen. Dry tetrahydrofuran (THF) ( $\sim 150 \text{ cm}^3$ ) was added and the stirred solution irradiated overnight. The resulting orange-coloured solution of the metal pentacarbonyl–THF complex was filtered and added dropwise to the appropriate ligand ( $2.6 \text{ mmol}$ ) contained in an ice-cold Schlenk tube. After continuous stirring for 4–6 h, displacement of THF by the ligand was indicated by a colour change of the solution from orange to yellow. All volatile material was evaporated under reduced pressure and the unreacted metal hexacarbonyl removed by sublimation at approx.  $0.01 \text{ mmHg}$  ( $40\text{--}50^\circ\text{C}$  for 4–6 h). The oily residue was extracted with hexane ( $10\text{--}15 \text{ cm}^3$ ) and cooled to  $-20^\circ\text{C}$  overnight to give an air-sensitive yellow/brown crude product. This was purified by column chromatography (alumina grade III) using hexane as eluent. After solvent removal, the orange/yellow solution was cooled to between  $-17$  and  $-80^\circ\text{C}$  for 4–6 h, when yellow/brown crystals were formed. The product was washed with hexane, dried under vacuum and stored under dry nitrogen. All the complexes were air-sensitive. Yields were in the range 40–60%. Analytical and IR characterization data are given in Table 2.

### X-Ray crystal structure

Crystals of  $[\text{W}(\text{CO})_5({}^t\text{BuSCH}_2\text{S}^t\text{Bu})]$  (**6**) were prepared as above and sealed under nitrogen in Lindemann capillaries.

*Crystal data.*  $\text{C}_{14}\text{H}_{20}\text{O}_5\text{S}_2\text{W}$ ,  $M = 516.28$ , monoclinic,  $a = 9.235(1) \text{ \AA}$ ,  $b = 9.367(2) \text{ \AA}$ ,  $c = 22.326(6) \text{ \AA}$ ,  $\beta = 90.40(2)^\circ$ ,  $U = 1930.72 \text{ \AA}^3$ , space group  $P2_1/n$ ,  $Z = 4$ ,  $D_c = 1.78 \text{ g cm}^{-3}$ ,  $\mu (\text{Mo-}K_\alpha) = 63.35 \text{ cm}^{-1}$ ,  $F(000) = 1000$ .

*Data collection.* Lattice parameters were determined by least-squares refinement of 25 reflections ( $13^\circ < \theta (\text{Mo-}K_\alpha) < 14^\circ$ ) automatically centred on a CAD4 diffractometer, 3933 intensity data ( $1.5^\circ < \theta < 25^\circ$ ;  $+h, +k, \pm l$ ) were recorded on the same instrument using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) and an  $\omega$ - $2\theta$  scan ( $\omega$  scan width =  $1.00 + 0.35 \tan \theta$ ) following standard procedures [14]. Semi-empirical absorption corrections were applied using the  $\psi$  scan values for 3 reflections (min and max transmission, 89.4 and 99.9%). Of the

Table 2

Synthesis and characterization of the mononuclear pentacarbonyltungsten(0) and -chromium(0) complexes of symmetrical dithioether ligands

