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# Selective Synthesis of Stannoles by 1,1-Carboboration of Bis(trimethylsilylethynyl)tin Compounds Using Weakly and Strongly Electrophilic Triorganoboranes: Characterization of a Zwitterionic Intermediate

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The triorganoboranes BEt<sub>3</sub>, BPh<sub>3</sub>, and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> were allowed to react with bis(trimethylsilylethynyl)diorganotin compounds [R<sup>1</sup><sub>2</sub>Sn(C=C-SiMe<sub>3</sub>)<sub>2</sub>; R<sup>1</sup><sub>2</sub> = -(CH<sub>2</sub>)<sub>5</sub>- (**a**), R<sup>1</sup> = *n*Bu (**b**), <sup>*n*</sup>Oct (**c**), Ph (**d**)] to give selectively and quantitatively stannoles. The reactions proceeded by 1,1-carboboration in two consecutive steps (inter- and intramolecular) and intermediates were detected by NMR spectroscopy. In one case, using the strongly electrophilic B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, a zwitterionic inter-

## Introduction

The properties of the  $\pi$  system in 1-heterocyclo-2,4dienes are a complex function of the heteroatom as well as of substituents at the 1-5 positions. There is increasing interest in metalloles because of their photophysical properties related to the tuneable band gap of the  $\pi$  system.<sup>[1,2]</sup> In this context, stannoles deserve attention as electron-rich cyclic dienes and potential starting materials for the synthesis of other metalloles. However, there are rather few straightforward routes available for their preparation,<sup>[3]</sup> and the majority of the more convenient synthetic strategies appear to be limited to aryl groups at the 2-5 positions.<sup>[3,4]</sup> This situation has been considerably improved by 1,1carboboration because the reactions of diethynyl(dimethyl)tin or bis(trimethylsilylethynyl)dimethyltin with trialkylboranes afford stannoles (e.g., Scheme 1).<sup>[5,6]</sup> In this manner, stannoles 1 and 2 were obtained in essentially quantitative yields under mild conditions.<sup>[7,8]</sup> In the same way, stannoles can be obtained selectively by using trialkylboranes and other diethynyltin compounds.<sup>[9]</sup> In contrast, 1,1-carboboration using triphenylborane, BPh<sub>3</sub>, has led to mixtures of stannoles and 1,4-stannaboracyclohexa-2,5-diene derivatives.<sup>[9]</sup> In addition, the use of tris(pentafluorophenyl)borane, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, for the 1,1-carboboration of R<sup>1</sup><sub>2</sub>Sn(C=C- $R_{2}$  ( $R^{1}$  = alkyl, Ph; R = H, nBu) selectively affords 1,4mediate was isolated and structurally characterized by X-ray diffraction analysis. The question of reversibility of the 1,1-carboboration is addressed. Multinuclear magnetic resonance spectroscopy (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F, <sup>29</sup>Si, <sup>119</sup>Sn NMR) was used to characterize the intermediates and the stannoles as the final products. Some of the NMR parameters (<sup>11</sup>B, <sup>13</sup>C, <sup>29</sup>Si) of the intermediates were calculated by DFT methods using the optimized gas-phase geometries.

stannabora-cyclohexa-2,5-diene derivatives instead of stannoles.<sup>[9]</sup>



Scheme 1. Two examples  $^{[5,6]}$  of 1,1-carboboration reactions as a viable route to stannoles.

In this work, we studied the 1,1-carboboration reactions of four bis(trimethylsilylethynyl)diorganotin compounds **3**  $[R^{1}_{2}Sn(C \equiv C-SiMe_{3})_{2}$  with  $R^{1}_{2} = -(CH_{2})_{5}$ , (**a**);  $R^{1} = nBu$ , (**b**), "Oct (**c**), Ph (**d**)] with triorganoboranes BEt<sub>3</sub>, BPh<sub>3</sub>, and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, which differ greatly in their electrophilic character. Previous work on the synthesis of **2** and related stannoles with Me<sub>3</sub>Si groups<sup>[6,8]</sup> had revealed no evidence for reactive intermediates, and it was hoped that more electrophilic triorganoboranes could be helpful in this respect. All the reactions were studied by multinuclear magnetic resonance methods (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>29</sup>Si, and <sup>119</sup>Sn NMR spectroscopy) to elucidate mechanistic aspects of the 1,1-carboboration reactions.

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## **Results and Discussion**

#### Bis(trimethylsilylethynyl)tin Compounds

The bis(trimethylsilylethynyl)tin compounds 3a-d were obtained (Scheme 2) in high yields as colorless solids or as an oil (3b), and are slightly sensitive to moisture. Before use, the purity of 3 was verified by NMR spectroscopy (Table 1). Only limited NMR spectroscopic data have been reported for 3b so far<sup>[10]</sup> and the NMR spectra for 3d in Figure 1 show the purity that can be achieved. In the case of 3a, the molecular structure was established by X-ray crystallography (Figure 2).



Scheme 2. Synthesis of bis(trimethylsilylethynyl)diorganotin compounds.

Few structural data are available for dialkynyl(diorgano)tin compounds,<sup>[12,13]</sup> and **3a** is the first example with trimethylsilylethynyl groups. All the bond lengths are in the usual range, but the bond angles at tin are of interest because in **3a**, as a consequence of the six-membered ring, the endocyclic bond angle C5–Sn–C9 is fairly small [100.97(8)°] when compared with the corresponding angles in other noncyclic examples (>115 and  $\leq$ 129°). However, the bond angle C1–Sn–C3 in **3a** [108.98(8)°] is similar to that in non-

Table 1. <sup>13</sup>C, <sup>119</sup>Sn, and <sup>29</sup>Si NMR parameters<sup>[a]</sup> for the bis(trimethylsilylethynyl)diorganotin compounds.

