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STERIC INFLUENCES ON SULPHUR INVERSION BARRIERS IN GROUP 6A TETRACARBONYL COMPLEXES OF DITHIOETHERS

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Summary

The complexes *cis*-[$M(CO)_4(RSCH_2CH_2SR)$] (M = Cr, Mo, W, R = ^{t}Bu; M = W, R = Me, Et, ^{i}Pr, ^{t}Bu) and *cis*-[$M(CO)_4$(*cis*-RSCH=CHSR)] (M = Cr, Mo, W; R = Me, ^{t}Bu) have been synthesised, and sulphur inversion studied using variable temperature ^{1}H and ^{13}C $\{^1H\}$ NMR techniques. For complexes of the saturated ligands, signals due to both *DL* and *meso* invertomers were observed at −90 °C, with the relative populations of these invertomers being dependent on the steric bulk of the alkyl groups attached to sulphur. Sulphur inversion barriers, which have been calculated via total bandshape analysis of the variable temperature NMR spectra of these complexes, show a marked dependence on the steric requirements of the dithioether ligand. For the complexes of the unsaturated ligands, only the *meso*-invertomers were observed at limiting low temperatures (ca. −90 °C), and sulphur inversion barriers were therefore not able to be calculated in these cases.

Introduction

Since the first observation of pyramidal sulphur inversion in a transition metal complex using variable temperature NMR spectroscopy [1], chalcogen inversion in a wide range of transition metal compounds has been studied using this technique, and accurate inversion barriers have been calculated in a number of cases by bandshape analysis [2] of the spectra so obtained. Many of the factors that influence the magnitude of these inversion barriers are now understood [3], but one aspect that has not previously been investigated quantitatively is the effect of attaching substituents of varying steric requirements to the inverting chalcogen centre. A small decrease in inversion energy has been observed for sulphur inversion barriers in dialkyl and diaryl sulphoxides [4,5] on increasing the steric requirements of the attached alkyl and aryl groups but inversion energy trends for thio- or seleno-ether ligand complexes have not been reported.

As part of a study of steric effects on sulphur inversion energies in a range of transition metal complexes of sulphur-containing ligands, we have prepared the

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TABLE 1

SYNTHETIC, ANALYTICAL AND INFRARED DATA FOR THE COMPLEXES *cis*-[$M(CO)_4(RSCH_2CH_2SR)$] (M = Cr, Mo, W; R = ^{t}Bu; M = W; R = Me, Et, ^{i}Pr) AND *cis*-[$M(CO)_4$(*cis*-RSCH=CHSR)] (M = Cr, Mo, W; R = Me, ^{t}Bu)

Complex		Method of preparation	Yield (%) [a]	ν [b](CO) (cm^{-1})				Analyses (Found (calc) (%))		Melting point (°C)
								C	H	
[$Cr(CO)_4(^tBuSCH_2CH_2SBu^t)$]	(1)	(a)-toluene	40.8	2016m	1909vs	1893m	1859m	45.3 (45.4)	6.2 (6.0)	88–90
[$Mo(CO)_4(^tBuSCH_2CH_2SBu^t)$]	(2)	(a)-xylene	82.6	2023m	1916vs	1893s	1859m	40.9 (40.6)	5.5 (5.4)	102–105
[$W(CO)_4(^tBuSCH_2CH_2SBu^t)$]	(3)	(a)-xylene	23.0	2025m	1906vs	1889vs	1868s	33.3 (33.5)	4.5 (4.4)	116–119
[$W(CO)_4(^iPrSCH_2CH_2SPr^i)$]	(4)	(a)-xylene	45.1	2020m	1905vs	1889vs	1859m	30.4 (30.4)	3.8 (3.8)	97–98
[$W(CO)_4(EtSCH_2CH_2SEt)$]	(5)	(a)-xylene	24.8	2020m	1916vs	1893s	1865s	26.9 (26.9)	3.1 (3.2)	129–130
[$W(CO)_4(MeSCH_2CH_2SMe)$]	(6)	(b)	40.6	2017m		1894vs,br	1865ms	22.9 (23.0)	2.3 (2.4)	185–187
[$Cr(CO)_4$(*cis*-MeSCH=CHSMe)]	(7)	(b)	11.6	2021m	1918vs	1903s	1869m	34.0 (33.8)	3.0 (2.8)	93–94
[$Cr(CO)_4$(*cis*-^{t}BuSCH=CHSBu^t)]	(8)	(a)-toluene	35.8	2025m	1915vs	1897vs	1877m	45.8 (45.6)	5.5 (5.5)	142–145(d)
[$Mo(CO)_4$(*cis*-MeSCH=CHSMe)]	(9)	(a)-toluene	8.5	2031m	1918vs,br		1871s	28.9 (29.3)	2.5 (2.6)	95–98(d)
[$Mo(CO)_4$(*cis*-^{t}BuSCH=CHSBu^t)]	(10)	(a)-toluene	46.7	2029m	1917vs	1903s	1863m	40.5 (40.8)	5.0 (4.9)	117–119
[$W(CO)_4$(*cis*-MeSCH=CHSMe)]	(11)	(b)	23.0	2020ms		1897vs,br	1860m	23.2 (23.1)	2.2 (1.9)	118–120
[$W(CO)_4$(*cis*-^{t}BuSCH=CHSBu^t)]	(12)	(b)	57.7	2023m	1904vs	1889s	1864m	33.9 (33.6)	4.2 (4.0)	126–129(d)

