Pyramidal Inversion in Configurational Isomers of Tetracarbonyl[1,1,2,2-Tetrakis(methylthio)ethane]chromium(0): A Two-dimensional Nuclear Magnetic Resonance Exchange Study

Edward W. Abel, Kevin M. Higgins, Keith G. Orrell,* and Vladimir Šik
Department of Chemistry, The University of Exeter, Exeter EX4 4QD
Eirian H. Curzon and Oliver W. Howarth
Department of Chemistry and Molecular Sciences, The University of Warwick, Coventry CV4 7AL

Pyramidal inversion of the co-ordinated sulphur atoms in the *cis* and *trans* configurational isomers of $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$ has been examined by n.m.r. spectroscopy. The two-dimensional NOESY method was used to identify individual invertomers of each isomer at low temperature. One-dimensional band-shape analyses performed at higher temperatures yielded $\Delta G^‡$ values in the ranges 45—50 and 50—54 kJ mol^{-1} for the *trans* and *cis* isomers respectively. No evidence for *cis–trans* interconversion was obtained, probably because of the limited thermal stability of the complex.

Pyramidal inversion of Group 6B atoms co-ordinated to transition metals is readily studied by n.m.r. spectroscopy.[1] Many instances have been noted in which rapid inversion of co-ordinated atoms leads to other fluxional movements. Of particular novelty and relevance here are the 1,3-metallotropic shifts observed in metal pentacarbonyl complexes with cyclic[2–5] and open-chain ligands.[6,7] With bridging-ligand complexes such as $[(PtXMe_3)_2L]$ [L = $\overline{SCH_2(SCH_2)_nS}CH_2$ (n = 1 or 2), X = halide][8,9] single-site sulphur inversion is precluded and instead the ligand undergoes a series of 60° or 90° pivots about each S–Pt bond.

In order to investigate further the interrelationship of such fluxional movements the chromium tetracarbonyl complex of the ligand 1,1,2,2-tetrakis(methylthio)ethane was prepared. This complex, $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$, was isolated as a mixture of configurational isomers arising from the mutual *cis* and *trans* dispositions of the unco-ordinated methylthio-groups. The stereodynamics of this isomer mixture were examined by n.m.r. spectroscopy with a view to studying (*i*) the inversion of the co-ordinated sulphur atoms and (*ii*) any *cis–trans* interconversion arising from 1,3-metal pivots about either co-ordinated sulphur.

Two-dimensional n.m.r. exchange spectroscopy[10] has important advantages over conventional one-dimensional n.m.r. methods for studying slow internal-exchange processes. First, all exchanging nuclei can be clearly identified from the off-diagonal (cross) peaks in highly complex slow-exchange two-dimensional spectra. Secondly, the intensities of these cross-peaks, measured as a function of the mixing time in the NOESY pulse sequence,[11] can be used in favourable cases to deduce exchange rate constants.[11–13] This allows rate data to be obtained from 'near static' spectra of compounds whose thermal instabilities prevent their being taken to higher temperatures for one-dimensional band-shape fittings. Thirdly, cross-peak intensities often enable distinctions to be made between different chemical exchange pathways.[14–17]

The complex $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$ represents a case where the high complexity of its slow-exchange spectrum, arising from the three distinct conformers (invertomers) of each configurational isomer, could only be analysed by two-dimensional spectroscopy. Because of a likely contribution of nuclear Overhauser effects (n.O.e.s) to certain cross-peak intensities,[18] it was thought preferable to base the subsequent inversion-energy studies on conventional one-dimensional band-shape analyses. We now report this new application of one- and two-dimensional n.m.r. methods for studying pyramidal atomic inversion.

Experimental

Materials.—1,1,2,2-*Tetrakis*(*methylthio*)*ethane.* Methanethiol (20.0 g, 0.41 mol) was introduced into a vigorously stirred mixture of glyoxal (40% aqueous solution, 12.6 g, 0.08 mol) and hydrochloric acid (25% aqueous solution, 10 cm^3) at −15 °C. The stirring was continued for 2.5 h and the solution allowed to warm to room temperature. The resulting yellow-pale green oil was extracted into diethyl ether (2 × 50 cm^3), separated from the aqueous layer, and dried over magnesium sulphate. After filtration, the predominant impurity, $(MeS)_2CHCHO$ [b.p. 67.8—69.5 °C, 0.7 mmHg (*ca.* 93 Pa)], was removed by vacuum distillation as a colourless liquid. On cooling, a light brown, semi-crystalline solid remained. This was recrystallised from diethyl ether to give white crystals of the required product (yield 5.09 g, 27.5%), m.p. 59.5—60.5 °C.