			$\delta$ [ppm]	]		
	$\frac{\delta_{\rm C}}{{ m R}^1}$	$\delta_{\rm C}$ Sn-C=	$\delta_{\rm C}$ =C-Si	$\delta_{\rm C}$ SiMe <sub>3</sub>	$\delta_{ m Sn}$	$\delta_{\mathrm{Si}}$
$Me_2Sn(C \equiv C -$	-5.8	109.4	118.6	0.1	-167.4	-19.1
$SiMe_3)_2$	[491.0]	[542.0]	[89.1]	56.2		[12.4]
$(C_6D_6)$		11.2	76.3			
3a	14.1 [444.3],	107.5	119.3	0.0	-216.1	-19.4
$R_{2}^{1} =$	27.0 [34.2]	[516.9]	[80.6]	56.1		[11.8]
-(CH <sub>2</sub> ) <sub>5</sub> -						
(CDCl <sub>3</sub> )	30.8 [70.1]	10.8	76.8			
3b	13.2 [477.9],	109.4	119.0	0.1	-167.3	-20.0
$R^1 = nBu$	28.5 [27.5],	[468.8]	[71.1]	56.2		[11.4]
$(CDCl_3)$	26.5 [67.8]	11.1	76.9			
	13.6					
3с	13.8 [475.9],	109.8	119.4	0.0	-168-0	-20.0
$R^1 = {^nOct}$	26.5 [27.4],	[459.4]	[70.6]	56.0		[11.0]
$(CDCl_3)$	33.7 [65.7],	11.0	76.3			
	29.6 [18.9],					
	29.5, 32.2,					
	23.0, 14.3					
3d	135.5	107.1	121.0	-0.2	-239.6	-18.9
	[735.4],					
$R^1 = Ph$	136.5 [50.3],	[632.3]	[99.9]	56.1		[13.4]
(CDCl <sub>3</sub> )	129.2 [68.6],	10.7	74.5			
	130 1 [13 9]					

[a] Coupling constants  ${}^{n}J({}^{119}\text{Sn},X)$  (X =  ${}^{13}\text{C}, {}^{29}\text{Si})$  in Hz in [], and  ${}^{n}J({}^{29}\text{Si},{}^{13}\text{C})$  in Hz in [].

cyclic dialkynyl(diorgano)tin compounds (103–108°). The six-membered ring in 3a deviates slightly from the ideal chair conformation.



Figure 1. 100.6 MHz  ${}^{13}C{}^{1}H$ , 79.47 MHz  ${}^{29}Si{}^{1}H$  (refocused INEPT<sup>[11]</sup>), and 149.2 MHz  ${}^{119}Sn{}^{1}H$  NMR spectra (refocused INEPT,<sup>[11]</sup>) measured at 296 K, in C<sub>6</sub>D<sub>6</sub>) of **3d** showing numerous satellite signals for the various isotopomers. In the expanded regions of the  ${}^{13}C$  NMR spectrum,  ${}^{117/119}Sn$  and  ${}^{29}Si$  satellites are marked by asterisks and crosses, respectively.





Figure 2. Molecular structure of **3a** (ORTEP, ellipsoids drawn at the 40% probability level; hydrogen atoms have been omitted for clarity). Selected bond lengths [pm] and angles [°]: Sn1–Cl 209.66(18), Sn1–C3 209.80(17), Sn1–C5 213.29(17), Sn1–C9 213.88(18), C1–C2 120.4(2), C3–C4 120.4(2), Si1–C2 185.30(18), Si2–C4 184.91(19), C2–C1–Sn1 173.55(15), C1–C2–Si1 177.17(15), C4–C3–Sn1 177.82(15), C3–C4–Si2 174.54(16), C1–Sn1–C3 106.98(8), C1–Sn1–C5 108.83(7), C3–Sn1–C5 108.83(7), C1–Sn1–C9 111.12(7), C3–Sn1–C9 113.09(7), C5–Sn1–C9 100.95(8).

### 1,1-Carboboration of Bis(trimethylsilylethynyl)diorganotin Compounds – General Remarks

As for other dialkynyltin compounds, the 1,1-carboboration of **3** proceeds in two major steps (Scheme 3). The first step is the intermolecular 1,1-carboboration, which may lead to the alkenyl(alkynyl)tin compounds **4** or **5**. The stereochemistry of **4** precludes ring closure, however, 1,1carboboration is readily reversible for such alkenes<sup>[8,14]</sup> (see also below). Therefore the equilibrium is driven towards **5**, in which the Sn–C= bond is activated owing to vicinity of the electron-deficient boron atom in the BR<sub>2</sub> group. This leads to migration of the alkynyl group from tin to boron and the formation of the zwitterionic intermediate **6**. Finally, irreversible rearrangement of **6** selectively affords the



Scheme 3. 1,1-Carboboration of bis(trimethylsilylethynyl)diorganotin compounds.

stannoles 7. Although some evidence has been collected previously for derivatives of type 4,<sup>[15,16]</sup> species such as 5 and 6 with Me<sub>3</sub>Si groups appeared to be too short-lived, and their intermediacy was proposed to explain the formation of the stannoles with this particular pattern of substituents.