[a] Rel. to $M(CO)_6$ or $M(CO)_4$(nbd) as appropriate. [b] In CH_2Cl_2 solution.

complexes *cis*-[$M(CO)_4(RSCH_2CH_2SR)$] (M = Cr, Mo, W, R = ^tBu; M = W, R = Me, Et, ^iPr) and *cis*-[$M(CO)_4$(*cis*-RSCH=CHSR)] (M = Cr, Mo, W; R = Me, ^tBu). Sulphur inversion in these complexes has been studied using variable temperature ^1H and ^{13}C $\{^1H\}$ NMR methods. Accurate chalcogen inversion barriers have previously been calculated for a limited range of Group 6A metal tetracarbonyl complexes, including *cis*-[$M(CO)_4(Me_2CDSeCD_2CH_2SeCDMe_2)$] [6], *cis*-[$M(CO)_4(MeSeCH_2CMe_2CH_2SeMe)$] [7], *cis*-[$M(CO)_4(PhCH_2SCH_2CH_2SCH_2Ph)$] [8] (M = Cr, Mo, W), and *cis,cis*- and *trans,cis*-[$Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}$] [9].

Experimental

General

All preparations were performed under dry nitrogen by use of standard Schlenk techniques [10]. Toluene and hexane were dried over sodium and distilled from sodium diphenylketyl under nitrogen prior to use. Xylene was dried over sodium and thoroughly degassed prior to use. The hexacarbonyls [$M(CO)_6$] (M = Cr, Mo, W) were obtained from Aldrich Chemical Co. and were used without further purification. The complexes [$M(CO)_4$(nbd)] (M = Cr, Mo, W; nbd = bicyclo[2.2.1]-hepta-2,5-diene) were prepared according to published procedures [11,12]. The ligands $EtSCH_2CH_2SEt$ and $^tBuSCH_2CH_2SBu^t$ were purchased from K&K Chemicals and were used without further purification. The ligands $MeSCH_2CH_2SMe$ [13], $^iPrSCH_2CH_2SPr^i$ [13], *cis*-MeSCH=CHSMe [14] and *cis*-$^tBuSCH=CHSBu^t$ [15] were synthesised according to published procedures. Infrared spectra were recorded on a Perkin–Elmer 398 spectrometer interfaced to a Perkin–Elmer 3600 Data Station, and were calibrated from the 1602 cm^{-1} signal of polystyrene. Elemental analyses were performed by Butterworth Laboratories Ltd., London.

Preparations of the complexes

The complexes were prepared by published procedures, either (a) by direct thermal reaction of [$M(CO)_6$] with the ligand in refluxing toluene or xylene [16–18], or (b) by refluxing the ligand with [$M(CO)_4$(nbd)] in hexane [8]. Details of the method of preparation employed and the yields obtained are given in Table 1.

NMR studies

^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker AM-250 FT NMR spectrometer operating at 250.13 MHz (^1H) and 62.90 MHz (^{13}C). A standard variable temperature unit was used to control the probe temperature in variable temperature runs and temperatures are considered accurate to $\pm 1°C$. All spectra, unless otherwise stated, were recorded in CD_2Cl_2 solution using Me_4Si as internal standard. Band-shape analyses of the variable temperature NMR spectra were performed using the authors' modified version of the DNMR program of Kleier and Binsch [2,19].

Results and discussion

The complexes **1** to **12** (Table 1) were conveniently prepared as described above, and were isolated as yellow, air-stable crystalline solids. The infrared spectra show four bands attributable to a $2A_1 + B_1 + B_2$ vibrational set as expected for *cis*-tetra-

TABLE 2

^{1}H NMR PARAMETERS FOR COMPLEXES **1–6**

Complex	Temperature (°C)	Chemical shifts and spin–spin coupling constants [a]		
		Methyl protons	Backbone methylene protons	Alkyl group methylene/methine protons
1	−90	1.41(s) [b]	2.99(d), 2.43(d) [7.12] (*DL*) 2.70 (m,br) (*meso*)	
	20	1.42(s)	2.66(s)	
2	−90	1.4(s) [b]	3.27(d), 2.25(d) [7.57] (*DL*) 2.78 (m,br) (*meso*)	
	20	1.42(s)	2.66(s)	
3	−90	1.43(s) [b]	3.27(d), 2.36(d) [8.06] (*DL*) 2.8 (m,br) (*meso*)	
	20	1.41(s)	2.74(s)	
4	−90	1.42(s) [b]	3.43(d), 2.28(d) [10.8] (*DL*) 2.83–2.97 (*meso*) [c]	2.83–2.97 (*meso* and *DL*) [c,d]
	20	1.41(d) [6.62]	2.78(s)	2.93(septet) [6.62] [d]
5	−90	1.34(t) [6.89] (*DL*) 1.37(t) [6.89] (*meso*)	3.40(d), 2.34(d) [10.3] (*DL*) 2.84–2.92 [c] (*meso*)	2.84–2.92 (*DL*) [c,e] 2.63(q) [6.89] (*meso*) [e]
	20	1.36(t) [7.38]	2.79(s)	2.81(q) [7.38]
6	−80	2.58(s) (*DL*) 2.75(s) (*meso*)	3.28(d), 2.46(d) [9.88] (*DL*) 3.05(m,br) (*meso*)	
	20	2.60(s)	2.79(s)	