Tetracarbonyl[1,1,2,2-*tetrakis*(*methylthio*)*ethane*]*chromium*(0). This preparation was carried out under an atmosphere of dry nitrogen. Excess of ligand (0.11 g, 5.1 × 10^{-4} mol) was heated under reflux in benzene (10 cm^3) with tetracarbonyl-(norbornadiene)chromium[19] for 2 h. After removal of solvent under reduced pressure, the resulting yellow solid was washed with light petroleum (b.p. 40—60 °C) to remove excess of ligand, and recrystallised from dichloromethane and light petroleum (b.p. 40—60 °C) to give bright yellow crystals (yield 0.10 g, 75.4%), m.p. 57.6—60.5 °C (Found: C, 31.65; H, 3.80. Calc. for $C_{10}H_{14}CrO_4S_4$: C, 31.75; H, 3.75%). I.r. (in hexane): 1 892s (B_1), 1 903s (B_2), 1 921m,br (A_1), and 2 020w cm^{-1} (A_1).

N.M.R. Spectra.—Spectra were obtained at 400.13 MHz using a Bruker WH400 instrument. Temperatures were calibrated independently with a Comark thermocouple in a dummy sample. One-dimensional spectra were obtained under standard conditions, with Lorentzian-to-Gaussian resolution enhancement where appropriate; two-dimensional NOESY spectra required 32 scans for each of 256 inter-pulse intervals τ, using a basic $[(1\ s)\text{—}\frac{\pi}{2}\text{—}\tau\text{—}\frac{\pi}{2}\text{—}(0.1\ s)\text{—}\frac{\pi}{2}\text{—f.i.d.}]_n$ sequence (f.i.d. = free induction decay). Under the conditions of the experiment, measurable off-diagonal peaks would not arise from internuclear Overhauser enhancements or couplings. The data were processed using a sine-bell window in both dimensions, followed by symmetrisation about the diagonal.

Band-shape analysis. This was performed on the methine-proton spectra measured in the temperature range −10 to −60 °C using the authors' version of the original program of Kleier and Binsch.[20] Computer-synthesised spectra were visually matched with experimental spectra. Energy parameters, derived from standard Arrhenius and Eyring plots, were based on least-squares fittings of at least five data points. Errors quoted for the Eyring parameters follow the recommended practice of Binsch and Kessler.[21]

Results and Discussion

Properties of the Complex.—The chromium complex prepared as above is a yellow crystalline solid, readily soluble in organic solvents. Although the solid is stable in air, it was prone to decomposition in solution. This precluded n.m.r. studies at above-ambient temperatures (see later). Analytical and i.r. data (see Experimental section) were consistent with a mononuclear, chelate structure.[22]

Variable-temperature N.M.R. Studies.—400-MHz Proton n.m.r. spectra of the methyl region of $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$ recorded in the range −70 to +20 °C are depicted in Figure 1. Four distinct signals at 20 °C indicated the presence of two configurational isomers. Lowering the temperature caused exchange broadenings, followed by line splittings until at *ca.* −60 °C nine sharp methyl signals were detected. A methyl signal due to free ligand was also present throughout this temperature range and was seen not to participate in the coalescence phenomena. A small impurity signal observed at 20 °C was attributed to slight decomposition of the complex in solution. All other spectral changes were totally reversible with temperature. Some additional line broadening observed at temperatures below *ca.* −60 °C was thought likely to be due to slowing down of S–C bond rotations in certain conformers (see later). After a close inspection of the spectral changes in the methyl region with temperature (Figure 1) it was not possible to deduce the relationship between the lines in the near-static spectrum at −60 °C with those in the exchange-averaged spectrum at 20 °C. It was therefore decided to use two-dimensional exchange spectroscopy. Using the NOESY pulse sequence, a homonuclear exchange-correlated two-dimensional proton spectrum of the methyl region at −50 °C was obtained. The contour-plotted spectrum is shown in Figure 2 and its one-dimensional counterpart in Figure 3. Using the cross-peaks to identify exchange between invertomers of the same configurational isomer, a strongly consistent assignment of all the lines was achieved as follows.

The complex can exist in three configurations, an enantiomeric *trans* pair and a *cis* isomer (Figure 4). Each configuration can adopt several different conformations when sulphur inversion is slow. These are represented schematically in Figure 5. In this representation, inversion is considered to occur independently at each co-ordinated sulphur atom, in an uncorrelated manner,[1] and the chelate ring assumed to adopt a pseudo-planar conformation. The spectrum at 20 °C clearly indicates the existence of both configurational isomers in the population ratio 74:26 (Table 1). Steric considerations of the unco-ordinated SMe groups strongly suggest that the *trans* isomer will predominate. Supporting evidence for this is provided by the analogous complexes $[PtXMe_3\{(MeS)_2CHCH(SMe)_2\}]$ (X = Cl, Br, or I).[23] These exist purely in the *trans* configuration in the solid, although in solution a variety of configurational forms are present.

A careful inspection of the two-dimensional contour plot (Figure 2) indicated some magnetisation exchange and/or n.O.e. effects associated with all signals except that near δ 2.2, which was identified as a free-ligand signal. Assuming exchange effects to be the dominant causes of the cross-peaks, the latter should be detected only between co-ordinated SMe protons in different invertomers of the same configuration. Exchange is not expected to occur between co-ordinated and unco-ordinated SMe groups at this low temperature.

