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SYNTHETIC AND STRUCTURAL STUDIES ON SOME 1,3-DISELENA-[3]FERROCENOPHANES OF CARBON, SILICON AND TIN. CRYSTAL AND MOLECULAR STRUCTURE OF BIS(FERROCENE-1,1′-DISELENATO)TIN(IV) AT 163 K

A.G. OSBORNE, R.E. HOLLANDS,
Department of Chemistry, University of Exeter, Exeter EX4 4QD (Great Britain)

R.F. BRYAN and S. LOCKHART
Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901 (U.S.A.)

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Summary

A series of 1,3-diselena-[3]ferrocenophanes of general formula $Fe(C_5H_4Se)_2Y$, ($Y = CH_2$, $C(C_6H_5)_2$, $Si(CH_3)_2$, $Si(C_6H_5)CH_3$, $Sn(CH_3)_2$ or $Sn(C_6H_5)_2$) and a spiro compound $[Fe(C_5H_4Se)_2]_2Sn$ have been prepared by reaction of ferrocene-1,1′-diselenol and halide complexes of the Group IV elements. Spectroscopic properties of the compounds are reported. In solution these compounds are fluxional by a bridge-reversal process. The crystal structure of bis(ferrocene-1,1′-diselenato)tin(IV) has been determined at 163 K. At that temperature crystals have space group *Pbcn* with *a* 7.515(3), *b* 11.159(5) and *c* 24.308(10) Å. Least-squares refinement gave $R = 0.040$ for 2357 unique reflections whose intensities were measured by counter diffractometry. The molecules have two-fold crystallographic symmetry ($Z = 4$) with the axis passing through the Sn atom. The Sn—Se bond lengths are 2.516(1) and 2.539(1) Å, and the Se—Sn—Se valence angles show considerable variation, that in the ferrocenophane moiety being 108.6(1), and the others 104.5(2), 108.5(1), and 117.4(2)°. The Se—C bond lengths are 1.901(4) and 1.903(4) Å, with C—Se—Sn angles of 98.6(1) and 99.7(1)°. The cyclopentadienyl rings are in an eclipsed conformation with a mean twist angle of 5.7°, and the Se atoms are displaced from the ring planes by 0.24 and 0.27 Å yielding a non-bonded Se···Se separation of 4.00 Å in the ferrocenophane moiety.

Introduction

We have recently been interested in the synthetic and structural chemistry of [1]ferrocenophanes [1,2] and [3]ferrocenophanes [3]. Previously we

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described [3] the synthesis of 1,2,3-triselena-[3]ferrocenophane, its conversion to ferrocene-1,1′-diselenol, and the use of the diselenol and the corresponding dithiol to synthesize [3]ferrocenophanes with symmetrical trichalcogen chains. We have now extended this study to a series of 1,3-diselena-[3]ferrocenophanes which incorporate a Group IV element in the 2-position in the bridge. Some analogous 1,3-dithia-[3]ferrocenophanes have been described [4]. In order to gain further insight into the factors influencing the structures of this class of compound, we have determined the crystal and molecular structure, at 163 K, of a member of the series, viz. bis(ferrocene-1,1′-diselenato)tin(IV). Comparisons have been drawn between the structure of this compound and the structures of two related [3]ferrocenophanes [3,5].

Experimental

^{1}H NMR spectra were recorded at 100 MHz using Jeol MH 100 and PS/PFT 100 spectrometers. Mass spectra were recorded on a V.G. Micromass 16F instrument. Analyses were obtained from the Exeter University departmental service or from Butterworth Laboratories, Teddington, Middlesex. All solvents were dried and degassed before use, and all reactions were carried out under purified nitrogen. Ferrocene-1,1′-dithiol and ferrocene-1,1′-diselenol were prepared by literature methods [3,4].

1,3-Diselena-[3]ferrocenophane

Diiodomethane (0.12 cm^3, 1.5 mmol) was added to a stirred solution of ferrocene-1,1′-diselenol (0.42 g, 1.2 mmol) in benzene (50 cm^3). Triethylamine (0.4 cm^3, 2.8 mmol) was then added and the reaction mixture refluxed for 6 h. The cooled mixture was filtered and the solvent removed from the filtrate to give the crude product which was subjected to dry-column chromatography on Grade II alumina. Elution with hexane gave a single diffuse band containing 1,3-diselena-[3]ferrocenophane which was subsequently crystallized from hexane. Yield 0.26 g (61%).

1,3-Diselena-2,2-diphenyl-[3]ferrocenophane

Benzophenone (0.32 g, 1.8 mmol) and a few crystals of *p*-toluene sulphonic acid were added to a stirred solution of ferrocene-1,1′-diselenol (0.55 g, 1.6 mmol) in benzene (50 cm^3). The reaction mixture was brought slowly to reflux and approximately 30 cm^3 of liquid was distilled off. The remaining mixture was cooled and filtered, and the solvent removed from the filtrate to give the crude product which was subjected to dry-column chromatography on Grade II alumina. Elution with hexane gave two bands. The first orange-red band contained 1,2,3-triselena-[3]ferrocenophane (0.8 g), characterized from its m.p. and mass spectrum. The second band contained 1,3-diselena-2,2-diphenyl-[3]ferrocenophane which was subsequently crystallized from hexane. Yield 0.16 g (19%).

