

A synthetic, structural and NMR spectroscopic study on 1,3-distanna-2-chalcogena-[3]ferrocenophanes

Max Herberhold^{*}, Udo Steffl, Wolfgang Milius, Bernd Wrackmeyer^{*}

Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany

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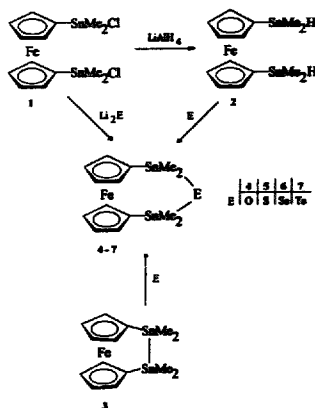
Abstract

Three synthetic routes to the first 1,3-distanna-2-chalcogena-[3]ferrocenophanes are described, and their ¹H, ¹³C, ⁷⁷Se, ¹¹⁹Sn and ¹²⁵Te NMR solution spectra are reported. The reaction of either 1,1'-bis(chlorodimethylstannyl)ferrocene (1) with the chalcogenide Li₂E (E = O, S, Se, Te) or 1,1'-bis(dimethylstannyl)ferrocene (2) with the chalcogen E (E = O, S, Se, Te) as well as the insertion of chalcogen into the tin–tin bond of 1,1,2,2-tetramethyl-1,2-distanna-[2]ferrocenophane (3) all give the corresponding 1,3-distanna-2-chalcogena-[3]ferrocenophane, Fe(C₂H₄SnMe₂)₂E (E = O (4), S (5), Se (6) and Te (7)), in reasonable yields (> 50%). The X-ray structure determinations of 6 and 7 indicate that the size of the chalcogen has a decisive influence upon the geometry of the sandwich moiety. Thus, the cyclopentadienyl rings are both bent away from the SnESn bridge in 6 (α = 3.4°) and 7 (α = 4.3°). The rings adopt a nearly staggered conformation in the selenium complex 6 (twist angle τ = 27.5°) but are almost eclipsed in the two crystallographically independent molecules of the tellurium compound, 7A (τ = 4.8°) and 7B (τ = 4.4°).

Keywords: Ferrocenophanes; Tin–tin bond; NMR; Iron; X-ray diffraction

1. Introduction

Among the [3]ferrocenophanes containing heteroelements in the triatomic bridge [1], a series of 1,3-dichalcogena-2-stanna-[3]ferrocenophanes (with the chalcogens directly attached to the ring) has been obtained [2]. Recently, 1,1'-bis(chlorodimethylstannyl)ferrocene (1) and 1,1'-bis(dimethylstannyl)ferrocene (2) have been used for the synthesis of 1,2-distanna-[2]- (3) and 1,2,3-tristanna-[3]ferrocenophane [3]. All three ferrocene derivatives 1–3 appeared to be promising candidates for the formation of 1,3-distanna-2-chalcogena-[3]ferrocenophanes. The present work describes the synthesis of the new [3]ferrocenophanes, Fe(C₂H₄SnMe₂)₂E (E = O (4), S (5), Se (6) and Te (7)), which were characterised by multinuclear magnetic resonance measurements. The molecular structures of both the selenium and the tel-



Scheme 1. Synthetic routes to the 1,3-distanna-2-chalcogena-[3]ferrocenophanes 4–7.

^{*} Corresponding authors.