#### 1,1-Carboboration Using BEt<sub>3</sub>, and BPh<sub>3</sub>

In the cases of trialkylboranes such as BEt<sub>3</sub>, monitoring the 1,1-carboboration reactions by <sup>29</sup>Si NMR spectroscopy proved successful for detecting intermediates of type 4(Et), readily identified by their characteristic NMR spectroscopic data (Table 2; see also Figure 3). Typically, mixtures of 4(Et) and 7(Et) were present after warming the reaction mixtures to room temperature. However, <sup>29</sup>Si NMR signals of the species 5 or 6 could not be observed. After 1 or 2 days at room temperature, the stannoles 7(Et) were the

Table 2. <sup>13</sup>C, <sup>11</sup>B, <sup>29</sup>Si, and <sup>119</sup>Sn NMR parameters<sup>[a]</sup> for the alkenyl(alkynyl)tin compunds 4a-c(Et).

					$\delta$ [ppm]				
			$\delta_{\mathrm{C}}$			δ	Si	$\delta_{\mathrm{B}}$	$\delta_{\mathrm{Sn}}$
	Sn–C=	=C-B	Sn–C≡	≡C–Si	Et/BEt <sub>2</sub>	SiMe <sub>3</sub> (alkene)	SiMe <sub>3</sub> (alkyne)		$(h_{1/2})$
<b>4a</b> <sup>[b]</sup>	136.8 [321.4]  60.0	183.1 (br.)	115.9 [275.1]  11.1]	117.9 [34.6] [77.4]	35.2 [135.7], 14.1/ 21.2 (br.), 9.3	-5.5 [95.5]	-20.9 [7.8]	85.7	-180.5 (39)
<b>4b</b> <sup>[c]</sup>	139.2 [229.6]	181.9 (br.)	116.7 [284.1]	119.2 [35.5]	36.7 [137.9], 14.0/ 21.9 (br.), 9.5	-6.2 [80.7]	-21.0 [8.5]	85.4	-135.7 (31)
<b>4c</b> <sup>[d]</sup>	139.2 [312.3]	182.0 (br.)	116.8 [266.4]	119.4 [34.5]	33.7, 13.8/ 22.0 (br.), 9.6	-6.2 [80.7]	-21.0 [8.4]	n.o.	-136.0 (13)

[a] Measured at 296 K in CDCl<sub>3</sub> (4a) or C<sub>6</sub>D<sub>6</sub> (4b, 4c), line widths  $h_{1/2}$  in () in Hz, coupling constants  ${}^{n}J({}^{119}Sn,X)$  (X =  ${}^{29}Si, {}^{13}C$ ) and  ${}^{n}J({}^{29}Si, {}^{13}C)$  in [] and ||, respectively, in Hz, br. denotes the broadened  ${}^{13}C$  NMR signal of a carbon linked to boron; n.o. means not observed. [b] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 0.2$  [55.7] (Me<sub>3</sub>Si-alkyne), 1.3 [13.0] [50.5] (Me<sub>3</sub>Si-alkene), 16.5 [334.3] (SnCH<sub>2</sub>), 27.8 [34.8] (CH<sub>2</sub>), 31.7 [46.2] (CH<sub>2</sub>) ppm. [c] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 0.2$  [55.6] (Me<sub>3</sub>Si-alkyne), 1.8 [49.8] (Me<sub>3</sub>Si-alkene), 15.6 [363.9] (Sn-CH<sub>2</sub>), 29.5 [24.0] SnCH<sub>2</sub>-CH<sub>2</sub>, 27.3 [62.4] (-CH<sub>2</sub>-), 13.9 (CH<sub>3</sub>) ppm. [d] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 0.1$  [55.4] (Me<sub>3</sub>Si-alkyne), 1.9 [50.8] (Me<sub>3</sub>Si-alkene) ppm, other  ${}^{13}C$  NMR signals were not assigned because of overlap with signals for the stannole **7c**(Et).



sole products (see Table 3 for the NMR spectroscopic data). The <sup>119</sup>Sn NMR spectra of the reaction mixtures were less informative because the <sup>29</sup>Si satellites due to  ${}^{n}J({}^{119}Sn,{}^{29}Si)$  are not always well resolved, in contrast to  ${}^{117/119}Sn$  satellites in the <sup>29</sup>Si NMR spectra.



Figure 3. 79.47 MHz <sup>29</sup>Si{<sup>1</sup>H} NMR spectra (at 296 K, in  $C_6D_6$ ; refocused INEPT<sup>[11]</sup>) for the reaction of **3b** with triethylborane. Upper trace: Recorded after warming the reaction mixture to room temp., removal of volatile materials, and dissolving in  $C_6D_6$ . Lower trace: The same mixture after 24 h at room temp.

The reactions of **3a** and **3b** with triphenylborane were already complete (>95%) by the time the samples had reached ambient temperature. In the case of **3a**, in one experiment, a weak broadened <sup>119</sup>Sn NMR signal was detected at  $\delta_{\text{Sn}} = -177$  ppm, tentatively assigned to **4a**(Ph), which was no longer visible after 12 h. The stannoles **7a**(Ph) and **7b**(Ph) were formed quantitatively (see Figures 4 and 5).