Reaction of ferrocene-1,1′-diselenol with acetone in the presence of p-*toluene sulphonic acid*

The reaction was carried out as described in the preparation of 1,3-diselena-

2,2-diphenyl-[3]ferrocenophane, but using the reactants ferrocene-1,1′-diselenol (0.55 g, 1.6 mmol), acetone (1,3 cm^3, 17.7 mmol) and a few crystals of *p*-toluene sulphonic acid. Elution of the chromatography column with hexane gave two bands. The first contained ferrocene (0.06 g) whilst the second contained 1,2,3-triselena-[3]ferrocenophane (0.23 g, 34%). Both compounds were identified by m.p. and mass spectra.

1,3-Diselena-2,2-dimethylsilyl-[3]ferrocenophane

This was prepared from dichlorodimethylsilane (0.26 g, 2.0 mmol), ferrocene-1,1′-diselenol (0.55 g, 1.6 mmol) and triethylamine (0.38 cm^3, 3.8 mmol) in a manner similar to that described for 1,3-diselena-[3]ferrocenophane, except that the reaction mixture was stirred at room temperature for 15 min and chromatography was omitted. Yield 0.39 g (61%).

1,3-Diselena-2-methyl-2-phenylsilyl-[3]ferrocenophane

This was prepared from dichloromethylphenylsilane (0.40 g, 2.1 mmol), ferrocene-1,1′-diselenol (0.57 g, 1.7 mmol) and triethylamine (0.56 cm^3, 4.0 mmol) in a manner similar to that described for 1,3-diselena-[3]ferrocenophane, except that the reaction mixture was stirred at room temperature for 2 h and chromatography was omitted. Yield 0.60 g (77%).

1,3-Diselena-2,2-dimethylstannyl-[3]ferrocenophane

This was prepared from dichlorodimethylstannane (0.41 g, 1.9 mmol), ferrocene-1,1′-diselenol (0.51 g, 1.5 mmol) and triethylamine (0.51 cm^3, 3.7 mmol) in a manner similar to that described for 1,3-diselena-[3]ferrocenophane, except that the reaction mixture was stirred at room temperature for 2 h and chromatography was omitted. Yield 0.66 g (91%).

1,3-Diselena-2,2-diphenylstannyl-[3]ferrocenophane

This was prepared from dichlorodiphenylstannane (0.73 g, 2.1 mmol), ferrocene-1,1′-diselenol (0.57 g, 1.7 mmol) and triethylamine (0.56 cm^3, 4.0 mmol) in a manner similar to that described for 1,3-diselena-[3]ferrocenophane, except that the reaction mixture was stirred at room temperature for 2 h and chromatography was omitted. Yield 0.76 g (73%).

Bis(ferrocene-1,1′-diselenato)tin(IV)

This was prepared from tin tetrachloride (0.09 cm^3, 0.8 mmol), ferrocene-1,1′-diselenol (0.53 g, 1.5 mmol) and triethylamine (0.50 cm^3, 3.6 mmol) in a manner similar to that described for 1,3-diselena-[3]ferrocenophane, except that the reaction mixture was stirred at room temperature for 2 h, chromatography was omitted and the product was crystallized from benzene. Yield 0.23 g (37%).

(Ferrocene-1,1′-diselenato)lead(II)

A solution of ferrocene-1,1′-diselenol (0.26 g, 0.7 mmol) in ethanol (20 cm^3) was added to a stirred solution of lead(II) acetate trihydrate (0.36 g, 1.0 mmol) in a water/ethanol (3/2) mixture (50 cm^3). A precipitate formed immediately and was filtered off, washed several times with water and dried in a vacuum desiccator. Yield 0.23 g (56%) of a maroon powder which decomposed without melting above 250°C. Anal. Found: C, 22.21; H, 1.51. $C_{10}H_8FePbSe_2$ calcd.: C, 21.87; H, 1.47%.

(Ferrocene-1,1′-dithiolato)lead(II)

This was prepared from ferrocene-1,1′-dithiol (0.52 g, 2.1 mmol) and lead(II) acetate trihydrate (1.00 g, 2.6 mmol) in a manner similar to that described for (ferrocene-1,1′-diselenato)lead(II). Yield 0.85 g (89%) of a brick-red powder which decomposed without melting above 250°C. Anal. Found: C, 25.78; H, 1.78. $C_{10}H_8FePbS_2$ calcd.: C, 26.38; H, 1.78%.

1,3-Dithia-2-methyl-2-phenylsilyl-[3]ferrocenophane

Dichloromethylphenylsilane (0.18 g, 0.9 mmol) was added to a suspension of (ferrocene-1,1′-dithiolato)lead(II) (0.33 g, 0.7 mmol) in toluene (50 cm^3) and the reaction mixture refluxed for 10 h. The cooled mixture was filtered and the solvent removed from the filtrate to give the crude product which was crystallized from hexane. Yield 0.05 g (18%), m.p. 170—171°C. Anal. Found: C, 54.88; H, 4.35. $C_{17}H_{16}FeS_2Si$ calcd.: C, 55.43; H, 4.38%.

