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Dynamic NMR studies of 1,1′,2,2′-bis(1,2,3-trithia-[3])ferrocenophane and some mixed sulphur/selenium-bridged derivatives *

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Abstract

The doubly trisulphur-bridged metallocene compound, 1,1′,2,2′-bis(1,2,3-trithia-[3])ferrocenophane (1) exists in solution as a mixture of chair–chair and chair–boat diastereomers arising from the orientations of the trisulphur linkages. Dynamic NMR studies have shown that the energies of the two bridge reversal processes, chair–boat to chair–chair and chair–boat to boat–chair, are, in terms of $\Delta G^{\ddagger}$ (298.15 K) data, 93.9 and 89.0 kJ mol^{-1} respectively. These values are compared with data obtained for the singly trichalcogen-bridged metallocenophanes, and the mechanism of bridge reversal is discussed. Relative populations of the two diastereomers were strongly solvent dependent, with the less abundant chair-boat conformer more favoured in polar solvents. An NMR analysis of the products resulting from conversion of the doubly-trisulphur-bridged compound, 1, to SSeS-bridged species, namely 1,1′,2,2′-(1,2,3-trithia-[3])(1,3-dithia, 2-selena-[3])ferrocenophane (2) and 1,1′,2,2′-bis(1,3-dithia,2-selena-[3])ferrocenophane (3) identified each compound and its individual diastereomers.

1. Introduction

Singly-trichalcogen-bridged [3]ferrocenophanes have been known for a number of years [1–4] and have been shown to undergo a restricted bridge reversal fluxion analogous to six-membered ring chair-chair conformation exchange. The process can be accurately monitored by dynamic NMR spectroscopy and activation energies for this fluxion are now known for all nine complexes in the series $[Fe(C_5H_4E)_2E']$ (E, E′ = S, Se or Te) [5–7]. These activation energies may be closely related to the total trichalcogen bridge lengths and the relative torsion energies of the chalcogen–chalcogen single bonds.

We now report dynamic NMR studies of the bridge reversal fluxion in the first multiply-trichalcogen-bridged ferrocenophane, namely 1,1′,2,2′-bis(1,2,3-trithia-[3])ferrocenophane (1), a species involving two separate bridges of three sulphur atoms linking the cyclopentadienyl rings. Owing to the presence of two conformers of the compound in solution, the chair–chair and chair–boat (or boat–chair) species (Fig. 1), two bridge reversal processes may occur. Their energies have been calculated and are compared with those for singly-trichalcogen bridged species, and a mechanism for the fluxion is proposed.

Conversion of the doubly-trisulphur-bridged compound, 1, to mixed sulphur/selenium-bridged derivatives is also discussed. All reaction products have been clearly identified and characterised by NMR techniques.

2. Experimental section

2.1. Materials

The preparation of 1,1′,2,2′-bis(1,2,3-trithia-[3])ferrocenophane has been described previously [8] and the syntheses of 1,1′,2,2′-(1,2,3-trithia-[3])(1,3-dithia,2-selena-[3])ferrocenophane and 1,1′,2,2′-bis(1,3-dithia, 2-selena-[3])ferrocenophane will be discussed elsewhere [9].

2.2. NMR studies

Room temperature ^{1}H NMR spectra were recorded on a Bruker AM 250 spectrometer operating at 250.13 MHz using a variety of solvents (see Table 1 for de-

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* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

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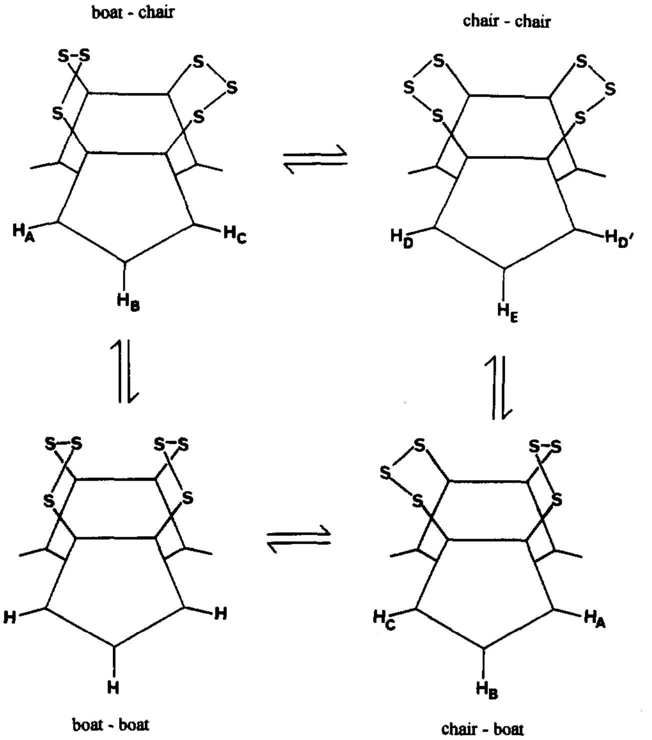


