Ring Reversal, Sulphur Inversion, and 1,3-Metal Shifts in Sulphur-containing Six-membered-ring Complexes of Chromium and Tungsten Carbonyls

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Complexes of the general formula $[M(CO)_5L]$ (M = Cr or W; L = $SCH_2SCH_2CH_2CH_2$, $SCH_2SCH_2SCH_2$, and β-SCHMeSCHMeSCHMe) have been prepared and studied by variable-temperature ^1H n.m.r. spectroscopy. Detailed computer syntheses of static and dynamic spectra indicate that the complexes exist in a number of conformations which are interconverted by fluxional processes. These processes are six-membered ligand ring reversal, pyramidal sulphur-atom inversion, and commutation of an $M(CO)_5$ moiety over three sulphur atoms *via* a 1,3-shift process. Accurate energy barriers ($\Delta G^{\ddagger}$) for all three processes have been calculated. It is interesting to note that only the β-SCHMeSCHMeSCHMe complexes undergo the 1,3-shift process at ambient temperature.

DYNAMIC nuclear magnetic resonance (d.n.m.r.) [1] has undergone rapid advancement in recent years and has been used to study a wide variety of motional phenomena.[2] A recent review [3] describes how the technique may be used to calculate accurate thermodynamic parameters for fluxional motions and how a distinction between alternative mechanistic pathways can sometimes be made.

Our own interests have been primarily concerned with accurate studies of fluxional phenomena occurring in Group 6B co-ordination complexes of palladium and platinum. In particular we have obtained accurate energy-barrier data for six-membered ligand ring reversal [4,5] and pyramidal atomic inversion,[4-10] as well as observing novel phenomena such as ligand-atom commutation [5,10-13] and Pt-methyl scrambling.[4,10,12,13]

We have now turned our attention to the study of related fluxional processes in complexes of organo-sulphur-containing ligands with Group 6 metal carbonyls. The only previous detailed d.n.m.r. studies on such complexes concerned those with the general formula $[M(CO)_4(L\text{–}L)]$, where M is Cr, Mo, or W and L–L is a bidentate organo-sulphur or -selenium ligand. These studies were concerned with the assignment of the observed spectral changes to either chelate ring reversal or pyramidal atomic inversion.[14] Other workers [15] have either ignored the current d.n.m.r. literature or have been concerned simply with the detection of a fluxional phenomenon rather than a detailed d.n.m.r. study.[16]

We now report the first accurate d.n.m.r. studies on complexes of the type $[M(CO)_5L]$, where M = Cr or W and L is an organosulphur six-membered ring of the general formula SCHRSCHRECHR (E = S or CH_2; R = H or Me). The energy data obtained refer to six-membered ring reversal, sulphur inversion, and to a novel fluxional commutation of the $M(CO)_5$ moiety over all sulphur-atom co-ordination sites.

EXPERIMENTAL

Preparation of the Complexes.—The ligands 1,3,5-trithian, β-2,4,6-trimethyl-1,3,5-trithian, and 1,3-dithian were prepared using standard literature procedures.[17-19] Their complexes with pentacarbonyl-chromium and -tungsten moieties have been reported previously,[16,20,21] the general method of preparation being u.v.-irradiation of the metal hexacarbonyl and ligand in tetrahydrofuran (thf) solution. This method was modified slightly [22] in order that several complexes could be prepared from a single u.v. exposure. It involved irradiation of a thf solution of metal carbonyl only, followed by displacement of thf from the metal pentacarbonyl complex formed, by stirring with the desired ligand at room temperature. All reactions and manipulations were carried out under an atmosphere of dry nitrogen using freshly distilled anhydrous solvents since solutions of the complexes rapidly decompose on exposure to air. The solid complexes are somewhat more stable.

A brief investigation confirmed the previously observed [16] low stability of the corresponding molybdenum complexes and so their preparations were not pursued in view of the handling difficulties which would arise in attempting n.m.r. studies. The chromium and tungsten complexes were obtained as crystalline solids and their analytical data are given in Table 1.

*Hydrogen-*1 *N.M.R. Studies.*—Owing to the rapid decomposition of solutions of the complexes on exposure to air, n.m.r. samples were prepared by adding the solid complex to an n.m.r. tube fitted with a Taperlok (Wilmad Glass Co. Inc.) joint and then the appropriate solvent and reference material were distilled into the tube under an atmosphere of dry nitrogen.