#### 1,1-Carboboration Using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

The enhanced electrophilic character of  $B(C_6F_5)_3$  can be usefully exploited in 1,1-carboboration reactions when compared with other triorganoboranes.<sup>[19]</sup> For instance, dialkynyl(dimethyl)silanes are converted quickly and selectively into siloles under mild reaction conditions,<sup>[20]</sup> whereas the analogous reaction with triethylborane requires heating at 100-110 °C for several days.<sup>[21]</sup> The first attempts at using  $B(C_6F_5)_3$  for the 1,1-carboboration of dialkynyl(diorgano)tin compounds other than 3 gave zwitterionic intermediates similar to  $6(C_6F_5)$  followed by the formation of 1,4-stannaboracyclohexa-2,5-dienes instead of stannoles.<sup>[9]</sup> Apparently, the Lewis acid strength of the  $B(C_6F_5)_2$  group in the elusive intermediates  $5(C_6F_5)$  has two functions: 1) It accelerates the migration of the alkynyl group from tin to boron to give  $6(C_6F_5)$  and 2) it stabilizes the zwitterionic intermediates  $6(C_6F_5)$  because of the relatively favored alkynylborate moiety (see Table 4 for relevant NMR spectroscopic data). The presence of  $6(C_6F_5)$  is already evident by monitoring the reaction progress using <sup>11</sup>B and <sup>29</sup>Si NMR spectroscopy (see Figure 6). The original <sup>29</sup>Si(≡C-Si) NMR signal of 3 vanishes and two new signals are observed, one broadened signal accompanied by <sup>117/119</sup>Sn satellites, corresponding to  ${}^{2}J({}^{119}\text{Sn}, {}^{29}\text{Si})$  across an olefinic carbon atom. The broadening can be traced to unresolved vicinal <sup>29</sup>Si-<sup>11</sup>B spin-spin coupling.<sup>[17]</sup> The sharper <sup>29</sup>Si NMR signal at higher frequency belongs to the silicon atom attached to the bridging  $C \equiv C$  unit. Apparently, this silicon atom is no longer linked to a typical alkynyl carbon atom (as in alkynylsilanes) and therefore its nuclear magnetic shielding is similar to that in alkenylsilanes.<sup>[22]</sup> This is to be expected for a bond angle C=C-Si of 155.1°, as determined for solid  $6a(C_6F_5)$  (see below), which is in excellent agreement with the value of 155.4° for the calculated optimized geometry [B3LYP/6-311G(d,p)<sup>[23]</sup> and Sn (LANL2DZ)<sup>[24]</sup> level of theory]. The  $\delta_{s_i}$  values and the assignments were confirmed by calculation of the <sup>29</sup>Si nuclear magnetic shielding.<sup>[25]</sup> The characteristic <sup>13</sup>C(Si-C=) NMR signal is accompanied by  $^{117/119}$ Sn satellites [ $^{1}J(^{119}$ Sn, $^{13}$ C $\equiv) \approx 102-105$  Hz], which indicates significant Sn-C(Si)≡ bonding interactions.



Figure 4. 79.47 MHz <sup>29</sup>Si{<sup>1</sup>H} NMR (refocused INEPT<sup>[11]</sup>) and 149.2 MHz <sup>119</sup>Sn{<sup>1</sup>H} NMR spectra (at 296 K, in C<sub>6</sub>D<sub>6</sub>) for the reaction of **3a** with triphenylborane, which selectively leads to the stannole **7a**(Ph). In the <sup>29</sup>Si NMR spectrum, satellite signals for <sup>2</sup>J(<sup>119</sup>Sn,<sup>29</sup>Si) and <sup>1</sup>J(<sup>29</sup>Si,<sup>13</sup>C) are marked by asterisks and crosses, respectively. The <sup>119</sup>Sn NMR spectrum shows a broadened signal ( $h_{1/2} = 26$  Hz) because of unresolved vicinal <sup>119</sup>Sn–<sup>11</sup>B spin–spin coupling.<sup>[17]</sup> The <sup>29</sup>Si satellites for <sup>2</sup>J(<sup>119</sup>Sn<sup>29</sup>Si) are barely visible at the bottom of the <sup>119</sup>Sn NMR signal.



