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Ferrocenylethynyltin Compounds – Characterization and Reactivity towards Triethylborane

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Dedicated to Professor Henri Brunner on the occasion of his 70th birthday

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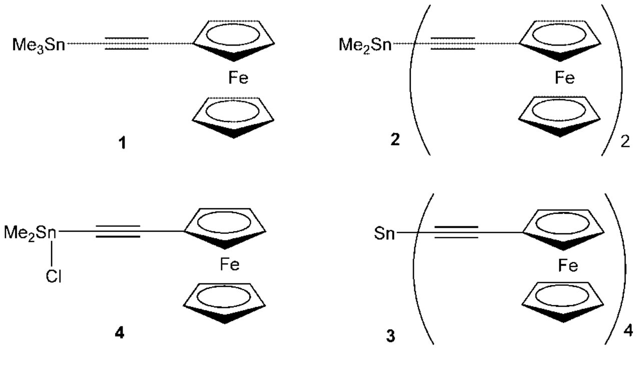
Ferrocenylethynyl(trimethyl)tin (**1**), bis(ferrocenylethynyl)dimethyltin (**2**), tetrakis(ferrocenylethynyl)tin (**3**), and chloro(ferrocenylethynyl)dimethyltin (**4**) have been prepared and characterized in solution by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. Solid-state MAS ^{13}C and ^{119}Sn NMR spectra were measured for **2** and **3**, and the molecular structure of one of the modifications of **2** was determined by X-ray analysis. The reactivity of **1**–**4** towards triethylborane has been explored. 1,1-Organoboration takes place in all cases, and the reactions are stereoselective for **1** and **4** to give the alkenes **5** and **6**, respectively, in which the stannyl and the boryl groups are in *cis*-positions at the C=C bond. In the case of **2**, the final products are the 1-stannacyclopenta-2,4-diene **7a** and the 1-stanna-4-boracyclohexa-2,5-diene **8a**, whereas the reaction of **2** with triisopropylborane leads selectively to the six-membered ring **8b**. Zwitterionic intermediates **9a**,**b**, in which the tin atom is coordinated side-on to the C≡C bond of an alkynylborate, have been detected by NMR spectroscopy. Compound **3** reacts with triethylborane to give a mixture of three spirotin compounds **10**–**12** as the final products, where the tin atom connects five- and six-membered rings.

Introduction

The synthetic potential of the C≡C bond in alkynes can be further enhanced by organometallic substituents.[1] This is well known for stannyl groups,[2] and the polar Sn–C≡ bonds in alkyn-1-yltin compounds are useful for various transformations. The reactivity of such alkyn-1-yltin compounds can be modified by the nature of other substituents at the tin atom and also by the second substituent at the C≡C bond, which may be hydrogen, an alkyl or aryl group, or another organometallic substituent. In the present work, we describe the synthesis and characterization of the ferrocenylethynyltin compounds **1**–**4** (Scheme 1) and report their reactivity towards triethylborane (BEt_3) and, in the case of **2**, triisopropylborane ($BiPr_3$).



Scheme 1. The ferrocenylethynyltin compounds studied.

Results and Discussion

Synthesis and NMR Spectroscopic Characterization of the Ferrocenylethynyltin Compounds

The most convenient synthesis of **1**–**3** starts from ethynylferrocene,[3] which is first converted into the alkynyllithium reagent and then treated with tin halides. (Scheme 2). Alternatively, the reaction of ethynylferrocene with the respective tin amides[4] [e.g. Me_3SnNEt_2, $Me_2Sn(NEt_2)_2$ and $Sn(NEt_2)_4$] can be used to obtain **1**–**3**. The reaction of **2** with one equivalent of dimethyltin dichloride at 110 °C in the presence of a small amount of toluene leads to **4**. A slight excess (10%) of Me_2SnCl_2 helps to convert **2** into **4** quantitatively. Compounds **1**–**4** are orange-red solids that are well soluble (**1**, **2**, **4**) or rather insoluble (**3**) in hydrocarbons. Single crystals of complex **2** suitable for X-ray structural analysis were isolated after recrystallization from hexane. The

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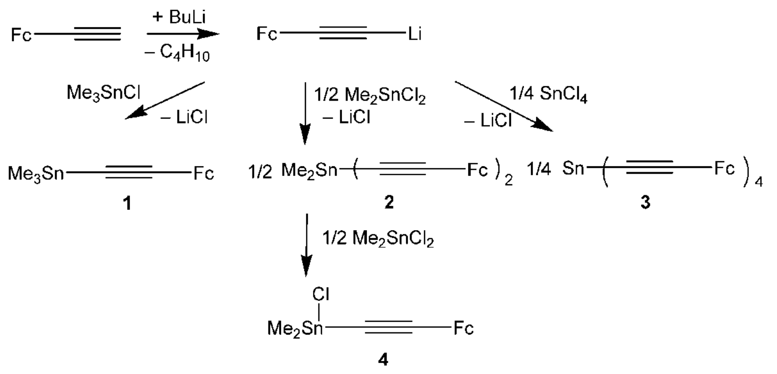


Scheme 2. Synthesis of the ferrocenylethynyltin compounds (Fc = Ferrocenyl).

Table 1. ^{13}C and ^{119}Sn NMR spectroscopic data[a] of the ferrocenylethynyltin compounds **1**–**4**.