Table 1

Data relevant to the single crystal X-ray structure analyses of 6 and 7

Parameter	6	7
<i>Crystal data</i>		
Formula; M_r	$C_{14}H_{20}FeSeSn_2$; 560.5	$C_{14}H_{20}FeTeSn_2$; 609.1
Crystal habit	Platelet	Irregular
Dimensions (mm^3)	$0.45 \times 0.30 \times 0.08$	$0.30 \times 0.25 \times 0.20$
Crystal system; space group	Triclinic; $P\bar{1}$	Triclinic; $P\bar{1}$
Unit cell dimensions		
a, b, c (Å)	6.602(2), 8.990(2), 15.427(3)	9.707(2), 13.609(2), 15.160(2)
α, β, γ (deg)	92.61(3), 91.21(3), 107.79(3)	64.49(2), 88.93(2), 77.47(2)
V (Å ³); Z ; $F(000)$	870.3(4); 2; 528	1758.0(5); 4; 1128
D_{calc} ($g\ cm^{-3}$)	2.139	2.301
Absorption coefficient (mm^{-1})	5.744	5.243
<i>Diffractometer</i>		
	Siemens P4, Mo K α ; $\lambda = 71.073$ pm, graphite monochromator	
Temperature (K); scan mode; range (deg)	296; ω ; $2.0 \leq 2\theta \leq 55.0$	173; ω ; $2.0 \leq 2\theta \leq 55.0$
No. of measured reflections	4757	9093
Indep. reflections (int. R)	3781 (0.0436)	7728 (0.0237)
No. of observed reflections (limit)	3357 ($F > 3.0\sigma(F)$)	7270 ($F > 2.0\sigma(F)$)
Absorption correction	Semi-empirical (ψ -scans)	Semi-empirical (ψ -scans)
Min./max. transmission	0.2614/0.6492	0.2350/0.2971
<i>Solution</i>		
	Direct methods (program SHELTXL-PLUS)	
<i>Refinement</i>		
No. of refined parameters	164	326
Final R ; wR	0.0477; 0.0463	0.0282; 0.0230
Weighting scheme w^{-1}	$\sigma^2(F)$	$\sigma^2(F)$
Residual electron density ($e\ \text{Å}^{-3}$)	1.46/–1.39	1.10/–0.96

Table 2

Selected bond distances (pm) and angles (deg) for compounds 6 and 7

Fe($C_2H_4SnMe_2$) ₂ Se 6		Fe($C_2H_4SnMe_2$) ₂ Te 7			
		7A		7B	
Sn(1)–Se	252.6(1)	Sn(1)–Te(1)	273.6(1)	Sn(3)–Te(2)	272.6(1)
Sn(2)–Se	253.5(1)	Sn(2)–Te(1)	273.6(1)	Sn(4)–Te(2)	273.2(1)
Sn(1)–C(11)	210.9(7)	Sn(1)–C(1)	210.9(4)	Sn(3)–C(15)	211.4(4)
Sn(1)–C(11)	213.9(9)	Sn(1)–C(11)	214.1(5)	Sn(3)–C(25)	212.9(6)
Sn(1)–C(12)	213.3(11)	Sn(1)–C(12)	213.2(8)	Sn(3)–C(26)	213.9(5)
Sn(2)–C(6)	211.9(6)	Sn(2)–C(6)	212.4(4)	Sn(4)–C(20)	212.2(4)
Sn(2)–C(13)	213.9(11)	Sn(2)–C(13)	213.2(7)	Sn(4)–C(27)	213.0(7)
Sn(2)–C(14)	211.2(12)	Sn(2)–C(14)	213.9(6)	Sn(4)–C(28)	213.6(6)
Fe–center(1–5)	165.4	Fe(1)–center(1–5)	165.5	Fe(2)–center(15–19)	165.5
Fe–center(6–10)	165.3	Fe(1)–center(6–10)	165.5	Fe(2)–center(20–24)	165.4
Se–Sn(1)–C(1)	107.0(2)	Te(1)–Sn(1)–C(1)	109.9(1)	Te(2)–Sn(3)–C(15)	109.8(1)
Se–Sn(1)–C(11)	104.5(2)	Te(1)–Sn(1)–C(11)	106.6(2)	Te(2)–Sn(3)–C(25)	111.7(2)
Se–Sn(1)–C(12)	111.8(3)	Te(1)–Sn(1)–C(12)	110.0(1)	Te(2)–Sn(3)–C(26)	106.6(2)
C(1)–Sn(1)–C(11)	110.4(0)	C(1)–Sn(1)–C(11)	110.0(2)	C(15)–Sn(3)–C(25)	109.8(2)
C(1)–Sn(1)–C(12)	109.1(3)	C(1)–Sn(1)–C(12)	108.8(2)	C(15)–Sn(3)–C(26)	107.3(2)
C(11)–Sn(1)–C(12)	114.1(4)	C(11)–Sn(1)–C(12)	111.4(3)	C(25)–Sn(3)–C(26)	111.4(2)
Se–Sn(2)–C(6)	115.2(2)	Te(1)–Sn(2)–C(6)	109.9(1)	Te(2)–Sn(4)–C(20)	111.4(1)
Se–Sn(2)–C(13)	102.3(3)	Te(1)–Sn(2)–C(13)	111.0(1)	Te(2)–Sn(4)–C(27)	109.8(1)
Se–Sn(2)–C(14)	107.5(3)	Te(1)–Sn(2)–C(14)	107.5(2)	Te(2)–Sn(4)–C(28)	107.3(2)
C(6)–Sn(2)–C(13)	109.1(4)	C(6)–Sn(2)–C(13)	110.3(2)	C(20)–Sn(4)–C(27)	107.3(2)
C(6)–Sn(2)–C(14)	108.7(3)	C(6)–Sn(2)–C(14)	106.2(2)	C(20)–Sn(4)–C(28)	109.9(2)
C(13)–Sn(2)–C(14)	114.1(5)	C(13)–Sn(2)–C(14)	111.8(2)	C(27)–Sn(4)–C(28)	111.1(2)
Sn(1)–Se–Sn(2)	101.0(1)	Sn(1)–Te(1)–Sn(2)	92.5(1)	Sn(3)–Te(2)–Sn(4)	91.8(1)