Table 3.	$^{13}C, ^{1}$	<sup>1</sup> B, <sup>1</sup>	<sup>9</sup> F, <sup>2</sup>	<sup>29</sup> Si,	and	<sup>119</sup> Sn NMR	parameters <sup>[a]</sup>	for	the	stannoles	5 7(Et,	Ph,	$C_5F_5$	).
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					$\delta$ [ppm]				
				$\delta_{ m C}$		δ	Si	$\delta_{\mathrm{B}}$	$\delta_{\mathrm{Sn}}$
	C2	C3	C4	C5	R/BR <sub>2</sub>	2-SiMe <sub>3</sub>	5-SiMe <sub>3</sub>	$(h_{1/2})$	$(h_{1/2})$
7a(Et) <sup>[b]</sup>	144.5	181.7	166.7	138.3	31.5 [89.6],	-9.7	-8.2	86.5	83.1
	[167.6]	(br.)	[89.4]	[231.8]	16.1 [10.7]/	[100.2]	[100.4]	(1400)	(33.8)
	65.2		11.8	63.8	22.3 (br.), 9.4	(0.5)	(0.5)		
7b(Et) <sup>[c]</sup>	145.5	183.7	168.5	139.5	32.1 [83.9],	-10.5	-9.2	87.0	141.8
	[166.0]	(br.)	[83.9]	[229.3]	16.2 [9.8]/	[96.0]	[96.2]	(1450)	(36.7)
	65.0		[11.3]	64.1	22.7 (br.), 9.7	(1.2)	(1.2)		
7c(Et) <sup>[d]</sup>	145.5	183.8	168.5	139.5	34.6 [49.9],	-10.5	-9.1	87.7	141.6
	[166.5]	(br.)	[83.7]	[228.7]	16.2 [10.1]/	[96.0]	[96.2]	(1840)	(13.7)
	[64.7]		[11.9]	[64.0]	22.7 (br.), 9.8	(1.2)	(1.2)		
7d(Et) <sup>[e]</sup>	142.8	184.0	169.8	136.8	31.8 [97.4],	-8.7	-7.2	87.1	50.4
	[200.0]	(br.)	[103.3]	[273.5]	16.1 [10.3]/	[95.5]	[96.9]	(2200)	(24.5)
	{64.7}	. /	{10.9}	{71.8}	22.3 (br.), 9.5				
7a(Ph) <sup>[f]</sup>	152.5	179.4	167.7	143.4	146.5 [96.1] ( <i>i</i> ),	-8.3	-6.9	70.0	79.6
, í	[161.8]	(br.)	[94.7]	[214.1]	129.1, 127.6, 126.4/	[99.0]	[95.7]	(3200)	(25.2)
	[63.6]		111.4	62.6	142.1 (br.) (i), 138.1 (o),	51.7	52.2		
					127.7 (m), 131.4 (p)				
<b>7b</b> (Ph) <sup>[g]</sup>	153.7	181.0	168.8	144.5	146.5 [92.2] ( <i>i</i> ),	-9.0	-7.7	70.0	138.1
, í	[160.9]	(br.)	[88.8]	[210.7]	129.2, 127.5,	[94.5]	[91.5]	(2500)	(24.0)
	[63.1]	. /	111.7	[62.1]	126.3/142.2 (br.)	51.9	52.1		
					( <i>i</i> ) 138.2 ( <i>o</i> ),				
					127.7 (m), 131.4 (p)				
$7a(C_6F_5)^{[h]}$	163.8	172.0	144.8	156.3	[h]	-8.3	-6.6	62.0	94.2
	[144.6]	(br.)	[n.o.]	[184.4]		[81.1]	[78.1]	(4000)	(30.0)
	[61.5]	. /		[57.7]				× /	. ,
$7b(C_6F_5)^{[i]}$	165.5	173.8	146.1	158.0	[i]	-9.0	-7.6	63.5	151.6
( 0 5)	[139.2]	(br.)	[96.9]	[178.2]		[73.7]	[76.2]	(5000)	(24.8)
	[59.7]		. ,	[57.7]					( )
$7d(C_6F_5)^{[j]}$	162.3	174.6	147.3	155.2	[3]	-7.4	-5.9	61.0	45.8
1 0 57	[179.8]	(br.)	[n.o.]	[227.3]		[75.7]	[75.4],	(5400)	(27.0)
	60.1	. /		57.4				· /	

[a] Measured at 296 K in  $C_6D_6$ , line widths  $h_{1/2}$  in () in Hz, coupling constants  ${}^nJ({}^{119}Sn,X)$  (X =  ${}^{29}Si, {}^{13}C$ ),  ${}^nJ({}^{29}Si, {}^{13}C$ ), and  $\overline{{}^nJ({}^{19}F, {}^{13}C)}$  in [], ||, and {}, respectively, in Hz, br. denotes the broadened  ${}^{13}C$  NMR signal of a carbon linked to boron, n.o means not observed. [b] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 1.9$  [10.8] [51.5] (5-SiMe<sub>3</sub>), 2.2 [9.8] [51.7] (2-SiMe<sub>3</sub>), 2.2 [9.3] [51.8] (5-SiMe<sub>3</sub>), 1.5.3 [272.5] (Sn-CH<sub>2</sub>), 29.9 [18.6] (CH<sub>2</sub>), 27.4 [51.7] (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>) ppm. [d] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 2.1$  [10.0] [51.6] (2-SiMe<sub>3</sub>), 2.2 [9.3] [51.8] (5-SiMe<sub>3</sub>), 15.7 [272.8] (Sn-CH<sub>2</sub>), 27.8 [18.7] (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>). 14.3 (CH<sub>3</sub>) ppm. [e] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 2.0$  [11.2] [52.1] (2-SiMe<sub>3</sub>), 1.9 [10.6] [52.1] (5-SiMe<sub>3</sub>), 141.5 [409.3] (Sn-C-*i*), 137.0 [39.0] (C-*o*), 128.5 [46.9] (C-*m*), 128.7 [5.9] (C-*p*) ppm. [f] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 2.3$  [10.3] [51.9] (2-SiMe<sub>3</sub>), 1.9 [7.7] [25.1] (CF<sub>2</sub>) ppm. [g] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 2.3$  [10.3] [51.9] (2-SiMe<sub>3</sub>), 1.9 [7.7] [25.2] (Sn-CH<sub>2</sub>), 27.6 [49.4] (CH<sub>2</sub>), 14.2 (CH<sub>3</sub>) ppm. [h] Other  ${}^{13}C$  NMR spectroscopic data:  $\delta_C = 2.3$  [10.3] [51.9] (2-SiMe<sub>3</sub>), 1.9 [7.7] [25.2] (SiMe<sub>3</sub>), 14.9 [269.2] (Sn-CH<sub>2</sub>), 27.6 [49.4] (CH<sub>2</sub>), 17.7 [61.4] (CH<sub>2</sub>), 120.5 t {22.6} (C-*i*), 114.4 t {20.9} (C-*i*) ppm, other  ${}^{13}C$  NMR signals were not assigned.  ${}^{19}F$  NMR spectroscopic data:  $\delta_C = 0.0$  [53.0] (SiMe<sub>3</sub>), 1.7 [52.0] (SiMe<sub>3</sub>), 14.9 [269.2] (Sn-CH<sub>2</sub>), 27.5 [30.7] (CH<sub>2</sub>), 31.7 [61.4] (CH<sub>2</sub>), 120.5 t {22.6} (C-*i*), 114.4 t {20.9} (C-*i*) ppm, other  ${}^{13}C$  CMR signals were not assigned.  ${}^{19}F$  NMR spectroscopic data:  $\delta_C = 0.0$  [53.0] (SiMe<sub>3</sub>), 1.7 [52.0] (SiMe<sub>3</sub>), 16.5 [27.7] (Sn-2(h<sub>2</sub>), 13.8 (CH<sub>3</sub>), 120.2 t {22.0} (C-*i*), 114.0 t {20.8} (C-*i*) pm, other  ${}^{13}C(C_6F_5)$  NMR signals were not assigned.  ${}^{19$ 