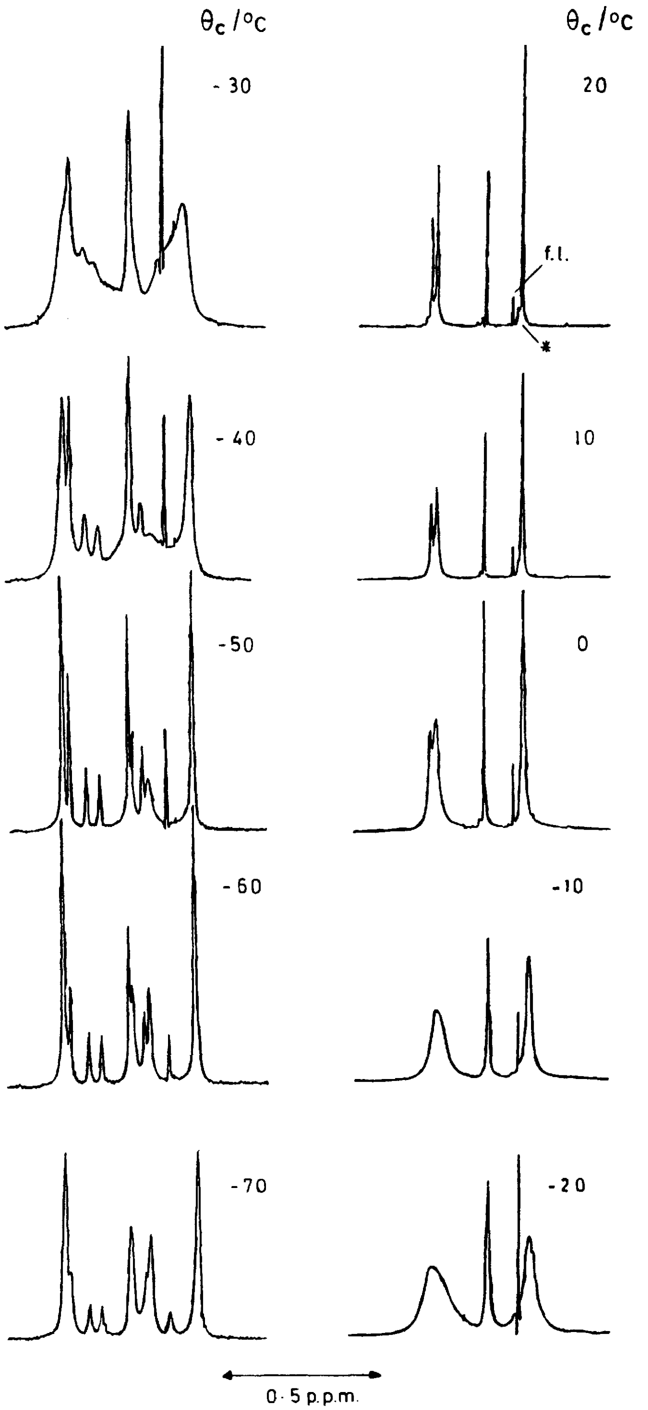

Figure 1. 400-MHz Proton n.m.r. spectra of the methyl region of $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$; f.l. = free ligand. The asterisk indicates an impurity peak

Inspection of Figure 2 shows cross-peak connections between peaks numbered 1 and 5, 2 and 3, 2 and 4, 3 and 4, 5 and 6, and 7 and 9. Peak 8, due to free ligand, shows no exchange. This