^a The crystal of 7 contains two symmetrically independent molecules, 7A and 7B.

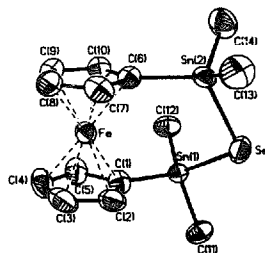


Fig. 1. Molecular structure of 1,3-distanna-2-selena-[3]ferrocenophane (**6**).

lurium compound, **6** and **7** respectively, were determined by single crystal X-ray structure analyses.

2. Results and discussion

2.1. Synthesis

Three preparative routes to the [3]ferrocenophanes **4–7** are shown in Scheme 1; all three are useful for the synthesis of **4–7**. Clean reactions are observed if 1,2-distanna-[2]ferrocenophane (**3**) is used as a starting material; in the cases of sulfur, selenium and tellurium, insertion into the tin–tin bond of **3** takes place quantitatively. The [3]ferrocenophanes **4–7** are orange crystalline solids, which are soluble in benzene, toluene and dichloromethane.

2.2. Molecular structures of the 1,3-distanna-2-chalcogeno-[3]ferrocenophanes **6** and **7**

Data relevant to the X-ray structure determinations of **6** and **7** are given in Table 1,¹ and selected bond lengths and angles are listed in Table 2. The molecular structures of **6** and **7** are shown in Figs. 1 and 2.

The geometry of the sandwich moiety, $\text{Fe}(\text{C}_5\text{H}_4)_2$, is only slightly distorted in the [3]ferrocenophanes **6** and **7**. The two cyclopentadienyl rings are almost parallel, the angle δ at iron (ring center–Fe–ring center) being 177.3° in **6** and 176.6° in **7A** or 176.7° in **7B**. The triatomic bridge is somewhat too large for the metallocene unit; therefore the cyclopentadienyl ring planes are slightly bent away from the bridge, the dihedral angle ('tilt angle' α) between the planar cyclopentadi-

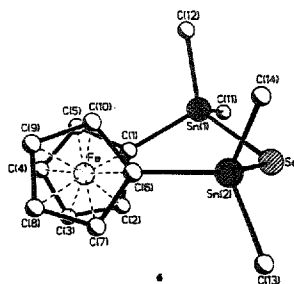


Fig. 2. Comparison of the ring conformations of **6** and **7A** (**7B** is closely similar to **7A**).

Table 3
 ^1H , ^{13}C , ^{77}Se , ^{119}Sn and ^{125}Te NMR data for the ferrocenophanes **4–7** (in C_6D_6)