	$\delta_{^{13}C_{2,5}}$	$\delta_{^{13}C_{3,4}}$	$\delta_{^{13}C_{1}}$	$\delta_{^{13}C_{Cp}}$	$\delta_{^{13}C_{\equiv C\text{–}Sn}}$	$\delta_{^{13}C_{\equiv C\text{–}Fc}}$	$\delta_{^{13}C_{Me}}$	$\delta_{^{119}Sn}$
1[b]	71.6	68.4	65.6 [12.8]	70.1	89.3 [433.2] {–58.5}	107.6 [94.4] {–14.1}	–7.4 [404.6] {+2.7}	–65.4
2	72.6 [5.0]	69.5	66.3 [15.5]	71.0	87.8 [625.9] {–26.7}	109.6 [134.3] {–2.2}	–5.7 [495.1] {+20.2}	–152.8[c]
3	72.4	69.7	63.5 [23.4]	70.7	82.7 [1167.3]	109.8 [241.8]	–	–342.2
4	72.8 [5.0]	69.9	65.0	71.1	89.7 [563.6]	111.3 [133.3]	–0.1 [493.4]	+21.7

[a] In CD_2Cl_2 at 296 K; coupling constants $J_{^{119}Sn,^{13}C} \pm 0.5$ Hz are given in brackets; isotope-induced chemical shifts $^{n}\Delta^{12/13}C(^{119}Sn) \pm 0.5$ ppb in braces with a negative sign for the shift of the more heavy isotopomer to lower frequency. [b] In $CDCl_3$ at 296 K. [c] Solid-state MAS ^{119}Sn NMR: $\delta_{^{119}Sn}$ = –144.0 (minor) and –150.5 ppm (major).

identity of the compounds **1**–**4** in solution follows from a consistent set of NMR parameters (Table 1). Even in the case of the sparingly soluble complex **3**, the ^{13}C NMR spectra could be recorded for determination of the $J_{^{117/119}Sn,^{13}C}$ coupling constants (Figure 1). The large magnitude of the $^{n}J_{^{119}Sn,^{13}C}$ coupling constants is typical of tetraalkyn-1-yltin derivatives.[5,6] In the cases of **1** and **2**, the ^{119}Sn NMR spectra were recorded in order to measure isotope-induced chemical shifts $^{n}\Delta^{12/13}C(^{119}Sn)$ (Figure 2). Both the $^{n}J_{^{119}Sn,^{13}C}$ coupling constants and isotope-induced chemical shifts $^{n}\Delta^{12/13}C(^{119}Sn)$ are observed in the expected ranges of the data previously determined for other alkyn-1-yltin compounds.[5–7] This indicates that the ferrocenyl group does not exert a special influence on the bonding situation in the Sn–C≡C–Fc fragment.

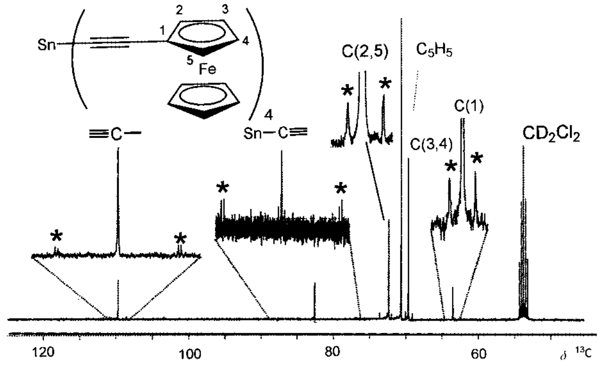


Figure 1. $^{13}C\{^{1}H\}$ NMR spectrum (100.5 MHz) of tetrakis(ferrocenylethynyl)tin (**3**; saturated solution in CD_2Cl_2) showing the $^{117/119}$Sn satellites (marked by asterisks) for spin-spin coupling across one, two, three, and four bonds.

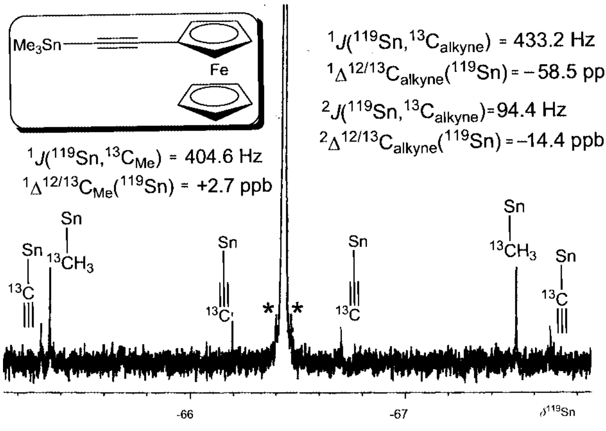


Figure 2. $^{119}Sn\{^{1}H\}$ NMR spectrum (refocused INEPT[25]; 186.5 MHz) of ferrocenylethynyl(trimethyl)tin (**1**; 5% in $CDCl_3$ at 296 K; acquisition time 5 s, repetition delay 2.5 s; 64 transients). The ^{13}C satellites are marked, and coupling constants and isotope-induced chemical shifts $\Delta^{12/13}C(^{119}Sn)$ are given. The ^{13}C satellites indicated by asterisks correspond to $^{3}J_{^{119}Sn,^{13}C_{Fc}}$ = 12.8 Hz.

Structural Studies of Bis(Ferrocenylethynyl)Dimethyltin (2) and Tetrakis(Ferrocenylethynyl)tin (3)

The molecular structure of **2** in the solid state, determined by X-ray analysis, is shown in Figure 3. All bond lengths and angles are close to the expected values, when compared with other alkynes[1a] or ferrocenyl derivatives.[8,9] The cyclopentadienyl rings are almost exactly parallel to each other, and deviate by 6.3° from the eclipsed positions. The C2–C3 bond forms an angle of 2.7° (pointing away from the iron atom) with the C_5H_4 plane. There are no appreciable intermolecular interactions ($d_{Fe\cdots Fe}$ = 956.6 pm). The literature does not contain structural data on comparable di(alkyn-1-yl)dimethyltin compounds.