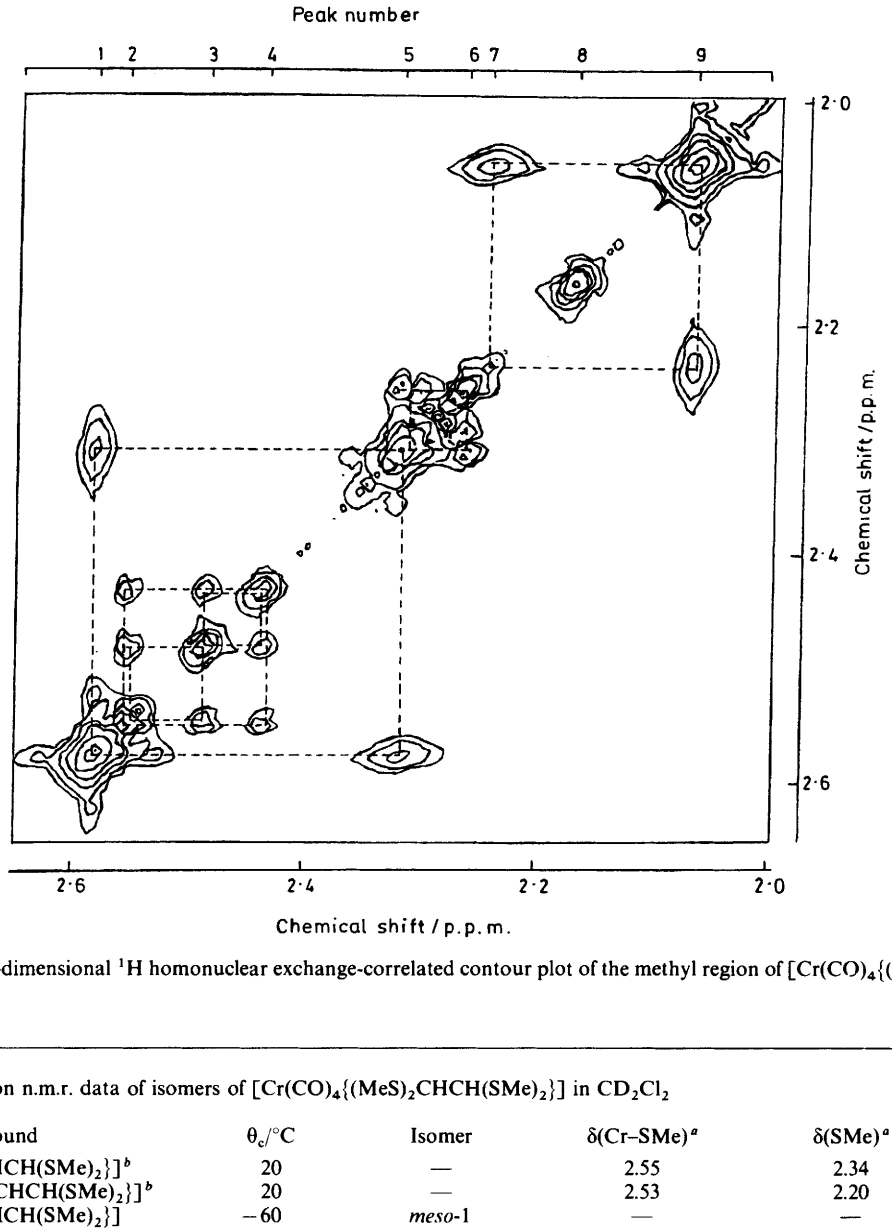

Figure 2. 400-MHz Two-dimensional ^{1}H homonuclear exchange-correlated contour plot of the methyl region of $[\mathrm{Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}}]$ at −50 °C

Table 1. 400-MHz Proton n.m.r. data of isomers of $[\mathrm{Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}}]$ in $\mathrm{CD_2Cl_2}$

Compound	θ_c/°C	Isomer	δ(Cr–SMe)[a]	δ(SMe)[a]	δ(CH)[a]
cis-$[\mathrm{Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}}]$[b]	20	—	2.55	2.34	3.98
trans-$[\mathrm{Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}}]$[b]	20	—	2.53	2.20	3.33
cis-$[\mathrm{Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}}]$	−60	*meso*-1	—	—	—
		DL-1, -2	2.48, 2.43	2.32, 2.26	4.24, 3.82 (3.9 Hz)[c]
		meso-2	2.55	2.30	3.93
trans-$[\mathrm{Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}}]$	−60	DL-1	2.32 (two signals)	2.24 (two signals)	3.12, 3.13 (2.2 Hz)[c]
		DL-2	—	—	3.50
		DL-3	2.57	2.06	3.13

[a] Chemical shifts relative to $\mathrm{SiMe_4}$. [b] Populations: *cis*, 26.2; *trans*, 73.8%. [c] $^3J(^1\mathrm{H{-}C{-}C{-}}^1\mathrm{H})$.

information, together with the integrated intensities of the lines in the one-dimensional spectrum (Figure 3), allows a fairly definitive assignment of each line to be made. From steric considerations the *trans* (DL-3) invertomer possessing *trans* orientations between *all* neighbouring SMe groups will be the most populous species in solution, and the two most intense signals 1 and 9 are respectively assigned to the protons of the co-ordinated and unco-ordinated SMe groups of this invertomer. As co-ordination to transition metals usually produces high-frequency shifts of ligand signals,[1] the signals 2—4 are assigned to protons of co-ordinated SMe and, as they show no connections with peak 1, are attributed to the *cis* isomer. The enantiomeric pair *cis* (DL-1 and -2) each has a pair of non-equivalent co-ordinated SMe groups. The equal-intensity pair of signals 3 and 4 is therefore assigned to these, and signal 2 to one of the *cis* (*meso*) invertomers, almost certainly *cis* (*meso*-2). The cross-peak between signals 1 and 5 implies that 5 is due to one of the other *trans* invertomers, probably *trans* (DL-1), both on steric grounds and from its statistical weighting of two. The greater width of signal 5 is attributed to a small chemical shift distinction between the two non-equivalent co-ordinated SMe groups. A similar effect was observed for the methine and unco-ordinated SMe groups of this invertomer (see later).

Turning to the resonances of unco-ordinated SMe, only signals 7 and 9 show any mutual exchange. Thus, signal 7 must be due to the other *trans* invertomer, *trans* (DL-1). The broadness of this single signal is due to the very slightly anisochronous nature of the two SMe groups. Finally, the remaining two signals, signal 6 and the shoulder of signal 5, are attributed to the anisochronous SMe groups of the *cis* (DL-1, -2) pair. The signal of unco-ordinated SMe of *cis* (*meso*-2) is not separately identified but is thought to be obscured by signal 5 by virtue of its expected chemical shift.