Variable-temperature n.m.r. spectra were recorded at 5—10 °C intervals in a JEOL MH-100 spectrometer. A JES-VT-3 unit was used to control the probe temperatures which were measured, using a Comark digital thermometer type 5000 attached to a Cu/Cu-Ni thermocouple, to an accuracy of at least ±1 °C.

RESULTS AND DISCUSSION

The ^1H n.m.r. spectra of all the complexes listed in Table 1 were recorded between -80 and $+60$ °C in CD_2Cl_2 or $CDCl_3$ solvents under an atmosphere of nitrogen. The spectra of each type of ligand complex will be described in turn.

1,3-Dithian Complexes.—The spectra of both pentacarbonyl-chromium and -tungsten complexes $[M(CO)_5$-

TABLE 1

Analytical data for six-membered sulphur heterocycle complexes of Group 6A metal pentacarbonyls

Complex	Yield/ %	M.p./°C	Analysis/% [a] C	Analysis/% [a] H	I.r./cm^{-1} C=O stretch [b] A_1(m)	I.r./cm^{-1} C=O stretch [b] E(vs)	I.r./cm^{-1} C=O stretch [b] A_1(s)
$[Cr(CO)_5(SCH_2SCH_2CH_2CH_2)]$	26	51	35.1 (34.6)	2.80 (2.60)	2 072	1 947	1 938
$[W(CO)_5(SCH_2SCH_2CH_2CH_2)]$	20	67	24.5 (24.4)	2.00 (1.85)	2 080	1 944	1 937
$[Cr(CO)_5(SCH_2SCH_2SCH_2)]$	33	100	29.1 (29.1)	1.95 (1.85)	2 069	1 943	1 940
$[W(CO)_5(SCH_2SCH_2SCH_2)]$	39	110	21.3 (20.8)	1.50 (1.30)	2 078	1 943	1 937
$[Cr(CO)_5(SCHMeSCHMeSCHMe)]$	48	92—93	35.5 (35.5)	3.25 (3.25)	2 068	1 947	1 935
$[W(CO)_5(SCHMeSCHMeSCHMe)]$	85	102—103	26.3 (26.2)	2.35 (2.40)	2 078	1 945	1 932

[a] Calculated values in parentheses. [b] Intensities in parentheses; s = strong, m = medium, v = very.

$(SCH_2SCH_2CH_2CH_2)]$ show essentially the same features and only the chromium complex was chosen for a full d.n.m.r. analysis. There are two possible structures for the above complex depending on whether the $Cr(CO)_5$ moiety is axial or equatorial to the ligand ring, see Figure 1. These conformations can undergo two fluxional processes, namely ring reversal and sulphur inversion. The influence of these processes on the methylene protons attached to the SCH_2S carbon atom are shown in Figure 2. If both of these processes are slow on the n.m.r. time scale, the spectrum for the SCH_2S methylene group would be expected to consist of two AB quartet patterns in a ratio corresponding to the relative populations of the two conformers. The onset of one rate process would bring about a coalescence phenomenon leading to a single AB quartet which would then broaden and coalesce to give a single line when both rate processes were fast on the n.m.r. time scale.

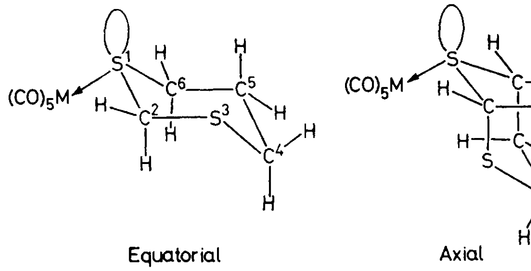


FIGURE 1 Possible conformations of $[M(CO)_5(SCH_2SCH_2CH_2CH_2)]$

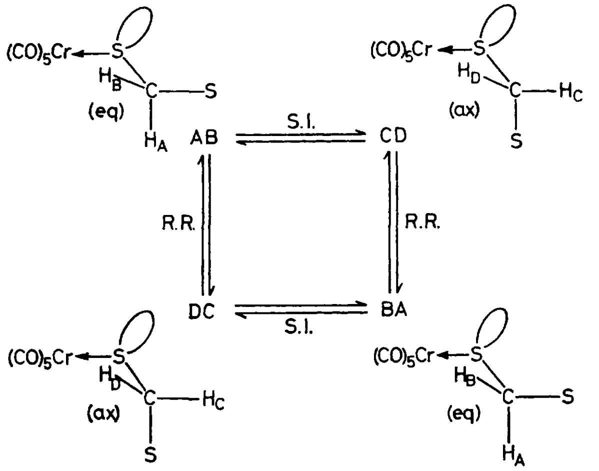


FIGURE 2 The effect of ring reversal (R.R.) and sulphur inversion (S.I.) on the environments of the SCH_2S protons of $[Cr(CO)_5(SCH_2SCH_2CH_2CH_2)]$