No.	Complex	Yield (%)	m.p. (°C)	$\nu(\text{C}=\text{O})^a$ ( $\text{cm}^{-1}$ )	Analytical data			
					Found (%)		Calculated (%)	
					C	H	C	H
1	$[\text{W}(\text{CO})_5\text{MeSCH}_2\text{SMe}]$	40	56–57	2076(s), 1983(s,b), 1943(s,b)	22.2	2.1	22.2	1.9
2	$[\text{W}(\text{CO})_5\text{EtSCH}_2\text{SEt}]$	44	Oil	2076(s), 1980(s), 1934(s,b), 1915(sh)	Not obtained <sup>b</sup>			
3	$[\text{Cr}(\text{CO})_5\text{EtSCH}_2\text{SEt}]$	60	Oil	2070(s), 1984(s), 1938(s,b), 1915(sh)	Not obtained <sup>b</sup>			
4	$[\text{W}(\text{CO})_5\text{PrSCH}_2\text{S}^i\text{Pr}]$	40	Oil	2076(s), 1980(s), 1934(s,b), 1915(sh)	Not obtained <sup>b</sup>			
5	$[\text{Cr}(\text{CO})_5\text{PrSCH}_2\text{S}^i\text{Pr}]$	52	Oil	2070(s), 1986(s), 1944(s), 1940(sh,w)	Not obtained <sup>b</sup>			
6	$[\text{W}(\text{CO})_5\text{BuSCH}_2\text{S}^i\text{Bu}]$	46	66–67	2076(s), 1985(s), 1948(s,b)	32.2	3.9	32.6	3.9
7	$[\text{Cr}(\text{CO})_5\text{BuSCH}_2\text{S}^i\text{Bu}]$	61	47.3–48	2069(s), 1988(s), 1944(s), 1939(sh,w)	43.6	5.1	43.7	5.2

<sup>a</sup> Solvent chloroform. s, sharp; b, broad; sh, shoulder; w, weak. <sup>b</sup> No data available because of physical state of product.

total of 3386 unique data, 2614 with  $F_0 > 3\sigma$  ( $F_0$ ) were used in the final refinement.

**Structure analysis and refinement.** The structure was solved by the standard heavy atom procedures and refined using full matrix least squares methods [15]. Refinement of all non-hydrogen atoms with anisotropic temperature factors finally converged at  $R = 0.031$  and  $R_w = 0.0371$ . No attempts were made to locate the hydrogen atoms. The weighting scheme used was  $w = 1/[\sigma^2(F_0) + 0.000317(F_0)^2]$  and this gave flat analyses of variance.

Sources of scattering factors are as in [16]. All calculations were performed on a DEC VAX11/750 computer. A complete table of bond lengths and angles, and lists of thermal parameters and structure factors are available from the authors.

## Results

### NMR studies

The room temperature <sup>1</sup>H spectra of the complexes 1–7 were consistent with monodentate coordination of the  $\text{M}(\text{CO})_5$  moiety to one of the sulphur atoms of the dithioether ligand. In all cases the central  $-\text{SCH}_2\text{S}-$  methylene signal was a sharp singlet indicative of rapid pyramidal inversion of the coordinated S atom. Room temperature NMR data for all the complexes are collected in Table 3.

The solution stabilities of the tungsten complexes were considerably greater than those of the chromium complexes and enabled variable temperature NMR studies to be performed. On cooling the four tungsten complexes 1, 2, 4 and 6 to low temperatures, the methylene singlet signal first broadens, then splits into a doublet and finally resolves into a AB quartet, normally at about  $-80$  to  $-90^\circ\text{C}$ .

Table 3

$^1\text{H}$  NMR data <sup>a</sup> of the mononuclear pentacarbonyltungsten(0) and -chromium(0) complexes of symmetrical dithioether ligands in  $\text{CDCl}_3$  at room temperature

No.	Complex <sup>b</sup>	$-\text{SCH}_2\text{S}-$	$-\text{SCH}_3$ $-\text{SCH}_2\text{CH}_3$ $-\text{SCH}(\text{CH}_3)_2$	$-\text{SCH}_2\text{CH}_3$ $-\text{SCH}(\text{CH}_3)_2$ $-\text{SC}(\text{CH}_3)_3$		
1	$[\text{W}(\text{CO})_5\text{MeSCH}_2\text{SMe}]$	3.61(s)	2.71(s)	2.25(s)	–	–
2	$[\text{W}(\text{CO})_5\text{EtSCH}_2\text{SEt}]$	3.87(s)	3.03(q)	2.72(q)	1.37(t)	1.32(t)
3	$[\text{Cr}(\text{CO})_5\text{EtSCH}_2\text{SEt}]$	3.69(s)	2.84(q)	2.68(q)	1.37(t)	1.30(t)
4	$[\text{W}(\text{CO})_5\text{PrSCH}_2\text{S}^i\text{Pr}]$	3.88(s)	3.44(sp)	3.16(sp)	1.33(d)	1.31(d)
5	$[\text{Cr}(\text{CO})_5\text{PrSCH}_2\text{S}^i\text{Pr}]$	3.72(s)	3.46(sp)	3.14(sp)	1.36(d)	1.32(d)
6	$[\text{W}(\text{CO})_5\text{BuSCH}_2\text{S}^i\text{Bu}]$	4.05(s)	–	–	1.48(s)	1.41(s)
7	$[\text{Cr}(\text{CO})_5\text{BuSCH}_2\text{S}^i\text{Bu}]$	3.81(s)	–	–	1.45(s)	1.39(s)