X-ray crystallography

Crystal data. Crystals suitable for X-ray study were obtained from benzene solution as brown-red irregular plates having only {001} well developed. Crystal data for the specimen used are given in Table 1. The sample was cooled to 163 K by immersion in a stream of cold N_2 gas by use of the Nicolet LT-1 cooling device. Crystal symmetry and space group were derived from 25° precession photographs taken with Mo-K_α radiation at room temperature. No phase transition is apparent on cooling the sample. The systematic absences observed were: $0kl$ with k odd, $h0l$ with l odd, and $hk0$ with $h + k$, odd, and uniquely define

TABLE 1

CRYSTAL DATA

Molecular formula	$C_{20}H_{16}Fe_2Se_4Sn$
Molecular weight	802.6
Temperature (K)	163
Space group	*Pbcn*
a (Å)	7.515(3)
b (Å)	11.159(5)
c (Å)	24.308(10)
U (Å^3)	2038
Z	4 (Molecular symmetry 2)
D_x (g cm^{-3})	2.615
F(000)	1496
λ (Mo-K_α) (Å)	0.71069
μ (cm^{-1})	103
Crystal size (mm)	0.52 × 0.75 × 0.10
Crystal forms	{110}, {$\overline{110}$}, {001}
Independent reflections used	2357 (87.6% with $I > 3\sigma(I)$)
2θ max. (°)	60
Scan range (2θ) (°)	2.4—3.0
Scan speed (° min^{-1})	2.93—29.3

the space group. Unit cell parameters were derived for the cooled crystal by a least-squares fit to the observed angular settings for 15 strong general reflections measured with the same radiation on a Nicolet P3m automated diffractometer.

Intensity data. Intensity measurements for a single octant of reciprocal space were made on the cooled crystal by automatic diffractometry, with the $\theta-2\theta$ scan method and with scan rate dependent on reflection intensity as judged by a 2 *s* prescan. Background measurements were made at either end of the scan range for a total time equal to that spent on the scan. Mo-K_α radiation was used, made monochromatic by Bragg reflection from the (002) planes of a pyrolytic graphite crystal, with scintillation counting and pulse-height analysis. The intensities of two reference reflections, monitored after every 50 scans, showed an irregular variation of ±2% about their mean values over the course of the experiment. There is a ten-fold difference between the minimum and maximum calculated path lengths through the crystal, and absorption corrections were applied and structure amplitudes derived in the usual way *.

Structure determination and refinement. As there are only four molecules in the unit cell, the Sn atom is required to lie either at a center of symmetry or on a two-fold axis of symmetry of the space group, the latter being the obvious choice. Positions of the Sn, Se and Fe atoms were found from a three-dimensional sharpened Patterson function, and those of the carbon atoms from a difference electron-density map calculated using the heavy atom phases. Initial full-matrix least-squares refinement of atomic positions and isotropic thermal parameters converged at $R = 0.18$ in the absence of absorption corrections, and at $R = 0.08$ when these were applied. Adoption of anisotropic thermal parameters for Sn, Se and Fe, and subsequent refinement, reduced R to 0.049. Hydrogen atoms were identified from a difference electron-density map and their positional parameters refined. Their thermal parameters were held fixed and equal to the isotropic B value of the carbon of attachment. At convergence, ($\Delta(p)/\sigma(p) <$ 0.13), and with a ratio of observations to parameters of 23/1, the values of the conventional unweighted and weighted residuals were 0.040 and 0.046, respectively, for the 2357 independent reflections used **. The weighting factor used in the least-squares refinement was $1/[\sigma^2(F) + gF^2]$ with $g = 0.001$. A final difference electron-density map contained only peaks around the Sn and Se atoms indicative of an imperfect allowance for absorption effects (0.9 e Å^{-3}). The scattering factors used for the heavy atoms, with allowance made for the real part of the anomalous dispersion corrections, were taken from Cromer and Waber [6] and that for hydrogen from Stewart, Davidson and Simpson [7] ***.

Results and discussion

Ferrocene-1,1'-diselenol in benzene, in the presence of triethylamine, reacted with dihalides of Group IV elements to give good yields of 1,3-diselena-[3]ferro-

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* Initial data reduction and calculations involved in structure determination were carried out on an XDS Sigma 2 computer. Absorption corrections and refinement were carried out on a DEC PDP 11 computer using programs from the ENRAF-NONIUS structure solving package.

** Five strong reflections for which the count rate exceeded the useful response range of the counter were omitted from the refinement, and nine non-independent 00*l* data were included.

*** The Table of structure factors has been deposited with the British Library at Boston Spa, Wetherby LS23 7BQ (Great Britain) as Supplementary Publication No. SUP 90061 (12 pages).

cenophanes (eq. 1).

$$\mathrm{Fe(C_5H_4SeH)_2 + YX_2 + 2\ Et_3N \rightarrow Fe(C_5H_4Se)_2Y + 2\ Et_3NHX} \qquad (1)$$

$(\mathrm{X = I,\ Y = CH_2;\ X = Cl,\ Y = Si(CH_3)_2,\ SiCH_3(C_6H_5),\ Sn(CH_3)_2,\ Sn(C_6H_5)_2})$

