1,1′-Bis(stannyl)- and 1,1′-Bis(chlorostannyl)ferrocenes Studied by Multinuclear Magnetic Resonance, Temperature-Dependent ^{57}Fe- and ^{119}Sn-Mössbauer Spectroscopy, and Electrochemistry

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The 1,1′-bis(chlorostannyl)-substituted ferrocenes $Fe(C_5H_4–SnMe_2Cl)_2$ (**2**), $Fe(C_5H_4–SnMeCl_2)_2$ (**3**) and $Fe(C_5H_4–SnCl_3)_2$ (**4**) were prepared, starting from 1,1′-bis(trimethylstannyl)ferrocene (**1**). Treatment of the chlorides with $Li[AlH_4]$ afforded the 1,1′-bis(hydridostannyl)-subsituted ferrocenes $Fe(C_5H_4–SnMe_2H)_2$ (**5**), $Fe(C_5H_4–SnMeH_2)_2$ (**6**) and $Fe(C_5H_4-SnH_3)_2$ (**7**), respectively. All complexes **1**–**7** were studied by ^{1}H-, ^{13}C-, and ^{119}Sn-NMR spectroscopy with 1D and 2D techniques. The compounds **1**–**4** were investigated by temperature-dependent ^{119}Sn- and ^{57}Fe-Mössbauer spectroscopy. The electrochemistry of **1**–**5** gave evidence of reversible one-electron oxidation processes. The molecular structure of 1,1′-bis(trichlorostannyl)ferrocene (**4**) was determined by X-ray structural analysis, and there was no indication of intra- or intermolecular Sn···Cl···Sn interactions. This direct structural information proved to be consistent with both the Mössbauer and the solution NMR spectroscopic data.

1. Introduction

In spite of the multifaceted chemistry of organotin compounds,[1] ferrocene derivatives bearing stannyl substituents at the cyclopentadienyl rings have received only scant attention.[1−4] Recent interest has focused on ferrocenophanes with one,[5] two,[6] and three[6,7] diorganostannylene moieties in the bridge. Other [3]ferrocenophanes with tin atoms in 1,3-positions and chalcogen,[7,8] nitrogen,[9] phosphorus,[9] or arsenic[9] in 2-position have been reported. The 1-stanna-[1]ferrocenophane undergoes ring-opening polymerization,[5,10] and transition-metal fragments can be inserted into the Sn−C(1) bond by oxidative addition.[11] The reaction of 1,2-distanna-[2]ferrocenophane with $Pt(C_2H_4)(PPh_3)_2$ provides access to 1,3-distanna-2-platina-[3]ferrocenophanes,[12,13] which are examples of the active intermediates in the Pt^0-catalyzed distannation of alkynes.[6,14,15]

In the present work we report on the synthesis and properties of potential precursors of ferrocenophanes containing two tin atoms, the 1,1′-disubstituted ferrocenes **1** bearing trimethylstannyl groups ($SnMe_3$), **2**−**4** bearing chlorostannyl groups ($SnMe_2Cl$, $SnMeCl_2$, and $SnCl_3$), and **5**−**7** bearing hydridostannyl groups ($SnMe_2H$, $SnMeH_2$, SnH_3) (Scheme 1). Obviously, all these ferrocene derivatives can serve as starting materials for novel organotin compounds. Their structures are of interest with respect to intra- and intermolecular interactions through chloro or hydrido bridges between tin atoms. Therefore, we have studied the compounds **1**−**7** by NMR spectroscopy in solution, by temperature-dependent ^{57}Fe- and ^{119}Sn-Mössbauer spectroscopy (**1**−**4**), by X-ray crystallography (**4**) and by electrochemical techniques (**1**−**5**).

2. Results and Discussion

2.1. Syntheses

1,1′-Bis(trimethylstannyl)ferrocene (**1**) served as starting material for all preparative work. It reacts with tin tetrachloride to give the complexes **2**−**4** as stable products which can be isolated and purified by recrystallization from hexane or pentane. However, as shown in Scheme 1, the compounds **2**−**4** are obtained in higher yield and purity by using a slightly different approach. Thus, the reaction of **1** with dimethyltin dichloride affords **2** in ca. 90% yield; the properties of **2** are in agreement with those reported previously.[3f] Both **1** or **2** react with an excess of tin tetrachloride to give **4**, whereas **3** is best accessible in the pure state by the reaction of **4** with tetramethyltin in a 1:1 ratio.

Treatment of the chlorides **2**−**4** with $Li[AlH_4]$ in ether at 0°C (**5**) or −30°C (**6**, **7**) affords the tin hydrides **5**−**7**. These are more labile than the parent chlorides and were isolated as orange-yellow oils. Although they were pure according to the NMR spectra, they could not yet be crystallized.