Parameter ^a	4	5	6	7
$\delta^1\text{H}(\text{2,5})$	4.06	4.09	4.10	4.10
$^2J(\text{Sn}^{13}\text{H}(\text{2,5}))$	10.4	11.0	11.1	11.0
$\delta^1\text{H}(\text{3/4})$	4.26	4.22	4.21	4.18
$^2J(\text{Sn}^{13}\text{H}(\text{2,4}))$	7.2	7.6	7.4	7.0
$\delta^1\text{H}(\text{SnMe})$	0.37	0.45	0.51	0.61
$^2J(^{119}\text{Sn}^{13}\text{C}_{\text{Me}})$	60.5	58.4	57.6	56.6
$\delta^{13}\text{C}(1)$	72.1	71.2	71.7	70.7
$^1J(^{119}\text{Sn}^{13}\text{C}(1))$	520.0	507.5	491.1	466.5
$^3J(\text{Sn}^{13}\text{C}(1))$	5.1	9.0	9.3	9.0
$^2J(^{119}\text{Sn}^{13}\text{C}(1))$	—	—	5.9	—
$\delta^{13}\text{C}(2/5)$	74.1	74.1	74.5	74.8
$^2J(\text{Sn}^{13}\text{C}(2/5))$	60.8	61.8	60.5	56.9
$\delta^{13}\text{C}(3/4)$	71.4	70.9	71.1	71.0
$^3J(\text{Sn}^{13}\text{C}(3/4))$	47.0	47.4	45.8	43.6
$\delta^{13}\text{C}(\text{SnMe})$	-4.4	-3.7	-3.4	-3.4
$^1J(^{119}\text{Sn}^{13}\text{C}_{\text{Me}})$	439.2	383.0	364.1	336.8
$^3J(\text{Sn}^{13}\text{C}_{\text{Me}})$	3.4	4.6	4.2	3.1
$^2J(^{119}\text{Sn}^{13}\text{C}_{\text{Me}})$	—	—	6.5	—
$^2J(^{125}\text{Te}^{13}\text{C}_{\text{Me}})$	—	—	—	11.0
$\delta^{119}\text{Sn}$	64.6	66.5	28.1	-70.7
$^2J(^{119}\text{Sn}^{117}\text{Sn})$	334.0 ^M	188.1	204.8	206.9
$^1J(^{119}\text{Sn}^{77}\text{Se})$	—	—	1133.0	—
$^1J(^{125}\text{Te}^{119}\text{Sn})$	—	—	—	2971.4
$\delta^{77}\text{Se}$	—	—	-549.0	—
$\delta^{125}\text{Te}$	—	—	—	-1250.0

^a J (Hz); if resolved, the coupling to ^{119}Sn is given.

^b in CDCl_3 , 306 Hz.

¹ Further details of the two crystal structure analyses are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldsdorfer, Germany, on quoting the depository numbers CSD-406432 and CSD-406433, the names of the authors and the journal citation.

Table 4
 ^1H , ^{13}C , ^{77}Se , ^{119}Sn and ^{125}Te NMR data for 1–3 and 1,1'-bis(trimethylstanny)ferrocene (8)

Parameter ^a	$\text{Fe}(\text{C}_2\text{H}_4\text{SnMe}_2\text{Cl})_2$ 1	$\text{Fe}(\text{C}_2\text{H}_4\text{SnMe}_2\text{H})_2$ 2	$\text{Fe}(\text{C}_2\text{H}_4\text{SnMe}_2)_2$ 3	$\text{Fe}(\text{C}_2\text{H}_4\text{SnMe}_2)_2$ 8 [8]
$\delta^1\text{H}(2/5)$	4.08	3.99	4.34	4.07
$^3J(\text{Sn}^1\text{H}(2,5))$	9.6	9.4	9.8	10.5
$\delta^1\text{H}(3/4)$	4.25	4.23	4.22	4.28
$^4J(\text{Sn}^1\text{H}(3,4))$	—	—	—	5.6
$\delta^1\text{H}(\text{SnMe})$	0.55	0.26	0.40	0.29
$^3J(\text{Sn}^1\text{H}_{\text{Me}})$	—	—	15.4	—
$^3J(^1\text{H}^1\text{H}_{\text{Me}})$	—	2.2	—	—
$^2J(^{119}\text{Sn}^1\text{H}_{\text{Me}})$	60.9	57.9	50.2	56.0
$\delta^{13}\text{C}(1)$	70.7	65.8	77.8	69.2
$^1J(^{119}\text{Sn}^{13}\text{C}(1))$	590.0	515.4	338.9	492.5
$^2J(\text{Sn}^{13}\text{C}_{\text{Me}})$	—	—	49.9	—
$\delta^{13}\text{C}(2/5)$	74.5	75.0	74.8	74.4
$^2J(\text{Sn}^{13}\text{C}(2/5))$	66.9	53.8	44.6	51.8
$\delta^{13}\text{C}(3/4)$	72.0	71.4	69.5	71.2
$^3J(\text{Sn}^{13}\text{C}(3/4))$	51.2	42.4	32.7	40.3
$\delta^{13}\text{C}(\text{SnMe})$	-1.1	-7.5	-8.2	-8.6
$^2J(\text{Sn}^{13}\text{C}_{\text{Me}})$	—	—	74.2	—
$^1J(^{119}\text{Sn}^{13}\text{C}_{\text{Me}})$	415.6	371.8	227.0	357.8
$\delta^{119}\text{Sn}$	125.5	-102.4	-43.4	-4.2
$^1J(^{119}\text{Sn}^{117}\text{Sn})$	—	—	5274.0	—