[a] Chemical shifts (δ, rel. to Me_4Si) and spin–spin coupling constants (in parentheses), (^3J(HH) Hz). [b] Distinct signals not observed for *meso* and *DL* invertomers. [c] Complete assignment not possible due to signal overlap. [d] Methine protons. [e] Methylene protons. Abbreviations employed are: (s) = singlet; (d) = doublet; (t) = triplet; (q) = quartet.

carbonyl complexes, although in some cases complete resolution of the A_1 and B_1 bands at ca. 1900 cm^{-1} was not possible. Satisfactory elemental analyses were also obtained for the complexes. Infrared and microanalytical data are presented in Table 1. The complexes **1–3** [17], **5** [20], **6** [16], and **8** [18] have previously been reported.

*Variable temperature ^{1}H NMR spectra of complexes **1–6***

^{1}H NMR data for complexes **1** to **6** at −90 °C and at +20 °C are presented in Table 2.

Single-site sulphur inversion in complexes of this type would proceed according to the pathway shown in Fig. 1, and would involve the interconversion of two *DL* invertomers and two degenerate *meso* invertomers. However, the two *DL* invertomers are enantiomeric and isochronous, and so only two sets of signals would be expected in the NMR spectra of these complexes at temperatures where sulphur inversion is slow on the NMR timescale. The ^{1}H NMR spectra at −90 °C of all of these complexes show features consistent with the presence of these invertomers; the ^{1}H NMR spectrum of **5** at −90 °C is shown in Fig. 2 as an example. In all cases, the methylene protons of the ligand backbone give rise, in principle, to an AA′BB′ multiplet. However, the internal chemical shift ($\nu_A - \nu_B$), and the proton coupling

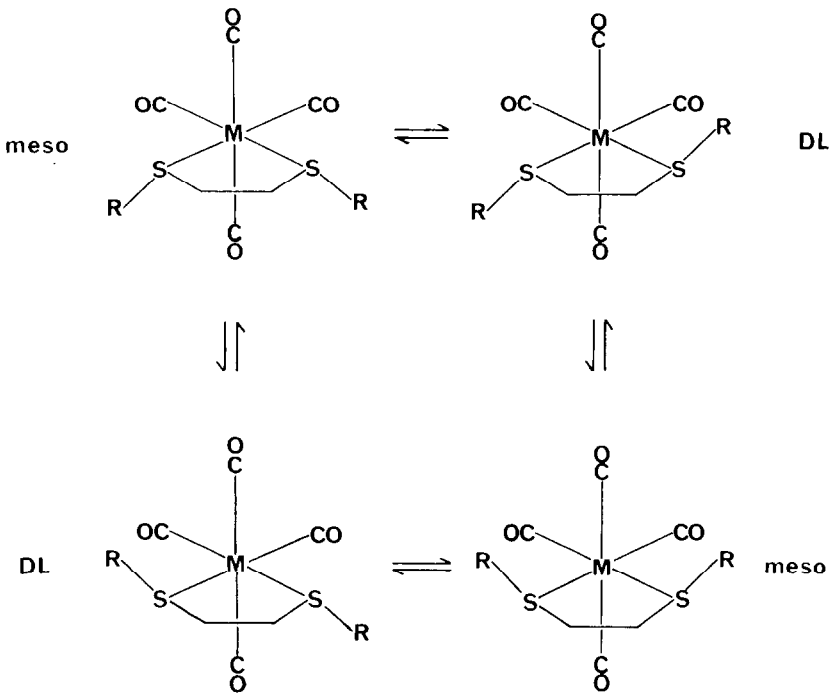

Fig. 1. Interconversion between *DL* and *meso* invertomers of *cis*-[M(CO)$_4$(RSCH$_2$CH$_2$SR] via single-site sulphur inversion.

constants for each invertomer were such that for the *DL*-invertomer this signal approximated to an AB quartet whereas for the *meso*-invertomer an ill-resolved multiplet was observed. In the spectra of **4** and **5**, this region of the spectrum was additionally complicated by overlap of the ligand backbone methylene signals of the *meso*-invertomer with those of the methine and methylene groups respectively of the alkyl substituents on sulphur for both invertomers. Complete assignment of signals in this region was not always possible. The methyl region of the spectra for complexes **1** to **3** showed a broad singlet at ca. 1.42 ppm in each case, indicating that the chemical shift difference between the signals for the $(CH_3)_3C$ protons of *meso* and *DL* invertomers was too small for separate signals to be resolved. The methyl region of **4** also shows a broad singlet at $-90\,^{\circ}C$, which implies that the static state spectrum for this region has not been reached at this temperature, again presumably as a result of small chemical shift differences between the signals for the two invertomers. For **5**, separate signals for each invertomer in the methyl region were observed as overlapping triplets at δ 1.34 (*DL*) and δ 1.37 (*meso*), whilst for **6** the methyl region showed singlets at δ 2.58 and 2.75 for the *DL* and *meso* invertomers respectively.