<sup>a</sup>  $\delta$  values relative to  $\text{Me}_4\text{Si}$  (int). s, singlet; d, doublet; t, triplet; q, quartet; sp, septet.

This is clearly indicative of a slowing down of the pyramidal inversion of the metal-coordinated S atom, causing the diastereotropic pair of methylene protons of the  $-\text{SCH}_2\text{S}-$  group to be individually detected. This inversion process may be represented by Fig. 1, and the spectra of  $[\text{W}(\text{CO})_5(^i\text{BuSCH}_2\text{S}^i\text{Bu})]$  (**6**) arising from this process are shown in Fig. 2. Total bandshape analysis was carried out on the methylene signals and the best-fit rate constants for each temperature were deduced. These yielded the Arrhenius and Eyring activation parameters collected in Table 4.

#### X-Ray crystallography

A single crystal X-ray determination of the complex  $[\text{W}(\text{CO})_5(^i\text{BuSCH}_2\text{S}^i\text{Bu})]$  (**6**) was performed. Atomic coordinates are listed in Table 5 and a labelled structure depicted in Fig. 3. This displays the expected six-coordination for W and the monodentate nature of the ligand, in accordance with the solution NMR studies discussed earlier. Bond lengths and bond angles are given in Tables 6 and 7, respectively.

Bond lengths are fairly unexceptional. The W–S length of 2.571(5) Å is comparable to that found in other compounds of tungsten(0) bonded to S ligands [17–19]. The W–C distance *trans* to S at 1.965(13) Å is significantly shorter than the corresponding distances *cis* to S at 2.023(13)–2.040(13) Å. This effect has been observed in other metal–sulphur bonded derivatives of Group VI metal carbonyls

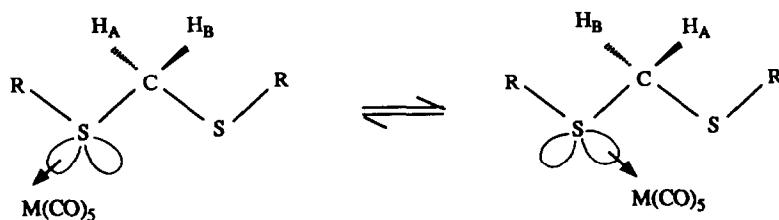


Fig. 1. Pyramidal inversion in the complexes  $[\text{M}(\text{CO})_5(\text{RSCH}_2\text{SR})]$  showing the exchange of geminal methylene environments.