In summary, the SMe signals can be assigned to *two* invertomers of both the *trans* isomer (namely *trans* DL-1 and DL-3) and the *cis* isomer (namely *cis* DL-1, -2 and *meso*-2). No evidence was found for the *trans* (DL-2) or *cis* (*meso*-1) isomers. It is not surprising that the latter isomer is absent in view of the strong steric interactions between both co-ordinated and unco-ordinated SMe groups. However, the absence of *trans* (DL-2) is somewhat unexpected but is attributed to the relatively low abundance of this isomer (Table 2) and the likely broadness of its two SMe signals due to restricted S–C bond rotations (see later).

These methyl-region assignments, which are summarised in Table 1, were then used to provide a definitive assignment of the methine region of the spectrum (Figure 6). Isomer-population measurements from the methyl region indicated that the methine signals due to either configurational isomer were totally separated, with the *cis* signals appearing at higher frequencies. The assignments given in Figure 6 and Table 1 were aided by the two-dimensional spectrum of this region (not shown) and by the observation of vicinal coupling (^3J = 3.9 Hz) between the methine signals 10 and 13. These signals are clearly due to the most abundant *cis* invertomer, the DL-1, -2 pair, by virtue of this scalar coupling and because of the cross-peak between signals 10 and 13 in the two-dimensional spectrum. A strong cross-peak relating signals 15 and 16 confirms the assignments of these signals to *trans* (DL-1) and *trans* (DL-3) respectively. Signal 15 can be interpreted as a partially resolved AB quartet with a very small internal chemical shift and a scalar coupling of *ca.* 2 Hz, due to the slightly anisochronous nature of the two CH protons.

In this region of the spectrum it is particularly noteworthy that the *trans* (DL-2) species is identified for the first time (signal 14). This signal is notably broad as is also that of *cis* (*meso*-2) (signal 12). This broadness, which becomes much more apparent on further cooling of the sample, is attributed to restricted rotation about the S–C bonds of the unco-ordinated SMe groups in these sterically crowded species.

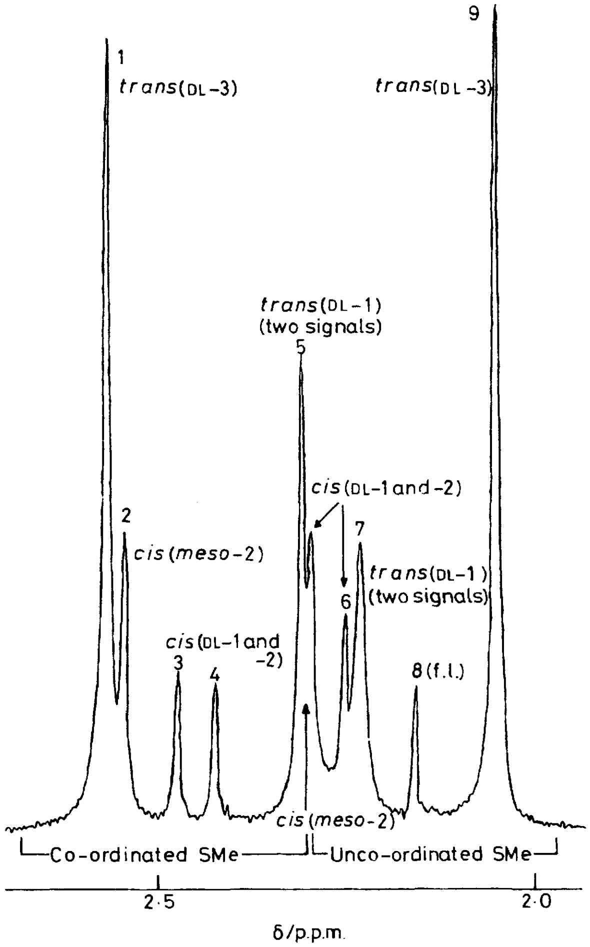

Figure 3. 400-MHz Proton n.m.r. spectrum of the methyl region of $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$ at −60 °C. The peak numbering is in accordance with Figure 2

Table 2. Static parameters and 'best-fit' rate constants used in the computer simulation of 400-MHz ^{1}H n.m.r. spectra (CH region) of $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$

(*a*) *trans*

Isomer	δ^a/Hz	$^3J^b$/Hz	p^c/%	T_2^*/s	θ_c/°C	k_{12}/s^{-1}	k_{14}/s^{-1}
	1 334.0			0.0796	−10	5 065.0	505.0
DL-1		2.2	44.2		−20	2 091.0	200.0
	1 332.2			0.0796	−30	802.0	70.0
					−40	284.0	22.5
DL-2	1 402.0	—	13.2	0.0796	−50	91.5	0.0
					−60	26.5	0.0
DL-3	1 250.0	—	42.6	0.0796			

(*b*) *cis*

Isomer	δ^a/Hz	$^3J^b$/Hz	p^c/%	T_2^*/s	θ_c/°C	k_{12}/s^{-1}	k_{13}/s^{-1}
meso-1	—	—	—	—	−10	100.0	450.0
	1 691.0			0.0095	−20	50.0	125.0
DL-1 and -2		3.9	58.4		−30	15.0	50.0
	1 530.2			0.0095	−40	7.0	7.0
					−50	1.0	4.0
meso-2	1 576.3	—	41.6	0.0095	−60	—	—

[a] Chemical shifts relative to $SiMe_4$. [b] $^3J(^1H–C–C–^1H)$. [c] Population.