The populations of the invertomers were unequal and showed a small dependence on the steric bulk of the thioalkyl group. Molecular models show that nonbonded interactions between the thioalkyl groups are reduced in the *DL* invertomer relative to the *meso* invertomer, and the more populous invertomer in each case was attributed to the *DL* invertomer. Supporting evidence for this is

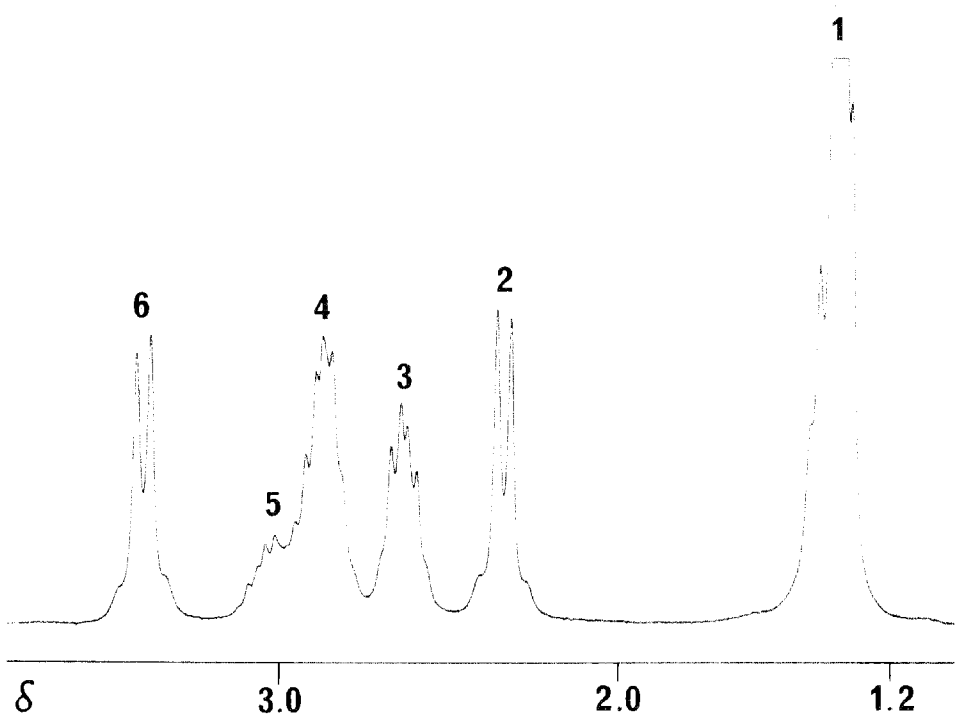

Fig. 2. ^{1}H NMR spectrum of *cis*-[W(CO)$_4$(EtSCH$_2$CH$_2$SEt)] (**5**) at −90 °C. Signal assignments as follows: 1, CH$_3$ (*DL* and *meso*), 2, 6, backbone CH$_2$ (*DL*), 3, CH$_2$CH$_3$ (*meso*)?, 4, CH$_2$CH$_3$ (*DL*)?, 5, backbone CH$_2$ (*meso*)?.

provided by the published X-ray crystal structures of **1** [21], **3** [22], and of *cis*-[Cr(CO)$_4$(EtSCH$_2$CH$_2$SEt)] [23], which all show a *trans* orientation of the alkyl groups in the solid state. It has previously been noted that, for species where both solid-state and solution data are available, the favoured invertomer in solution is the one which resembles the solid-state structure most closely [24], and thus these X-ray structures strongly suggest that the *DL* invertomer would predominate in solution.

On increasing the temperature of solutions of **1**–**6**, broadening and coalescence of signals in all regions of the spectra occurred until at ambient temperatures averaged spectra were observed consistent with rapid interconversion of the invertomers by sulphur inversion (Table 2). A singlet at ca. δ 2.7 was observed for the ligand backbone methylene protons in each case, and the expected signals according to the nature of the thioalkyl group were observed for all complexes.

^{13}C NMR spectra for complexes 1–6

Proton-decoupled ^{13}C NMR spectra have been obtained for complexes **1**–**6** at −90 and at +20 °C, and the parameters for all complexes are presented in Table 3.

The ^{13}C {^{1}H} NMR spectra at −90 °C are again consistent with the presence of two invertomers in unequal proportions. Generally, individual resonances were detected in each region of the spectrum for both invertomers; however, for **1** and **2** it was not possible to detect separate signals for the methyl carbons of the *meso* and *DL* invertomers, and for **3** separate signals were not detected for the quaternary carbons of the t-butyl groups.