The experimental spectrum however, shows only one AB quartet pattern coalescing to a single sharp line at high temperatures. There are two possible explanations for this unanticipated result: either one of the fluxional processes has a low energy barrier (<40 kJ mol^{-1}) and is therefore already rapid at *ca.* -80 °C, or the population of one of the conformers is small ($<1\%$) and cannot be detected by ^1H n.m.r. We strongly favour the latter explanation for the following reasons. The ring reversal energy for 1,3-dithian is 43 kJ mol^{-1},[23] and typical sulphur inversion energies for organosulphur ligands co-ordinated to chromium carbonyl moieties are 52 kJ mol^{-1} for $[Cr(CO)_4\{PhS(CH_2)_3SPh\}]$ [16] and 43 kJ mol^{-1} for $[Cr(CO)_5(SC_4H_6)]$.[15] These values indicate that both motional processes should be slow at -80 °C and therefore detectable if both conformers were present. A small population for the axial conformer is not surprising in view of the fact that for the analogous compound 1,3-dithian 1-oxide, the axial conformer population is only 16%[24] and that the equatorial conformation for $[Fe(CO)_4(SCH_2SCH_2CH_2CH_2)]$ is favoured, as shown by *X*-ray crystallography.[25]

We therefore conclude that the complex exists in a single equatorial conformation and that the spectral band-shape changes are a result of sulphur inversion averaging the axial and equatorial methylene proton environments. The spectral syntheses were limited to the methylene protons of the SCH_2S carbon atoms, which exhibited an AB quartet pattern, the lower frequency lines of which were considerably broader (5 Hz) than the higher frequency lines (2 Hz). The reason for this broadening is long-range W-type (zigzag) coupling[24] between equatorial protons. The equatorial proton of the methylene group is therefore assigned to the lower frequency proton of the AB quartet.

TABLE 2

Arrhenius and transition-state parameters for the motional processes in the complexes $[M(CO)_5L]$

Complex	Solvent	Process	E_a/ kJ mol^{-1}	$\log_{10}A$	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}	$\Delta G^\ddagger$ */ kJ mol^{-1}
$[Cr(CO)_5(SCH_2SCH_2CH_2CH_2)]$	CD_2Cl_2	Sulphur inversion	50.22 ±1.45	12.72 ±0.31	48.23 ±1.43	−7.91 ±5.88	50.59 ±0.33
$[Cr(CO)_5(SCH_2SCH_2SCH_2)]$	CD_2Cl_2	Ring reversal	61.14 ±3.41	14.30 ±0.70	59.03 ±3.39	21.79 ±13.31	52.53 ±0.60
$[Cr(CO)_5(SCH_2SCH_2SCH_2)]$	CD_2Cl_2	Sulphur inversion	57.13 ±1.16	13.82 ±0.24	55.08 ±1.16	12.71 ±4.54	51.23 ±0.20
$[W(CO)_5(SCH_2SCH_2SCH_2)]$	CD_2Cl_2	Ring reversal	54.56 ±0.69	13.06 ±0.14	52.48 ±0.69	1.81 ±2.75	53.02 ±0.14
$[W(CO)_5(SCH_2SCH_2SCH_2)]$	CD_2Cl_2	Sulphur inversion	54.56 ±0.69	13.06 ±0.14	52.48 ±0.69	1.81 ±2.75	53.02 ±0.14
$[Cr(CO)_5(SCHMeSCHMeSCHMe)]$	$CDCl_3$	1,3-Shift	75.68 ±2.70	14.53 ±0.46	73.60 ±2.70	26.18 ±8.72	65.80 ±0.08
$[W(CO)_5(SCHMeSCHMeSCHMe)]$	$CDCl_3$	1,3-Shift	73.16 ±3.65	13.62 ±0.63	70.67 ±3.66	7.38 ±12.12	68.47 ±0.02

* $\Delta G^\ddagger$ was calculated for $T = 298.15$ K.