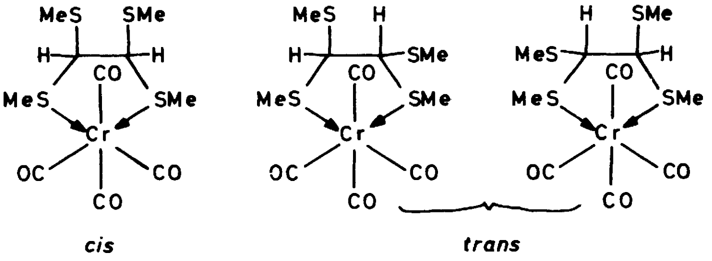

Figure 4. Configurational isomers of $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$

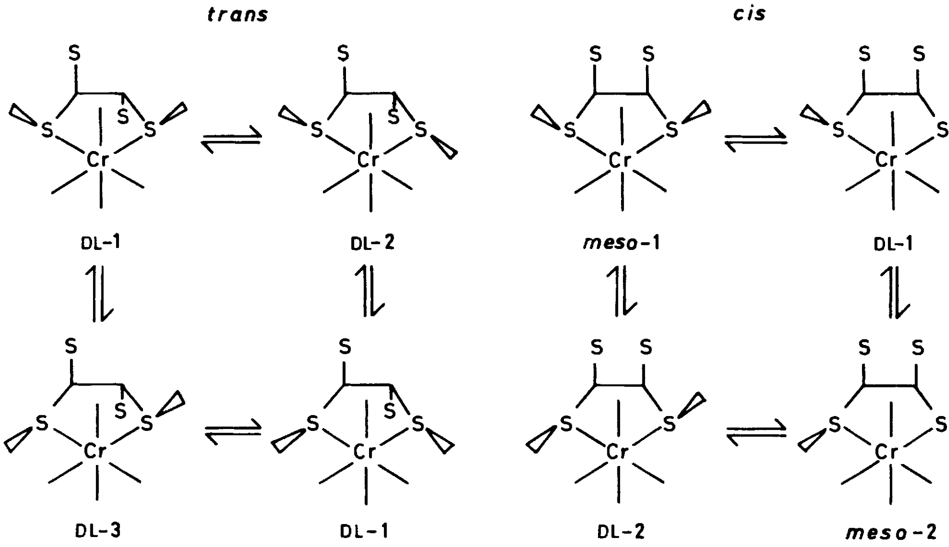

Figure 5. Conformational isomers of *cis*- and *trans*-$[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$

