

## DYNAMIC NMR STUDIES OF PENTACARBONYL-CHROMIUM(0) AND -TUNGSTEN(0) COMPLEXES OF 2,4,6-TRITHIAHEPTANE AND 2,4,6,8-TETRATHIANONANE

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### Summary

The mono- and bis-(metal pentacarbonyl) complexes  $\{[M(CO)_5]_m\{MeS(CH_2S)_n-$   
 $Me\}$  ( $M = Cr, W; m = 1, n = 2; m = 2, n = 2,3$ ) have been synthesised and studied  
 by dynamic NMR methods. Total band shape fitting of temperature variable  $^1H$   
 NMR spectra of the complexes has enabled the determination of very accurate data  
 for pyramidal ligand atom sulphur inversions. At higher temperatures line shape  
 changes that would accord with 1,3 intramolecular shifts of the  $M(CO)_5$  moieties  
 between ligand sulphur atoms were observed. Concurrent dissociation, however,  
 prevented access to the high quality spectra required for accurate determination of  
 kinetic data of such shifts.

### Introduction

Recent work has seen the report of a range of different fluxional behaviours of  
 the complexes of Group VI metal carbonyls with organosulphur and organoselenium  
 ligands. In the complexes  $[M(CO)_5(\dot{S}CHR\dot{S}CHRE\dot{C}HR)]$  ( $M = Cr, W; E = S, CH_2;$   
 $R = H, CH_3$ ) accurate energy barriers have been obtained for ring reversal, sulphur  
 atom inversion and 1,3-shift of the  $M(CO)_5$  moiety of all possible ligand coordina-  
 tion sites [1,2]. In open chain ligands chalcogen inversion and 1,2-metal shifts have  
 been reported in complexes  $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$  ( $M = Cr, Mo, W;$   
 $E = S, Se$ ) [3]; and chalcogen inversion and 1,3-metal shifts were characterized in  
 complexes  $[W(CO)_5(MeECH_2E'Me)]$  ( $E = E' = S$  or  $Se; E = S, E' = Se$ ) [4].

The present extension of this field examines the metal pentacarbonyl complexes  
 of the linear polysulphur ligands 2,4,6-trithiaheptane  $MeSCH_2SCH_2SMe$ , and  
 2,4,6,8-tetrathianonane  $MeSCH_2SCH_2SCH_2SMe$ .

### Experimental

The ligands were prepared according to literature methods [5] 2,4,6-trithiahep-  
 tane, b.p. 104–108°C/15 mmHg (lit. [6] b.p. 106°C/5 mmHg),  $^1H$  NMR  $\delta(Me)$

2.15,  $\delta(\text{CH}_2\text{S})$  3.77 ppm: 2,4,6,8-tetrathianonane, b.p. 106–108°C/0.1 mmHg (lit. [5] b.p. 117.5°C/0.7 mmHg),  $^1\text{H NMR}$   $\delta(\text{Me})$  2.15,  $\delta(\text{CH}_2(\text{outer}))$  3.77,  $\delta(\text{CH}_2(\text{inner}))$  3.92 ppm.

Tetraethylammonium bromopentacarbonyl metallates were prepared by standard methods [7], and triethyloxonium tetrafluoroborate was prepared by a literature method [8].

#### *Preparation of $[\text{Cr}(\text{CO})_5(\text{MeSCH}_2\text{SCH}_2\text{SMe})]$*

A two-fold excess of 2,4,6-trithiaheptane (1.16 g, 7.5 mmol) was added to a solution of tetraethylammonium bromopentacarbonylchromate (1.5 g, 3.73 mmol) in dry dichloromethane (25 cm<sup>3</sup>) in a Schlenk tube under dry nitrogen. After cooling the solution to 0°C triethyloxonium tetrafluoroborate (0.7 g, 3.73 mmol) in dichloromethane (10 cm<sup>3</sup>) was added very slowly (5 min). The bright yellow colour changed to orange-green. All volatiles were removed (20°C/0.1 mmHg), and the solid residue was extracted with freshly distilled hexane (3 × 10 cm<sup>3</sup>). The extracts were filtered through a Schlenk sinter and the volume reduced to 10 cm<sup>3</sup>. Chromatography on a silica gel column with hexane as eluant under nitrogen give an initial light-orange band followed by a main deep yellow band. Removal of solvent from the deep yellow solution yielded yellow crystals of 2,4,6-trithiaheptanepentacarbonylchromium(0) (0.49 g, 38%). These were recrystallized from hexane by cooling to –78°C and dried under vacuum. Yellow crystals of 2,4,6-trithiaheptane-pentacarbonyltungsten(0) (0.61 g, 46%) were prepared in an analogous manner.