2.2. NMR-Spectroscopic Studies

All NMR spectra (Table 1) support the proposed structures of **1**−**7**. No indication of intermolecular association can be found in C_6D_6 or $CDCl_3$ solutions. Chemical shifts and coupling constants vary in such a regular way that intramolecular interactions between the stannyl groups also

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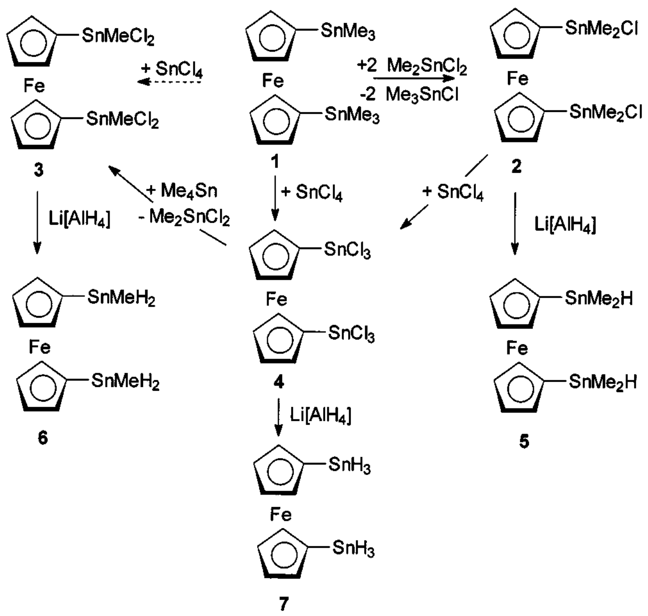

Scheme 1. Synthesis of complexes **2−7**

appear to be unlikely. Thus, intramolecular hydride exchange between the two tin atoms in **5−7** must be slow on the NMR time scale, since the magnitude of the coupling constants $|^1J(^{119}Sn,^1H)|$ is observed in the usual range [e.g. $PhSnH_3$: $^1J(^{119}Sn,^1H)$ = 1920 Hz[16]]. $^1H/^1H$-NOE difference spectra[17] show the proximity of the methyltin groups to the hydrogen atoms in 2,5- and 2′,5′-positions of the cyclopentadienyl rings, as expected, but also to the hydrogen atoms in 3′,4′- and 3,4-positions. This indicates that the stannyl groups on average avoid close mutual contacts.

^1H- and ^{13}C-resonance signals of the ferrocene unit were assigned on the basis of 2D heteronuclear $^{13}C/^1H$ shift correlations, of ^{13}C-^{13}C coupling constants (e.g. in **4**, as has been described for **1**[4]), and of the consistent trend in the ^{119}Sn-^{13}C coupling constants. The signal-to-noise ratio of the ferrocene-$^{13}C(1,1')$ resonances was much improved by using the refocused INEPT pulse sequence[18] based on $^{2,3}J(^{13}C,^1H)$, as has been suggested previously.[19] The observation of relevant cross peaks for ^{119}Sn satellites in the 2D experiments[20] revealed that the signs of the coupling constants $^3J[^{119}Sn,^1H(2,5)]$, $^4J[^{119}Sn,^1H(3,4)]$, $^2J[^{119}Sn,^{13}C(2,5)]$, and $^3J[^{119}Sn,^{13}C(3,4)]$ are alike. A typical example is shown in Figure 1. Taking into account the negative sign of $\gamma(^{119}Sn)$ and the presumably negative sign of $^3J(^{119}Sn,^1H)$ or $^3J(^{119}Sn,^{13}C)$ (reduced coupling constants $^3K > 0$), all these coupling constants should be < 0.

The changes in the coupling constants $^1J(^{119}Sn,^{13}C)$ in **1−4** are best explained by the concept of rehybridization[21] as a consequence of replacing the methyl groups in **1** by the more electronegative chloro substituents. The “s character” of the remaining Sn−C hybrid orbitals increases with increasing number of Sn−Cl bonds. The analogous trend, although less pronounced, is found in the case of the hydrides. An increasing number of Sn−H bonds leads to larger coupling constants $^1J(^{119}Sn,^{13}C)$. At the same time, the magnitude of $^1J(^{119}Sn,^1H)$ increases from **5−7**.

The tin chemical shifts $\delta^{119}Sn$ are known to be extremely sensitive even to weak associative interaction.[16] In the case of compounds **1−7**, only small changes in the $\delta^{119}Sn$ values result from solvent effects, dilution, or changes in temperature. The similarity between phenyl and ferrocenyl groups is reflected by the $\delta^{119}Sn$ data, e.g. of **1** (−4.2) and $PhSnMe_3$ (−28.6[16]), **4** (−23.2) and $PhSnCl_3$ (−63[16]), and **7** (−330.7) and $PhSnH_3$ (−320[16]). Spin-spin coupling between ^{119}Sn and ^{117}Sn nuclei was not observed in the complexes **1−7**. Altogether, the $\delta^{119}Sn$-NMR data indicate negligible inter- or intramolecular interactions in **1−7**.