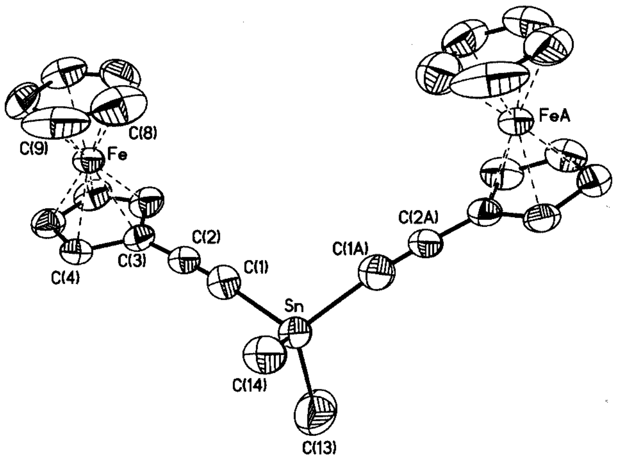


Figure 3. ORTEP representation (50 % probability; hydrogen atoms have been omitted) of the molecular structure of bis(ferrocenylethynyl)dimethyltin (**2**). Selected bond lengths [pm] and angles [°]: Sn–C1 211.3(8), Sn–C13 211.3(12), Sn–C14 210.0 (12), C1–C2 119.0(9), C2–C3 141.3(9), C3–C4 143.0(8)m, C3–C7 142.2(9), C4–C5 146.1(8), C5–C6 149.2(9), Fe–centroid(C_5H_4) 165.6, Fe–centroid(C_5H_5) 164.4; C1–Sn–C1A 107.0(4), C1–Sn–C13 108.5(3), C1–Sn–C14 109.2(3), C13–SnC14 114.3(5), Sn–C1–C2 174.0(6), C1–C2–C3 177.1(7), centroid–Fe–centroid 178.7.

The symmetry in the solid-state structure of **2** is remarkable, and would be somewhat surprising if this structure is the sole modification of **2**. Therefore, solid-state MAS $^{13}C\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra were recorded (Figure 4). These measurements clearly show that the bulk material of crystalline **2** contains a second modification. There are two sites for tin with rather similar isotropic ^{119}Sn chemical shifts, close to the value for solutions of **2**. The solid-state MAS ^{13}C NMR spectrum reveals one set of alkynyl ^{13}C resonances, corresponding to the symmetric molecular structure found by X-ray analysis, and there are two additional sets of alkynyl ^{13}C resonances which can be expected for a less symmetric arrangement of the ferrocenylethynyl units in the second crystalline modification.

In the case of **3**, we have not been able to obtain single crystals so far. Only one tin site was detected in the solid-state MAS ^{119}Sn NMR of the microcrystalline powder of **3**, and this site shows an expectedly small chemical shift anisotropy.[10] Similarly, only one set of alkynyl ^{13}C resonances is observed in the solid-state MAS ^{13}C NMR spectrum. If there are several modifications of **3** present, it can be assumed that their structures are very similar.

Reactivity of the Ferrocenylethynyltin Compounds Towards Triethylborane

The reactivity of Sn–C≡ bonds in alkyn-1-yltin compounds towards triorganoboranes is well documented.[11,12] The results of the reactions of **1** and **4** with triethylborane (BEt_3) are fully consistent with previous observations for 1,1-organoboration reactions, all of which proceed by cleavage of the Sn–C≡ bond via a borate-like zwitterionic intermediate.[12] The 1,1-ethylboration is regio- and stereospecific, and affords the alkenyltin compounds **5** and **6** in essentially quantitative yield (Scheme 3). The proposed structures follow from the NMR spectroscopic data (Table 2), and the *cis*-positions of the stannyl and boryl groups are confirmed by selective $^1H/^1H$ NOE experiments.[13]

The reaction of **2** with BEt_3 leads to a mixture of the stannacyclopenta-2,4-diene **7a** and the 1-stanna-4-boracyclohexa-2,5-diene **8a** in a ratio close to 1:2. This ratio was reproduced in several experiments in different solvents (toluene or CH_2Cl_2). The structural assignment follows conclusively from the NMR spectroscopic data (Table 3 and

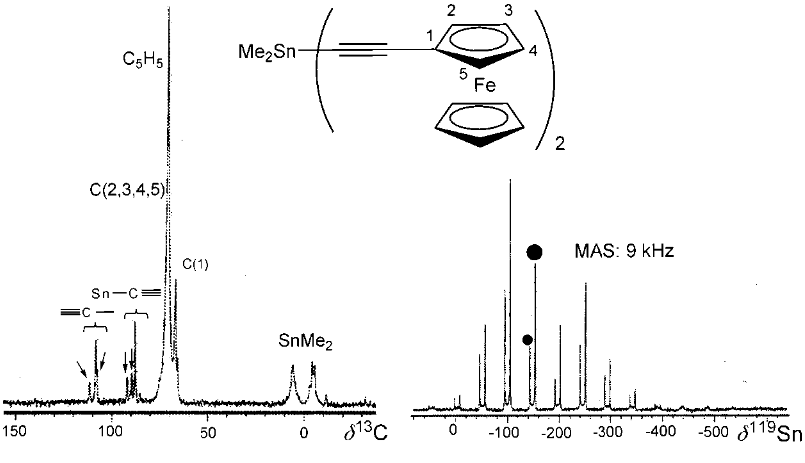
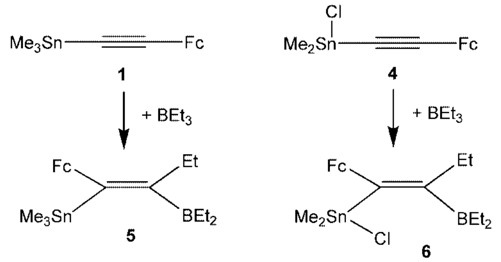