The spectra were fitted as an AB $\rightleftharpoons$ BA spin problem using the DNMR8 computer program. Owing to the negligible population of the axial conformer the rate constants obtained refer to the higher energy fluxional process. These rate constants were treated in the usual way to give the Arrhenius and transition-state parameters listed in Table 2. The $\Delta G^\ddagger$ value of 50.6 kJ mol^{-1} is significantly higher than that for ring reversal in the free ligand (43 kJ mol^{-1}).[23] Since co-ordination to a transition-metal moiety has no appreciable influence on the ring reversal barrier,[4] we are confident in concluding that this energy barrier refers to sulphur inversion. Hydrogen-1 n.m.r. static parameters are listed in Table 3.

1,3,5-*Trithian Complexes*.—At −66 °C the 'static' spectra of the complexes $[M(CO)_5(SCH_2SCH_2SCH_2)]$ (M = Cr or W) exhibit two AB quartets with an intensity ratio 2 : 1, for each of two isomers giving a total of 16 lines, Figure 3. In contrast to the 1,3-dithian complexes, it was therefore possible to observe signals for both conformers, with the equatorial conformer being assumed to have the greater population.

TABLE 3

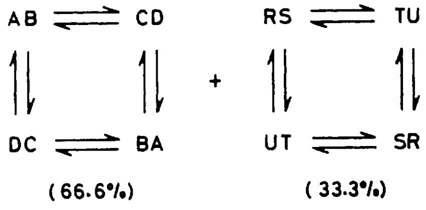
Hydrogen-1 n.m.r. parameters (Hz) [a] for the SCH_2S methylene protons in the complexes $[M(CO)_5L]$

Complex	Conformer	Population	$\nu_{A/C}$	$\nu_{B/D}$	$J_{AB/CD}$	$\nu_{R/T}$	$\nu_{S/U}$	$J_{RS/TU}$	T_2^{*b}/s
$[Cr(CO)_5(SCH_2SCH_2CH_2CH_2)]$	Eq.	1.00	403.6	360.2	−13.2				0.127
$[Cr(CO)_5(SCH_2SCH_2SCH_2)]$	Eq.	0.82	441.5	391.2	−13.5	452.5	377.0	−15.5	0.086
$[W(CO)_5(SCH_2SCH_2SCH_2)]$	Eq.	0.68	455.0	413.0	−14.0	455.0	385.0	−14.0	0.150
$[Cr(CO)_5(SCH_2SCH_2SCH_2)]$	Ax.	0.18	483.4	353.0	−15.0	456.0	380.0	−15.0	0.086
$[W(CO)_5(SCH_2SCH_2SCH_2)]$	Ax.	0.32	498.5	364.0	−14.0	440.0	370.0	−14.0	0.1 5

[a] In CD_2Cl_2 relative to $SiMe_4$. [b] Effective transverse relaxation time, $T_2^* = (\pi\Delta\nu_{\frac{1}{2}})^{-1}$ (where $\Delta\nu_{\frac{1}{2}}$ is the natural linewidth at half-height).

Above −50 °C the spectral changes which occur are consistent with an increased rate of ring reversal and sulphur inversion (Figure 4). A set of spectra for $[W(CO)_5(SCH_2SCH_2SCH_2)]$ is shown in Figure 5. In order to calculate separate energy barriers for the two fluxional processes it is essential to correctly assign each signal in the experimental spectrum to the different protons shown in Figure 4. The assignments were made on the assumption that the equatorial $M(CO)_5$ conformer had the greater population and that equatorial ring protons exhibited broader lines than their axial counterparts due to W-type (zigzag) coupling.[24] These assignments are shown in Figure 3 and the n.m.r. parameters, which are temperature independent, are given in Table 3.

The two motional processes will produce completely different band-shape changes since ring reversal averages the axial protons of one conformer with the equatorial protons of the other (*e.g.* AA′ $\rightleftharpoons$ D′D), whereas sulphur inversion averages axial with axial and equatorial with equatorial (*e.g.* AA′ $\rightleftharpoons$ C′C). The complete dynamic nuclear-spin problem is shown in Figure 4. Such a problem is too complex for our largest version of the standard DNMR computer program[26] but can be simplified without appreciable error to the two spin problems shown in the Scheme.