#### *Preparation of the bis(metal pentacarbonyl) complexes $[\{M(\text{CO})_5\}_2\{\text{MeS}(\text{CH}_2\text{S})_n\text{Me}\}]$ ( $M = \text{Cr}, \text{W}; n = 2, 3$ )*

All four complexes have essentially the same preparation, and the general method is outlined below.

The metal hexacarbonyl (5 mmol) in dry tetrahydrofuran was irradiated by a Hanovia 125W lamp in a water cooled jacket for 24 h under dry nitrogen. The resulting orange coloured solution of  $[\text{THFM}(\text{CO})_5]$  was filtered and added to the appropriate ligand (2.5 mmol) in a Schlenk tube. The mixture was stirred for 6 h at 20°C, when the displacement of THF by sulphur ligand was indicated by the orange to yellow colour change. All volatiles were removed at 40°C/0.001 mmHg/4 h. The oily residue was extracted with hexane (3 × 10 cm<sup>3</sup>) followed by cooling to –20°C. The yellow crystals deposited were contaminated with a small amount of free ligand.

Subsequent chromatography on an alumina column with hexane eluant gave a pure sample of the bis(metal pentacarbonyl) complex. The products were air-sensitive, yellow and were stored under nitrogen until used for spectroscopic measurements. Yields were 35–45% and characterisations are noted in Table 1.

### **Properties and structures**

The carbonyl stretching region of the infrared spectra are reported in Table 1 for these metal pentacarbonyls. Four active bands  $2A_1 + B_1 + E$  result from the bulky linear nature of the ligands.

The room temperature 100 MHz  $^1\text{H NMR}$  spectra of the mononuclear complexes  $[\text{M}(\text{CO})_5\{\text{MeSCH}_2\text{SCH}_2\text{SMe}\}]$  showed two distinct methyl and two distinct meth-

ylene absorptions, indicating that the  $M(CO)_5$  group is attached to an outer sulphur atom of the ligand.

In the dinuclear complexes of the same ligand  $[\{M(CO)_5\}_2\{MeSCH_2SCH_2SMe\}]$  only one methyl and one methylene peak is observed, again showing the attachment of the metal groups to the outer sulphurs of the ligand.

For the complexes  $[\{M(CO)_5\}_2\{MeSCH_2SCH_2SCH_2SMe\}]$  one methyl absorption and two methylene absorptions (intensity ratio 2/1) were observed. Such a simple pattern indicates either a structure where both metal carbonyl groups are attached to the inner two sulphur atoms, or alternatively to the outer two sulphur atoms. We favour the latter, both from steric requirements and the chemical shift values of the protons.

Representative room temperature  $^1H$  NMR spectra of these three types of complex are illustrated in Fig. 1 for  $[Cr(CO)_5\{MeSCH_2SCH_2SMe\}]$ ,  $[\{Cr(CO)_5\}_2\{MeSCH_2SCH_2SMe\}]$  and  $[\{Cr(CO)_5\}_2\{MeSCH_2SCH_2SCH_2SMe\}]$ .

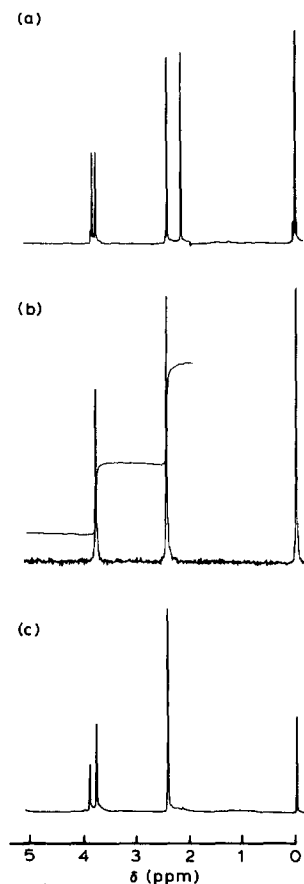


Fig. 1. Room temperature  $^1H$  NMR spectra of (a)  $[Cr(CO)_5\{MeS(CH_2S)_2Me\}]$ , (b)  $[\{Cr(CO)_5\}_2\{MeS(CH_2S)_2Me\}]$  and (c)  $[\{Cr(CO)_5\}_2\{MeS(CH_2S)_3Me\}]$  in  $CD_2Cl_2$ .