Figure 4. Solid-state VACP[27] MAS $^{13}C\{^1H\}$ (100.5 MHz) and $^{119}Sn\{^1H\}$ (149.1 MHz) NMR spectra of **2**, showing the presence of two modifications in the crystalline state. The signals for the isotropic $\delta_{^{119}Sn}$ values are marked by filled circles. The alkynyl ^{13}C NMR signals for the modification that is not represented by the crystal structure (Figure 3) are marked by arrows.



Scheme 3. 1,1-Ethylboration of the (ferrocenlyethynyl)tin compounds **1** and **4**.

Table 4), and in particular from the ^{119}Sn and ^{13}C NMR spectra (Figure 5).

The formation of a mixture is reminiscent of the results of the 1,1-ethylboration of bis(phenylethynyl)dimethyltin.[14] Monitoring of the reaction of **2** with BEt_3 by NMR spectroscopy shows that there is a fairly stable intermediate **9a** which must be regarded as the immediate precursor of the heterocycles. Zwitterionic complexes similar to **9a** have been observed before,[12] and they have been fully characterized by NMR spectroscopic data in solution,[15] in the

Table 2. ^{11}B, ^{13}C, and ^{119}Sn NMR spectroscopic data[a] of the alkenyltin compounds **5** and **6**.

	$\delta_{^{13}C}$ (Sn–C=)	$\delta_{^{13}C}$ (B–C=)	$\delta_{^{13}C}$ (Et)	$\delta_{^{13}C}$ (SnMe)	$\delta_{^{13}C}$ (BEt_2)	$\delta_{^{119}Sn}$	$\delta_{^{11}B}$
5[b]	134.1 [543.5]	165.3 (br)	29,7 [87.3] 14.0 [10.2]	–5.7 [321.6]	21.9 (br), 9.2	–54.1	82.0
6[c]	136.0 [650.1]	170.0 (br) [65.0]	26.4 [104.7] 14.6 [12.9]	2.4 [348.4]	21.8 (br) 10.7	+46.4	76.0

[a] In CD_2Cl_2 at 296 K; coupling constants $J_{^{119}Sn,^{13}C} \pm 0.5$ Hz are given in brackets; br. denotes ^{13}C NMR signals of carbon atoms bonded to boron. [b] Other ^{13}C NMR spectroscopic data: δ = 90.5 [64.9] (C_1), 70.0 ($C_{2,5}$), 67.4 ($C_{3,4}$), 69.2 ppm (C_5H_5). [c] Other ^{13}C NMR spectroscopic data: δ = 90.1 [98.3] (C_1), 68.9 [5.0], 70.0 (C_5H_4), 68.4 ppm (C_5H_5).

Table 3. ^{11}B, ^{13}C, and ^{119}Sn NMR spectroscopic data[a] of the intermediates **9a** and **9b**.

	$\delta_{^{13}C}$ (B–C≡)	$\delta_{^{13}C}$ (Fc-C≡)	$\delta_{^{13}C}$ (Sn–C=)	$\delta_{^{13}C}$ (B–C=)	$\delta_{^{13}C}$ (R)	$\delta_{^{13}C}$ (SnMe)	$\delta_{^{13}C}$ (BR_2)	$\delta_{^{11}B}$	$\delta_{^{119}Sn}$
9a[b]	103.6 (br)	128.2 [21.7]	134.5 [679.1]	183.9 (br)	27.5 [137.8] 16.1 [16.1]	1.4 [264.7]	20,5 (br) 13.5	+0.2	147.0
9b[b,c]	106.7 (br)	127.4 [21.4]	134.7 [708.5]	192.7 (br)	34.4 (CH) [145.4]	1.9 [272.8]	[c]	+34	66.0

[a] In CD_2Cl_2 at 296 K; coupling constants $J_{^{119}Sn,^{13}C} \pm 0.5$ Hz are given in brackets; br. denotes ^{13}C NMR signals of carbon atoms bonded to boron. [b] Other ^{13}C NMR spectroscopic data: δ = 69.0–75.0 ppm (numerous overlapping signals, not assigned, for C_5H_5 and C_5H_4). [c] Other ^{13}C NMR signals were not assigned.

Table 4. ^{11}B, ^{13}C, and ^{119}Sn NMR spectroscopic data[a] of the stannacyclopenta-3,5-diene **7a** and the 1-stanna-4-boracyclohexa-2,5-dienes **8**.