2.3. X-ray Structural Analysis of 1,1′-Bis(trichlorostannyl)ferrocene 4

In addition to the ferrocenophanes mentioned in the introduction, there is only one report of an X-ray analysis of a 1,1′-bis(stannyl)ferrocene, namely 1,1′-bis(triphenylstan-

Table 1. ^1H-, ^{13}C-, and ^{119}Sn-NMR parameters[a] of the 1,1′-bis(stannyl)ferrocenes **1−7**

			δ^1H			$\delta^{13}C$			$\delta^{119}Sn$
	Stannyl	2/5-H	3/4-H	H_{Me}	C-1	C-2/5	C-3/4	C_{Me}	
1	$SnMe_3$	4.07 [10.5]	4.28 [5.6]	0.29 [56.0]	69.2 [492.5]	74.4 [51.8]	71.2 [40.3]	−8.68 [357.8]	−4.2
2	$SnMe_2Cl$	4.08 [9.6]	4.25 [6.3]	0.55] [60.9]	70.7 [590.0]	74.5 [66.9]	72.0 [51.2]	−1.1 [415.6]	125.5
3	$SnMeCl_2$	4.25 [10.6]	4.28 [13.0]	0.65 [74.7]	73.2 [776.4]	74.7 [96.9]	73.1 [75.4]	5.77 [508.9]	100.4
4	$SnCl_3$	3.89 [14.5]	4.18 [20.8]		73.0 [1191.7]	74.2 [134.6]	74.0 [113.5]		−23.2
5	$SnMe_2H$[b]	3.99 [9.4]	4.23 [n.r.]	0.26 [57.9]	65.8 [514.4]	75.0 [53.8]	71.4 [42.8]	−7.5 [371.8]	−102.4
6	$SnMeH_2$[c]	3.93 [n.r.]	4.17 [n.r.]	0.25 [61.0]	62.6] [546.6]	75.9 [56.5]	71.8 [44.9]	−13.0 [387.0]	−210.5
7	SnH_3[d]	3.89 [n.r.]	4.12 [n.r.]		59.2 [583.2]	76.8 [59.6]	72.3 [46.5]		−330.7

[a] In C_6D_6 at 25°C (ca. 5−15%), coupling constants $J(^{119}Sn,^1H)$ and $J(^{119}Sn,^{13}C)$ are given in brackets [±0.3 and ±1 Hz, respectively]; n.r.: not resolved. − [b] $\delta^1H(SnH)$ = 5.45 [1824]; $^3J(^1H,Sn,C,^1H)$ = 2.2 Hz. − [c] $\delta^1H(SnH)$ = 5.24 [1876]; $^3J(^1H,Sn,C,^1H)$ = 2.5 Hz. − [d] $\delta^1H(SnH)$ = 4.97 [1947].

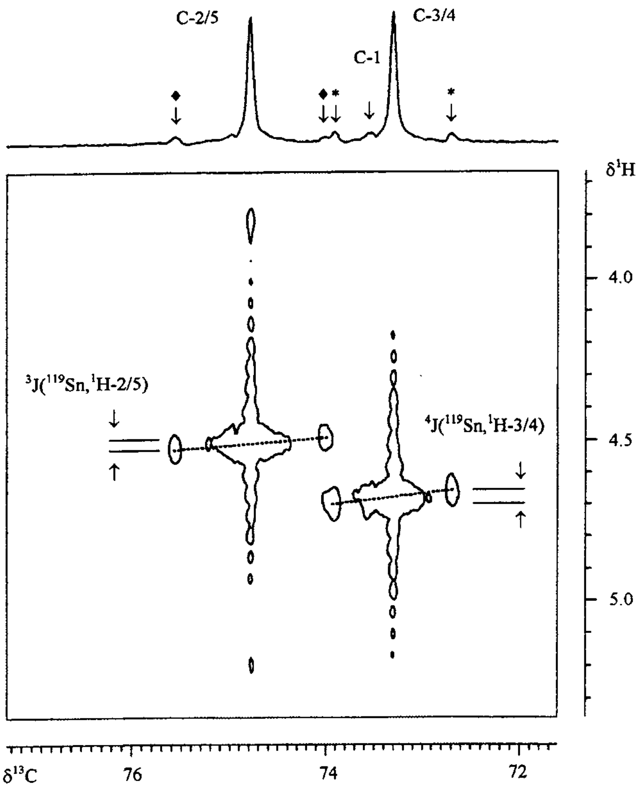

Figure 1. Contour plot of the 62.9-MHz 2D $^{13}C/^{1}H$ HETCOR experiment for $Fe(C_5H_4SnMeCl_2)_2$ (**3**) in $CDCl_3$ {$\delta^1H(2,5) = 4.51$ [12.6 Hz] and $\delta^1H(3,4) = 4.68$ [13.2]}, based on $^1J(^{13}C,^1H)$, showing the region of $^{13}C(2,5)$ and $^{13}C(3,4)$ resonances together with the $^{117/119}Sn$ satellites; the positive tilt of the cross peaks for these satellites indicates like signs of $^nJ(Sn,^{13}C)$ and $^{n+1}J(Sn,^1H)$ ($n = 2, 3$)