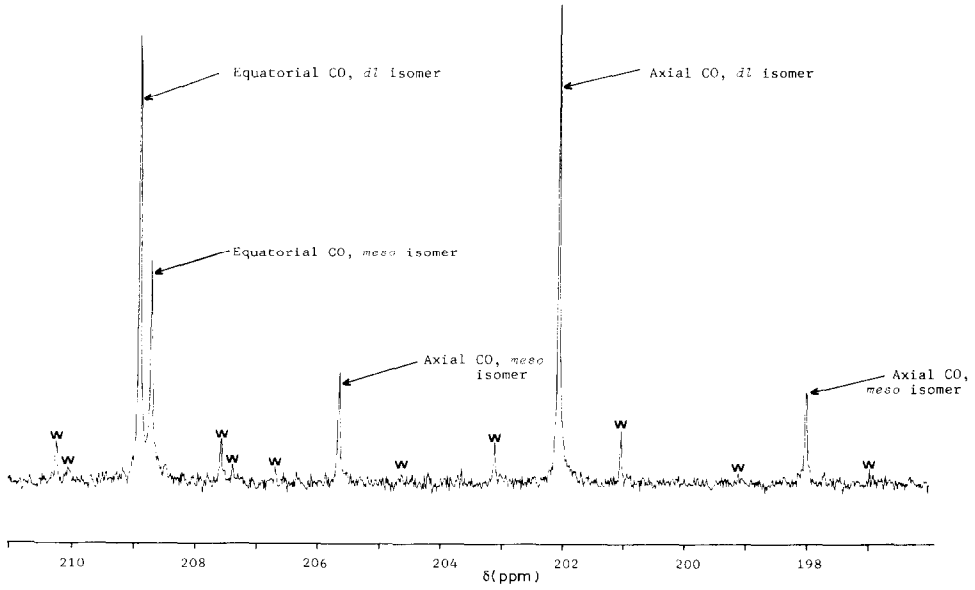

Fig. 3. Carbonyl region of the ^{13}C $\{^1H\}$ NMR spectrum of *cis*-$[W(CO)_4(^tBuSCH_2CH_2SBu^t)]$ (**3**) at $-90°C$; W = ^{183}W satellite.

The carbonyl regions of these spectra provide unequivocal support for the assignment of signals to individual isomers. A typical example of the type of spectrum observed for these complexes in this region is given in Fig. 3. The *DL* invertomer gave rise to two signals in the carbonyl region, one for the equatorial carbonyl groups and one for the chemically equivalent axial carbonyls.

In contrast, the *meso* invertomer gave rise to a single equatorial carbonyl resonance, and two signals for the non-equivalent axial carbonyl groups. Comparison of the intensities of the *DL* and *meso* signals in this region confirmed that the *DL* invertomer predominated in solution.

For the tungsten complexes **3**–**6** it proved possible to observe satellite signals of the carbonyl resonances due to coupling to ^{183}W, the exception being as noted in Table 3. The values of $^2J(CW)$ were approximately 167–168 Hz for the equatorial carbonyl groups (*trans* to sulphur) and 130–132 Hz for the axial carbonyl groups (*cis* to sulphur), although a rather lower value of 119.5 Hz was observed for the *meso* invertomer of **4**. These compare with coupling constants of 138–142 Hz (*trans* to L) and 125–129 Hz (*cis* to L) for complexes of the type $[W(CO)_5L]$, where L = tertiary phosphine or phosphite [25]. Owing to the poor solubility of **6**, particularly at low temperatures, carbonyl ^{183}W satellites were not observed in this case.

At 20 °C, spectra consisting simply of two signals in the CO region were observed for **1** to **6**, these being consistent with rapid interconversion of invertomers via sulphur inversion (Table 3). The chemical shifts noted in Table 3 for these carbonyl signals are similar in magnitude to those observed previously for sulphur-coordinated chromium, molybdenum and tungsten carbonyl complexes [26–29]. For the tungsten complexes, ^{183}W satellites were again observed in most cases, the values of $^1J(CW)$ being similar to those observed at -90 °C for the individual invertomers.

TABLE 3

$^{13}C\{^1H\}$ NMR PARAMETERS FOR COMPLEXES **1–6**

Complex	Temperature (°C)	Chemical shifts and spin–spin coupling constants [a]				
		Methyl carbons	Ligand backbone carbons	Alkyl group carbons	Axial carbonyl carbons	Equatorial carbonyl carbons
1	−90	29.42 [b]	31.21 (*DL*)	48.53 (*DL*) [c]	216.98 (*DL*)	228.14 [b]
			31.52 (*meso*)	48.69 (*meso*) [c]	213.45, 220.59 (*meso*)	
	20	29.70	31.21	48.58 [c]	217.36	228.23
2	−90	29.39 [b]	30.34 (*DL*)	48.52 (*DL*) [c]	207.27 (*DL*)	218.61 (*DL*)
			31.85 (*meso*)	48.57 (*meso*) [c]	203.81, 210.61 (*meso*)	218.36 (*meso*)
	20	29.56	31.03	48.40 [c]	207.39	218.43
3	−90	29.24 (*DL*)	31.96 (*DL*)	50.13 [b,c]	202.08 [130.6] (*DL*)	208.92 [168.1] (*DL*)
		29.38 (*meso*)	33.24 (*meso*)		198.02, 205.65 [132.8] (*meso*)	208.73 [167.7] (*meso*)
	20	29.55	32.84	50.11 [b]	202.44 [130.5]	208.50 [167.8]
4	−90	22.29 [d] (*DL*)	32.71 (*DL*)	43.01 (*DL*) [e]	201.37 [131.5] (*DL*)	208.76 [168.3] (*DL*)
		22.42, 22.56 (*meso*)	34.05 (*meso*)	45.20 (*meso*) [e]	199.47, 203.28 [119.5] (*meso*)	208.84 [168.3] (*meso*)
	−30	22.13	33.82	44.40 [e]	201.90 [131.1]	208.47 [167.4]
5	−90	14.40 (*DL*)	33.36 (*DL*)	36.38 (*DL*) [f]	201.48 [131.2] (*DL*)	208.91 [167.2] (*DL*)
		14.85 (*meso*)	35.50 (*meso*)	38.46 (*meso*) [f]	200.26, 202.89 [g] (*meso*)	209.13 [g] (*meso*)
	30	14.15	34.84	37.54 [f]	201.73 [g]	208.42 [166.9]
6	−50	26.39 (*DL*)	35.18 (*DL*)		201.76 [g] (*DL*)	208.81 [g] (*DL*)
		27.64 (*meso*)	37.51 (*meso*)		200.59, 202.87 [g] (*meso*)	208.98 [g] (*meso*)
	20	27.10	36.84		[h]	208.59 [g]