An analogous reaction with tin tetrachloride yielded the spiro compound, bis(ferrocene-1,1′-diselenato)tin(IV). 1,3-diselena-2,2-diphenyl[3]ferrocenophane was prepared in comparatively low yield by the acid-catalysed condensation reaction of ferrocene-1,1′-diselenol and -benzophenone. An attempt to prepare the 2,2-dimethyl derivative from acetone by the same method did not yield the desired [3]ferrocenophane. Ferrocene-1,1′-diselenol and ferrocene-1,1′-dithiol reacted with lead(II) acetate in aqueous ethanol to give (ferrocene-1,1′-diselenato)lead(II) and (ferrocene-1,1′-dithiolato)lead(II), respectively. Both products are air-stable solids insoluble in all common organic solvents. The interaction of lead dithiolates and Group IV organometallic dichlorides is a convenient method [8] for the synthesis of dithiacyclopentane and dithiacyclohexane derivatives, and we attempted to apply this method to the synthesis of [3]ferrocenophanes. However, reaction of (ferrocene-1,1′-dithiolato)lead(II) with dichloromethylphenylsilane gave 1,3-dithia-2-methyl-2-phenylsilyl-[3]ferrocenophane in only 18% yield, and the lead salt offered no particular advantage over use of the dithiol.

All the [3]ferrocenophanes are air-stable crystalline solids, soluble in organic solvents, and gave satisfactory analytical results. Reaction yields, analytical results and some physical properties of the compounds are listed in Table 2. In the mass spectrometer the [3]ferrocenophanes all show molecular ions, often

TABLE 2

REACTION YIELDS, ANALYTICAL DATA AND PHYSICAL PROPERTIES OF SOME 1,3-DISELENA-[3]FERROCENOPHANES

Bridge groups [a] Y	Yield (%)	M.p. (°C)	Colour	Mass spectrum [b] (Calcd.) (Abundance) [c]	Analysis [c] (Found (calcd.) (%))	
					C	H
CH_2	61	220—222 dec.	Orange	358 (358) (100)	36.96 (37.12)	2.76 (2.83)
$C(C_6H_5)_2$	19	175—195 dec.	Orange	510 (510) (72)	53.91 (54.36)	3.73 (3.57)
$Si(CH_3)_2$	61	187 dec.	Yellow	402 (402) (86)	36.13 (36.02)	3.42 (3.53)
$SiCH_3(C_6H_5)$	77	182—184 dec.	Orange	464 (464) (100)	44.11 (44.18)	3.53 (3.49)
$Sn(CH_3)_2$	91	188—190	Orange	492 (492) (100)	29.18 (29.37)	2.78 (2.88)
$Sn(C_6H_5)_2$	73	232—234	Orange	616 (616) (100)	42.71 (42.98)	2.92 (2.95)
Sn [d]	37	>250 dec.	Dark red	804 (804) (5)	29.75 (29.93)	2.10 (2.01)

[a] See eq. 1 for explanation of symbols.

[b] Base peak of molecular ion.

[c] Percentage abundance related to the most abundant ion.

[d] Spiro compound.

TABLE 3

^{1}H NMR DATA OF SOME 1,3-DISELENA-[3] FERROCENOPHANES

Bridge group [d] Y	Chemical shifts (multiplicity) (relative intensity) [a,b,c]				
	Ferrocenyl signals	Phenyl signals		Other signals and assignments	
		H(2,4,6)	H(3,5)		
CH_2 [e]	4.08(t,4) 4.31(t,4)			4,16(t',2) [f]	CH_2
$C(C_6H_5)_2$	3.81(t,4) 4.23(t,4)	7.36(m,3)	7.72(m,2)		
$Si(CH_3)_2$	4.08(t,4) 4.27(t,4)			0,95(q,6) [g]	CH_3
$Si(CH_3)C_6H_5$	3.89(m,2) 4.12(m,2) 4.18(m,2) 4.23(m,2)	7.46(m,3)	7.88(m,2)	1,11(q,3) [h]	CH_3
$Sn(CH_3)_2$	4.04(t,4) 4.22(t,4)			0,97(h,6) [i]	CH_3
$Sn(C_6H_5)_2$	3.94(t,4) 4.11(t,4)	7.44(m,6)	7.69(m,4)		
Sn [j]	4.20(t,4) 4.36(t,4)				

[a] δ(ppm, δ(TMS) = 0. [b] $CDCl_3$ solution unless otherwise indicated. [c] m = multiplet, t = unsymmetrical triplet, h = non-binomial heptet, q = non-binomial quintet, t' = non-binomial triplet. [d] See eq. 1 for explanation of symbol. [e] $CDCl_2/CS_2$ mixture as solvent. [f] $^2J(^{77}Se-H)$ 16.7 Hz. [g] $^2J(^{29}Si-H)$ 6.9 Hz, $^3J(^{77}Se-H)$ 4.3 Hz. [h] $^2J(^{29}Si-H)$ 7.2 Hz, $^3J(^{77}Se-H)$ 4.2 Hz. [i] $^2J(^{117}Sn-H)$ 53.8 Hz, $^2J(^{119}Sn-H)$ 56.4 Hz, $^3J(^{77}Se-H)$ 1.5 Hz. [j] Spiro compound.

as the most abundant species (Table 2) with good agreement of the isotope pattern with theory.