nyl)ferrocene.[22] In this complex, the stannyl groups are in *trans* positions, and the torsional angle τ between the cyclopentadienyl rings is 163.4(4)° (with respect to the positions of the substituted cyclopentadienyl carbon atoms). To the best of our knowledge, there is also just one example of a molecular structure of an organotin trichloride, namely methyltin trichloride, in which the surroundings of the tin atoms correspond to compressed tetrahedrons [CSnCl 120.3(3), 113.5(1)°; ClSnCl 103.58(6)°], and weak intermolecular Sn···Cl···Sn interactions [$d_{Sn-Cl} = 371.4(2)$ pm] are proposed in order to account for the arrangement of the $MeSnCl_3$ molecules in infinite chains.[23] The molecular structure of **4** is depicted in Figure 2 together with selected bond lengths and angles.[24] The $SnCl_3$ groups are not in *trans* positions; the torsional angle τ between the cyclopentadienyl rings is 85.3°. All intramolecular Sn···Cl···Sn contacts must be extremely weak [shortest distance $d_{Sn-Cl} = 526$ pm], and the same is true for intermolecular contacts [shortest distance $d_{Sn-Cl} = 395$ pm] in spite of the infinite chains built by molecules of **4**, as shown in Figure 3. Figure 3 also shows the separation of the $SnCl_3$ from the ferrocene parts in the crystal structure. The distortion from tetrahedral symmetry around the tin atoms in **4** is even less than in $MeSnCl_3$. The complete absence of intramolecular Sn···Cl···Sn bridging in **4** is surprising, since this type of bonding is well established in other organotin halides, e.g. in tris(dialkylhalostannyl)amines.[25]

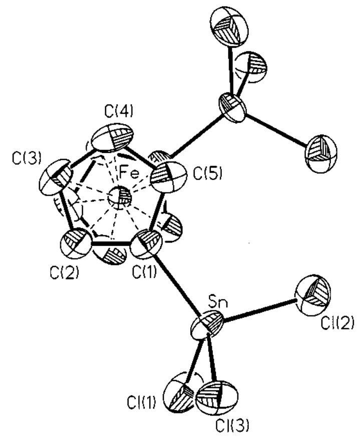

Figure 2. ORTEP plot (thermal ellipsoids represent a 50% probability; hydrogen atoms are not shown) of the molecular structure of 1,1′-bis(trichlorostannyl)ferrocene **4**; selected bond lengths [pm] and angles [°]: Sn−Cl(1) 229.2(1), Sn−Cl(2) 230.4(1), Sn−Cl(3) 230.4(1), Sn−C(1) 207.1(4), Fe−C 204.1−205.3, C−C 140.0−143.9; Cl(1)−Sn−Cl(2) 104.4(1), Cl(1)−Sn−Cl(3) 104.7(1), Cl(2)−Sn−Cl(3) 111.6(1), Cl(1)−Sn−C(1) 115.6(1), Cl(2)−Sn−C(1) 111.6(1), Cl(3)−Sn−C(1) 116.6(1)

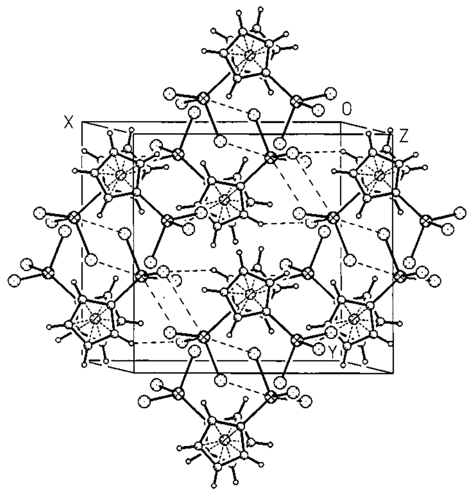

Figure 3. Packing of 1,1′-bis(trichlorostannyl)ferrocene **4** in the crystal lattice (perspective view on the *xy* plane [001])

2.4. ^{57}Fe- and ^{119}Sn-Mössbauer Spectroscopy

The Mössbauer parameters at 90 K as well as their temperature dependencies are summarized in Table 2. All of the ^{57}Fe-resonance spectra consist of well-resolved doublets having isomer shifts (I.S.) of about 0.52−0.53 mm s^{-1} at 90 K and quadrupole splittings (Q.S.) of 2.3 mm s^{-1}. These values are characteristic[26] of ferrocenyl moieties in which each cyclopentadienyl ring is ligated by a single σ bond to a main-group atom, including Sn, and are otherwise not remarkable. A typical spectrum (of **4** at 90 K) is shown in the upper part of Figure 4. The M_{eff} values, calculated[27] from the temperature dependence of the I.S. parameter fall in the range of 112−142 Da, consistent with the predomi-

Table 2. Mössbauer data (^{57}Fe and ^{119}Sn) for the compounds **1**−**4**

	I.S. (90 K) [mm s^{-1}]	Q.S. (90 K) [mm s^{-1}]	$-\mathrm{d}\ln A/\mathrm{d}T$ $\times 10^{3}$[c]	$-\mathrm{dI.S.}/\mathrm{d}T$ $\times 10^{4}$[c]
Fe[a] resonances				
1	0.536(2)	2.336(4)	12.07	3.07(18)
2	0.536(1)	2.343(3)	8.56	3.59(15)
3	0.521(2)	2.327(5)	5.29	2.93(18)
4	0.523(1)	2.270(3)	5.55	3.71(11)
Sn[b] resonances				
1	1.235(3)	0.30(2)	31.67	3.12(57)
2	1.368(4)	3.006(6)	21.85	1.61(47)
3	1.131(6)	1.781(7)	22.08	2.22(63)
4	1.414(26)	3.137(4)	17.11	2.91(24)