^a J (Hz); if resolved, the coupling to ^{119}Sn is given.

enyl rings being 3.4° in **6** and 4.3° in both **7A** and **7B**. The ring–tin bond lies nearly in the plane of the corresponding cyclopentadienyl ring in **6** ($\beta_1 = 1^\circ$, $\beta_2 = 2.3^\circ$), whereas it is somewhat more bent out of this plane (away from Fe) in **7A** ($\beta_1 = 5.5^\circ$, $\beta_2 = 7.5^\circ$) and **7B** ($\beta_1 = 7.9^\circ$, $\beta_2 = 4.5^\circ$). The most significant difference between **6** and **7** lies in the conformations of the two rings in the ferrocene moieties. Whereas the rings are close to staggered in the selenium complex **6** (twist angle $\tau = 27.5^\circ$), they are close to eclipsed in **7A** ($\tau = 4.8^\circ$) and **7B** ($\tau = 4.4^\circ$); the ideal staggered and eclipsed conformations require 36° and 0° respectively. (For the definition of angles α , β , δ and τ see also Ref. [3].)

The bond distances in the SnESn bridge system correspond to normal single bonds, cf. $[\text{SeSnMe}_2]_3$ 253 pm av. [4] and $[\text{TeSnMe}_2]_3$ 275 pm av. [5]. The angles at selenium ($101.0(1)^\circ$ in **6**) and tellurium

($92.5(1)^\circ$ in **7A**, $91.8(1)^\circ$ in **7B**) are also observed in the expected range; analogous angles are found in the 1,2,3-trichalcogena-[3]ferrocenophanes, $\text{Fe}(\text{C}_2\text{H}_4\text{Se})_2\text{Se}$ (Se–Se–Se 100.7° [6]) and $\text{Fe}(\text{C}_2\text{H}_4\text{Te})_2\text{Te}$ (Te–Te–Te $91.6(1)^\circ$ and $93.9(1)^\circ$ in molecules A and B respectively [7]); the angles at Se (100.8° av. [4]) and Te (96° av. [5]) in the six-membered rings $[\text{ESnMe}_2]_3$ are quite similar.

2.3. NMR spectroscopy

NMR data of the new [3]ferrocenophanes **4–7** are given in Table 3, whereas Table 4 contains selected NMR data of 1–3 and of 1,1'-bis(trimethylstanny)ferrocene (**8**), and Table 5 relevant NMR data of the bis(trimethylstanny)chalcogenides **9–12** for comparison. Assignments of ^1H and ^{13}C NMR signals were achieved as described previously [11]. A typical ^1H NMR spectrum

Table 5
 Selected NMR data of the bis(trimethylstanny)chalcogenides **9–12**, in C_6D_6 solution

Parameter	$(\text{Me}_3\text{Sn})_2\text{O}$ 9 [9]	$(\text{Me}_3\text{Sn})_2\text{S}$ 10 [10]	$(\text{Me}_3\text{Sn})_2\text{Se}$ 11 [10]	$(\text{Me}_3\text{Sn})_2\text{Te}$ 12 [10]
$\delta^{13}\text{C}(\text{SnMe})$	-1.9	-2.5	-2.3	-3.4
$^1J(^{119}\text{Sn}^{13}\text{C}_{\text{Me}})$	394.3	353.7	337.8	316.4
$^3J(\text{SnESn}^{13}\text{C}_{\text{Me}})$	n.m. ^a	5.5	—	—
$^2J(^{77}\text{SeSn}^{13}\text{C}_{\text{Me}})$	—	—	6.4	—
$\delta^{119}\text{Sn}$	124.1	87.1	42.7	-68.2
$^2J(^{119}\text{Sn}^{117}\text{Sn})$	347.3	215.8	232.7	226.8
$^1J(^{119}\text{Sn}^{77}\text{Se})$	—	—	1087.0	—
$^1J(^{125}\text{Te}^{119}\text{Sn})$	—	—	—	2817.0
$\delta^{77}\text{Se}$	—	—	-549.9	—
$\delta^{125}\text{Te}$	—	—	—	-1232.1

^a n.m. = not measured.