The details of the ^{1}H NMR spectra of the [3]ferrocenophanes are listed in Table 3. For those compounds which have a symmetrical group at the 2-position of the bridge, the spectra contain a pair of unsymmetrical triplets in the range δ 3.81 to 4.40 ppm, corresponding to the ferrocenyl protons, and a single absorption for the substituents in the 2-position. These spectral features are similar to those observed for other [3]ferrocenophanes, and have been rationalized in terms of a rapid bridge reversal process [4]. Detailed studies of the process and of the energy barriers involved have been made for a number of [3]ferrocenophanes by variable temperature ^{1}H NMR [9,10]. Whilst it was possible [4] to obtain low-temperature limiting spectra for some 1,3-dithia-[3]ferrocenophanes, it was also found that an increase in bridge length resulted in a lower energy barrier to bridge reversal. Thus, replacement of sulphur by selenium would be expected to result in lower barriers for the process. Indeed, in an attempt to obtain a low-temperature limiting spectrum for 1,3-diselena-[3]ferrocenophane, we cooled samples to —116°C, but there was no indication that the rate of bridge reversal was altered significantly. The corresponding 1,3-dithia-[3]ferrocenophane showed a low-temperature limiting spectrum at —86°C [9]. Variable temperature ^{1}H NMR studies were not undertaken on 1,3-diselena-[3]ferrocenophanes of silicon or tin, as it was not expected that low-temperature limiting spectra would be obtained. Because of the lower symmetry of the molecule, the ^{1}H NMR evidence for the 2-methyl-2-phenyl derivative is less conclusive but, by analogy with the more symmetrical derivatives, we expect that it is also undergoing a rapid bridge reversal at room temperature.

The $^3J(^{77}\mathrm{Se—H})$ coupling constants at 4.3, 4.2 and 1.5 Hz, observed for the 2,2-dimethylsilyl, 2-methyl-2-phenylsilyl and 2,2-dimethylstannyl derivatives, respectively, are in the same range as those reported for other selenium compounds [11]. The $^2J(^{29}\mathrm{Si—H})$ couplings of 6.9 and 7.2 Hz for the 2,2-dimethylsilyl and the 2-methyl-2-phenylsilyl derivatives, respectively, compare with a value of 6.9 Hz for $[(CH_3)_3Si]_2S$ [12]. The values of 53.8 and 56.4 Hz, observed for $^2J(^{117}\mathrm{Sn—H})$ and $^2J(^{119}\mathrm{Sn—H})$ couplings, respectively, in the 2,2-dimethylstannyl derivative compare with 53.5 and 56.0 Hz for the same couplings in $[(CH_3)_3Sn]_2Se$ [12].

In the ^{13}C NMR spectra (Table 4) those [3]ferrocenophanes with a symmetrical grouping at the 2-position show three signals for the cyclopentadienyl carbon atoms. Two of these absorbances, in the range δ 68.8 to 75.3 ppm, are of approximately equal intensity and correspond to the C(2,5) and C(3,4) atoms. The third signal, of low intensity, in the range δ 77.2 to 84.3 ppm, is attributable to the C(1) atom. These spectral features are again consistent with a rapid fluxional motion of the bridge.

Atomic parameters for the asymmetric unit of the crystal structure at 163 K of bis(ferrocene-1,1′-diselenato)tin(IV) are given in Table 5. In the solid state the molecule has two-fold symmetry, the Sn atom lying on the crystallographic symmetry axis at $x = 0$, $z = 1/4$. The axis thus relates one ferrocenophane moiety to the other, but there is no symmetry implied within the individual ferrocenophane units. The coordinates of the symmetry related part of the molecule are derived from those of Table 5 by the operations: $x' = —x$, $y' =$

(Continued on p. 140)

TABLE 4

^{13}C NMR DATA OF SOME 1,3-DISELENA-[3]FERROCENOPHANES

Bridge Group [c] Y	Chemical Shifts [a, b]						
	Ferrocenyl signals		Phenyl signals			Other signals and assignments	
	C(1)	C(2,3,4,5)	C(1)	C(2,3,5,6)	C(4)		
CH_2	[d]	70.4, 74.5				33.9	CH_2
$C(C_6H_5)_2$	84.3	70.1, 74.8	142.2	128.2, 130.4	128.0	[d]	C
$Si(CH_3)_2$	77.2	69.1, 75.3				5.0	CH_3
$Si(CH_3)C_6H_5$	77.2	69.1, 69.2, 74.8, 75.3	134.2	134.5, 128.3	130.9	4.8	CH_3
$Sn(CH_3)_2$	78.4	68.8, 75.2				1.2	CH_3
$Sn(C_6H_5)_2$	77.6	69.0, 75.2 (5.3)	139.3	129.1(61), 135.8(50)	130.2		

[a] δ(ppm), δ(TMS) = 0, $CDCl_3$ solution.

[b] Coupling constants (Hz) for Sn—C (average value) in parentheses.

[c] See eq. 1 for explanation of symbol.

[d] Not observed.