[a] Relative to metallic iron at room temperature. − [b] Relative to $BaSnO_3$ at room temperature. − [c] Assuming linear regression fits.

nantly covalent character of the ferrocenyl ligand bond. As noted previously,[28] the Q.S. is temperature-insensitive and reflects primarily the thermal expansion coefficients of the covalent lattice.

With the exception of the results for **1**, the ^{119m}Sn-Mössbauer spectra also consist of well-resolved doublets, and these data (at 90 K) are again summarized in Table 2. A representative spectrum (of **4** at 90 K) is shown in the lower half of Figure 4. In contrast, the ^{119m}Sn-Mössbauer spectrum of **1** appears to consist of a single resonance maximum, despite the obvious lack of cubic symmetry around the metal atom. This lack of a resolvable quadrupole splitting in the case where the Sn^{IV} atom is ligated to nearest-neighbor atoms lacking nonbonding lone pairs has been extensively discussed in the literature.[29−33] When lone-pair electrons are present on the atom(s) σ-bonded to the Sn, a π-electron back donation into empty 6p orbitals of the tin atom is assumed to give rise to a large electric field gradient at the metal center. In the present case, the three $Sn-CH_3$ and the single $Sn-C_{Cp}$ bonds, although clearly not of T_d symmetry, give rise to four sp^3-hybrid orbitals on the tin atom which are sufficiently similar to produce a very small field gradient at the Mössbauer-active atom site. Using a Lorentzian line shape minimization procedure, the quadrupole splitting at 90 K is calculated to be ca. 0.30(2) mm s^{-1}; that is less than the natural line width.

The other three compounds **2**−**4** represent an interesting series of bonding interactions, especially with respect to the field gradients generated by the σ and π bonds around the metal center. In previous studies of organotin chlorides, the question of the effect of coordination around the Sn atom has always posed a complication in the interpretation of the relevant Mössbauer data. Thus, Me_3SnCl, which is monomeric in the vapor phase,[34] is polymeric in the solid[35] with a distorted trigonal-bipyramidal environment around the Sn atom. Similarly, the X-ray diffraction data for Me_2SnCl_2[36] reflect a sixfold coordination around the Sn atom, in which two chlorine atoms bridge adjacent Sn atoms and the two methyl groups occupying axial positions around the quasi-octahedral metal atom. Recent X-ray diffraction data[23] for $MeSnCl_3$ have been referred to above and indicate weak intermolecular Sn−Cl−Sn bonding to account for the infinite chain formation suggested by the NQR data of Petrosyan et al.,[37] but the theoretical calculations of Manning and Grodzicki[38a] and Grodzicki et al.[38b] have assumed four-coordinate metal centers in their discussion of the Q.S. and I.S. parameters of this molecule. Clearly, these variable coordinations around Sn complicate the interpretation of the Mössbauer parameters of the methyl Sn halides. In the present series of compounds, in which the bulky nature of the ferrocenyl ligand(s) clearly precludes coordination numbers larger than 4, this complication is obviated. The absence of a resolvable Q.S. in the Sn spectra of **1** has already been noted (above). The readily observed non-zero Q.S. parameter for **2**, **3**, and **4** is readily accounted for by the π back-donation effect, and the relative similarity of the Q.S. parameters for **2** and **4**, and its much smaller value for **3**, is consistent with this rationalization. Thus, **2** has one Sn−Cl and three Sn−C and **4** has three Sn−Cl and one Sn−C bond. The distortion from tetrahedral symmetry arising from one and three π bonds to the metal atom should have similar influences but with opposite sign on the field gradient at the metal center. The