After several days in  $C_6D_6$  or toluene at room temp., the intermediates  $6(C_6F_5)$  rearrange completely into the stannoles  $7(C_6F_5)$ . This process is indicated by the <sup>11</sup>B NMR spectra in which the relatively sharp <sup>11</sup>B NMR signal in the borate region disappears and the typically broad <sup>11</sup>B NMR signal for the trigonal-planar boron atom grows.<sup>[26]</sup> Similarly, two new <sup>29</sup>Si NMR signals emerge, both accompanied by <sup>117/119</sup>Sn satellites for <sup>2</sup> $J(^{117/119}Sn,^{29}Si)$ ,<sup>[6]</sup> and a new broadened <sup>119</sup>Sn NMR signal appears at lower frequencies

than that for the corresponding intermediate. The pattern typical for the olefinic C-2–5 of the 3-borylated stannoles is observed in the <sup>13</sup>C NMR spectra<sup>[6]</sup> (Table 3). The temperature-dependent complex <sup>19</sup>F NMR spectra of 7(C<sub>6</sub>F<sub>5</sub>) can partially be analyzed<sup>[27]</sup> with respect to hindered rotation about the C–C<sub>6</sub>F<sub>5</sub> and all B–C bonds ( $\Delta G^{\#}$  at coalescence = 11.5±0.5 kcal/mol). The stannoles 7(C<sub>6</sub>F<sub>5</sub>) do not rearrange upon irradiation with Pyrex-filtered UV light<sup>[28a]</sup> as has been found for comparable siloles.<sup>[28b]</sup>





Figure 5. 100.6 MHz  ${}^{13}C{}^{1}H$  NMR spectrum of the stannole **7a**(Ph), obtained from the reaction mixture without further purification. Expansions are shown for the C-2,3,4,5 and C-*ipso* signals with  ${}^{117/119}$ Sn (asterisks) and  ${}^{29}$ Si satellites (crosses). The latter correspond to the  ${}^{13}$ C satellites in the  ${}^{29}$ Si NMR spectrum (Figure 2) and confirm the assignment for Si-2 and Si-5. Note the typically<sup>[18]</sup> broadened C-3 signals for the boron-bonded carbon atom.

Table 4. <sup>13</sup>C, <sup>11</sup>B, <sup>19</sup>F, <sup>29</sup>Si, and <sup>119</sup>Sn NMR parameters<sup>[a]</sup> for the zwitterionic intermediates 6(C<sub>5</sub>F<sub>5</sub>).

	$\delta$ [ppm]								
	$\delta_{5}$	Si	$\delta_{\rm C}$	$\delta_{\mathrm{C}}$	$\delta_{\mathrm{C}}$	$\delta_{ m F}$	$\delta_{ m F}$	$\delta_{\mathrm{B}}$	$\delta_{\mathrm{Sn}}$
	Si-C=	Si-C≡	B-C≡	Si-C≡	R′ <sub>2</sub> Sn	$C_6F_5$	$B(C_6F_5)_2$	$(h_{1/2})$	$(h_{1/2})$
<b>6a</b> (C <sub>6</sub> F <sub>5</sub> ) <sup>[b]</sup>	-7.8 [143.0]	-5.9 [<2]	175.0 (br.) <sup>[c]</sup>	116.5 [102.5]	22.9 [242.4] (Sn-CH <sub>2</sub> ), 27.2 [29.0] (CH <sub>2</sub> ), 30.2 [74.2] (CH <sub>2</sub> )	-140.0 m ( <i>o</i> ), -157.9 t   20.9   ( <i>p</i> ), -164.2 m   7.6     20.9   ( <i>m</i> )	-130.5 m ( <i>o</i> ), -158.7 t   20.9   ( <i>p</i> ), -165.2 m   8.5     20.9   ( <i>m</i> )	-12.8 (97)	200.6 (124)
$\pmb{6b}(C_6F_5)^{[d]}$	-9.3 [145.0]	-6.8 [<2]	175.0 (br.) <sup>[c]</sup>	124.3 [n.o.]	22.9 [272.9] (Sn-CH <sub>2</sub> ), 28.3 [60.1] (Sn-CH <sub>2</sub> -CH <sub>2</sub> ), 27.1 [73.8] (CH <sub>2</sub> ), 13.4 (CH <sub>3</sub> )	-139.3  m(o), -157.9  t   20.9  (p), -164.2  m   7.5     20.9  (m)	-130.2 m ( <i>o</i> ), -159.1 t   20.4   ( <i>p</i> ), -165.3 m   8.3     20.4   ( <i>m</i> )	-12.9 (140)	247.7 (99)
$\boldsymbol{6d}(C_6F_5)^{[e]}$	-7.2 [149.0]	-5.6 [<2]	173.0 (br.) <sup>[c]</sup>	116.9 [105.0]	135.5 [448.5], 136.2 [48.1], 129.3 [62.5], 131.6 [12.1]	-138.9 m ( <i>o</i> ), -156.9 t   21.2   ( <i>p</i> ), -163.7 m   7.9     21.2   ( <i>m</i> )	-129.7 m ( <i>o</i> ), -158.2 t   21.2   ( <i>p</i> ), -164.7 m   7.9     21.2   ( <i>m</i> )	-12.7 (90)	76.3 (55)