	$\delta_{^{13}C}$ [Sn–C(2)]	$\delta_{^{13}C}$ [Sn–C(5)]	$\delta_{^{13}C}$ (B–C=)	$\delta_{^{13}C}$ (=C-Et)	$\delta_{^{13}C}$ (R)	$\delta_{^{13}C}$ (SnMe)	$\delta_{^{13}C}$ (BR)	$\delta_{^{119}Sn}$	$\delta_{^{11}B}$
7a[b]	138.1 [446.0]	136.2 [489.0]	165.8 (br)	152.5 [115.8]	28.7 [55.9] 14.7 [9.5]	–5.5 [302.1]	22.7 (br) 10.3	+11.7	82.0
8a[c]	147.7 [472.0]	–	165.7 (br) [33.8]	–	27.9 [63.5] 16.2 [9.5]	–3.9 [327.7]	18.1 (br) 10.4	–145.7	71.4
8b[d]	133.6 [452.2]	–	174.9 (br)	–	32.9 (CH)[d] [66.1]	–3.8 [313.7]	[d]	–131.7	76.0

[a] In CD_2Cl_2 at 296 K; coupling constants $J_{^{119}Sn,^{13}C} \pm 0.5$ Hz are given in brackets; br. denotes ^{13}C NMR signals of carbon atoms bonded to boron. [b] Other ^{13}C NMR signals: δ = 91.1 [71.6], 88.3 [69.0] (C_1), 68–75 ppm (numerous overlapping signals for C_5H_4 und C_5H_5). [c] δ = 89.3 [58.9], 68–75 ppm (numerous overlapping signals for C_5H_4 und C_5H_5). [d] Other signals were not assigned owing to strong overlap.

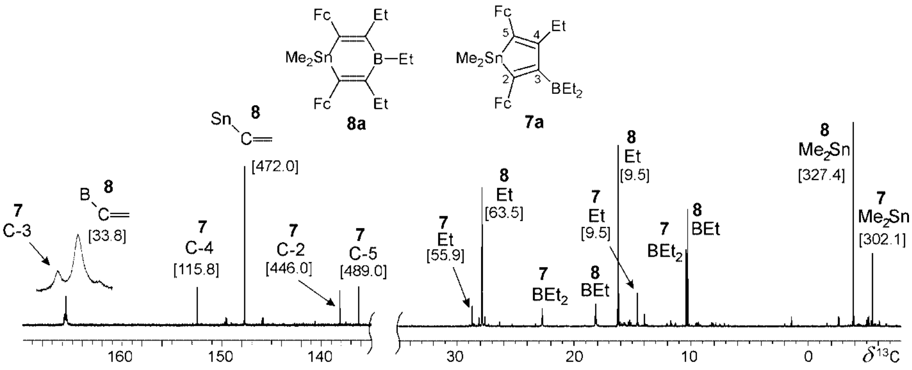
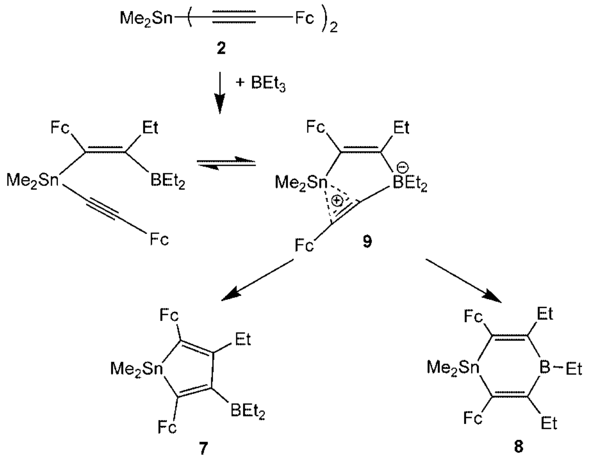


Figure 5. $^{13}C\{^1H\}$ NMR spectrum (100.5 MHz) of the mixture of products **7a** and **8a** showing the assigned ^{13}C NMR signals in the ranges expected for the olefinic and the aliphatic carbon atoms. $^{117/119}Sn$ satellites are indicated and $J_{^{119}Sn,^{13}C}$ coupling constants are given in brackets.

solid state,[16] and also by X-ray analysis.[15,17,18] In such related derivatives, with alkyl instead of the ferrocenyl groups, the ^{119}Sn resonances[15] ($\delta_{^{119}Sn}$ = +160 to +215 ppm) are found at slightly higher frequencies than for **9a** ($\delta_{^{119}Sn}$ = +147 ppm at 23 °C and +159 ppm at –20 °C). It is known, that the ferrocenyl group can stabilize a vinyl-cationic structure,[19] which may be considered for **9a** as an extreme case of unsymmetrical bridging. It should also be noted that triorganostannyl groups in the β-position to the carbocationic center exert a stabilizing effect.[20] The NMR spectroscopic evidence indicates that the ferrocenyl group stabilizes the bridged structure in **9a** much better than a phenyl group. In previous work, where the ferrocenyl was replaced with phenyl groups, the equilibrium shown for the intermediate **9a** in Scheme 4 was found, even at –10 °C, to be much more on the side of the nonbridged species[15] (cf. $\delta_{^{119}Sn}$ = +11.6 ppm and $\delta_{^{11}B}$ = +33.3 ppm at –10 °C[15] with $\delta_{^{119}Sn}$ = +147 ppm and $\delta_{^{11}B}$ = +0.2 ppm for **9a** at 23 °C).



Scheme 4. 1,1-Organoboration of the bis(ferrocenylethynyl)dimethyltin (**2**).

When the reaction of **2** with triisopropylborane (B*i*Pr$_3$) was studied under similar conditions, the formation of the intermediate **9b** took place more slowly than that of **9a**. The rearrangement of **9b** was also slow (several days at room temperature); however, in contrast to the behavior of **9a**, the six-membered ring **8b** was formed selectively. The ^{119}Sn and ^{11}B NMR spectroscopic data for **9b** at room temperature ($\delta_{^{119}Sn}$ +66 ppm and $\delta_{^{11}B}$ +34 ppm) indicate that the equilibrium is shifted towards the nonbridged species.