Fig. 1. Static conformers of **1** showing the labelling of the ring methine protons.

tails). A ^{1}H NMR spectrum was also recorded on a 400 MHz Bruker spectrometer at the University of Warwick, with (CD_2Cl_2) as the solvent.

Variable temperature ^{1}H NMR spectra were also run on the Bruker AM 250 spectrometer with $C_6D_5NO_2$ as the solvent. A standard B-VT1000 unit was used to control the NMR probe temperature, the calibration of this unit being checked periodically against a Comark digital thermometer. The temperatures are considered accurate to at least ±1°C. NMR bandshape analyses were carried out as previously [5–6] using the authors' version of the DNMR3 program [10].

TABLE 1. Hydrogen-1 NMR chemical shifts [a] for [Fe{[$C_5H_3(S_3)]_2$}] (**1**) in a range of solvents

Solvent	Chemical shift [b]	
	δ_C	$\delta_{D,D'}$
C_6D_6	3.47	3.63
$C_6D_5NO_2$	4.02	4.07
$CDCl_3$	4.11	4.18
$CDCl_2.CDCl_2$	4.11	4.17
CD_2Cl_2	4.14	4.09
$(CD_3)_2SO$	4.31	4.36

[a] At 250.13 MHz, relative to Me_4Si (int.). [b] The shifts of protons C and D/D' are listed as there is no ambiguity in assignment of these signals.

3. Results and discussion

3.1. Studies on the 'static' spectra of 1,1',2,2'-bis(1,2,3-trithia-[3])ferrocenophane (1)

Spectra of **1** at room temperature exhibited no fluxional molecular motion, and were recorded in a range of solvents. Two effects were observed:

Firstly, chemical shifts of the cyclopentadienyl ring hydrogens were quite solvent-sensitive. Table 1 lists the solvent dependence of the ring protons adjacent to an S_3 bridge in a chair conformation (see Fig. 1 for hydrogen labelling). Chemical shifts in most cases increased with the dipolar character of the solvent with the exception of the aromatic solvents C_6D_6 and $C_6D_5NO_2$, where clearly the C and DD' hydrogens of **1** experience significant deshielding from the aromatic ring currents of these solvents.

Secondly, the relative populations of the chair–chair and chair–boat conformers were greatly affected (see Table 2). The data clearly indicate that the chair–chair conformer is always the preferred species. However, as the dipole moment of the solvent increases so does the proportion of the chair–boat conformer. It is clear (Fig. 1) that the chair–boat form will have a somewhat greater dipole moment due to the greater asymmetry of this molecule compared to the chair–chair form. Therefore, it is reasonable to expect that this species becomes more favoured as the polarity of the solvent increases.

3.2. NMR bandshape analysis of 1,1',2,2'-bis(1,2,3-trithia-[3])ferrocenophane (1)

The bridge reversal conformational change in [3]ferrocenophanes with chalcogen bridging atoms is well-established and its rate can be monitored very precisely from its averaging effects on the ring methine proton NMR signals [5,7].

TABLE 2. Relative populations of chair–chair and chair–boat conformers of **1**, [Fe{[$C_5H_3(S_3)]_2$}] in a variety of solvents with their dipole moments [a]

Solvent	μ(D)[11]	Relative populations [b]		Difference in relative populations
		chair–chair	chair–boat	
C_6D_6	0	0.86	0.07	0.79
$CDCl_3$	1.01	0.80	0.10	0.70
$CDCl_2.CDCl_2$	1.32	0.70	0.15	0.55
CD_2Cl_2	1.60	0.59	0.20	0.39
$(CD_3)_2SO$	3.96	0.54	0.23	0.31
$C_6D_5NO_2$	4.22	0.48	0.26	0.22

[a] Dipole moments, μ(D), are given at 20°C. [b] Values taken from spectral integrations, with the chair–boat conformer having a statistical weighting of 2.