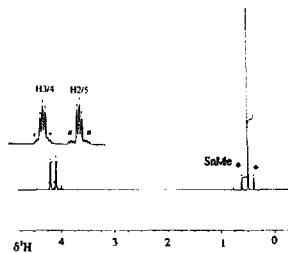


Fig. 3. 250 MHz ^1H NMR spectrum of **6** showing $^{117/119}\text{Sn}$ satellites as marked.

is shown in Fig. 3. Reaction mixtures are readily analyzed by ^{13}C NMR spectroscopy as shown in Fig. 4 for a mixture of **3** and **4**. Mutual assignment of ^1H and ^{13}C NMR signals follows from 2D $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlations as shown in Figs. 5 and 6, together with the information on relative signs of coupling constants $J(^{117/119}\text{Sn}, ^{13}\text{C})$ and $J(^{117/119}\text{Sn}, ^1\text{H})$.

The NMR data set for the new [3]ferrocenophanes **4–7** is in full accordance with the proposed structure. The regular changes in both $\delta^{119}\text{Sn}$ values and coupling constants $^1J(^{119}\text{Sn}, ^{13}\text{C}_{\text{Me}})$ (parallel to those in the series **9–12** in Table 5) as well as $^1J(^{119}\text{Sn}, ^{13}\text{C}(1))$ indicate that the ferrocenophane structure does not enforce any particular strain on the $\text{Me}_2\text{Sn}-\text{E}-\text{SnMe}_2$ moiety, as is confirmed by the structural parameters for **6** and **7**.

A linear relationship between the bond angle $\text{Me}-\text{Sn}-\text{Me}$ (ϕ) and the coupling constant $^1J(^{119}\text{Sn}, ^{13}\text{C}_{\text{Me}})$ has been proposed [13]: $^1J = 11.4\phi - 875$. This correlation does not hold for compounds **6** with $^1J = 364.1\text{ Hz}$ and $\phi = 114.1^\circ$ ($\phi_{\text{calcd}} = 108.7^\circ$) and **7** with $^1J = 336.8\text{ Hz}$ and $\phi = 111.4^\circ$ ($\phi_{\text{calcd}} = 106.3^\circ$). An

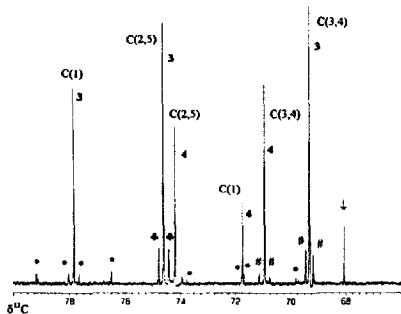


Fig. 4. 125.8 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a reaction mixture of **3** and **4**, recorded by using the reformatted INEPT pulse sequence [12] based on $^2J(^{13}\text{C}, ^1\text{H})$. The $^{117/119}\text{Sn}$ satellites are marked by asterisks. Ferrocene (**1**) is present as an impurity.

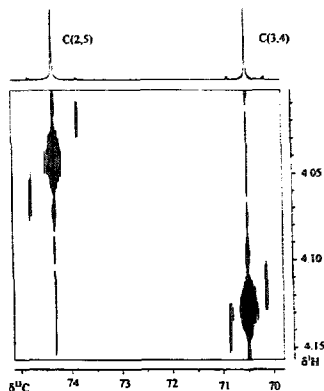


Fig. 5. Contour plot of the 62.9 MHz 2D $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlation of **7** showing the $^{13}\text{C}(2,5)$ and $^{13}\text{C}(3,4)$ resonances with cross-peaks according to $J(^{117/119}\text{Sn}, ^{13}\text{C})$ and $J(^{117/119}\text{Sn}, ^1\text{H})$. The tilt of the cross-peaks indicates alike signs of the coupling constants.

additional relationship between ϕ and $^2J(^{119}\text{Sn}, ^1\text{H}_{\text{Me}})$ has also been proposed [13]: $\phi = 0.0161 |^2J|^2 - 1.32|^2J| + 133.4$. The calculated values $\phi_{\text{calcd}} = 111.0^\circ$ (**6**) and $\phi_{\text{calcd}} = 110.3^\circ$ (**7**) also differ somewhat from the experimental values of 114.1° (**6**) and 111.4° (**7**).