The reaction of **3** with BEt$_3$ proceeds slowly to give a mixture of three final products, the spirotin compounds **10**–**12** (in a ratio of 45:50:5). When the progress of the reaction was monitored by ^{119}Sn NMR spectroscopy (see Figure 6), the ^{119}Sn NMR signals for various intermediates were observed. In analogy to previous work,[17,21] these were assigned to the zwitterionic intermediates **13**–**15**, which have to be considered as precursors of the final products (Scheme 5). The structural assignment of the final products is based on the $\delta_{^{119}Sn}$ values together with the observation of relevant ^{13}C NMR signals in the olefinic region. The latter correspond closely to those for compounds **7a** and **8a** (see Figure 5). The ^{119}Sn resonances differ significantly, depending on whether the tin atom is part of a five- or six-membered ring. ^{119}Sn nuclei as part of five-membered rings are typically deshielded.[22]

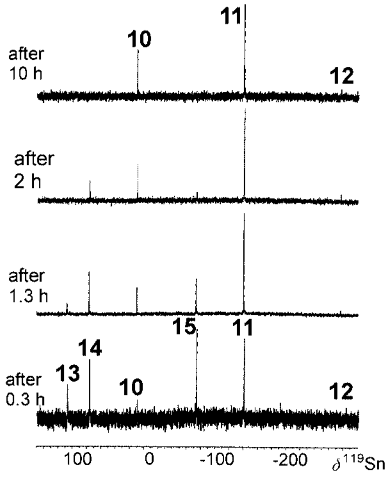
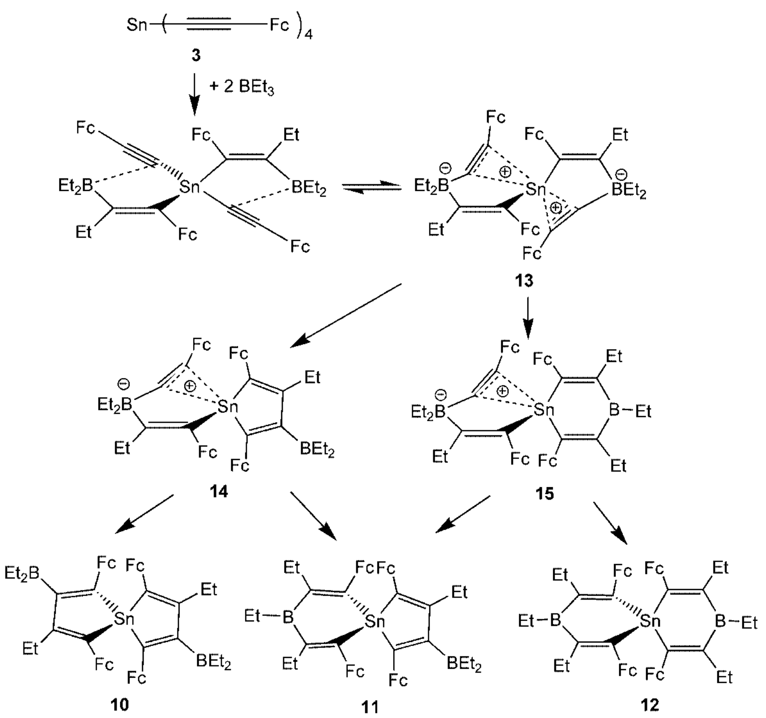


Figure 6. $^{119}Sn\{^1H\text{-inverse-gated}\}$ NMR spectra (149.1 MHz) of the CD$_2$Cl$_2$ solution from the reaction of tetrakis(ferrocenylethynyl)tin (**3**) with an excess of BEt$_3$. ^{119}Sn NMR signals of the zwitterionic intermediates **13**–**15** are observed in the beginning, and after 10 h at room temperature only ^{119}Sn NMR signals of the spirotin compounds **10**, **11** and **12** (ratio 45:50:5) are left.



Scheme 5. 1,1-Ethylboration of tetrakis(ferrocenylethynyl)tin (**3**).

Conclusions

All structural and spectroscopic data indicate that the ferrocenyl group does not exert any special effects on the C≡C bond in ferrocenylethynyltin compounds. This is also supported by the results of the 1,1-organoboration reactions. Novel organometallic-substituted alkenes with stannyl and boryl groups in *cis*-positions are accessible by 1,1-ethylboration of the mono(ferrocenylethynyl)tin compounds **1** and **4**. Fairly stable zwitterionic intermediates were detected in the course of 1,1-organoboration reactions of bis(ferrocenylethynyl)dimethyltin (**2**) and tetrakis(ferrocenylethylnyl)tin (**4**). These reactions give access to 1-stannacyclopenta-2,4-diene or 1-stanna-4-boracyclohexa-2,5-diene derivatives and the corresponding spirotin compounds. The product distribution is apparently dependent on the nature of the trialkylborane.