The rate of bridge reversal in **1** is slow on the NMR timescale at room temperature and at temperatures up to *ca.* 90°C. These 'static' spectra consist of a number of signals relating to chair-chair and chair–boat species. The boat–chair isomer is the enantiomer of the chair–boat form and as such is indistinguishable by NMR but nevertheless must be included in the dynamic exchange scheme. The labelling of the ring protons is shown in Fig. 1. Each proton has an isochronous but magnetically non-equivalent counterpart in the other cyclopentadienyl ring. However, as there is no evidence of long range couplings between protons in different rings, the spin system can be accurately described in terms of the spins of a single cyclopentadienyl ring. There was also no evidence of the boat–boat conformer presumably because of strong bridgehead sulphur–sulphur interactions. The onset of bridge reversal at higher temperatures will therefore average pairs of protons according to the dynamic spin system:

$$\begin{tikzcd} \mathrm{ABC} \arrow[rr, shift left, "k_1"] \arrow[dr, shift right, "k_2"'] & & \mathrm{DED'} \arrow[ll, shift left] \arrow[dl, shift left, "k_1"] \\ & \mathrm{CBA} \arrow[ul, shift right] \arrow[ur, shift left] & \end{tikzcd}$$

The chemical shifts and scalar H–H couplings were measured from the static spectra and are recorded in Table 3.

The assignment of the signals to the ring protons was based on careful consideration of the environment of individual protons. The higher degree of symmetry of the chair–chair conformer enabled its protons D/D′ and E to be assigned unambiguously to the signals at δ 4.070 and δ 4.671 respectively. The other low frequency signal at δ 4.012 was therefore attributed to the C protons of the boat-chair (chair–boat) form since they, like the D/D′ protons, are adjacent to an S_3 bridge in a chair conformation. Distinction between the A and B proton signals was achieved by a careful examination of their multiplet structures.

TABLE 3. Hydrogen-1 NMR data for compound 1

Hydrogen [a]	δ [b]	ν [c]/Hz	
		a′	b′
A [d]	4.646	1162	0.130
B [e]	4.618	1155	0.175
C [f]	4.012	1004	0.193
D,D′ [g]	4.070	1018	0.200
E [g]	4.671	1168	0.180

[a] See Fig. 1 for labelling. [b] Relative to Me_4Si(int) $\delta = 0$. [c] At 250.13 MHz, values based on eqn. $\nu = a' + b'\theta/°C$. [d] $^3J_{AB} = 3.0$ Hz, $^4J_{AC} = 1.54$ Hz. [e] $^3J_{BA} = 3.0$ Hz, $^3J_{BC} = 2.76$ Hz. [f] $^3J_{CB} = 2.76$ Hz, $^4J_{CA} = 1.54$ Hz. [g] $^3J_{DE} = {}^3J_{D'E} = 2.81$ Hz.