TABLE 5

POSITIONAL AND THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS [a, b, c]

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Sn	0.00000(—)	−0.20721(4)	0.25000(—)	0.93(1)	1.09(1)	1.15(2)	0.00(—)	−0.13(1)	0.00(—)
Se(1)	0.09164(7)	−0.06912(4)	0.32675(2)	1.76(2)	0.83(1)	1.71(2)	−0.06(1)	−0.43(2)	−0.07(2)
Se(2)	−0.27107(7)	−0.32540(5)	0.28076(2)	1.05(2)	2.30(2)	1.43(2)	−0.54(2)	−0.28(2)	0.05(2)
Fe	0.01648(9)	−0.34700(6)	0.40204(3)	0.84(2)	0.98(2)	1.21(3)	−0.10(2)	0.00(2)	−0.12(2)
C(1)	0.1360(6)	−0.1864(4)	0.3819(2)	1.08(7)					
C(2)	0.0619(7)	−0.1815(5)	0.4361(2)	1.42(8)					
C(3)	0.1446(7)	−0.2733(5)	0.4676(2)	1.72(9)					
C(4)	0.2688(7)	−0.3346(5)	0.4336(2)	1.46(8)					
C(5)	0.2635(7)	−0.2821(4)	0.3800(2)	1.15(7)					
C(6)	−0.1800(6)	−0.3941(4)	0.3465(2)	1.20(7)					
C(7)	−0.2529(7)	−0.3730(5)	0.3997(2)	1.34(8)					
C(8)	−0.1711(7)	−0.4543(5)	0.4375(2)	1.57(9)					
C(9)	−0.0470(7)	−0.5252(5)	0.4071(2)	1.57(9)					
C(10)	−0.0537(7)	−0.4881(5)	0.3509(2)	1.40(8)					
H(2)	−0.028(8)	−0.132(5)	0.448(3)						
H(3)	0.112(7)	−0.290(5)	0.500(3)						
H(4)	0.343(8)	−0.394(5)	0.448(3)						
H(5)	0.317(7)	−0.306(5)	0.345(2)						
H(7)	−0.343(9)	−0.315(5)	0.410(3)						
H(8)	−0.186(8)	−0.451(5)	0.475(3)						
H(9)	0.033(8)	−0.585(5)	0.422(3)						
H(10)	0.009(7)	−0.514(6)	0.321(3)						

[a] Positional parameters are given as fractions of the unit cell edges. [b] Thermal parameters are given for Sn, Se and Fe as coefficients for the exponent: $[-(b_{11}a^{*2}h^2 + ...)/4 + b_{12}a^*b^*hk + ...)/2]$. [c] E.s.d's, in parentheses, are applicable to the least significant digits.

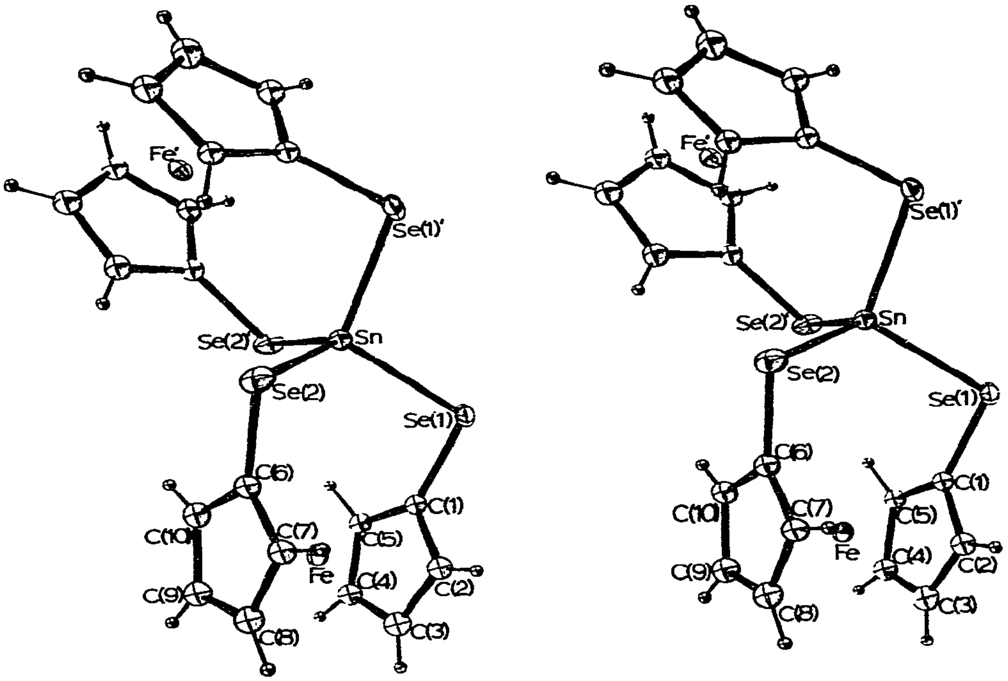

Fig. 1. Stereoscopic view of the molecular conformation as found in the crystal, showing the numbering scheme adopted. Hydrogen atoms are labelled to correspond to the carbon of attachment.