[a] Chemical shifts (δ, rel. to Me_4Si) and spin–spin coupling constants (in parentheses) ($^1J(CW)$ Hz). [b] Distinct signals for *DL* and *meso* invertomers not observed. [c] Quaternary carbons. [d] Distinct signals for the anisochronous methyl groups not observed. [e] Methine carbons. [f] Methylene carbons. [g] ^{183}W satellites not observed for this signal. [h] Not observed. The higher inversion energy for this complex could result in this signal still being broad at 20 °C.

Determination of activation parameters for pyramidal sulphur inversion in complexes ***1–6***

Computer simulations of the methylene region of the $^{13}C\{^1H\}$ variable temperature NMR spectra of complexes **1** to **5** were performed using the static parameters noted in Table 4, the spin problem being a simple two-site exchange:

$$A(DL) \rightleftharpoons B(meso)$$

For complex **5**, signals due to the methylene protons of both the ligand backbone and the ethyl group were simulated simultaneously, and simulated and experimental spectra for this complex are shown in Fig. 4. For complex **6**, the poor solubility of the complex precluded the use of ^{13}C NMR spectra for computer simulation, and rate constants for sulphur inversion in this complex were obtained from simulation of the methyl region of variable temperature ^1H NMR spectra, again using the static parameters listed in Table 6.

The rate constants obtained from these simulations were used to evaluate Arrhenius and Eyring activation parameters for sulphur inversion in these complexes (Table 5). The free energies of activation, $\Delta G^{\ddagger}_{298}$, of **3** to **6** show a marked dependence on the size of the thioalkyl group, varying from 53.7 kJ mol^{-1} for **6** down to 42.5 kJ mol^{-1} for **3**. These values may be compared with that of 51.5 kJ mol^{-1} reported for the complex, *cis*-$[W(CO)_4(PhCH_2SCH_2CH_2SCH_2Ph)]$ [6]. Sulphur inversion in these species would proceed via a planar transition state at each sulphur, and the value of $\Delta G^{\ddagger}_{298}$ would therefore be determined by the ease of access to this transition state. Comparison of the X-ray crystal structures of $[Cr(CO)_4(EtSCH_2CH_2SEt)]$ [23] and **1** [21] shows that on increasing the steric bulk of the thioalkyl group the Cr–S–C(alkyl group) bond angles increase markedly from 112.0° (av.) to 118.7° (av.). A similar effect occurs for the C(alkyl group)–S–C(ligand backbone) angle which increases from 100.6° (av.) to 104.5° (av.). Thus on increasing the steric requirements of the alkyl group a considerable distortion towards a planar sulphur geometry is seen which would provide easier access to the planar transition state at the onset of rapid sulphur inversion, and these effects are reflected in the values of $\Delta G^{\ddagger}_{298}$ for these complexes. Additionally, molecular models suggest that the pseudo-planar geometry at each sulphur that is afforded by

TABLE 4

STATIC PARAMETERS USED IN THE CALCULATION OF PYRAMIDAL SULPHUR INVERSION ENERGIES FOR COMPLEXES **1–6** [a]

Complex	Temperature (°C)	ν_A [b] (Hz)	p_A	ν_B [c] (Hz)	p_B	T_2^* (s)
1	−90	1955.5	0.745	1983.5	0.255	0.028
2	−100	1908.9	0.730	2002.8	0.270	0.048
3	−90	2010.0	0.716	2090.5	0.284	0.054
4	−70	2057.6	0.630	2141.4	0.370	0.080
5	−80 [d]	2098.3	0.650	2232.9	0.350	0.077
	−80 [e]	2288.2	0.650	2419.0	0.350	0.064
6 [f]	−40	636.2	0.648	680.8	0.352	0.138

[a] All simulations were performed on the methylene region of variable temperature $^{13}C\{^1H\}$ NMR spectra unless otherwise stated. [b] *DL*-isomer. [c] *meso*-isomer. [d] Data for SCH_2CH_2S signals. [e] Data for CH_3CH_2S signals. [f] Simulation performed on methyl region of variable temperature ^1H NMR spectra.