TABLE 1  
ANALYTICAL AND INFRARED DATA FOR THE COMPLEXES  $\{[M(\text{CO})_5]_m(\text{MeS}(\text{CH}_2\text{S})_n\text{Me})\}$  ( $M = \text{Cr}, \text{W}; m = 1, n = 2, m = 2, n = 2, 3$ )

Compound	M.p. (°C)	Analysis (Found (calcd.)(%))				$\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) (in hexane solution)
		H	C	S	M	
$[\text{Cr}(\text{CO})_5(\text{MeS}(\text{CH}_2\text{S})_2\text{Me})]$	32-33	2.85 (2.90)	31.15 (31.21)	-	-	2063w, 1985w, 1947s, 1937m(sh)
$[\text{W}(\text{CO})_5(\text{MeS}(\text{CH}_2\text{S})_2\text{Me})]$	35-36	1.57 (2.11)	21.84 (22.60)	-	-	2070w, 1987w, 1943s, 1935m(sh)
$[\{\text{Cr}(\text{CO})_5\}_2(\text{MeS}(\text{CH}_2\text{S})_2\text{Me})]$	49-50	1.73 (1.87)	31.15 (31.32)	-	-	2069w, 1988w, 1952s, 1944m(sh)
$[\{\text{W}(\text{CO})_5\}_2(\text{MeS}(\text{CH}_2\text{S})_2\text{Me})]$	60	1.37 (1.25)	21.53 (20.96)	13.10 (11.99)	-	2080w, 1979w, 1947s, 1938m(sh)
$[\{\text{Cr}(\text{CO})_5\}_2(\text{MeS}(\text{CH}_2\text{S})_3\text{Me})]$	54-55	2.62 (2.06)	32.65 (30.82)	23.20 (21.94)	17.40 (17.79)	2067w, 1990w, 1948s, 1942m(sh)
$[\{\text{W}(\text{CO})_5\}_2(\text{MeS}(\text{CH}_2\text{S})_3\text{Me})]$	77	1.65 (1.42)	20.15 (21.24)	15.21 (15.12)	-	2075w, 1985w, 1949s, 1943m(sh)

## Recording, simulation and computation of NMR spectra

For low temperature studies the solvent was an equimolar  $\text{CD}_2\text{Cl}_2/\text{CS}_2$  mixture with  $\text{Me}_4\text{Si}$  as reference. In the high temperature studies an equimolar  $\text{C}_6\text{D}_6\text{NO}_2/\text{C}_6\text{D}_6$  mixture was used with  $\text{Me}_3\text{SiOSiMe}_3$  as reference. All solutions were very air sensitive, and samples were contained in Taperlok (Wilmad) tubes under nitrogen. Spectra were recorded at 100 MHz using a JEOL PS/PFT-100 spectrometer equipped with a standard variable temperature accessory. Temperatures were recorded with a calibrated copper-constantan thermocouple, and were considered accurate to  $< 1^\circ\text{C}$ . NMR band shape analyses were performed with the authors' modified version of the DNMR program of Kleier and Binsch [9,10].

## Dynamic NMR studies

(a) Low temperature  $^1\text{H}$  NMR studies of  $[\text{M}(\text{CO})_5\{\text{MeSCH}_2\text{SCH}_2\text{SMe}\}]$  ( $\text{M} = \text{Cr}, \text{W}$ )

In these complexes, the metal coordinated sulphur atom is a chiral centre, and both methylene groups in the ligand chain are prochiral (Fig. 2a). The diastereotopic hydrogen pairs  $\text{H}_\text{A}$  and  $\text{H}_\text{B}$ , and  $\text{H}_\text{C}$  and  $\text{H}_\text{D}$  only become isochronous by the inversion process about the coordinated sulphur atom as illustrated in Fig. 3.