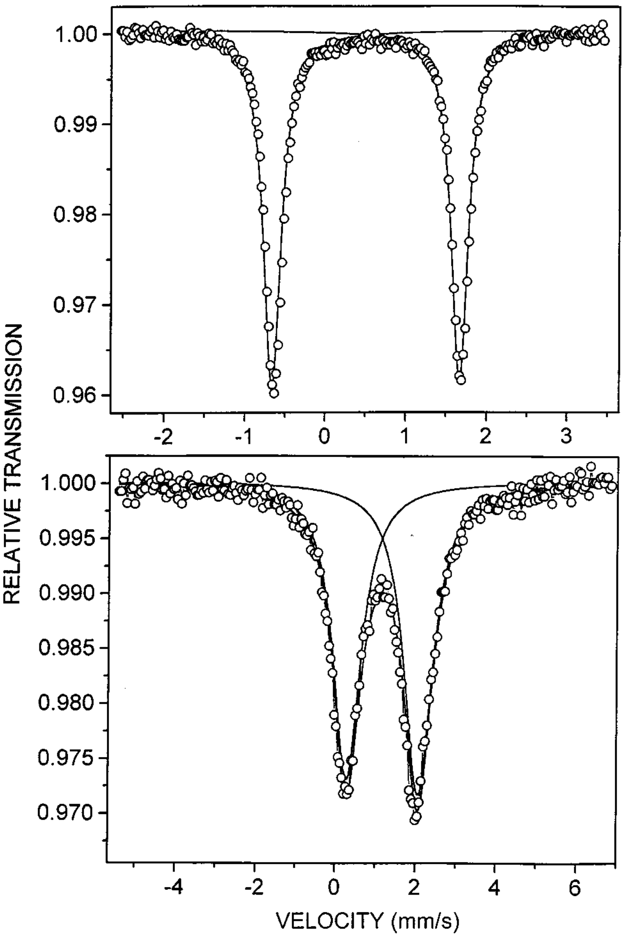

Figure 4. Representative Mössbauer spectra for **4** at 90 K; the upper trace is that of the ^{57}Fe-resonance effect, while the lower trace is that for the ^{119}Sn resonance; the full lines are the fitted data to the experimental points with each component of the doublet fitted separately; the velocity scales are relative to the centroid of a metallic iron absorbance (upper trace) and a $BaSnO_3$ absorber spectrum absorbance (lower trace) at room temperature

effect of the bonding in **3** (i.e. two Sn−Cl bonds and one $Sn-C_{CH3}$ and one $Sn-C_{Cp}$ bond) is reflected in the ca. 40% reduction in the Q.S.

Finally, with respect to both the ^{57}Fe- and the ^{119}Sn-Mössbauer data, it is appropriate to observe that the temperature dependencies of the I.S., Q.S. and resonance effect (as reflected in the area under the resonance curve for optically “thin” absorbers) are all smooth, continuous functions in the temperature range from 90 to ca. 300 K. Thus, there is no evidence of either structural or crystallographic phase transitions in this interval for any of the compounds examined in this study. As can be noted in Table 2, the $-\mathrm{dln}A/\mathrm{d}T$ parameter of the ^{57}Fe resonance for **1** is significantly larger than for **2**, which in turn is larger than the value of this parameter for **3** and **4**, indicating a larger mean-square amplitude of vibration of the iron atom in **1** than in **4** under comparable conditions. Similarly (but less pronounced) is the decrease of the $-\mathrm{dln}A/\mathrm{d}T$ parameter extracted from the ^{119}Sn spectra, again reflective of a larger mean-square amplitude of vibration of the Sn atom in **1** than in **4**. This observation is clearly consistent with the fact that **1** is a liquid at room temperature, **2** is a low-melting solid, and **3** and **4** are crystalline materials, and thus the lattice temperature (as reflected in the lattice phonon spectrum) increases with the ratio of the number of chlorine to methyl group ligands in this series. However, there is persuasive evidence from the Mössbauer hyperfine parameters and their temperature dependencies that there are no significant intermolecular interactions in these complexes in the solid state, in agreement with the solution (C_6D_6 or $CDCl_3$) NMR data cited above.

2.5. Electrochemistry of 1−5

The typical redox behavior of the stannylferrocenes **1**−**5** is shown in Figure 5 for the example of $Fe(C_5H_4-SnMe_3)_2$ (**1**).

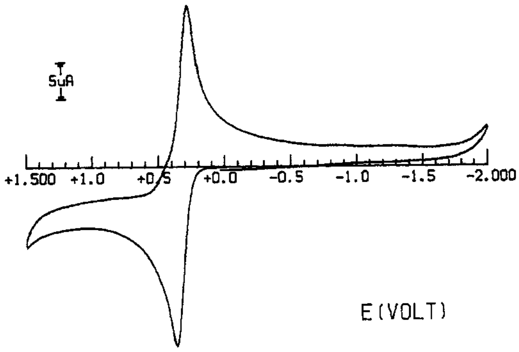

Figure 5. Cyclic voltammetric response recorded at a platinum electrode in a CH_2Cl_2 solution containing **1** ($1.1\ 10^{-3}$ mol dm^{-3}) and $[NBu_4][PF_6]$ (0.2 mol dm^{-3}); scan rate 0.2 Vs^{-1}

As expected, it is only the oxidation of the ferrocene unit which can be observed, and it is a chemically reversible process. As a matter of fact, controlled potential coulometric tests ($E_W = +0.7$ V) show the consumption of one electron per molecule. The originally yellow solution turns blue and exhibits an absorption band at $\lambda_{max} = 636$ nm which confirms the iron-centered oxidation to the ferricenium cation. The chemical reversibility of the one-electron removal is proven by the fact that the exhaustively oxidized solution of **1** displays a cyclic voltammetric profile quite complementary to that shown in Figure 5.