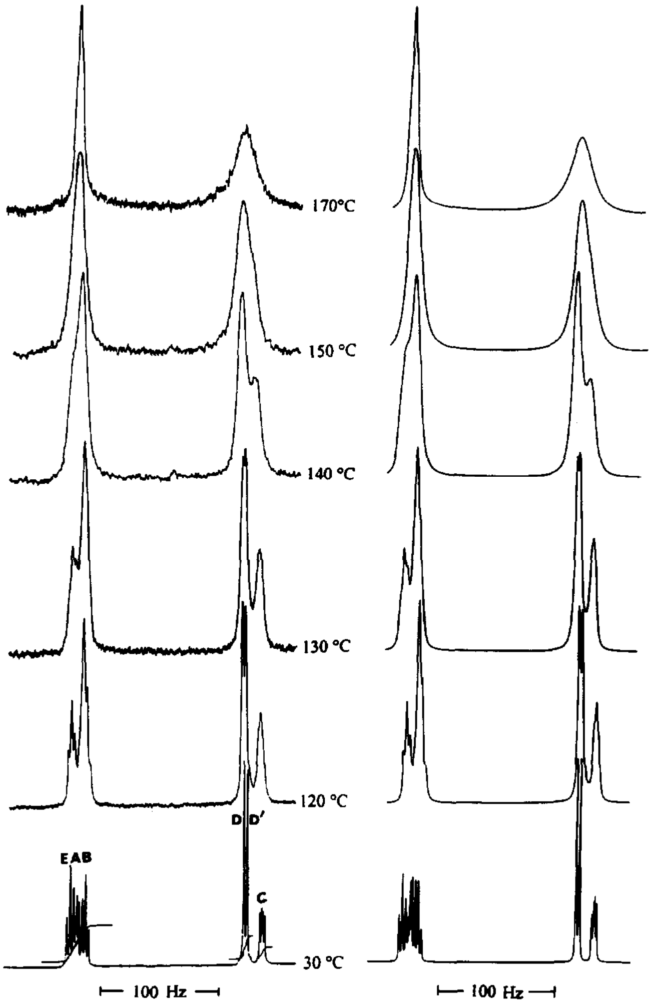


Fig. 2. Variable temperature ^1H NMR spectra of **1**, in the range 30–170°C. "Best-fit" computer synthesised spectra are shown alongside experimental spectra.

Having measured the 'static' NMR parameters, variable temperature ^1H spectra were recorded in the range 30 → 170°C. From such spectra (Fig. 2) it can been seen that initially the signals for D/D′ and E change little but those for all other protons begin to broaden. At 120°C, C appears as a broad singlet, A and B have collapsed into one signal, and E has started to collapse alongside, but its triplet structure is still visible. As the temperature is increased further, the spectra become composed of two broad signals. The high frequency signal sharpens at 170°C whilst the other collapses further. As the temperature rises, exchange of proton environments due to the bridge reversal processes is controlled by two rate constants k_1, for chair–boat to chair–chair and k_2, for chair–boat to boat–chair exchange (see Fig. 1). Bandshape analysis was performed on this basis. Chemical shifts were

TABLE 4. Exchange rate data obtained for the bridge reversal processes in $[Fe\{[C_5H_3(S_3)]_2\}]$ (1)

T (°C)	k_1 (s^{-1})	k_2 (s^{-1})
30	~0	~0
100	0.6±0.1	~0
110	1.9±0.1	~0
120	4.2±0.2	~0
130	7.5±0.3	~0
140	16.5±0.8	8.0±0.5
150	40.0±2.0	14.0±1.0
160	54.0±2.5	22.0±1.0 [a]
170	116.0±6.0	37.0±2.0 [a]

[a] Extrapolated values.

found to be linearly temperature dependent for spectra up to 100°C (Table 3).

It was assumed that the relative populations of the conformers are the same throughout the analysis. A study of the signal integrations in spectra at 70, 80 and 100°C showed this to be a safe assumption. It was found that the values of k_2 did not make any major contribution to the spectra at temperatures above 150°C. Values of k_2 above 150°C were therefore based on extrapolations of values for the spectra at 140 and 150°C.

A list of the 'best-fit' rate constants is given in Table 4, and the data obtained were utilised to give the Eyring activation parameters listed in Table 5. These parameters refer to the boat–chair → chair–chair process. The energy of the exchange between the boat-chair and chair-boat enantiomers was rather less accurately calculated to be $\Delta G^{\ddagger} = 89 \pm 1$ kJ mol^{-1}. It is pertinent to compare these values with corresponding data for bridge reversal in singly-trichalcogen-bridged ferrocenophanes (Table 5). Earlier studies have shown there to be a correlation between activation energies and (i) the total length of the bridge (as determined from standard covalent radii) and more significantly (ii) the torsional energies of the bonds which constitute the bridging unit. Such a correlation has been shown to be valid for six-membered alicyclic ring reversals [12] and pseudo, six-membered heterocyclic ring systems [5]. These trends are again followed in this doubly-bridged system but, interestingly, the bridge reversal energy is significantly higher than for the singly-trisulphur-bridged [3]ferrocenophane $[Fe\{(C_5H_4)_2S_3\}]$ (80.4 kJ mol^{-1}). This is reasonable if one considers the fact that the two S_3 bridges are adjacent and this close proximity must hinder the reversal of either bridge.