Experimental Section

General Procedures: All reactions were carried out using the usual techniques to exclude oxygen and moisture. The starting materials ethynylferrocene,[3] tin amides,[23] and triisopropylborane[24] were prepared following literature procedures. BuLi, tin chlorides, and triethylborane were used as commercial products without further purification. Melting points were measured (Büchi 510 melting point apparatus) in sealed capillaries under argon and are uncorrected. Mass spectra (EI ionization, 70 eV) were obtained using a Finnigan MAT 8500 spectrometer with direct inlet. IR spectra: Perkin–Elmer, Spectrum 2000 FTIR instrument. NMR spectra: Bruker ARX 250, Bruker DRX 500 (both for ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR spectra of solutions), and Varian Inova 400 (for solutions and for solid-state MAS ^{13}C and ^{119}Sn NMR spectra). ^{119}Sn NMR spectra of solutions were measured by using the refocused INEPT pulse sequence[25] for methyltin compounds, and by ^{1}H inverse-gated decoupling for all other cases. The chemical shifts are given relative to SiMe$_4$ [$\delta_{^1\mathrm{H}}$(C$_6$D$_5$H) = 7.15 ppm; $\delta_{^1\mathrm{H}}$(CHCl$_3$)/CDCl$_3$ = 7.23 ppm; $\delta_{^1\mathrm{H}}$(CHDCl$_2$/CD$_2$Cl$_2$) = 5.33 ppm; $\delta_{^{13}\mathrm{C}}$(C$_6$D$_6$) = 128.0 ppm; $\delta_{^{13}\mathrm{C}}$(CDCl$_3$) = 77.0 ppm; $\delta_{^{13}\mathrm{C}}$(CD$_2$Cl$_2$) = 53.8 ppm], SnMe$_4$ [$\delta_{^{119}\mathrm{Sn}}$ = 0 ppm for Ξ(^{119}Sn) = 37.290665 MHz], or BF$_3$·OEt$_2$ [$\delta_{^{11}\mathrm{B}}$ = 0 ppm for Ξ(^{11}B) = 32.083971 MHz]. For solid-state MAS NMR spectra, the $\delta_{^{13}\mathrm{C}}$ and $\delta_{^{119}\mathrm{Sn}}$ NMR spectroscopic data are given relative to external adamantane and Sn(chex)$_4$, respectively, and recalculated to the SiMe$_4$ and SnMe$_4$ scales.

Ferrocenylethynyltrimethyltin (1): [26] ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ [$J_{^{119}\mathrm{Sn},^1\mathrm{H}}$] = 0.31 [60.0] (s, 9 H, SnMe$_3$), 3.39, 4.13 [2m, 2×2 H, H(3,4,2,5)], 4.11 (s, 5 H, Cp) ppm. MS: *m*/*z* (%) = 374 (100) [M$^+$], 344 (82) [M$^+$ – 2Me], 329 (19) [M$^+$ – 3Me].

Bis(ferrocenylethynyl)dimethyltin (2): A THF (5 mL) solution of Me$_2$SnCl$_2$ (0.98 g, 4.46 mmol) was added, at 0 °C, to a solution of the Li salt of Fc-C≡C–H [prepared from 1.87 g of Fc-C≡C–H (8.92 mmol and an equimolar amount of BuLi (1.6 M in hexane)] in THF (15 mL). The mixture was kept stirring overnight, THF was removed under reduced pressure, and the residue was taken up in hexane (15 mL). After filtration, the product **2** was crystallized at –30 °C to give 1.21 g (48%) of orange crystals (m.p. 140–144 °C). ^{1}H NMR (400 MHz, C$_6$D$_6$, 296 K): δ [$J_{^{119}\mathrm{Sn},^1\mathrm{H}}$] = 0.30 [68.6] (s, 6 H, Me$_2$Sn), 3.84 (m, 4 H, C$_5$H$_4$), 4.05 (s, 10 H, C$_5$H$_5$), 4.41 (m, 4 H, C$_5$H$_4$) ppm. IR (toluene): $\tilde{\nu}$ = 2140, 2114 cm^{-1} (C≡C). MS: *m*/*z* (%) = 598 (80) [M$^+$], 418 (100) [M$^+$ – SnMe$_2$].

Tetrakis(ferrocenylethynyl)tin (3): A hexane (5 mL) solution of SnCl$_4$ (0.205 g, 1.74 mmol) was added, at 0 °C, to a solution of the Li salt of Fc-C≡C–H (prepared as above; 1.46 g, 6.94 mmol) in THF (15 mL). After stirring for 12 h at room temperature, insoluble materials were filtered off, and the solid was washed with toluene and dried to give the product **3** as an orange-yellow powder (0.877 g, 52%; m.p. 210–214 °C). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 296 K): δ = 4.26 (m, 8 H, C_5H_4), 4.27 (s, 20 H, C_5H_5), 4.56 (m, 8 H, C_5H_4) ppm. IR (toluene): $\tilde{\nu}$ = 2147 cm^{-1} (C≡C).

Chloro(ferrocenylethynyl)dimethyltin (4): A mixture of the stannane **2** (213 mg, 0.376 mmol) and Me_2SnCl_2 (90.1 mg, 0.414 mmol) in toluene (1 mL) was heated at for 1 h. After removal of the solvent and the excess of Me_2SnCl_2 in vacuo, the tin chloride **4** was left as a brownish-red solid that could be used without additional purification. The purity of **4** (according to NMR spectroscopic data) was ≥ 95%. ^1H NMR (400 MHz, C_6D_6, 296 K): δ [$J_{^{119}Sn,^{1}H}$] = 0.55 [69.1] (s, 6 H, Me_2Sn); 4.20 (m, 2 H, C_5H_4); 4.22 (s, 5 H, C_5H_5); 4.45 (m, 2 H, C_5H_4) ppm.

Organoboration the of Stannanes 1–4 with Triethylborane (General Procedure): A twofold excess of BEt_3 (four equivalents were used in the case of **3**) was added, at –78 °C, to a solution of the respective alkyn-1-yltin compound **1**–**4** (0.2–0.4 mmol) in CH_2Cl_2 and the reactions were monitored by ^{119}Sn NMR spectroscopy. For multinuclear NMR characterization of the zwitterionic intermediates **9a** and **9b** the same reactions were carried out with 0.1 mmol of **2** in CD_2Cl_2. The reaction of **2** with B*i*Pr_3 was also done on a small scale (0.05 mmol) in CD_2Cl_2 for NMR studies.