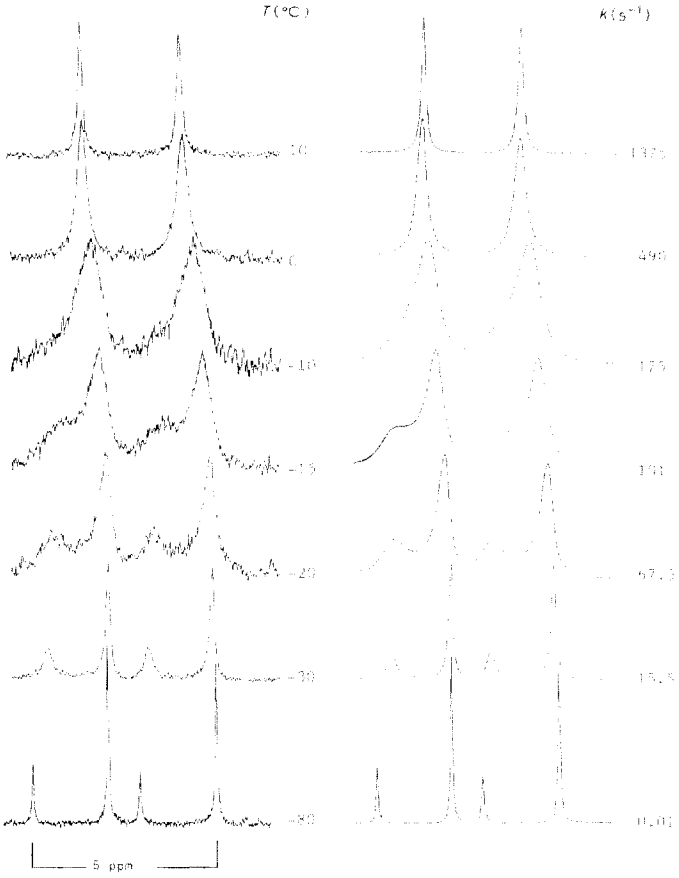

Fig. 4. Experimental and computer-simulated ^{13}C $\{^1H\}$ NMR spectra of the methylene region of *cis*-[$W(CO)_4(EtSCH_2CH_2SEt)$] (**5**) in the temperature range −80 to +10°C.

TABLE 5

ARRHENIUS AND EYRING ACTIVATION PARAMETERS FOR PYRAMIDAL SULPHUR INVERSION IN COMPLEXES **1–6** [a]

Complex	E_a (kJ mol^{-1})	$\log_{10}$ (A/s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
1	50.99 ± 1.23	14.37 ± 0.31	49.27 ± 1.22	24.9 ± 5.9	41.85 ± 0.53
2	46.63 ± 0.79	13.89 ± 0.20	44.89 ± 0.77	15.6 ± 3.7	40.25 ± 0.33
3	54.98 ± 0.71	14.97 ± 0.16	53.11 ± 0.70	35.7 ± 3.1	42.46 ± 0.23
4	57.38 ± 1.26	14.54 ± 0.27	55.37 ± 1.26	26.8 ± 5.2	47.39 ± 0.29
5	60.54 ± 1.33	14.28 ± 0.26	58.31 ± 1.31	21.0 ± 4.9	52.06 ± 0.15
6 [b]	65.53 ± 3.37	14.87 ± 0.66	63.33 ± 3.36	32.3 ± 12.7	53.69 ± 0.42

[a] Calculated from simulation of the methylene region of $^{13}C\{^1H\}$ variable temperature NMR spectra unless otherwise stated. [b] Calculated from simulation of the methyl region of ^1H variable temperature NMR spectra.

TABLE 6

^{1}H NMR PARAMETERS FOR COMPLEXES **7–12** AT 30 °C

Complex	Chemical shift (δ)	
	Methyl protons [a]	Ligand backbone protons [a]
7	2.56	6.95
8	1.44	6.99
9	2.63	6.92
10	1.44	6.95
11	2.81	7.00
12	1.45	7.00

[a] All signals are singlets.

rapid sulphur inversion considerably reduces the nonbonded interactions both between alkyl groups and between the alkyl groups and the ligand backbone hydrogens.

The variations in $\Delta G^{\ddagger}_{298}$ observed for complexes **1** to **3** are consistent with the trends observed previously for sulphur inversion in analogous series of chromium, molybdenum and tungsten complexes [3], with the inversion energy for **1** (M = Cr) intermediate between those of **2** (M = Mo, lowest energy) and **3** (M = W, highest energy), the values of the barriers being controlled by a combination of metal electronegativity and $p\pi$–$d\pi$ stabilisation of the planar transition state. On electronegativity arguments alone the chromium complex should show a higher inversion barrier than the tungsten complex. However, the inversion energy for the chromium complex is probably lowered further by significant $(3p$–$3d)\pi$ stabilisation of the planar transition state, whilst the $(3p$–$5d)\pi$ interaction for the tungsten complex is much less significant.

From Table 4 it can be seen that the relative invertomer populations are also slightly dependent on the steric bulk of the alkyl group attached to sulphur, with larger populations of the *DL* invertomer for complexes **1–3** than for **4–6**. However, for complexes **4–6** there is very little variation of the relative isomer populations, the *DL/meso* ratio remaining approximately 64/36 for all three complexes.