At ca.  $-90^\circ\text{C}$  the methylene region of the spectra of these complexes consisted of

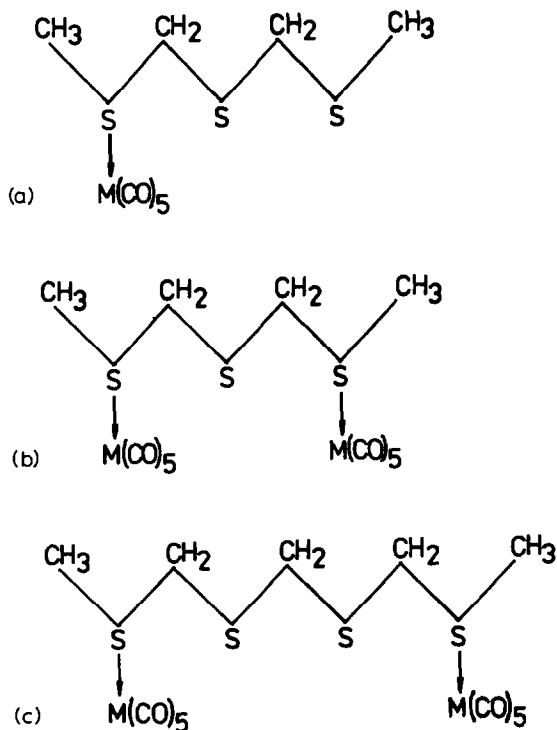


Fig. 2. Molecular structures of (a)  $[\text{M}(\text{CO})_5\{\text{CH}_3\text{S}(\text{CH}_2\text{S})_2\text{CH}_3\}]$  ( $\text{M} = \text{Cr}, \text{W}$ ), (b)  $[\{\text{M}(\text{CO})_5\}_2\{\text{CH}_3\text{S}(\text{CH}_2\text{S})_2\text{CH}_3\}]$  ( $\text{M} = \text{Cr}, \text{W}$ ) and (c)  $[\{\text{M}(\text{CO})_5\}_2\{\text{CH}_3\text{S}(\text{CH}_2\text{S})_3\text{CH}_3\}]$  ( $\text{M} = \text{Cr}, \text{W}$ ).

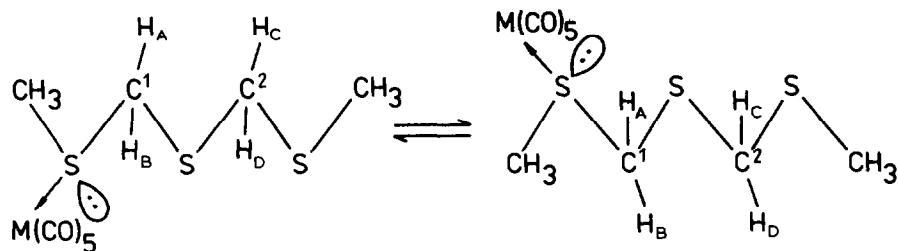


Fig. 3. Interconversion of invertomers of  $[M(CO)_5(CH_3S(CH_2S)_2CH_3)]$  by the inversion of the coordinated sulphur atom.

two well resolved AB quartets. On warming, broadening and eventual coalescence reduced each quartet to a sharp singlet at ca.  $-45^\circ\text{C}$ . These changes were reversible and concentration independent, and there was no exchange with a small amount of added free ligand. These spectral changes are undoubtedly due to the ligand atom sulphur inversion illustrated in Fig. 3. After determination of the static parameters (Table 2), and any temperature dependencies of these parameters over a wide range of temperature where the inversion process was slow, the spectra were simulated by a complete band shape analysis on the basis of  $AB \rightleftharpoons BA$  and  $CD \rightleftharpoons DC$  spin interconversions. Computer synthesised and experimental spectra for a range of temperatures for  $[Cr(CO)_5(MeSCH_2SCH_2SMe)]$  are illustrated in Fig. 4.

(b) *High temperature  $^1\text{H}$  NMR studies of  $[M(CO)_5\{MeSCH_2SCH_2SMe\}]$  ( $M = Cr, W$ )*

By analogy with other complexes [4], there was a likelihood that 1,3-metal shifts would take place in this type of complex. Such intramolecular 1,3-shifts in combination with ligand atom inversions would allow the metal moiety to commute over all six possible coordination sites in the ligand. Such movements would average the two methyl signals to a singlet, and similarly the methylene signals would coalesce to a singlet at fast exchange conditions. As expected, the methyl and methylene signals in both regions moved towards coalescence at ca.  $70^\circ\text{C}$ , but above  $85^\circ\text{C}$  decomposition began, and prevented the acquisition of spectra of sufficient quality to obtain accurate numerical parameters for the 1,3-metal shift process in this type of complex.