TABLE 5. Activation parameters for bridge reversal in trichalcogen-bridged [3]ferrocenophanes

Compound	$\Delta G^{\ddagger}$ (298 K) (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	Ref.
$[Fe\{(C_5H_4)_2S_3\}]$	80.4±0.2	77.0±0.9	−11.7±2.3	5
$[Fe\{(C_5H_4)_2S_2Se\}]$	72.6±0.2	69.8±1.1	−9.5±2.9	5
$[Fe\{(C_5H_4)_2S_2Te\}]$	62.5±0.02	60.5±1.3	−6.8±4.3	5
$[Fe\{(C_5H_4)_2Se_3\}]$	67.2±0.1	65.8±2.4	−5.0±7.8	5
$[Fe\{(C_5H_4)_2Se_2S\}]$	71.0±0.1	67.3±0.8	−12.4±2.4	5
$[Fe\{(C_5H_4)_2Se_2Te\}]$	59.9±0.1	57.0±1.1	−9.8±3.5	5
$[Fe\{(C_5H_4)_2Te_3\}]$	51.8±0.2	61.5±1.2	32.5±4.6	7
$[Fe\{(C_5H_4)_2Te_2S\}]$	56.3±0.04	61.9±1.3	18.9±4.5	7
$[Fe\{(C_5H_4)_2Te_2Se\}]$	55.4±0.07	63.0±1.4	25.7±4.9	7
$[Fe\{[C_5H_3(S_3)]_2\}]$	93.9±0.8 [a]	97.0±3.0	10.0±7.0	This work

[a] k_1 process, most analogous to the process measured in the singly-trichalcogen-bridged [3]ferrocenophanes. Value based on 8 spectra in the range 100 → 170°C.

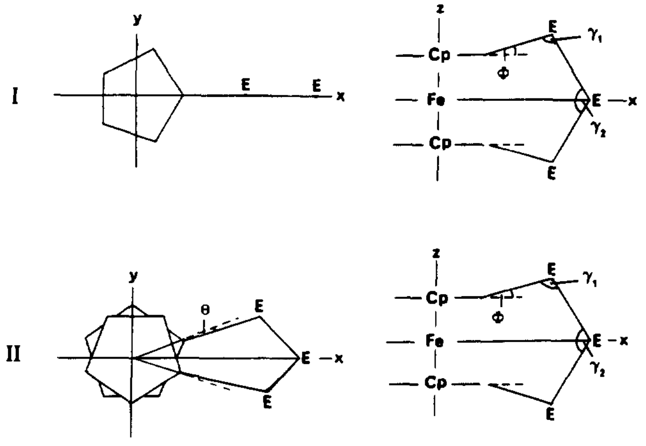


Fig. 3. Transition state geometries of $[Fe\{(C_5H_4)_2E_3\}]$. See ref. 7 for definitions of angles.

Consideration should also be given to the mechanism of the bridge reversal process. In earlier studies on singly-bridged compounds [5,13], a mechanism involving rotation about the Cp ··· Fe and chalcogen–chalcogen bridge bonds to produce a conformation with staggered cyclopentadienyl rings, similar to the half-chair conformation of cyclohexane (Fig. 3, structure II) was postulated. This intermediate, or transition state species, was thought likely to be energetically favoured over the intermediate with eclipsed cyclopentadienyl rings and a planar bridge system (Fig. 3, structure I). CNDO/2 molecular orbital calculations [7] performed on the ground state and transition state structures of these singly-bridged ferrocenophanes provided quantitative support for a staggered ring rather than an eclipsed ring intermediate.

However, in the present case, there are two sets of bridging units and so, the cyclopentadienyl rings may only rotate to a staggered form if both S_3 bridges change in a cooperative manner. This is likely to be a high energy and improbable process. If the S_3 bridges interconvert independently the transition state must involve eclipsed cyclopentadienyl rings and a planar S_3 bridge system, the other bridge retaining its boat or

TABLE 6. Theoretical rate data obtained for the bridge reversal processes in [Fe{($C_5H_3(S_3)$)$_2$}] at elevated temperatures.

T (°C)	k_1 (s^{-1})	k_2 (s^{-1})
180	216	64
200	668	159
220	1880	367
240	4880	794
260	11810	1620
280	26780	3140
300	57370	5810
320	116750	10310

chair conformation. It is, therefore, most relevant to note that CNDO/2 calculations [7] predict a value of 89.87 kJ mol^{-1} for the singly-trisulphur-bridged compound via a planar-bridged intermediate. This is in close agreement with 93.9 kJ mol^{-1} for **1**, the doubly-trisulphur-bridged compound, especially when allowing for the fact that there will be additional steric hindrance of another adjacent bridge, thus increasing the bridge reversal energy slightly.