Analysis of the cyclic voltammetric responses with scan rates varying from 0.02 to 1.00 Vs^{-1} is diagnostic for an essentially electrochemically reversible anodic step: The current ratio i_{pe}/i_{pa} is constantly equal to unity; the current function $i_{pa}v^{-1/2}$ remains constant; the peak-to-peak separation ΔE_p slightly departs from the theoretical value of 60 mV.[41]

The same behavior is exhibited by the complexes **2**, **3**, and **5**. In contrast, although the oxidation process of **4** also appears uncomplicated on the cyclic voltammetric time scale ($E^{0\prime} = +0.73$ V), its monocation $\mathbf{4}^+$ proved to be unstable on the longer time scale of macroelectrolysis, and the electrogenerated blue solution gives rise to a reversible reduction process at $E^{0\prime} = +0.37$ V (ferrocene).

Table 3 compiles the electrochemical parameters for the oxidation process of the complexes **1**−**5**, together with some related parameters. It is easy to conclude that the formal electrode processes are exclusively governed by the inductive effects of the methyl and chloro substituents of the stannyl groups. As a matter of fact, a plot of $E^{0\prime}$ values vs. the inductive (Hammett) parameters F[42] of these substituents affords a linear correlation coefficient of 0.99, according to the equation

$$E^{0\prime}\ [\mathrm{V}] = 0.16\ \Sigma F + 0.33$$

Table 3. Electrochemical and spectroscopic characteristics for the oxidation process of the complexes **1**−**5** in dichloromethane solution; ΣF represents the inductive effects of the substituents present in the stannyl groups

$Fe(C_5H_4-X)_2$ X =	$E^{0\prime}(0/+)$ [V]	ΔE_p[a]	λ_{max}[b] [nm]	ΣF
$SnMe_3$ (**1**)	+0.32	76	636	0.06
$SnMe_2Cl$ (**2**)	+0.46	73	634	0.88
$SnMeCl_2$ (**3**)	+0.65	92	−	1.70
$SnCl_3$ (**4**)	+0.73	70	[c]	2.52
$SnMe_2H$ (**5**)	+0.36	80	635	0.04
H	+0.37	78	620	−

[a] Measured at 0.1 Vs^{-1}. − [b] Referred to the oxidized species. − [c] See text.

3. Conclusions

Synthetic routes to 1,1′-bis(stannyl)ferrocenes are straightforward, both for chlorostannyl and hydridostannyl groups. These functionally substituted compounds should be useful starting materials for ferrocenophanes and other 1,1′-bis(stannyl)ferrocenes. There are no indications for intra- or intermolecular interactions between the stannyl groups, neither by Sn···Cl···Sn nor Sn···H···Sn bridging. This is obvious from investigations in the solid state by temperature-dependent ^{119}Sn- and ^{57}Fe-Mössbauer spectroscopy (**1**−**4**) and X-ray crystallography (**4**), and also in solution by multinuclear magnetic-resonance spectroscopy (**1**−**7**). The electrochemistry of **1**−**5** revealed the expected result by reversible one-electron oxidation processes involving the respective ferricenium cations.

Experimental Section

General: All compounds were handled in dry argon, and carefully dried solvents were used for syntheses and preparation of the samples for NMR measurements. Starting materials were either used as commercial products without further purification (ferrocene, Me_3SnCl, Me_2SnCl_2, $SnCl_4$, *n*-butyllithium 1.6 M in hexane) or prepared as described [$Fe(C_5H_4SnMe_3)_2$ (**1**)[4]].In general, all reactions were monitored by ^{119}Sn-NMR spectroscopy. − Electron impact (EI) mass spectra: Finnigan MAT 8500 with direct inlet. − NMR measurements: Bruker ARX 250 or DRX 500 {^1H, ^{13}C, ^{119}Sn NMR [inverse gated ^1H-decoupled or refocused INEPT spectra,[19] based on $^2J(^{119}Sn,^1H) = 55-75$ Hz]}. Chemical shifts are given relative to Me_4Si [$\delta^1H(CHCl_3/CDCl_3) = 7.24$, $\delta^1H(C_6D_5H) = 7.14$, $\delta^{13}C(CDCl_3) = 77.0$, $\delta^{13}C(C_6D_6) = 128.0$, $\delta^{13}C(C_6D_5CD_3\ ) = 20.4$], and Me_4Sn [($\delta^{119}Sn = 0$ for $\Xi(^{119}Sn) = 37.290665$ MHz].

X-ray Structural Analysis of 4: $C_{10}H_8Cl_6FeSn_2$; $M = 634.1$; orange crystal of irregular shape; size [mm] 0.35 × 0.20 × 0.18, monoclinic; space group *C*2/c, $a = 12.859(2)$, $b = 11.867(2)$, $c = 12.212(2)$ Å, $\beta = 109.21(2)°$, $V = 1759.6(5)$ Å^3, $Z = 4$, ρ(calcd.) = 2.394 Mg/m^3; absorption coefficient $\mu = 4.523$ mm^{-1}, $F(000) = 1184$. − Data collection: Siemens *P*4 diffractometer, Mo-K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator, 296 K; the single crystal was mounted in a Lindemann capillary; 2θ range 3.0−55.0°; scan type ω; reflections collected 4406, independent reflections 2026, observed reflections 1982 [$F > 2.0\ \sigma(F)$]; semi-empirical absorption correction; min./max. transmission 0.5335/1.000. − Structure solution: direct methods [SHELXTL PLUS (VMS)]; extinction correction $\chi = 0.00059(3)$, all atoms except the hydrogen atoms are described with anisotropic temperature factors, all hydrogen positions were refined by using the riding model and fixed *U*; weighting scheme $w^{-1} = \sigma^2(F)$; number of parameters refined 88; $R = 3.29\%$, $wR = 3.30\%$ (observed data); largest difference peak/hole 1.74/−0.53 e/Å^3.