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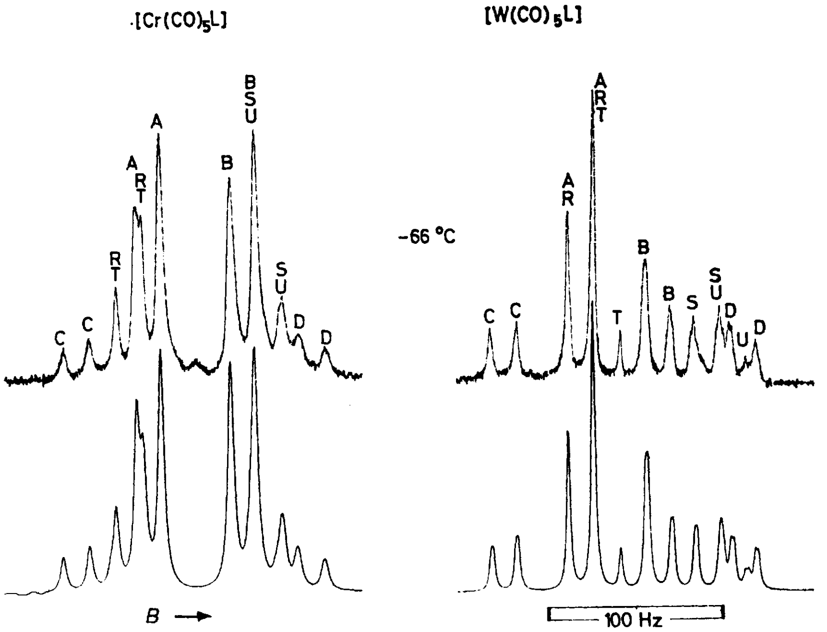

FIGURE 3 Low-temperature ^{1}H n.m.r. spectra of [M(CO)$_5$(SCH$_2$SCH$_2$SCH$_2$)] showing proton assignments and synthesised spectra

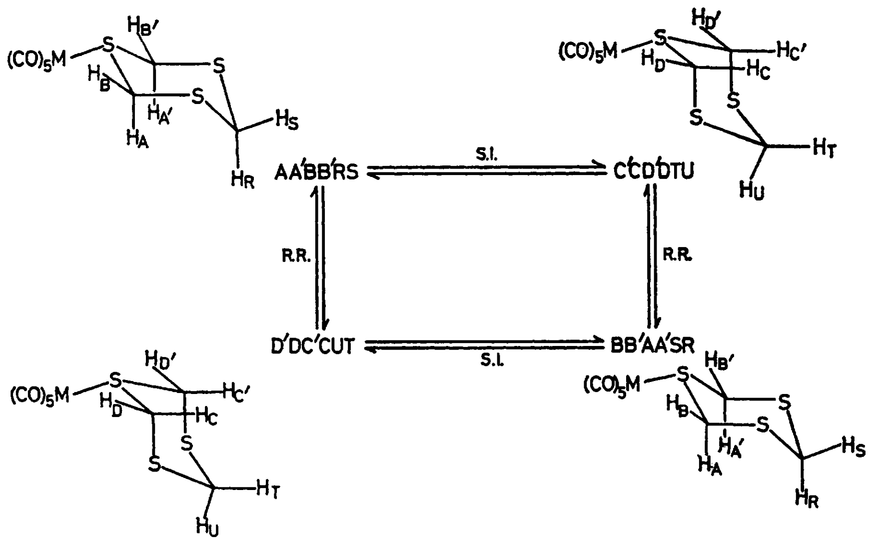

FIGURE 4 Dynamic nuclear-spin problem for the complexes [M(CO)$_5$(SCH$_2$SCH$_2$SCH$_2$)]

In making this type of approximation previously [8] the long-range ^4J couplings have been included in the value of the effective transverse relaxation time, T_2^*. In this case, however, the ^4J couplings vary in magnitude with the W-type couplings having the greater value, and hence the resulting variations in spectral bandwidths were reproduced by allowing each AB quartet to couple to a ' remote ' proton. It should be noted that in all cases the axial protons resonated at higher frequencies than their equatorial counterparts, a situation which, although opposite to that for cyclohexane, is not unusual for sulphur-containing six-membered rings.[24,27]

Synthesising spectra based on the above spin problem and using various independent values for the rates of ring reversal, k(R.R.), and sulphur inversion, k(S.I.), gave good fits between −50 °C and ambient temperatures. An example for [W(CO)$_5$(SCH$_2$SCH$_2$SCH$_2$)] is shown in Figure 5. Of the two complexes, the one with W(CO)$_5$ was the more amenable to accurate band-shape fitting due to the greater similarity of conformer populations and larger chemical-shift differences. The pentacarbonylchromium complex has the lower percentage of axial conformer due to the shorter M–S bond producing larger steric interactions compared to the pentacarbonyltungsten complex. For both complexes, the