The NMR analysis was then extended in a theoretical fashion to encompass exchange rates and temperatures out of range of the NMR spectrometer as it was clear that the signals due to protons A,D/D' and C had not reached coalescence even at 170°C. Theoretical rate constants were calculated from the Eyring equation (and are listed in Table 6) using the same NMR and thermodynamic parameters obtained previously. Selected spectra from this predicted bandshape analysis are given in Fig. 4.

The high frequency signal is a triplet which becomes more resolved as the temperature increases. The lower frequency signal broadens to a maximum between 190 and 200°C, and at higher temperatures sharpens to form a doublet. The predicted high temperature (320°C) limiting spectrum comprises a triplet (coupling constant 3.0 Hz) and a doublet (3.0 Hz) and arises from the bridge-averaged structure of the molecule. The two trisulphur bridges are now equivalent, being intermediate between chair and boat configurations. The triplet signal arises from the central methine hydrogen coupling to the two adjacent hydrogens and its shift is the "average" of signals B and E. The doublet is made up of the "average" signals of hydrogen A, C and D/D'.

3.3. NMR investigations of 1,1',2,2'-(1,2,3-trithia-[3])(1,3-dithia,2-selena-[3])ferrocenophane (2) and 1,1',2,2'-bis(1,3-dithia,2-selena-[3])ferrocenophane (3)

From reaction of 1,1',2,2'-(1,2,3-trithia-[3])ferrocenophane with lithium aluminium hydride followed by addition of selenium dichloride and triethylamine, a mixture of products was obtained and then analysed by various NMR experiments.

Hydrogen-1 NMR spectra, measured at 250 and 300 MHz operating frequencies, exhibited complex sets of signals which fell into two main regions, namely δ 4.08–4.16 and 4.55– 4.72. Unambiguous assignments of signals, however, proved impossible due to insufficient chemical shift dispersion. It was apparent, however, that three chemically distinct doubly chalcogen-bridged ferrocenophanes were present and each existed as 'static' equilibrium conformational mixtures. A 400 MHz ^{1}H spectrum of the mixture in $(CDCl_2)_2$ solvent was therefore obtained and this spectrum was fully analysed as described below.

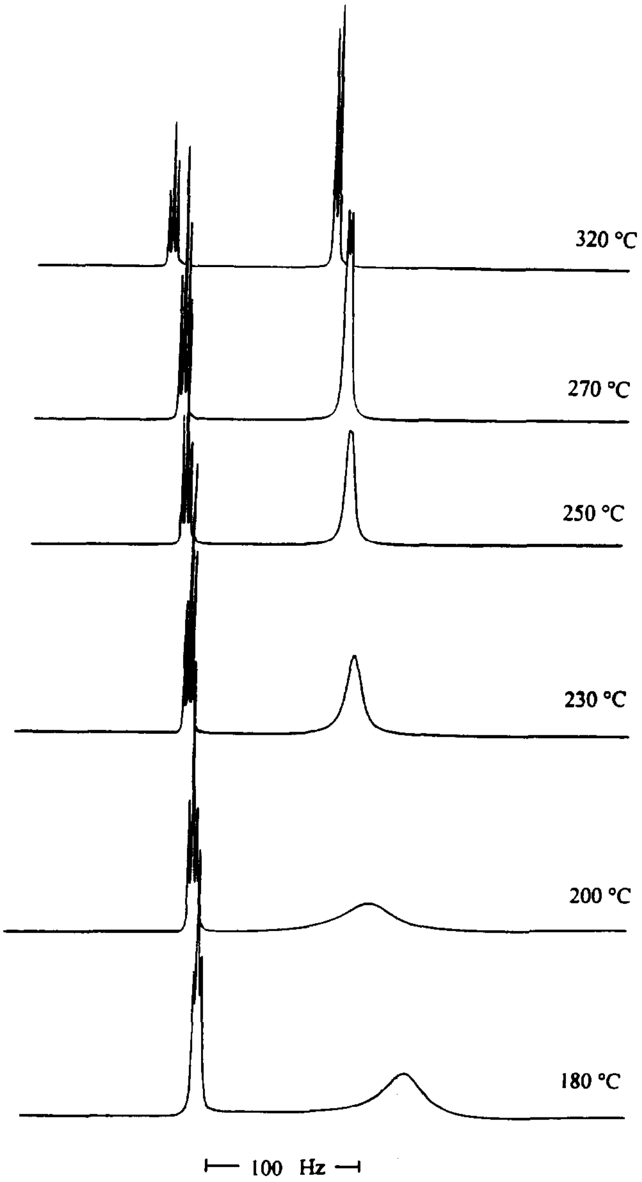


Fig. 4. Selected spectra from the predicted bandshape analysis of **1** at high temperatures.