[a] Measured at 296 K in C<sub>6</sub>D<sub>6</sub>, linewidths  $h_{1/2}$  in () in Hz, coupling constants  ${}^{n}J({}^{119}\text{Sn},X)$  (X =  ${}^{29}\text{Si},{}^{13}\text{C}$ ),  ${}^{n}J({}^{29}\text{Si},{}^{13}\text{C})$ ,  ${}^{n}J({}^{19}\text{F},{}^{13}\text{C})$ , and  ${}^{n}J({}^{19}\text{F},{}^{19}\text{F})$  in [], ||, and |||, respectively, in Hz, br. denotes the broadened  ${}^{13}\text{C}$  NMR signal of a carbon linked to boron, n.o means not observed. [b]  $\delta_{Si}(\text{Si-C} =)_{caled.} = -4.4$  ppm,  $\delta_{Si}(\text{Si-C} \approx)_{caled.} = -3.7$  ppm; other  ${}^{13}\text{C}$  NMR spectroscopic data:  $\delta_{C} = -0.3$  (SiMe<sub>3</sub>), 0.1 (SiMe<sub>3</sub>), 119.1 br. (B-C<sub>6</sub>F<sub>5</sub>, *i*), 121.8 t {21.7} (C<sub>6</sub>F<sub>5</sub>, *i*), 152.1 (Sn-C=), 175.0 br. (=C-B) ppm. [c] Assignment uncertain, because of overlap with  ${}^{13}\text{C}$  (C-B) NMR signal. [d] Other  ${}^{13}\text{C}$  NMR spectroscopic data:  $\delta_{C} = -0.5$  (SiMe<sub>3</sub>), 0.1 (SiMe<sub>3</sub>), 119.7 br. (B-C<sub>6</sub>F<sub>5</sub>, *i*), 122.4 t {21.8} (C<sub>6</sub>F<sub>5</sub>, *i*), 157.4 (Sn-CH=), 175.0 br. (=C-B) ppm. [e] Other  ${}^{13}\text{C}$  NMR spectroscopic data:  $\delta_{C} = -1.1$  (SiMe<sub>3</sub>), 0.2 (SiMe<sub>3</sub>), 119.2 br. (B-C<sub>6</sub>F<sub>5</sub>, *i*), 122.2 t {21.5} (C<sub>6</sub>F<sub>5</sub>, *i*), 155.8 (Sn-CH=), 180.0 br. (=C-B) ppm.

#### Zwitterionic Intermediates in the Course of 1,1-Carboboration

As shown in Scheme 3, among the first products formed in the intermolecular 1,1-carboboration reactions are the alkene derivatives 4, unsuitable for further intramolecular 1,1-carboboration. Apparently, Z/E isomerization readily takes place to give zwitterionic intermediates 6 and finally stannoles 7 via the elusive alkene 5. There is evidence (Scheme 4) that this particular Z/E isomerization takes place by 1,1-decarboboration, a process in which not only notoriously labile Sn–C but also C–C bonds are cleaved under mild conditions. This can be concluded from earlier observations by Hagelee and Köster using rather forcing conditions [Scheme 4 (a)],<sup>[29]</sup> and later on from our work under much milder conditions [Scheme 4 (b,c)].<sup>[7,8,14]</sup>

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Scheme 4. Examples of organometallic-substituted alkenylboranes known to undergo 1,1-decarboboration.



Figure 6. 79.47 MHz <sup>29</sup>Si{<sup>1</sup>H} NMR (at 296 K, in C<sub>6</sub>D<sub>6</sub>; refosused INEPT<sup>[11]</sup>) for the reaction of **3d** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> leading at first almost selectively to the zwitterionic intermediate **6d**(C<sub>6</sub>F<sub>5</sub>). The satellite signals for <sup>2</sup>J(<sup>119</sup>Sn,<sup>29</sup>Si) are marked by asterisks.

The 1,1-decarboboration requires the formation of a borate-like intermediate by charge separation (A, B, or C, Scheme 4) when the Me<sub>3</sub>Sn or Me<sub>3</sub>M groups move along the C=C bond. The relative contributions of the respective structures A, B, or C may be reflected in the <sup>11</sup>B and <sup>13</sup>C chemical shifts and, in favorable cases, by structural parameters such as Sn-C bond lengths (Figure 7). Given the shortcomings of the theoretical model (e.g., by using the LAN<sup>[24]</sup> data set for the heavy atom Sn), the trends in the experimental data are fairly well reproduced by the calculations. Particularly noteworthy are the strongly deshielded <sup>13</sup>C(B-C=) nuclei in  $6(C_6F_5)$  (Figure 7 and Table 4), which indicate significant contributions of structure A (Scheme 4). Such a structure, similar to a β-metal-stabilized carbocation,<sup>[30]</sup> can be considered as a prerequisite for the final intramolecular 1,1-carboboration. This process is usually fast for 6(Et) and 6(Ph), and becomes moderately slow in  $6(C_6F_5)$  because the  $C_6F_5$  groups on the boron lead to an increase in the Lewis acidity of boron to favor a longerlived borate structure.