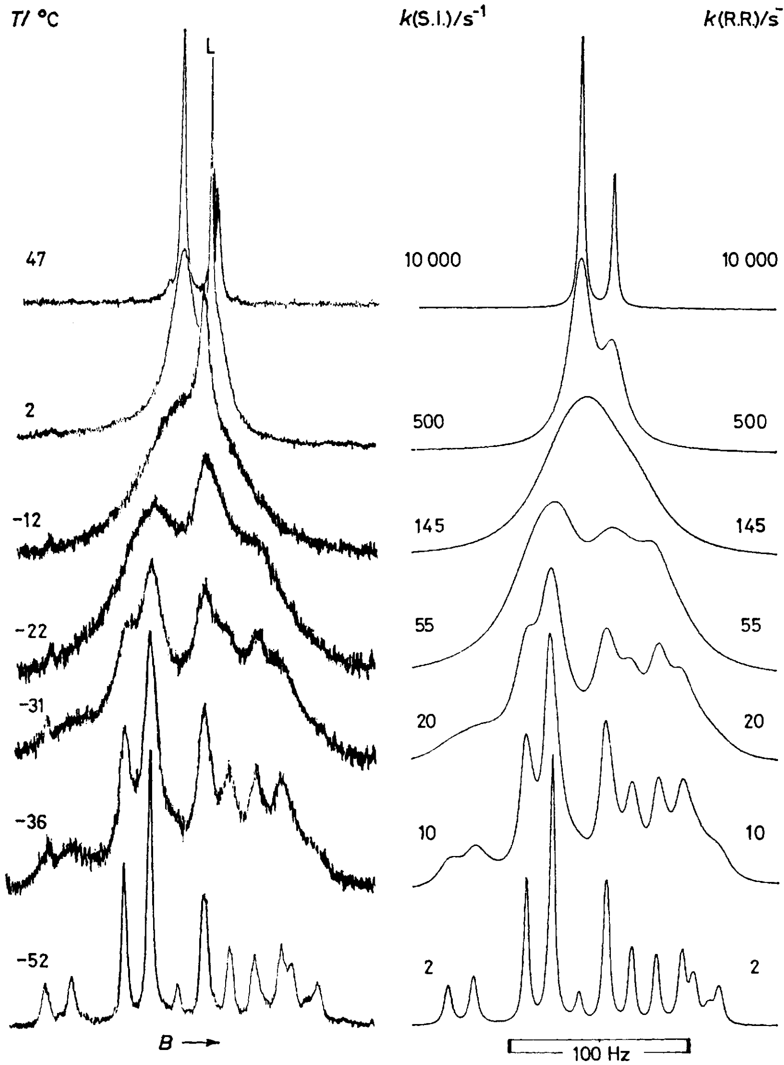

FIGURE 5 Variable-temperature ^{1}H n.m.r. spectra of the complex $[W(CO)_5(SCH_2SCH_2SCH_2)]$ and their computer syntheses

experimental spectra ceased to be sensitive to k(S.I.) above coalescence because of the much smaller chemical-shift differences that are averaged by sulphur inversion compared to ring reversal. The free ligand (L), produced during sample preparation, is present above coalescence (Figure 5) and confirms the intramolecular nature of both processes. The apparent disappearance of this signal at lower temperatures is due to a reduction in solubility and the slowing down of free-ligand ring reversal which causes the line to broaden. The two sets of ' best-fit ' rate constants k(R.R.) and k(S.I.) were used to calculate the energy barriers for ring reversal and sulphur inversion given in Table 2. In all cases the values of $\Delta G^\ddagger$ refer to the equatorial–axial conformer averagings.

β-2,4,6-*Trimethyl*-1,3,5-*trithian Complexes*.—The spectra of the complexes $[M(CO)_5(SCHMeSCHMeSCHMe)]$ (M = Cr or W) were similar to those reported previously.[16] Below −25 °C the methyl regions consisted of two doublets of intensity ratio 1 : 2. It was decided to confine our d.n.m.r. studies to the methine region, and in order to obtain the best spectral dispersion the spectra were recorded in $CDCl_3$ between −60 and +60 °C. An example of the methine region of the complex $[Cr(CO)_5(SCHMeSCHMeSCHMe)]$ is shown together with its computer syntheses in Figure 6.