5: Orange-red oil. ^1H NMR (500.1 MHz. $CDCl_3$, 296 K): δ [$J_{^{119}Sn,^{1}H}$] = 0.05 [53.0] (s, 9 H, Me_3Sn), 2.19, 0.85 (q and t, 2 H and 3 H, =C-Et), 1.30, 1.11 (m and t, 10 H, BEt_2), 3.85–4.00 (m, 4 H. C_5H_4), 3.83 (s, 5 H, C_5H_5) ppm.

6: Orange-red, waxy solid.: ^1H NMR (400 MHz, 296 K, CD_2Cl_2): δ [$J_{^{119}Sn,^{1}H}$] = 0.59 [55.0] (s, 6 H, Me_2Sn); 2.21 [8.5], 0.86 (q and t, 2 H nd 3 H, =C-Et), 1.36, 1.16 (m and t, 4 H and 6 H, BEt_2), 3.87 (s, 5 H, C_5H_5), 3.9–4.0 (m, 4 H, C_5H_4) ppm.

7a: Obtained as a mixture with **8a**. ^1H NMR (400 MHz, 296 K, CD_2Cl_2): δ [$J_{^{119}Sn,^{1}H}$] = 0.73 [52.6] (s, 6 H, Me_2Sn), 0.9 1.1 (m, 9 H, Et, BEt_2), 1.5 (q, $^3J_{^{119}Sn,^{1}H}$ = 7.6 Hz, 4 H, BEt_2), 2.2 (q, $^3J_{^{119}Sn,^{1}H}$ = 7.6 Hz, 2 H, Et), 4.18 (s, 10 H, C_5H_5), 4.1–4.3 (m, 8 H, C_5H_4) ppm.

8a: Obtained as a mixture with **7a**. ^1H NMR (CD_2Cl_2, 296 K): δ [$J_{^{119}Sn,^{1}H}$] = 0.53 [52.6] (s, 6 H, Me_2Sn), 0.9–1.1 (m, 9 H, Et, BEt), 1.5 (q, 2 H, BEt), 2.2 (q, 4 H, Et), 4.18 (s, 10 H, C_5H_5), 4.1–4.3 (m, 8 H, C_5H_4) ppm.

10: Obtained as a mixture with **11** and **12**. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 296 K): δ [$J_{^{119}Sn,^{13}C}$] = 22.9 (br), 9.9 (BEt_2). 28.3 [67.3], 16.2 [9.6] (Et), 68.9–69.9 (overlapping signals for C_5H_4 and C_5H_5), 87.6 [71.4] [C_5H_4-(1)], 89.9 [72.8] [C_5H_4-(1)], 134.2 [454.7] (C-1), 165.3 [43.6] (br) (C-2), 152.3 [117.8] (C-3), 139.0 [473.8] (C-4) ppm. $^{119}Sn\{^1H$ inverse-gated$\}$ NMR (149.1 MHz, CD_2Cl_2, 296 K): δ = 10.3 ppm.

11: Obtained as a mixture with **10** and **12**. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2, 296 K): δ [$J_{^{119}Sn,^{13}C}$] = 22.3 (br), 9.9 (BEt_2); 18.4 (br), 8.3 (BEt); 28.5 [57.6], 13.6 [10.1] (3-Et), 28.4 [56.4], 14.4 [9.5] (7-Et), 68.9–69.9 (overlapping signals for C_5H_4 and C_5H_5), 87.5 [79.7], 88.2 [71.0] [1,4-C_5H_4-(1)], 89.7 [76.1] [6-C_5H_4-(1)], 137.1 [409.0] (C-1), 164.5 [44.4] (br) (C-2), 153.7 [117.6] (C-3), 141.1 [428.8] (C-4), 150.0 [441.5] (C-6), 167.3 [36.6] (br) (C-7) ppm. $^{119}Sn\{^1H$ inverse-gated$\}$ NMR (149.1 MHz, CD_2Cl_2, 296 K): δ = –139.6 ppm.

12: A small amount as a mixture with **10** and **11**. ^{13}C NMR (125.8 MHz, CD_2Cl_2, 296 K): δ = 18.6 (br), 8.2 (BEt), 28.5, 14.3 (2-Et), 68.9–69.9 (overlapping signals for C_5H_4 and C_5H_5), 87.9 [1-C_5H_4-(1)], 152.4 (C-1), 166.1 (br) (C-2) ppm. $^{119}Sn\{^1H\}$ NMR (149.1 MHz, CD_2Cl_2, 296 K): δ = –275.7 ppm.

X-ray Crystallography: An orange-colored crystal of compound **2** of dimensions 0.18×0.16×0.12 mm^3 was sealed in a glass capillary under argon and measured on a Siemens P4 four-circle diffractometer at 293(2) K with Mo-K_α radiation (graphite monochromator). The structure was solved by direct methods and refined by a full-matrix least-squares procedure. A numerical absorption was carried out. The positions of the hydrogen atoms were calculated and refined isotropically by applying the riding model. All non-hydrogen atoms were refined anisotropically revealing wR^2 = 0.124 and $R1$ = 0.056 as final R values. The final difference map had no peaks of chemical significance (min./max. residual electron density –0.76/0.62 e 10^{-6} pm^{-3}).

CCDC-275737 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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