^{1}H and ^{13}C {^{1}H} NMR parameters for complexes 7–12

^{1}H and ^{13}C {^{1}H} NMR spectra were recorded for complexes **7–12** at both low temperatures and at 30 °C. ^{1}H NMR parameters for these complexes at 20 °C are given in Table 6, and ^{13}C {^{1}H} NMR parameters at 30 °C and at low temperatures are given in Table 7.

The ^{1}H NMR spectra at 20 °C were consistent with the rapid interconversion of invertomers via sulphur inversion. Complexes **7**, **9** and **11** showed one signal at δ 2.5–2.8 for the methyl group, with complexes **8**, **10** and **12** having a methyl resonance at δ ca. 1.44. The ligand backbone signal for all complexes fell in the range δ 6.92–7.00.

On cooling solutions of these complexes to ca. −90 °C no changes in the ^{1}H NMR spectra were observed. This would have arisen for one of two reasons, either (a) the sulphur inversion barriers were too low for static spectra to be obtained; or (b) only one invertomer was present in solution at −90 °C. Confirmation that the latter of these possible explanations was in fact the correct one was supplied by the

TABLE 7

^{13}C $\{^1H\}$ NMR PARAMETERS FOR COMPLEXES 7–12

Complex	Temperature (°C)	Chemical shift (δ) [a]			
		Methyl carbons	Quaternary carbons	Ligand backbone carbons	Carbonyl carbons
7	30	26.98	–	134.30	215.79 (*ax*) 227.88 (*eq*)
	−100	26.98	–	134.30	215.73 [b] (*ax*) 228.05 (*eq*)
8	30	29.80	52.07	130.14	216.70 (*ax*) 228.08 (*eq*)
	−90	29.49	51.93	130.01	213.03, 219.50 (*ax*) 227.98 (*eq*)
9	30	28.11	–	133.37	206.02 (*ax*) 218.02 (*eq*)
	−90	28.24	–	133.27	205.74, 206.07 (*ax*) 218.35 (*eq*)
10	30	29.78	51.98	129.37	206.94 (*ax*) 217.99 (*eq*)
	−90	29.48	51.84	129.20	203.62, 209.52 (*ax*) 218.02 (*eq*)
11	30	29.93	–	134.92	200.09 [c] (*ax*) 208.67 [c] (*eq*)
	−80	29.97	–	134.76	200.82 [b,c] (*ax*) 209.29 [c]
12	30	29.72	53.46	131.20	201.39 [129.9] [d] (*ax*) 208.18 [166.9] (*eq*)
	−90	29.43	53.46	130.98	197.74 [131.5], 204.20 [129.0] (*ax*) 208.54 [168.4] (*eq*)

[a] ^1J(CW) (Hz) values in parentheses. [b] Separate signals for the two axial carbonyl environments not resolved. [c] ^{183}W satellites not observed.

low temperature ^{13}C $\{^1H\}$ NMR spectra (Table 7) where the carbonyl region shows three signals (int. 1/1/2), consistent with the presence of only the *meso* isomer in solution at these temperatures. Admittedly for complexes 7 and **11** separate signals for the two axial carbonyl environments were not observed and so it is not therefore totally certain that static spectra pertained at −90 °C for these complexes; however the chemical shift difference between the two axial environments can be small (e.g. complex **9**) and therefore it would be most reasonable to assume that static spectra have been obtained in these complexes also, and that the absence of separate signals was due to resolution limitations.

On raising the temperature the axial carbonyl signals coalesced such that at 20 °C two signals, consistent with rapid sulphur inversion, were observed. All other regions of the ^{13}C $\{^1H\}$ spectra were similar at both low temperature and 20 °C, and parameters for other regions of the spectra at 20 °C are given in Table 7.

The invertomer populations for these complexes are in marked contrast to those observed for complexes **1**–**6**, where the *DL* invertomer was the most populous in

solution. However, the unsaturated nature of the ligand backbone constrains the chelate ring to a planar geometry, and models show that this results in much more serious nonbonded interactions between the alkyl groups and the axial carbonyl ligands than occurs with the saturated ligands, and furthermore these interactions are much more serious for the *DL* invertomer than for the *meso* invertomer. It therefore seems that invertomer populations in complexes **7–12** are controlled by alkyl group – carbonyl group non-bonded interactions, whereas for **1–6** the controlling factor is alkyl group – alkyl group nonbonded interactions. The invertomer populations observed for **7–12** are reflected in the X-ray crystal structure of **8** [18], which shows a *cis* arrangement of the t-butyl groups relative to a planar chelate ring.

^{183}W satellites for the carbonyl signals were observed for **12** at both −90 and 20 °C, values of $^{1}J(CW)$ being similar to those noted for complexes **3–5**. The poorer solubility of **11** precluded the observation of ^{183}W satellites for the carbonyl signals of this complex.

Calculation of inversion barriers for these complexes could only have been achieved by computer simulation of the variable temperature $^{13}C\ \{^{1}H\}$ NMR spectra in the axial carbonyl region where separate signals were resolved, and in order to detect these signals when broadened by the exchange process ^{13}CO enrichment of the complexes would have been necessary. We did not feel that the information to be obtained from this procedure warranted the preparation of enriched samples, as the effects of introducing unsaturation into a ligand backbone on sulphur inversion energies are already well documented [3].

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