Mössbauer Spectra: The experimental details relating to the acquisition of both ^{57}Fe- and ^{119}Sn-Mössbauer data have been described previously.[39][40] All samples were prepared as optically thin absorbers, and mixed with BN to minimize preferential crystallite orientation with respect to the γ-ray axis of the spectrometer. The isomer shift standards used in this study are the centroids of metallic iron and $BaSnO_3$ spectra at room temperature. Spectrometer calibration was effected by the use of a 1.85 mg m cm^{-2} metallic iron absorber at room temperature. Temperature control over the period of data acquisition (generally 4−24 h, depending on temperature) was stable to better than ±0.5 K. To minimize statistical errors, more than 10^6 counts per channel were accumulated at each temperature point.

Electrochemistry: Materials and apparatus for electrochemistry have been described elsewhere.[43] All potential values are referred to the Saturated Calomel Electrode (SCE).

1,1′-Bis(chlorodimethylstannyl)ferrocene (2): A Schlenk tube was filled with $Fe(C_5H_4SnMe_3)_2$ (**1**) (1.41 g; 2.8 mmol) and Me_2SnCl_2 (1.23 g; 5.6 mmol) was added at 0°C. The mixture was heated at 140°C for 3 h while Me_3SnCl sublimed and was collected at a cooling finger (15°C). Then the mixture was cooled to room temperature and remaining traces of Me_3SnCl und Me_2SnCl_2 were removed in vacuo. A viscous dark orange oil was left which crystallized upon cooling in hexane to give an orange solid (1.4 g; 90%; m.p. 85°C). − EI MS; *m/z* (%): 554 (100) [M$^+$].

1,1′-Bis(dichloromethylstannyl)ferrocene (3): A two-necked flask containing $Fe(C_5H_4SnCl_3)_2$ (**4**) (1.79 g; 2.82 mmol) was cooled to 0°C and tetramethyltin (0.429 ml; 3.10 mmol, slight excess) was added. After warming slowly to 60°C, the mixture was stirred at this temperature for 4 h. After cooling, Me_2SnCl_2 and Me_3SnCl were removed in vacuo. Extraction with toluene (15 ml), filtration, removal of toluene, and washing with hexane afforded 0.79 g (65%) of a yellow solid (m.p. 126°C, dec.). − EI MS; *m/z* (%): 594 (100) [M$^+$].

1,1′-Bis(trichlorostannyl)ferrocene (4): Tin tetrachloride (0.9 ml; 7.54 mmol) was added to a solution of $Fe(C_5H_4SnMe_2Cl)_2$ (**2**) (1.60 g; 2.90 mmol) in CH_2Cl_2 (5 ml) and hexane (15 ml) at 0°C. The color of the reaction mixture changed rapidly from yellow to green; the mixture was stirred for 2 h at 30°C. Then all volatile material was removed in vacuo and CH_2Cl_2/hexane (1:10, v/v; 20 ml) was used to extract the product. After filtration of the yellow solution and removal of the solvents, the product **4** (1.56 g; 85%; m.p. 122°C dec.) was obtained as a yellow solid. Recrystallization from hexane afforded single crystals suitable for X-ray analysis. − EI MS; *m/z* (%): 634 (100) [M$^+$].

1,1′-Bis(dimethylstannyl)ferrocene (5): A solution of $Fe(C_5H_4SnMe_2Cl)_2$ (0.73 g; 1.3 mmol) in ether (20 ml) was added to a suspension of $LiAlH_4$ in ether (30 ml) at −30°C. The mixture was stirred for 5 h at room temperature. After filtration and removal of ether, a yellow oil was left (6.07g; 96%). − EI MS; *m/z* (%): 486 (100) [M$^+$].

1,1′-Bis(methylstannyl)ferrocene (6): A solution of $Fe(C_5H_4SnMeCl_2)_2$ (490 mg; 0.83 mmol) in ether (20 ml) was added dropwise to a suspension of $LiAlH_4$ (120 mg; 3.16 mmol) in ether (30 ml) at −30°C. The mixture was stirred for 2 h at room temperature. After removal of the solvent in vacuo, the residue was extracted with hexane, insoluble material was filtered off and hexane was removed in vacuo from the yellow-orange solution. A yellow-orange oil was left (0.37 g; 98%). − EI MS; *m/z* (%): 456 (30) [M$^+$].

1,1′-Bis(stannyl)ferrocene (7): The same procedure with **4** as starting material, as described for **6**, afforded **7** in almost quantitative yield as a yellow-orange oil. − EI-MS; *m/z* (%): 429 (30) [M$^+$].

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