The ' static ' spectra were interpreted by analogy with related complexes. The 1 : 2 ratio of signals is a result of the $M(CO)_5$ moiety co-ordinating to a single sulphur atom in the ligand ring. The observation of *one* pair of quartets at −60 °C implies that only one of two possible conformers has a significant population (assumed axial, see later). The static n.m.r. parameters are given in Table 4.

Upon raising the temperature to ambient, the two quartets coalesce giving rise to a single quartet at +50 °C, a sharp free-ligand quartet (L) being observed throughout the temperature range (Figure 6). These spectral changes imply a rapid intramolecular com-

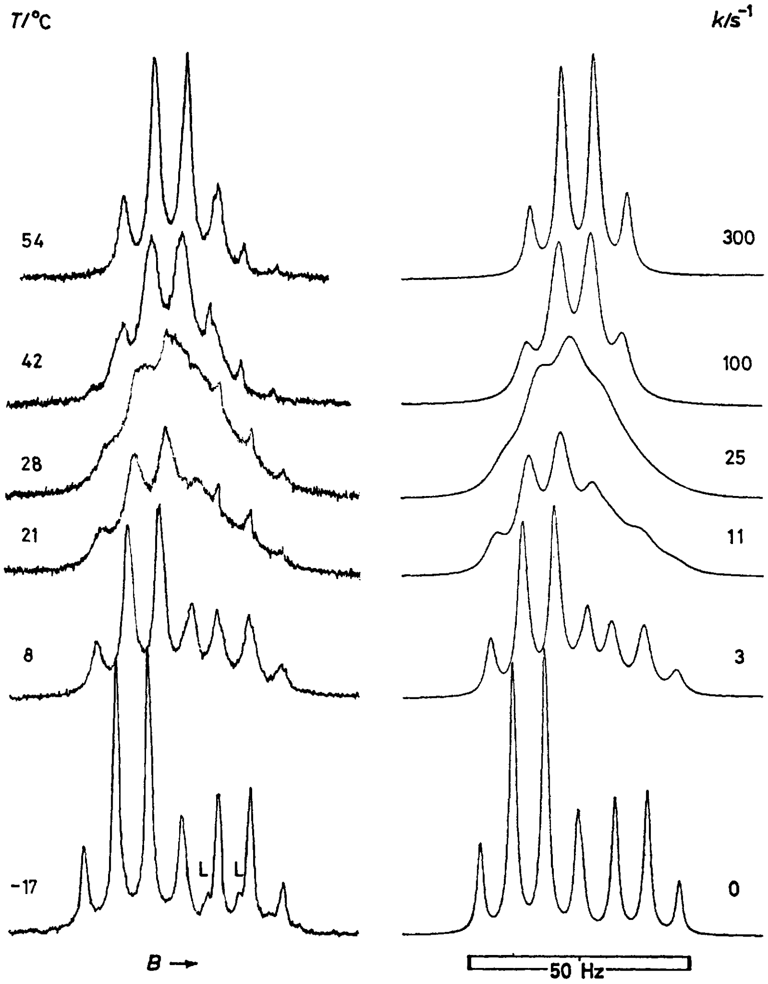

FIGURE 6 Variable-temperature ^1H n.m.r. spectra of the complex $[\mathrm{Cr(CO)_5(SCHMeSCHMeSCHMe)}]$ and their computer syntheses; L = free ligand

mutation of the $\mathrm{M(CO)_5}$ moiety over all three sulphur-atom co-ordination sites *via* a series of 1,3-shifts, see Figure 7. Examination of molecular models indicates that, in order to facilitate such a fluxional process, the $\mathrm{M(CO)_5}$ moiety must occupy an axial environment with respect to the ligand ring. This conformation was considered to be the less favoured in the 1,3-dithian and 1,3,5-trithian complexes (see above), but in this case the presence of equatorial methyl groups introduces steric factors which favour an axial attachment of $\mathrm{M(CO)_5}$.

The full dynamic nuclear-spin problem is shown in Figure 7. The lack of long-range ^4J coupling permits the reduction of this complex situation to $X_3A(66.6\%) \rightleftharpoons Y_3B(33.3\%)$, which is readily handled by the computer program. A set of spectral syntheses are shown in Figure 6. The rate constants obtained were used to calculate the Arrhenius and transition-state parameters for the 1,3-shift process (in Table 2). It should be noted that, due to the complex existing in a single conformation, sulphur inversion and ring reversal have no effect on the experimental spectra, and their energies are indeterminate.