Fourteen major chemically shifted signals were identified together with five minor signals. A 400 MHz 2D-COSY spectrum indicated that the main signals could be collected into 4 groups of 3 signals and one group of 2 signals as scalar couplings were clearly detected between signals in each group. This suggested that the total spectrum was consistent with two doubly bridged [3]ferrocenophanes, $[Fe(C_5H_3)_2(SSS)(SSeS)]$ (**2**) and $[Fe(C_5H_3)_2(SSeS)_2]$ (**3**), each existing as chair–chair, chair–boat and boat–chair conformers. The boat–boat conformer was discounted in view of its absence in the case of $[Fe(C_5H_3)_2(SSS)_2]$, **1**. The assignments of individual chemical shifts were based on the following assumptions:

(1) 3,3′,5,5′ methine protons adjacent to a trichalcogen bridge in a chair ring conformation are considerably shielded relative to other methine protons and appear in the region δ 4.08–4.16;

(2) 3,3′,5,5′ methine protons adjacent to a trichalcogen boat bridge and central 4,4′ methine protons appear in the higher frequency region of δ 4.55–4.72;

(3) replacement of a central S atom by Se in a trichalcogen chair bridge in most cases causes appreciable high frequency shifts of the adjacent methine protons, and smaller shifts of the other methine protons;

(4) replacement of a central S atom by Se in a trichalcogen boat bridge produces less well defined effects on the chemical shifts of the 3,3′ and 5,5′-methines, but the central 4,4′ methine protons experience small low frequency shifts.

There were certain exceptions to guide-lines (3) and (4) depending on which pairs of conformers are considered, but the full assignment of the 400 MHz spectrum (Table 7) is considered to be relatively firm. The methine proton labelling A–P refers to the conformer structures in Figs. 5 and 6. The results indicate that the main product of the reaction to replace the central S atoms of the S_3 bridges of $[Fe(C_5H_3)_2(SSS)_2]$ (**1**) is the compound with a single incorporated Se atom, namely $[Fe(C_5H_3)_2(SSS)(SSeS)]$ (**2**) with a smaller amount of $[Fe(C_5H_3)_2(SSeS)_2]$ (**3**) being formed. These two compounds account for *ca.* 95% of the total NMR signal intensity. The remaining 5% arises from weak signals in positions associated with the original unreacted $(SSS)_2$ bridged compound, **1**. Integrated intensities of the main signals indicated that the (SSS)(SSeS)- and $(SSeS)_2$-bridged ferrocenophanes were present in proportions of *ca.* 74 and 21% in solution. Due to certain signal overlaps these values are accurate to only *ca.* ±2%.

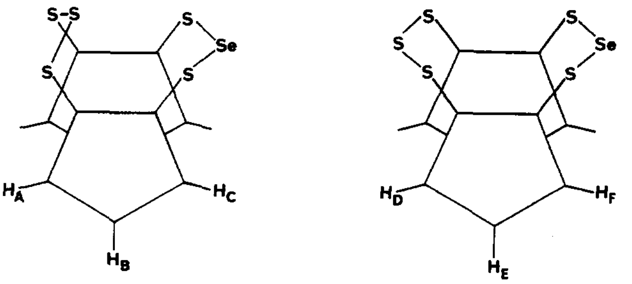
It was possible to measure the relative proportions of individual conformers of these compounds with rather greater accuracy and these are given in Table 8.

TABLE 7. NMR data for 1,1′,2,2′-(1,2,3-trithia-[3])(1,3-dithia,2-selena-[3]) ferrocenophane (**2**) and 1,1′,2,2′-bis(1,3-dithia,2-selena-[3]) ferrocenophane (**3**) in $CDCl_2 \cdot CDCl_2$ at 293 K.