Geminal coupling constants $^2J(^{119}\text{SnE}^{117}\text{Sn})$ depend mainly on the bond angle $\text{Sn}-\text{E}-\text{Sn}$ and on the nature of E. In order to discuss these data, the knowledge of the sign of 2J is required. In the cases of $\text{E} = \text{S}$ [14,10],

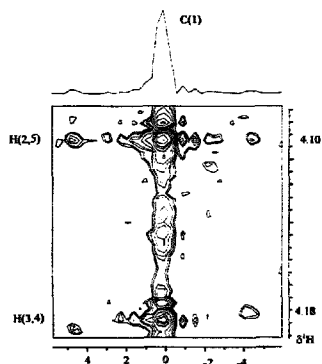


Fig. 6. Contour plot of the 62.9 MHz 2D $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlation of **7** showing the $^{13}\text{C}(1)$ resonance with cross-peaks according to $^3J(^{117/119}\text{Sn}, ^{13}\text{C}(1))$ without tilt for $^1\text{H}(2,5)$ cross-peaks and with a small positive tilt for $^1\text{H}(3,4)$ (corresponding to alike signs of $^2J(^{117/119}\text{Sn}, ^{13}\text{C}(1))$ and $^6J(^{117/119}\text{Sn}, ^1\text{H}(3,4))$).

Se [10] and Te [10], a negative sign of $^2J(\text{Sn},\text{Sn})$ has been experimentally determined. In the case of $E = \text{O}$, a positive sign was proposed for $\text{R}_2\text{Sn}-\text{O}-\text{SnR}_2$, including derivatives with a linear $\text{Sn}-\text{O}-\text{Sn}$ arrangement [15]. This is in agreement with the observed solvent dependence of $^2J(\text{Sn},\text{Sn})$ in stannoxanes [9], where smaller values $^2J(\text{Sn},\text{Sn})$ indicate a more acute bond angle $\text{Sn}-\text{O}-\text{Sn}$. However, a change of the sign of $^2J(\text{Sn},\text{Sn})$ in the fragment $\text{Sn}-E-\text{Sn}$ was not considered in the discussion of the relationship between $^2J(\text{Sn},\text{Sn})$ and the bond angle $\text{Sn}-E-\text{Sn}$ [16].

The magnitudes of the coupling constants $^2J(^{119}\text{Sn}, ^{117}\text{Sn})$ for 4–7 are similar to those for 9–12 (Table 5). In the case of 4, the solvent dependence of $^2J(\text{Sn},\text{Sn})$ is analogous to 9. Therefore, a positive sign of $^2J(\text{Sn},\text{Sn})$ is proposed for 4, although the coupling constants $^2J(\text{Sn},\text{Sn})$ are negative in 5–7.

3. Experimental section

3.1. General comments

All compounds were routinely handled under an atmosphere of Ar, and solvents were carefully dried and freshly distilled before use. Chromatography was carried out using columns (diameter 2–3 cm, length 30 cm) filled with degassed and Ar-saturated silica (Merck, Kieselgel 60, 60–200 mesh). The starting compounds 1,1'-bis(chlorodimethylstanny)ferrocene (1) [3], 1,1'-bis(dimethylstanny)ferrocene (2) [3] and 1,2-tetra-methyl-1,2-distanna-[2]ferrocenophane (3) [3], were prepared following literature procedures. Melting points: Büchi 510. EI (70 eV) mass spectra: Finnigan MAT 8500. The most intense peak of the computer-simulated mass pattern is listed. NMR spectra: ^1H , ^{13}C , ^{119}Sn NMR: Bruker ARX 250, recorded for diluted solutions (ca. 5–10%) in 5 mm tubes at $25 \pm 1^\circ\text{C}$ if not mentioned otherwise. Chemical shifts are given with respect to Me_4Si [$\delta^1\text{H}(\text{C}_6\text{D}_6\text{H})$ 7.15; $\delta^{13}\text{C}(\text{C}_6\text{D}_6)$ 128.0], Me_4Sn [$\Xi(^{119}\text{Sn}) = 37.290665 \text{ MHz}$], Me_2Se [$\Xi(^{77}\text{Se}) = 19.071523 \text{ MHz}$] and Me_2Te [$\Xi(^{125}\text{Te}) = 31.5497 \text{ MHz}$].