Energies of the Fluxional Processes.—We have already argued that the value of $\Delta G^{\ddagger}$ quoted in Table 2 for $[\mathrm{Cr(CO)_5(SCH_2SCH_2CH_2CH_2)}]$ refers to sulphur inversion and not to ring reversal. This value is similar to sulphur

TABLE 4

Hydrogen-1 n.m.r. parameters (Hz) [a] for the complexes $[\mathrm{M(CO)_5(\beta\text{-}SCHMeSCHMeSCHMe)}]$

Complex	ν_A		ν_B		ν_X	ν_Y	J_{AX}	J_{BX}	$T_2{}^{*b}$/s
	a	b	a	b					
$[\mathrm{Cr(CO)_5(SCHMeSCHMeSCHMe)}]$	432.0	−0.0816	409.4	0.0000	160.0	160.0	7.20	7.15	0.190
$[\mathrm{W(CO)_5(SCHMeSCHMeSCHMe)}]$	422.3	−0.1015	409.2	−0.0310	156.0	163.0	7.05	7.10	0.318

[a] In $CDCl_3$ relative to $SiMe_4$ at temperature T (°C); $\nu_i = a + bT$ Hz. [b] See footnote b, Table 3.

inversion barriers obtained for related complexes [14] and to that for $[Cr(CO)_5(SCH_2SCH_2SCH_2)]$ in this work (Table 2). Sulphur inversion energies calculated here for the complexes $[M(CO)_5(SCH_2SCH_2SCH_2)]$ are slightly dependent on the nature of the Group 6 metal, that for M = Cr being *ca.* 2 kJ mol^{-1} less than that for M = W, as was the case in related complexes.[14] This result may reflect a more efficient p_π–d_π overlap in the transition state of the Cr complexes compared to those of W, as was postulated to explain the different sulphur inversion barriers for complexes of dialkyl sulphides with Pd^{II} and Pt^{II}.[6-8]

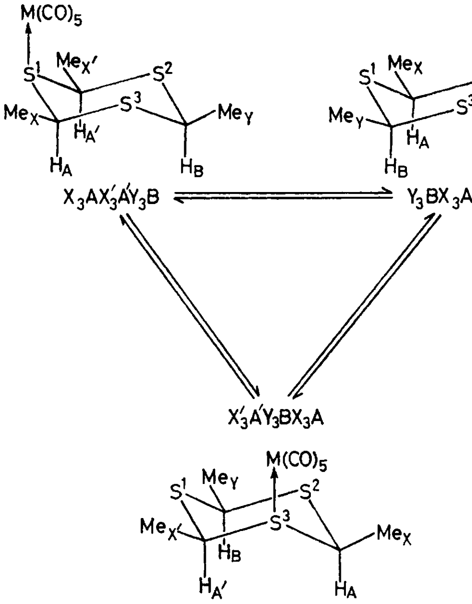

FIGURE 7 Dynamic nuclear-spin problem for the 1,3-shift process in the complexes $[M(CO)_5(SCHMeSCHMeSCHMe)]$

In contrast, ring reversal energies ($\Delta G^\ddagger$) obtained for $[M(CO)_5(SCH_2SCH_2SCH_2)]$ are, within experimental error, independent of the transition metal. This result supports the previous observation that transition-metal moieties have little effect on the ring reversal process.[4] It should be noted that in this study the ring reversal energies are *ca.* 6 kJ mol^{-1} greater than that for the free ligand.[28] However, the free-ligand data were obtained under difficult experimental conditions and may well be prone to a large experimental error.

The values of $\Delta G^\ddagger$ quoted for the 1,3-shift process in $[M(CO)_5(SCHMeSCHMeSCHMe)]$ show a lower value for the Cr complex which possibly reflects the more ready movement of the lighter $Cr(CO)_5$ moiety. Of greater significance is the fact that the above complexes are undergoing 1,3-shifts rapidly at room temperature whereas those of 1,3-dithian and 1,3,5-trithian are static. This is due to the fixed axial conformation of the $M(CO)_5$ group in the β-2,4,6-trimethyl-1,3,5-trithian complexes and the rigid conformation of the ligand with all methyl groups equatorial. In such a structure the other axial sulphur lone pairs are held at a constant distance from the $M(CO)_5$ moiety and directed in such a way as to facilitate a 1,3-shift. In the other types of complex, ring reversal and sulphur inversion change the relative positions of $M(CO)_5$ groups and sulphur lone pairs, making the probability of a 1,3-shift more remote. We are at present investigating the possibility of a 1,3-shift process occurring in these more flexible complexes at elevated temperatures.

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