(c) *Variable-temperature  $^1\text{H}$  NMR studies of the dinuclear complexes  $[\{M(CO)_5\}_2\{MeSCH_2SCH_2SMe\}]$  ( $M = Cr, W$ )*

From Fig. 2(b) it may be seen that the plane of symmetry through the centre

TABLE 2

STATIC PARAMETERS USED IN THE CALCULATION OF PYRAMIDAL INVERSION ENERGIES IN THE COMPLEXES  $[\{M(CO)_5\}\{MeS(CH_2S)_2Me\}]$

$M^a$	Temperature ( $^\circ\text{C}$ )	$\nu_A$ (Hz) <sup>b</sup>	$\nu_B$ (Hz)	$^2J$ (Hz) <sup>c</sup>	$\nu_C$ (Hz)	$\nu_D$ (Hz)	$^2J$ (Hz)	$T_2^*$ (s)
Cr	-90.4	413.8	360.5	13.9	393.5	369.3	14.4	0.102
W	-99.1	429.9	371.8	13.5	393.0	368.4	14.5	0.104

<sup>a</sup> Solvent was  $\text{CD}_2\text{Cl}_2/\text{CS}_2$  mixture. <sup>b</sup> Chemical shifts measured relative to  $\text{Me}_4\text{Si}$ . <sup>c</sup>  $^2J(\text{H}-\text{C}-\text{H})$ .

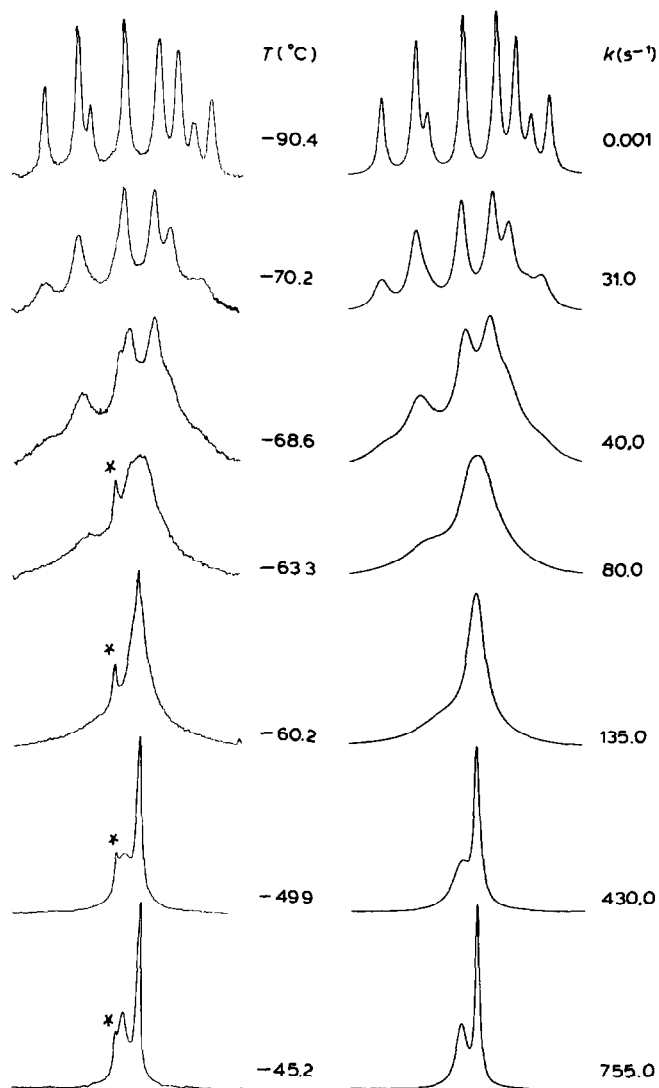


Fig. 4. Experimental and computer-synthesised spectra of the methylene region of  $[\text{Cr}(\text{CO})_5\text{-(MeS}(\text{CH}_2)_2\text{Me)}]$  showing the effect of sulphur inversion. The asterisked band is due to an impurity.

sulphur atom of these complexes produces two isochronous methylene groups and two isochronous methyl groups. Both methylene groups, however, are prochiral and at  $-80^\circ\text{C}$  the methylene region exhibited the four peaks of an AB quartet. Temperature rise caused collapse to a singlet without involvement of added excess ligand, as in (a) above. The inversion processes at the two sulphur ligand atoms, as illustrated in Fig. 5 are proposed. Whilst in the figure both sulphur atoms are inverted, this should not be taken as an indication of either synchronous or correlated atomic inversion. Indeed, on balance, the long flexible chain would be unlikely to require any element of inversion correlation. Static parameters are noted