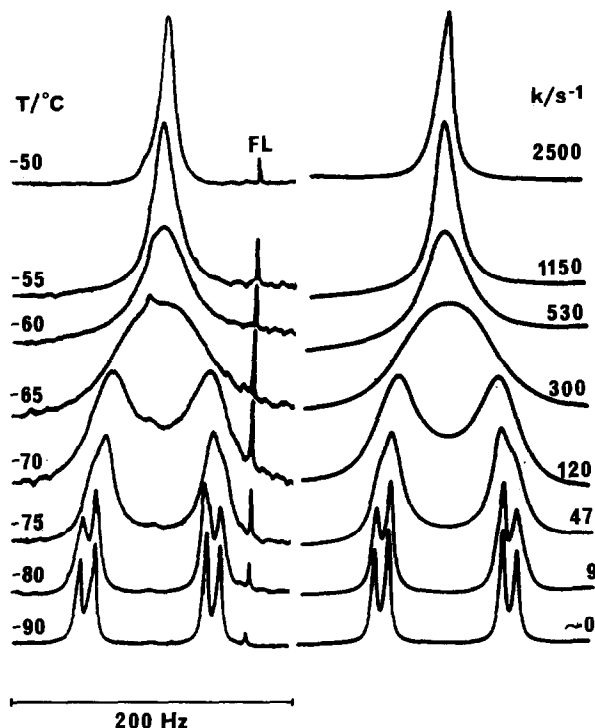


Fig. 2. Experimental and computer simulated  $^1\text{H}$  NMR spectra of the methylene signals of  $[\text{W}(\text{CO})_5(^1\text{BuSCH}_2\text{S}^1\text{Bu})]$  showing the effects of pyramidal inversion of the W-bonded sulphur atom. FL, free ligand.

and has been attributed to competition of the *trans* carbonyl ligands for the electron density from the W atom [18,20]. The C–S bonds fall within the normal range with the bonds from the coordinated S atom being somewhat longer than those from the uncoordinated S atom.

The bond angles at W indicate a slight distortion from regular octahedral symmetry with the equatorial carbonyl C(2)O(2) in particular being forced away from the pendant arm of the ligand, causing an opening up of the S(1)–W–C(2)

Table 4

Arrhenius and Eyring activation parameters for pyramidal sulphur inversion in mononuclear pentacarbonyl tungsten(0) complexes of symmetrical dithioether ligands

No.	Complex <sup>a</sup>	$E_a$ (kJ mol <sup>-1</sup> )	$\log(A)$ (s <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^\ddagger$ <sup>b</sup> (kJ mol <sup>-1</sup> )
1	$[\text{W}(\text{CO})_5\text{MeSCH}_2\text{SMe}]$ <sup>c</sup>	$53.5 \pm 2.7$	$14.8 \pm 0.6$	$51.7 \pm 2.7$	$31.8 \pm 12.1$	$42.2 \pm 0.9$
2	$[\text{W}(\text{CO})_5\text{EtSCH}_2\text{SEt}]$	$51.8 \pm 0.4$	$15.1 \pm 0.1$	$50.1 \pm 0.4$	$38.6 \pm 2.0$	$38.6 \pm 0.2$
4	$[\text{W}(\text{CO})_5\text{PrSCH}_2\text{S}^1\text{Pr}]$	$51.7 \pm 0.6$	$15.8 \pm 0.2$	$50.1 \pm 0.6$	$52.4 \pm 3.1$	$34.4 \pm 0.3$
6	$[\text{W}(\text{CO})_5^1\text{BuSCH}_2\text{S}^1\text{Bu}]$	$52.2 \pm 1.5$	$16.8 \pm 0.4$	$55.5 \pm 1.5$	$71.0 \pm 7.1$	$34.3 \pm 0.6$

<sup>a</sup> All complexes in  $\text{CD}_2\text{Cl}_2$  solvent except complex 1. <sup>b</sup> Calculated at 298.15 K. <sup>c</sup> In toluene-*d*<sub>8</sub>.

Table 5

Fractional atomic coordinates ( $\times 10^4$ ) for  $[\text{W}(\text{CO})_5(\text{}^t\text{BuSCH}_2\text{S}^t\text{Bu})]$ 