TABLE 6

BOND DISTANCES (Å) [a]

Sn—Se(1)	2.516(1)	Sn—Se(2)	2.539(1)
Se(1)—C(1)	1.903(3)	Se(2)—C(6)	1.901(4)
C(1)—C(2)	1.431(5)	C(6)—C(7)	1.423(5)
C(1)—C(5)	1.436(5)	C(6)—C(10)	1.418(5)
C(2)—C(3)	1.421(5)	C(7)—C(8)	1.430(5)
C(3)—C(4)	1.421(5)	C(8)—C(9)	1.428(5)
C(4)—C(5)	1.431(5)	C(9)—C(10)	1.428(5)
Mean	1.428(6)	*Mean*	1.425(4)
Fe—C(1)	2.063(3)	Fe—C(6)	2.068(3)
Fe—C(2)	2.052(4)	Fe—C(7)	2.046(4)
Fe—C(3)	2.035(4)	Fe—C(8)	2.040(4)
Fe—C(4)	2.050(4)	Fe—C(9)	2.049(4)
Fe—C(5)	2.063(3)	Fe—C(10)	2.074(4)
Mean	2.053(10)	*Mean*	2.055(13)
C(2)—H(2)	0.92(6)	C(7)—H(7)	0.98(6)
C(3)—H(3)	0.85(6)	C(8)—H(8)	0.91(6)
C(4)—H(4)	0.94(6)	C(9)—H(9)	0.97(6)
C(5)—H(5)	0.96(6)	C(10)—H(10)	0.89(6)
Mean	0.92(4)	*Mean*	0.94(4)

[a] E.s.d's, given in parentheses, are applicable to the least significant digits. Values are uncorrected for the effects of thermal motion.

TABLE 7

SELECTED BOND ANGLES (°) [a]

Se(1)—Sn—Se(2)	108.6(1)	Se(1)—Sn—Se(2′)	108.5(1)
Se(1)—Sn—Se(1′)	104.5(2)	Se(2)—Sn—Se(2′)	117.4(2)
Sn—Se(1)—C(1)	98.6(1)	Sn—Se(2)—C(6)	99.7(1)
Se(1)—C(1)—C(2)	123.7(3)	Se(2)—C(6)—C(7)	123.9(3)
Se(1)—C(1)—C(5)	127.2(3)	Se(2)—C(6)—C(10)	127.1(3)
C(2)—C(1)—C(5)	108.6(3)	C(7)—C(6)—C(10)	108.2(3)
C(1)—C(2)—C(3)	107.3(3)	C(6)—C(7)—C(8)	108.2(3)
C(2)—C(3)—C(4)	108.8(3)	C(7)—C(8)—C(9)	107.5(3)
C(3)—C(4)—C(5)	108.3(3)	C(8)—C(9)—C(10)	108.1(3)
C(4)—C(5)—C(1)	107.0(3)	C(9)—C(10)—C(6)	108.1(3)

[a] E.s.d's, given in parentheses, are applicable to the least significant digits.

y, $z' = 1/2 - z$. A stereoscopic view of the molecule, drawn with the program ORTEP [13] and showing the numbering scheme adopted, is shown in Fig. 1. Bond distances, uncorrected for the effects of thermal motion, are given in Table 6, and bond angles are given in Table 7. The thermal motions of the heavy atoms have been treated anisotropically but, because of the low temperature at which the structure determination has been carried out, the carbon atoms have been treated as isotropic scatterers. Because of the likely errors introduced by the high absorption of the sample, no attempt has been made to analyze the thermal anisotropy in terms of rigid body motions.

A significant difference (20σ) is found between the lengths of the two chemically equivalent Sn—Se bonds. Whereas this difference may only reflect the differing thermal motions of the Se atoms, it is associated with a distinct asymmetry in the valence angles around Sn, that in the ferrocenophane moiety being 108.6(1)°, and the others being 104.5(2), 108.5(1) and 117.4(2)°.

Other aspects of the molecular geometry may be compared to those found in X-ray studies of two other ferrocenophanes having trichalcogen bridges, viz. 1,3-dithia-2-selena-[3]ferrocenophane [3], (DSF), and 1,2,3-trithia-[3]ferrocenophane [5], (TTF). The two Se—C bond lengths are equal, within the limits of error, though the two Sn—Se—C bond angles are significantly different and smaller than the Se—S—C angles of 101.9(1)° and 102.6(1)°, reported for DSF, and the S—S—C angles of 102.2(3)° and 103.3(4)°, reported for TTF.

The lengths of the 10 C—C bonds of the cyclopentadienyl rings do not differ significantly from one another. The mean values for the two rings are very close to those found for the thermally corrected C—C bond length means in DSF (1.423 and 1.426 Å), confirming that thermal motions of the molecule as a whole have been substantially reduced at the low temperature used.

The Fe—C distances, as is usual, do show significant differences amongst themselves, but the means are again very close to the thermally corrected values found for DSF (2.053 and 2.055 Å).