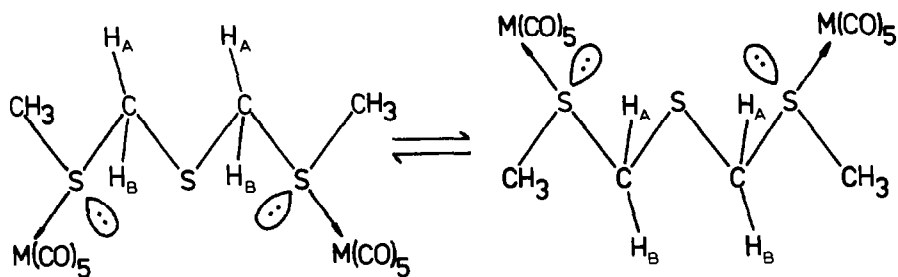


Fig. 5. Mutual exchange of the environments of  $H_A$  and  $H_B$  by inversion of the coordinated sulphur atoms in  $\{[M(CO)_5]_2(CH_3S(CH_2S)_2CH_3)\}$  ( $M = Cr, W$ ).

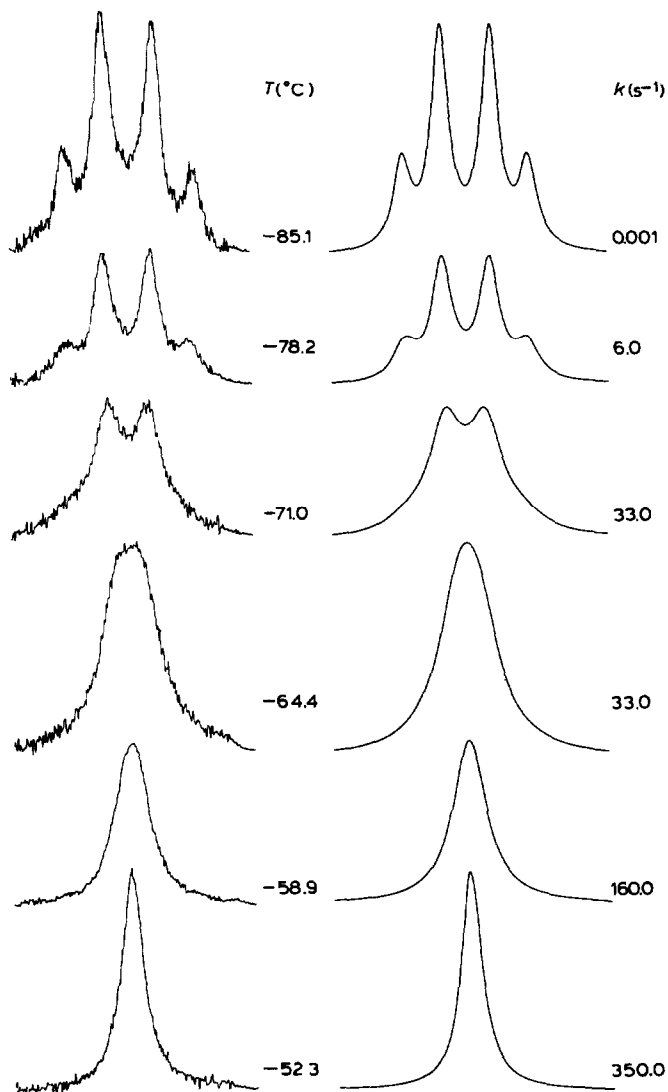


Fig. 6. Experimental and theoretical spectra of the methylene region of  $\{[Cr(CO)_5]_2(MeS(CH_2)_2Me)\}$  showing the effect of sulphur inversion.



TABLE 3

STATIC PARAMETERS USED IN THE CALCULATION OF PYRAMIDAL INVERSION ENERGIES IN THE COMPLEXES  $\{[M(CO)_5]\{MeS(CH_2)_3Me\}\}$

M	Temperature (°C)	$\nu_A$ (Hz)	$\nu_B$ (Hz)	$^2J$ (Hz)	$T_2^*$ (s)
Cr	-85.1	398.6	372.7	12.5	0.046
W	-84.1	416.5	386.3	14.5	0.071