δ [a]	Multiplet structure [b]	Assignment	
		Methine [c]	Species
4.665	d.d (2.64, 1.62)	A	**2** boat–chair
4.628	t (2.67)	B	
~4.11	d.d (2.70, 1.62)	C	
4.097	d.d (2.81, 1.46)	D	**2** chair–chair
4.686	t (2.79)	E	
4.158	d.d (2.77, 1.46)	F	
~4.09	d.d (2.79, 1.56)	G	**2** chair–boat
4.571	t (2.73)	H	
4.722	d.d (2.67, 1.56)	J	
~4.66	d.d (2.68, 1.52)	K	**3** chair–boat
4.547	t (2.72)	L	
~4.08	d.d (2.75, 1.52)	M	
4.081	d (2.76)	N/N′	**3** chair–chair
4.661	t (2.76)	P	

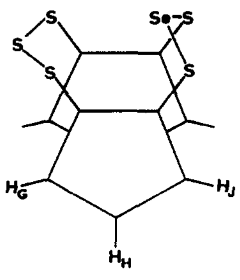
[a] In ppm rel. to Me_4Si (int). [b] d.d = doublets of doublets, t = 1:2:1 triplet, d = doublet, Figures in parentheses are $^2J(HH)$ and $^3J(HH)$ values in Hz. [c] Labels refer to Figs. 5 and 6.

No evidence of any boat–boat conformers was obtained. The intensity values imply that the bulkier Se atom is more easily accommodated when it forms part of a boat bridge. For a single (SSeS) bridge, *viz.* $[Fe(C_5H_3)_2(SSS)(SSeS)]$ the chair–chair form is still



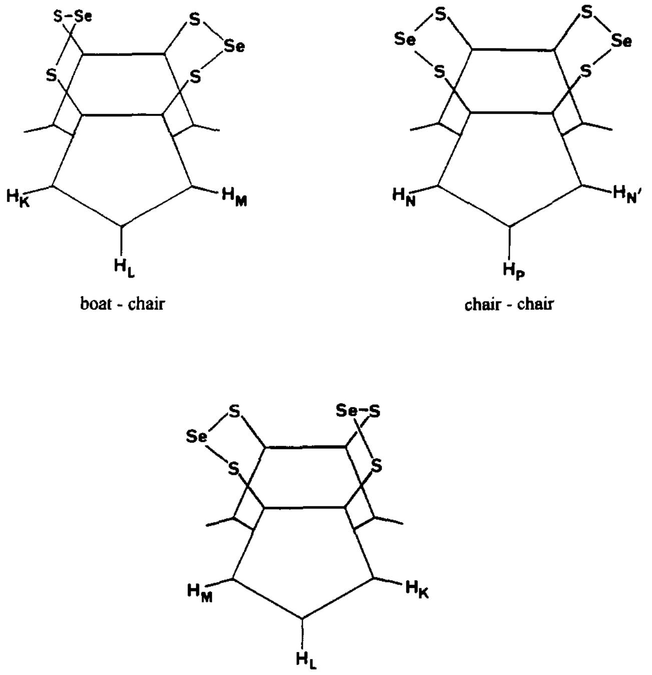
boat - chair

chair - chair



chair - boat

Fig. 5. Solution conformers of **2**.



boat - chair

chair - chair

chair - boat

Fig. 6. Solution conformers of 3.

most favoured in solution as found for $[Fe(C_5H_3)_2(SSS)_2]$, but in the case of two (SSeS) bridges, *viz.* $[Fe(C_5H_3)_2(SSeS)_2]$, the two equivalent chair–boat conformers dominate, suggesting that non-bonded interactions between the trichalcogen bridges and between the bridges and the cyclopentadienyl rings are most effectively accommodated in this structural form.

TABLE 8. Populations of compounds 1–3 in $(CDCl_2)_2$ solvent at 293 K.

Compound	Conformer	% Populations
2	chair–chair	62.5 [a]
	boat–chair	26.0 [a]
	chair–boat	11.5 [a]
3	chair–boat	35 [b]
	boat–chair	35 [b]
	chair–chair	30 [b]
1	chair–chair	~ 70
	boat–chair	~ 15
	chair–boat	~ 15

[a] Uncertainty ±0.5%. [b] Uncertainty ±1%.

These two new [3]ferrocenophane compounds incorporating one and two (SSeS) bridges presumably undergo bridge reversal at elevated temperatures by analogy with their $(SSS)_2$, (SSS) and (SSeS) bridged counterparts, but no investigations were made of any such fluxionality in view of the expected extreme complexity of their DNMR spectra. Attempts are being made to isolate the two new compounds in a pure state, in which circumstance DNMR studies would become a practical possibility.

Acknowledgment

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