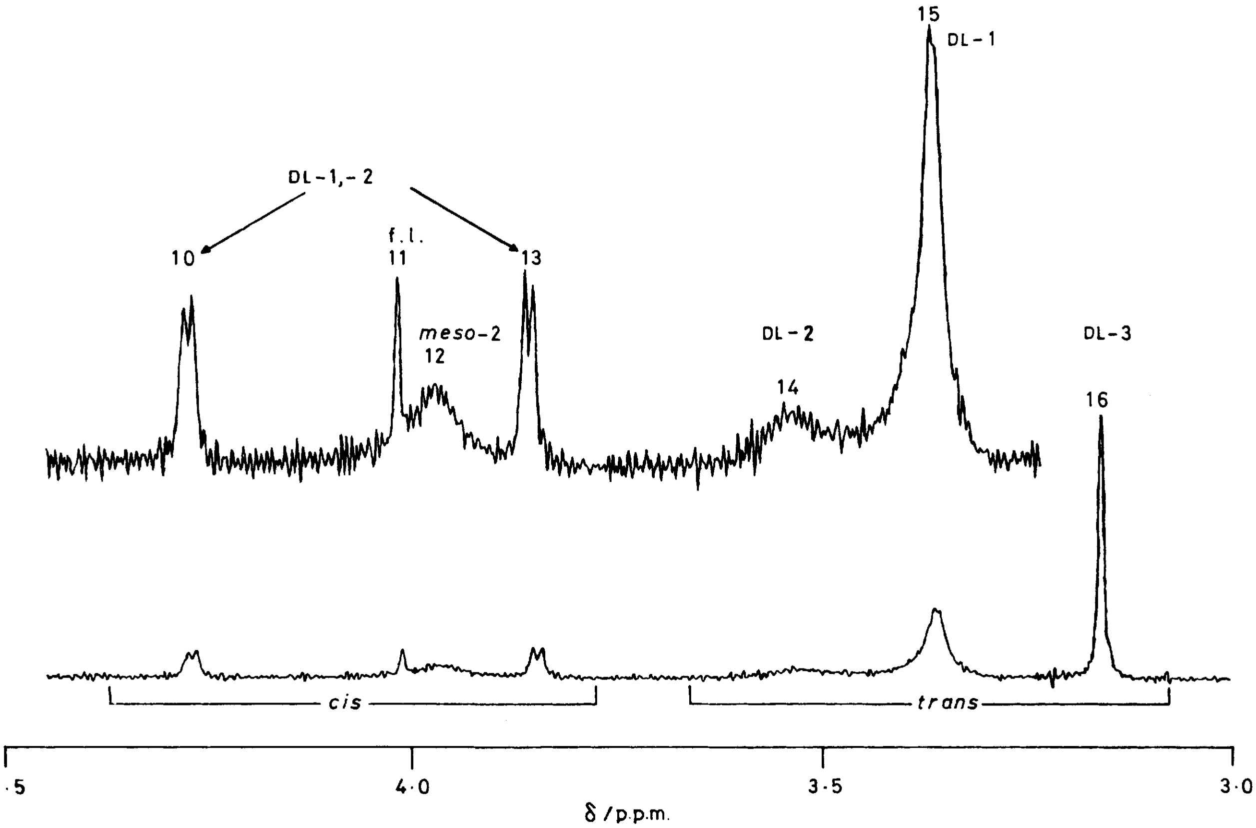

Figure 6. 400-MHz Proton n.m.r. spectrum of the methine region of $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$ at −60 °C

Figure 7. Experimental and computer-simulated spectra of $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$ (CH region only) showing the effects of pyramidal sulphur inversion. The 'best-fit' rate constants are given in Table 2

Having obtained a reliable assignment of the low-temperature methine spectrum, it was decided to carry out one-dimensional band-shape analyses on both the *cis* and *trans* methine regions. The dynamic spin problem for both isomers may be described as shown below. The static parameters and invertomer populations on which the band-shape analyses were based are listed in Table 2. The experimental and 'best-fit' computer-simulated spectra in the range −10 to −60 °C are shown in Figure 7. Very satisfactory fittings were achieved except at the very lowest temperatures where hindered rotation broadening became apparent.

trans

$$\begin{tikzcd}
{[\text{DL-1}]} \arrow[r, shift left] \arrow[d, shift left] & {[\text{DL-2}]} \arrow[l, shift left] \arrow[d, shift left] \\
{[\text{DL-3}]} \arrow[r, shift left] \arrow[u, shift left] & {[\text{DL-1}]} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}
\qquad
\begin{tikzcd}
AB \arrow[r, shift left, "k_{12}"] \arrow[d, shift left] & CC' \arrow[l, shift left] \arrow[d, shift left] \\
DD' \arrow[r, shift left] \arrow[u, shift left, "k_{14}"'] & BA \arrow[l, shift left, "k_{34}"] \arrow[u, shift left, "k_{23}"']
\end{tikzcd}$$

cis

$$\begin{tikzcd}
{[\textit{meso-}1]\ \text{(undetected)}} \arrow[r, shift left] \arrow[d, shift left] & {[\text{DL-1}]} \arrow[l, shift left] \arrow[d, shift left] \\
{[\text{DL-2}]} \arrow[r, shift left] \arrow[u, shift left] & {[\textit{meso-}2]} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}
\qquad
\begin{tikzcd}
& EF \arrow[d, shift left] \arrow[dl, shift left] \\
FE \arrow[r, shift left] \arrow[ur, shift left, "k_{13}"'] & GG' \arrow[l, shift left, "k_{23}"] \arrow[u, shift left, "k_{12}"']
\end{tikzcd}$$

Sulphur inversion-energy barriers were computed according to the usual Arrhenius and Eyring theories and the values given in Table 3. The spectra of both configurational isomers were sensitive to *two* rate constants and the energy data for each isomer refer to both possible inversion pathways from the DL-1 isomer. The intramolecular nature of the inversion process is confirmed by the $\log_{10}(A/s^{-1})$ values being around 13 and $\Delta S^{\ddagger}$ values being around 0 J K^{-1} mol^{-1}. The larger errors associated with the energy data for the *cis* isomer are due mainly to the additional line-broadening effects which occurred at temperatures below *ca.* −40 °C due to restricted S–C bond rotations. The band-shape analysis could not take these into account and accordingly the computer matchings were less certain.