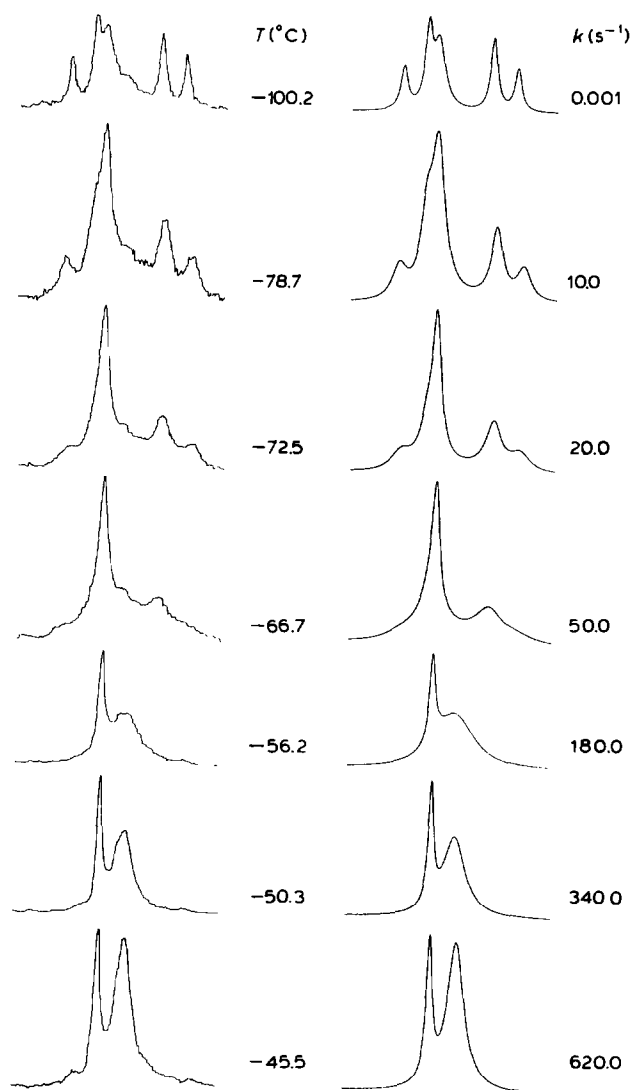


Fig. 7. Experimental and simulated spectra of the methylene region of  $\{[Cr(CO)_5]_2\{MeS(CH_2)_3Me\}\}$  showing the effect of pyramidal sulphur inversion.

TABLE 4

STATIC PARAMETERS USED IN THE CALCULATION OF PYRAMIDAL INVERSION ENERGIES IN THE COMPLEXES  $[\{M(\text{CO})_5\}_2\{\text{MeS}(\text{CH}_2\text{S})_3\text{Me}\}]$

M <sup>a</sup>	Temperature (°C)	AB-quartet of prochiral methylene protons				Singlet of achiral methylene protons	
		$\nu_A$ (Hz) <sup>b</sup>	$\nu_B$ (Hz)	<sup>2</sup> J (Hz) <sup>c</sup>	$T_2^*$ (s)	$\nu$ (Hz)	$T_2^*$ (s)
Cr	-100.2	404.8	354.4	14.3	0.065	393.3	0.038
W	-97.2	425.2	372.7	14.4	0.053	398.7	0.028

<sup>a</sup> Solvent was  $\text{CD}_2\text{Cl}_2/\text{CS}_2$  mixture. <sup>b</sup> Chemical shifts measured relative to  $\text{Me}_4\text{Si}$ . <sup>c</sup> <sup>2</sup>J(H-C-H).

in Table 3 and the spectra were simulated as an  $\text{AB} \rightleftharpoons \text{BA}$  spin interconversion.

Experimental and simulated spectra for  $[\{\text{Cr}(\text{CO})_5\}_2\{\text{MeSCH}_2\text{SCH}_2\text{SMe}\}]$  are reproduced in Fig. 6.

In these complexes no further line shape changes were observed up to 95°C, where decomposition became significant.

*(d) Variable temperature <sup>1</sup>H NMR studies of the binuclear complexes  $[\{M(\text{CO})_5\}_2\{\text{MeSCH}_2\text{SCH}_2\text{SCH}_2\text{SMe}\}]$*

In the class of complex, Fig. 2(c), we have several hydrogen environments. At -100°C the two isochronous methyl groups appear as a singlet, the pair of isochronous prochiral outer methylene groups appear as an AB quartet and the achiral central methylene group appears as a sharp singlet overlapping the AB quartet of the two other methylene groups. Warming caused only the collapse of the AB quartet. Spectra were simulated as an  $\text{AB} + \text{C} \rightleftharpoons \text{BA} + \text{C}$  system taking account of the unchanging singlet hydrogens (C) of the central methylene group. Static parameters used in spectral simulation are collected in Table 4, and experimental and computed spectra for  $[\{\text{Cr}(\text{CO})_5\}_2\{\text{MeSCH}_2\text{SCH}_2\text{SCH}_2\text{SMe}\}]$  are illustrated in Fig. 7. After sulphur inversion is rapid at ca. -40°C there are no further spectral changes until decomposition at ca. 90°C.