	x	y	z
W	6252.7(3)	3877.0(3)	8259.4(1)
S(1)	3625.9(17)	4276.2(16)	8576.5(7)
S(2)	4035.1(20)	2647.2(21)	9736.2(9)
O(1)	5520(8)	578(7)	8235(3)
O(2)	7636(6)	3492(6)	9557(2)
O(3)	9333(6)	3020(8)	7859(3)
O(4)	7392(7)	7053(7)	8346(3)
O(5)	5444(8)	4365(7)	6882(3)
C(1)	5747(9)	1767(9)	8244(3)
C(2)	7055(7)	3645(7)	9105(3)
C(3)	8197(8)	3346(9)	7998(3)
C(4)	6905(9)	5939(8)	8313(3)
C(5)	5685(8)	4174(8)	7379(3)
C(6)	3606(8)	4345(7)	9400(3)
C(7)	2733(8)	6007(7)	8382(3)
C(8)	3527(11)	7289(8)	8661(5)
C(9)	2692(11)	6085(10)	7691(4)
C(10)	1179(9)	5936(11)	8632(5)
C(11)	2324(8)	1656(8)	9771(3)
C(12)	1726(13)	1321(12)	9161(4)
C(13)	1175(11)	2591(13)	10115(5)
C(14)	2757(12)	350(12)	10153(6)

angle to  $94.9^\circ$  with a consequent reduction of the C(2)–W–C(3) angle to  $86.2^\circ$ . The axial carbonyl C(1)O(1) is surprisingly distorted towards the ligand such that the S(1)–W–C(1) angle is  $85.9^\circ$ , whereas its *trans* counterpart C(4)O(4) is not signifi-

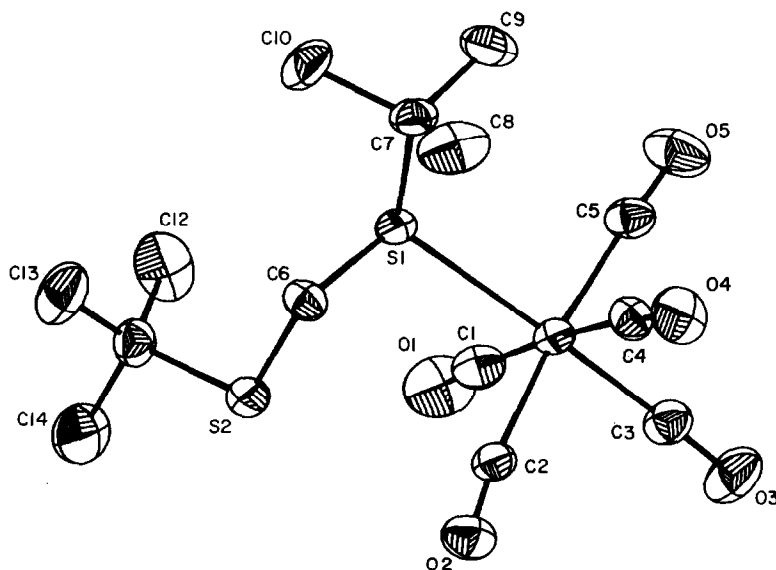


Fig. 3. View of the X-ray crystal structure of  $[\text{W}(\text{CO})_5(\text{}^t\text{BuSCH}_2\text{S}^t\text{Bu})]$  showing the atom labelling.

Table 6

Bond lengths (Å) for [W(CO)<sub>5</sub>(<sup>t</sup>BuSCH<sub>2</sub>S<sup>t</sup>Bu)]

S(1)–W	2.571(5)	C(1)–W	2.031(14)
C(2)–W	2.023(12)	C(3)–W	1.965(13)
C(4)–W	2.026(13)	C(5)–W	2.040(13)
C(6)–S(1)	1.840(11)	C(7)–S(1)	1.866(11)
C(6)–S(2)	1.799(12)	C(11)–S(2)	1.836(12)
C(1)–O(1)	1.134(15)	C(2)–O(2)	1.140(12)
C(3)–O(3)	1.143(13)	C(4)–O(4)	1.138(13)
C(5)–O(5)	1.140(13)	C(8)–C(7)	1.531(16)
C(9)–C(7)	1.543(17)	C(1)–C(7)	1.546(17)
C(12)–C(11)	1.491(17)	C(13)–C(11)	1.589(19)
C(14)–C(11)	1.538(19)		