Table 3. Arrhenius and Eyring activation parameters for pyramidal sulphur inversion in $[Cr(CO)_4\{(MeS)_2CHCH(SMe)_2\}]$

Isomer	Interconversion	E_a/kJ mol^{-1}	$\log_{10}(A/s^{-1})$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$(298.15 K)/ kJ mol^{-1}
trans	DL-1 ⟶ DL-2	48.99 ± 0.01	13.43 ± 0.01	46.98 ± 0.03	5.57 ± 0.12	45.31 ± 0.01
	DL-1 ⟶ DL-3	52.99 ± 0.37	13.23 ± 0.08	50.93 ± 0.40	1.57 ± 1.61	50.47 ± 0.08
cis	DL-1 ⟶ *meso*-2	54.91 ± 4.72	12.98 ± 1.02	52.90 ± 4.74	−3.00 ± 19.6	53.79 ± 1.10
	DL-1 ⟶ DL-2	60.01 ± 5.74	14.51 ± 1.24	58.00 ± 5.73	26.40 ± 23.67	50.13 ± 1.33

The $\Delta G^{\ddagger}$ data for the inversion process were in the range 45—50 kJ mol^{-1} for the *trans* isomer and 50—54 kJ mol^{-1} for the *cis* isomer. Only one previous study of sulphur inversion in a $Cr(CO)_4$ chelate complex has been reported,[24] namely of $[Cr(CO)_4(PhCH_2SCH_2CH_2SCH_2Ph)]$ for which a $\Delta G^{\ddagger}$ value of 48.7 kJ mol^{-1} was obtained. The two values for the *trans* isomer are clearly in good accord with this. The somewhat higher values for the *cis* isomer may be ascribed to additional constraint to a planar sulphur transition state in this more sterically crowded molecule.

The second aim of this study was to investigate any *cis–trans* interconversion which might arise at high temperatures as a result of a pivoting [8,9] about either co-ordinated sulphur. N.m.r. studies at above-ambient temperatures were attempted but unfortunately thermal instability of the complex prevented any evidence for such a process being obtained. It is planned to synthesise the tungsten tetracarbonyl complex in the hope that it will be more amenable to high-temperature studies. If this does not prove possible, two-dimensional spectra taken over a range of ambient temperatures may provide the required exchange information.

This would appear to be the first complex for which it has been possible simultaneously to compute energy-barrier data for more than one configurational form. The vital role played by two-dimensional n.m.r. exchange spectroscopy in this work is very apparent, and the method can clearly be extended to more complex isomeric mixtures.

References

1 E. W. Abel, S. K. Bhargava, and K. G. Orrell, *Prog. Inorg. Chem.*, 1984, **32**, 1.
2 E. W. Abel, M. Booth, K. G. Orrell, G. M. Pring, and T. S. Cameron, *J. Chem. Soc., Chem. Commun.*, 1981, 29.
3 E. W. Abel, M. Booth, K. G. Orrell, and G. M. Pring, *J. Chem. Soc., Dalton Trans.*, 1981, 1944.
4 E. W. Abel, G. D. King, K. G. Orrell, G. M. Pring, V. Šik, and T. S. Cameron, *Polyhedron*, 1983, **2**, 1117.
5 E. W. Abel, G. D. King, K. G. Orrell, and V. Šik, *Polyhedron*, 1983, **2**, 1363.
6 E. W. Abel, S. K. Bhargava, T. E. MacKenzie, P. K. Mittal, K. G. Orrell, and V. Šik, *J. Chem. Soc., Chem. Commun.*, 1982, 983.
7 E. W. Abel, M. Z. A. Chowdhury, K. G. Orrell, and V. Šik, *J. Organomet. Chem.*, 1984, **262**, 293.
8 E. W. Abel, M. Booth, G. D. King, K. G. Orrell, G. M. Pring, and V. Šik, *J. Chem. Soc., Dalton Trans.*, 1981, 1846.
9 E. W. Abel, G. D. King, K. G. Orrell, V. Šik, T. S. Cameron, and K. Jochem, *J. Chem. Soc., Dalton Trans.*, 1984, 2047.
10 J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, *J. Chem. Phys.*, 1979, **71**, 4546.
11 S. Macura and R. R. Ernst, *Mol. Phys.*, 1980, **41**, 95.
12 G. Bodenhausen and R. R. Ernst, *J. Am. Chem. Soc.*, 1982, **104**, 1304.
13 C. L. Perrin and R. K. Gipe, *J. Am. Chem. Soc.*, 1984, **106**, 4036.
14 B. H. Meier and R. R. Ernst, *J. Am. Chem. Soc.*, 1979, **101**, 6441.
15 Y. Huang, S. Macura, and R. R. Ernst, *J. Am. Chem. Soc.*, 1981, **103**, 5327.
16 R. Benn, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 626.
17 H. Meyer and A. Zschunke, *J. Organomet. Chem.*, 1984, **269**, 209.
18 S. Macura, Y. Huang, D. Suter, and R. R. Ernst, *J. Magn. Reson.*, 1981, **43**, 259.
19 M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2037.
20 D. A. Kleier and G. Binsch, DNMR3 Program 165, Quantum Chemistry Program Exchange, Indiana University, Indiana, U.S.A., 1970.
21 G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 411.
22 D. C. Harris and M. D. Bertolucci, 'Symmetry and Spectroscopy,' Oxford University Press, 1978, ch. 3.
23 E. W. Abel, T. S. Cameron, K. M. Higgins, K. G. Orrell, and V. Šik, unpublished work.
24 R. J. Cross, G. Hunter, and R. C. Massey, *J. Chem. Soc., Dalton Trans.*, 1976, 2015.

Received 11th February 1985; *Paper* 5/236