## Results and discussion

Rate constant values (usually 8 or 9, but at least 5) as extracted from the best-fit band shapes of the six complexes were used to evaluate Arrhenius and Eyring parameters for the pyramidal sulphur inversion of coordinated sulphur (Table 4). In addition to the non-exchange with added ligand during the spectral coalescence, further evidence of the intramolecular nature of the process is gained from all values of  $\log_{10} A \approx 13$  and  $\Delta S^\ddagger \text{ J K}^{-1} \text{ mol}^{-1}$  remaining close to zero. The inversion of the coordinated sulphur atoms proceeds via a planar transition state, and ease of access to this state controls the magnitude of the free energies of activation listed in Table 5. These rapid rates of inversion compared to for example sulphoxides [11] and sulphonium ions [12], are already well documented for metal carbonyl complexes; and whilst many factors contribute to lowering of these inversion energies, the actual magnitudes are primarily controlled by metal electronegativity and ligand-metal  $p\pi-d\pi$  bonding [13].

TABLE 5

## ARRHENIUS AND EYRING ACTIVATION PARAMETERS FOR PYRAMIDAL ATOMIC INVERSION

Complex	$E_a$ (kJ mol <sup>-1</sup> )	$\log_{10} A$	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )	${}^a\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )
$[\{\text{Cr}(\text{CO})_5\}\{\text{MeS}(\text{CH}_2\text{S})_2\text{Me}\}]$	$48.46 \pm 1.08$	$13.98 \pm 0.26$	$46.66 \pm 1.08$	$17.13 \pm 5.05$	$41.55 \pm 0.42$
$[\{\text{W}(\text{CO})_5\}\{\text{MeS}(\text{CH}_2\text{S})_2\text{Me}\}]$	$47.72 \pm 0.84$	$13.69 \pm 0.21$	$46.00 \pm 0.82$	$11.89 \pm 4.00$	$42.45 \pm 0.36$
$[\{\text{Cr}(\text{CO})_5\}_2\{\text{MeS}(\text{CH}_2\text{S})_2\text{Me}\}]$	$44.62 \pm 0.79$	$13.09 \pm 0.19$	$42.87 \pm 0.78$	$0.21 \pm 3.73$	$42.81 \pm 0.33$
$[\{\text{W}(\text{CO})_5\}_2\{\text{MeS}(\text{CH}_2\text{S})_2\text{Me}\}]$	$44.10 \pm 3.15$	$12.70 \pm 0.77$	$42.33 \pm 3.14$	$-7.16 \pm 14.85$	$44.47 \pm 1.28$
$[\{\text{Cr}(\text{CO})_5\}_2\{\text{MeS}(\text{CH}_2\text{S})_3\text{Me}\}]$	$45.71 \pm 1.07$	$13.25 \pm 0.26$	$43.98 \pm 1.07$	$3.46 \pm 5.13$	$42.95 \pm 0.46$
$[\{\text{W}(\text{CO})_5\}_2\{\text{MeS}(\text{CH}_2\text{S})_3\text{Me}\}]$	$44.89 \pm 0.32$	$12.76 \pm 0.08$	$43.19 \pm 0.33$	$-5.69 \pm 1.65$	$44.88 \pm 0.15$

<sup>a</sup> Calculated at 298.15 K.

Chromium has a higher electronegativity than tungsten, so upon that basis chromium complexes would be expected to have larger free energies of inversion than exactly analogous tungsten materials. However, this gross electronegativity effect appears to have been marginally modified to reverse this premise. We believe this is due to the inversion energy for chromium being further lowered by  $(3p-3d)\pi$  ligand interaction, whilst the  $(3p-5d)\pi$  interaction for tungsten is not significant.

The dinuclear complexes have slightly higher atomic sulphur inversion energies than the corresponding mononuclear complexes, but increase in chain length appears to have no notable effect upon the free energy of inversion.

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