Table 7

Bond angles (deg) for [W(CO)<sub>5</sub>(<sup>t</sup>BuSCH<sub>2</sub>S<sup>t</sup>Bu)]

C(1)–W–S(1)	85.9(4)	C(2)–W–S(1)	94.9(4)
C(2)–W–C(1)	89.4(5)	C(3)–W–S(1)	173.5(3)
C(3)–W–C(1)	87.7(6)	C(3)–W–C(2)	86.2(5)
C(4)–W–S(1)	97.3(4)	C(4)–W–C(1)	175.3(4)
C(4)–W–C(2)	86.9(5)	C(4)–W–C(3)	89.2(6)
C(5)–W–S(1)	91.3(4)	C(5)–W–C(1)	93.6(5)
C(5)–W–C(2)	173.3(4)	C(5)–W–C(3)	87.9(5)
C(5)–W–C(4)	89.8(5)	C(6)–S(1)–W	108.2(4)
C(7)–S(1)–W	118.5(4)	C(7)–S(1)–C(6)	100.8(6)
C(11)–S(2)–C(6)	106.5(6)	O(1)–C(1)–W	177.3(10)
O(2)–C(2)–W	173.2(9)	O(3)–C(3)–W	178.3(10)
O(4)–C(4)–W	174.1(10)	O(5)–C(5)–W	176.2(10)
S(2)–C(6)–S(1)	112.2(6)	C(8)–C(7)–S(1)	112.4(8)
C(9)–C(7)–S(1)	105.9(8)	C(9)–C(7)–C(8)	111.7(11)
C(10)–C(7)–S(1)	106.9(8)	C(10)–C(7)–C(8)	109.4(12)
C(10)–C(7)–C(9)	110.5(11)	C(12)–C(11)–S(2)	111.6(9)
C(13)–C(11)–S(2)	109.1(9)	C(13)–C(11)–C(12)	108.7(13)
C(14)–C(11)–S(2)	102.3(9)	C(14)–C(11)–C(12)	115.1(13)
C(14)–C(11)–C(13)	109.8(12)		

cantly affected. The most interesting feature of the ligand geometry is the relative orientation of the two <sup>t</sup>Bu groups. Non-bonded interactions between these groups are clearly being minimized by their adoption of a staggered conformation with the angle of stagger being about 90°.

## Discussion

The Arrhenius and Eyring activation energies for inversion of the coordinated S atoms (Table 4) show a clear dependence on the nature of the thioalkyl group. This trend is seen most clearly in the  $\Delta G^\ddagger$  (298.15 K) values which are least sensitive to systematic error [21]. The barrier energies are all relatively low and fall towards the lower limit of NMR detection by bandshape analysis. Values show a decrease as the mass/size of the R groups increases, although the difference



between the energies for the <sup>i</sup>Pr and <sup>t</sup>Bu ligands is very slight. The overall trend is most reasonably interpreted as due to the bulkier alkyl groups introducing greater degrees of distortion towards a planar S geometry, thus allowing easier access to this transition state geometry when inversion occurs.

Similar trends in S inversion energies have been noted for the complexes [Mo(CO)<sub>4</sub>(RSCH<sub>2</sub>CH<sub>2</sub>SR)] [22] and [W(CO)<sub>4</sub>(RSCH<sub>2</sub>CH<sub>2</sub>SR)] (R = Me, <sup>i</sup>Pr, <sup>t</sup>Bu) [23]. In the latter series of W(CO)<sub>4</sub> complexes, however, the magnitudes of activation energies,  $\Delta G^\ddagger$  (298.15 K), in the range 54–42 kJ mol<sup>-1</sup>, are significantly greater than in the present W(CO)<sub>5</sub> complexes. This is most probably the result of the S atoms being incorporated in a 5-membered ring whereby the stiffening effect of the ring lowers the ease of access to the planar transition state of the inversion process [1].

### Acknowledgement

We thank Mr. Nicholas G. Heaton for help with the bandshape analyses.

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