3.2. 1,3-Bis(dimethylstanna)-2-chalcogena-[3]ferrocenophanes 4–7

3.2.1. From 1 and Li_2E ($E = \text{O}, \text{S}, \text{Se}, \text{Te}$): general procedure

A solution of 0.25 g (0.45 mmol) of 1 in 10 ml of thf is added to 0.45 mmol Li_2E in 10 ml of thf, and the mixture is stirred for 2 h. The solvent thf is removed in vacuo and the residue is dissolved in hexane. Insoluble material is filtered off and the hexane solution is brought to dryness.

3.2.1.1. 1,3-Bis(dimethylstanna)-2-oxa-[3]ferrocenophane (4). Complex 4 was purified by sublimation to a cooling finger (15°C) to give 0.21 g (94.2%) of an orange crystalline solid (m.p. 74°C). EI MS: m/e (% rel. intensity) = 498 (80) [M^+]; 483 (20) [$\text{M}^+ - \text{Me}$]; 468 (100) [$\text{M}^+ - 2\text{Me}$]; 334 (30) [$\text{M}^+ - \text{SnMe}_2\text{O}$]; 304 (23) [$\text{Fe}(\text{C}_5\text{H}_4)_2\text{Sn}^+$].

3.2.1.2. 1,3-Bis(dimethylstanna)-2-thia-[3]ferrocenophane (5). Complex 5 was purified by chromatography on silica (using dichloromethane for elution) to give 0.19 g (82%) of 5 as an orange crystalline solid (m.p. 75°C). EI MS: m/e (% rel. intensity) = 514 (100) [M^+]; 499 (47) [$\text{M}^+ - \text{Me}$]; 484 (66) [$\text{M}^+ - 2\text{Me}$]; 334 (44) [$\text{M}^+ - \text{SnMe}_2\text{S}$]; 304 (60) [$\text{Fe}(\text{C}_5\text{H}_4)_2\text{Sn}^+$].

3.2.1.3. 1,3-Bis(dimethylstanna)-2-selena-[3]ferrocenophane (6). Complex 6 was purified by chromatography on silica (using dichloromethane–hexane (1/1) for elution) to give 0.22 g (85%) of 6 as an orange crystalline solid (m.p. 85°C). EI MS: m/e (% rel. intensity) = 560 (100) [M^+]; 545 (24) [$\text{M}^+ - \text{Me}$]; 530 (22) [$\text{M}^+ - 2\text{Me}$]; 515 (20) [$\text{M}^+ - 3\text{Me}$]; 334 (12) [$\text{M}^+ - \text{SnMe}_2\text{Se}$]; 304 (22) [$\text{Fe}(\text{C}_5\text{H}_4)_2\text{Sn}^+$].

3.2.1.4. 1,3-Bis(dimethylstanna)-2-tellura-[3]ferrocenophane (7). Complex 7 was purified by chromatography on silica (using dichloromethane–hexane (1/4) for elution) to give 0.08 g (28%) of 7 as an orange crystalline solid (m.p. 90°C). EI MS: m/e (% rel. intensity) = 610 (80) [M^+]; 595 (70) [$\text{M}^+ - \text{Me}$]; 580 (40) [$\text{M}^+ - 2\text{Me}$]; 334 (84) [$\text{M}^+ - \text{SnMe}_2\text{Te}$]; 304 (100) [$\text{Fe}(\text{C}_5\text{H}_4)_2\text{Sn}^+$].

3.2.2. From 2 and elemental chalcogen; general procedure

A toluene solution (20 ml) of 0.1 g (0.21 mmol) of 2 is prepared and excess chalcogen is added in one portion. The mixture is heated to reflux for 12 h. Toluene is removed and the residue is dissolved in hexane. After filtration the hexane is evaporated to give the [3]ferrocenophanes 4–7 in yields up to 90%.

3.2.3. From 3 and elemental chalcogen

In analogy to the procedure described in Section 3.2.2, the reaction of 0.1 g (0.21 mmol) of 3 in 10 ml of toluene in the presence of excess sulfur, selenium or tellurium affords 0.1 g of 5 (91%), 0.11 g 6 (93.5%) and 0.10 g 7 (79%) respectively.

3.2.3.1. 1,3-Bis(dimethylstanna)-2-oxa-[3]ferrocenophane (4). Method 1: a solution of 0.1 g (0.21 mmol) of 3 in 10 ml of toluene was stirred in the presence of air for 12 h. Yield: 0.03 g (29%) 4.

Method 2: a solution of 0.1 g (0.21 mmol) of 3 in

10 ml of thf was stirred in the presence of 5 mol% NaOEt under air. Yield: 0.04 g (38%) 4.

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