The overall conformation of the ferrocenophane moiety is similar to those of DSF and TTF, with some exaggeration of the minor differences between these two. There is a characteristic asymmetry of valence angles at C(1) and C(6), not quite so marked in this case as in that of DSF. The asymmetry is the same at the two centres, although Sn···C(5) and Sn···C(10) are quite different (3.82

TABLE 8

EQUATIONS OF SELECTED LEAST-SQUARES MEAN PLANES [a]

Cyclopentadienyl ring C(1)—C(5)					
$-0.7180X - 0.6403Y - 0.2729Z = 1.9314$					
Deviations (Å)					
C(1)	−0.004	C(6)	3.419	Sn	1.753
C(2)	0.001	C(7)	3.309	Se(1)	−0.237
C(3)	0.002	C(8)	3.199	Se(2)	3.857
C(4)	−0.005	C(9)	3.237	Se(1′)	1.770
C(5)	0.005	C(10)	3.381	Se(2′)	1.339
Cyclopentadienyl ring C(6)—C(10)					
$-0.7181X - 0.6720Y - 0.1811Z = 2.4023$					
Deviations (Å)					
C(1)	−3.420	C(6)	−0.002	Sn	−1.949
C(2)	−3.295	C(7)	−0.000	Se(1)	−3.817
C(3)	−3.192	C(8)	0.002	Se(2)	0.265
C(4)	−3.252	C(9)	−0.003	Se(1′)	−2.152
C(5)	−3.381	C(10)	0.003	Se(2′)	−2.390
Plane Se(1), Se(2), C(1), C(6)					
$0.6874X - 0.4594Y - 0.5625Z = 3.6055$					
Deviations (Å)					
C(1)	0.041	C(6)	−0.042	Sn	1.250
C(2)	−1.108	C(7)	−1.254	Se(1)	−0.035
C(3)	−0.640	C(8)	−0.931	Se(2)	0.035
C(4)	0.780	C(9)	0.489	Se(1′)	1.118
C(5)	1.218	C(10)	1.032	Se(2′)	3.676
Plane Sn, Se(1), Se(2)					
$-0.5968X - 0.7128Y - 0.3685Z = -0.5910$					
Deviations (Å)					
C(1)	−1.957	C(6)	1.429	Se(1′)	−2.197
C(2)	−2.149	C(7)	1.112	Se(2′)	1.880
C(3)	−2.071	C(8)	1.054		
C(4)	−1.836	C(9)	1.333		
C(5)	−1.749	C(10)	1.571		

[a] $X = aX$, $Y = bY$, $Z = cZ$.

and 4.00 Å) and neither is obviously a limiting contact.

The cyclopentadienyl rings are eclipsed, with a mean twist angle * of 5.7° compared to 0.08° in TTF and 1.5° in DSF. Each Se atom is displaced by about 0.25 Å from the plane of the cyclopentadienyl ring to which it is attached, in such a way as to increase the Se···Se separation. These displacements may be compared to the 0.04 Å displacement of the S atoms from the ring planes in DSF and to the coplanarity of rings and S atoms in TTF. The Van der Waals radius found for Se in the DSF structure was 1.80—1.85 Å. The centroid to centroid separation of the cyclopentadienyl rings is 3.32 Å, so that with no twist and no displacement of the Se atoms from the ring planes the Se atoms would be in too close contact. On the other hand, the Se(1)···Se(2) separation is 4.00 Å, quite a bit larger than the 3.7 Å apparently required to avoid crowding. Either the Van der Waals radius for Se found for DSF is not applicable in the present case, or some large component of both twist and displacement may be attri-

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* Defined as the mean of the torsion angles C(*n*)—CT(1)—CT(2)—C(*n* + 5), *n* = 1, 5, where CT is the ring centroid [5].

butable to the directional requirements of the Sn orbitals rather than to simple steric effects involving only Se.

Equations of selected mean planes are given in Table 8. The planes of the cyclopentadienyl rings are inclined at 5.6°, compared to 2.4° for DSF and 2.9° for TTF. The angle between the plane Se(1)—Sn—Se(2) and Se(1)—C(1)—C(6)—Se(2) is 97.1°, compared to the substantially larger corresponding angles of 112.2° in DSF and 110.9° in TTF. The angle between the two Se—Sn—Se planes of the symmetry related ferrocenophane moieties is 90.9°.

Intermolecular contacts are of normal Van der Waals type.

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References

1 A.G. Osborne, R.H. Whiteley and R.E. Meads, J. Organometal. Chem., 193 (1980) 345.
2 H. Stoeckli-Evans, A.G. Osborne and R.H. Whiteley, J. Organometal. Chem., 194 (1980) 91.
3 A.G. Osborne, R.E. Hollands, J.A.K. Howard and R.F. Bryan, J. Organometal. Chem., 205 (1981) 395.
4 A. Davison and J.C. Smart, J. Organometal. Chem., 174 (1979) 321.
5 B.R. Davis and I. Bernal, J. Cryst. Mol. Struct., 2 (1972) 107.
6 D.T. Cromer and J.T. Waber, International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, England, 1974.
7 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
8 R.H. Cragg and A. Taylor, J. Organometal. Chem., 99 (1975) 391.
9 E.W. Abel, M. Booth, C.A. Brown, K.G. Orrell and R.L. Woodford, J. Organometal. Chem., 214 (1981) 93.
10 E.W. Abel, M. Booth and K.G. Orrell, J. Organometal. Chem., 208 (1981) 213.
11 W. McFarlane, J. Chem. Soc. A, (1969) 670.
12 H. Schmidbaur and I. Ruidisch, Inorg. Chem., 3 (1964) 599.
13 C.K. Johnson, ORTEP-II: A Fortran Thermal Ellipsoid Plotting Program Crystal Structure Illustrations, ORNL Report 3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A. 1971.