Sn	Si B Si Si	Sn P B St	Sn B 1 2	N Sn 2 N	Sny B An An B
6a	$(C_6F_5)$	<b>8</b> (C <sub>6</sub> F <sub>5</sub> )	<b>9</b> (Et)	<b>10</b> (Et)	<b>11</b> (Et)
Sn-C1 [pm] exp. (calcd.)	247.8 (249.3)	252.0 (256.7)	233.5 (230.9)	262.6 (258.4)	235.5 (231.8)
Sn-C2 [pm] exp. (calcd.)	247.7 (251.4)	252.7 (243.7)	252.3 (267.3)	260.4 (253.8)	251.1 (267.6)
$\delta^{13}$ C(1) exp. (calcd.)	175.0 (155.6)	120.0 (140.1)	106.1 (117.0)	127.2 (143.4)	109.1 (104.7)
δ <sup>13</sup> C(2) exp. (calcd.)	116.5 (121.6)	90.8 (85.4)	123.3 (155.8)	97.9 (96.6)	124.9 (137.0)
δ <sup>11</sup> B exp. (calcd.)	-12.8 (-13.4)	-15,4 (-17.5)	-2.6 (-0.7)	-10.2 (-11.6)	-5.6 (-1.0)

Figure 7. Comparison of the experimental and calculated structural parameters and chemicals shifts  $\delta_{\rm C}$  and  $\delta_{\rm B}$  of some zwitterionic intermediates **6a**(C<sub>6</sub>F<sub>5</sub>), **8**(C<sub>6</sub>F<sub>5</sub>), **9**(Et),<sup>[31]</sup> **10**(Et),<sup>[32]</sup> and **11**(Et).<sup>[33]</sup>



The isolated and characterized intermediates  $6(C_6F_5)$  are the first examples in which a stannyl group is side-on coordinated to the C=C bond of an alkynylborate bearing a Me<sub>3</sub>Si group. Previously, such intermediates with C=C-SiMe<sub>3</sub> units were not observed at all, except when the cationic stannyl group was stabilized by a coordinative Sn-N bond, although direct structural evidence was missing.<sup>[16]</sup> Now we have succeeded in isolating and structurally characterizing  $6a(C_6F_5)$  (Figure 8). The unit B–C1–C33 is close to linear [178.9(5)°], whereas the unit C1–C33–Si1 is markedly bent [155.1(4)°], and both Sn-C1 and Sn-C33 distances are somewhat shorter than in the related derivative  $8(C_6F_5)$ .<sup>[9]</sup> All other bond lengths and angles of  $6a(C_6F_5)$ are in the expected ranges. The tetracoordinate boron atom is typically at the center of a slightly distorted tetrahedron. The surroundings of the tin atom deviate from trigonal planarity (sum of the bond angles 347.3°) as a result of bonding interactions with the  $C \equiv C$  bond. The sum of the bond angles at tin is larger in both  $8(C_6F_5)$  (354.4°)<sup>[9]</sup> and 9(Et) (351.1°),<sup>[31]</sup> which suggests stronger additional bonding interactions in  $6a(C_6F_5)$ . The atoms B1, Sn1, C8, C9, C1, and C33 form a plane within experimental error.



Figure 8. Molecular structure of the zwitterionic intermediate  $6a(C_6F_5)$  (ORTEP, ellipsoids drawn at the 40% probability level, hydrogen aroms have been omitted for clarity). Selected bond lengths [pm] and angles (°): Sn1–C22 213.3(5), Sn1–C26 215.1(5), Sn1–C9 215.4(4), Sn1–C33 247.5(5), Sn1–C1 247.8(4), Si2–C9 188.5(5), Si1–C33 188.1(5), C1–C33 122.7(6), C1–B1 161.1(7), C2–B1 166.3(7), B1–C8 163.8(7), B1–C16 165.5(7), C8–C9 135.6(6), C8–C10 150.9(6), C22–Sn1–C26 101.26(18), C22–Sn1–C9 121.94(19), C26–Sn1–C9 124.07(18), C9–Sn1–C13 105.63(16), C1–C33–Sn1 75.8(3), C9–Sn1–C1 79.16(16), C33–Sn1–C1 28.69(14), C33–C1–Sn1 75.5(3), C33–C1–B1 178.9(5), C1–B1–C8 107.5(4), C1–B1–C16 108.8(4), C1–B1–C2 103.3(4), C8–B1–C2 115.8(4), C16–B1–C2 112.6(4), C8–C9–Si2 130.5(3), C8–C9–Sn1 115.5(3), Si2–C9–Sn1 113.8(2), C1–C33–Si1 155.1(4).

## Conclusions

Confirming previous findings, it has been shown that the 1,1-carboboration of bis(trimethylsilylethynyl)tin compounds, irrespective of the other substituents on tin, provides a general route to stannoles bearing trimethylsilyl groups at the 2 and 5 positions. Moreover, the use of  $B(C_6F_5)_3$  has helped to establish firm evidence for the

mechanism of 1,1-carboboration by the characterization of zwitterionic intermediates prior to stannole formation, both in the solid state and in solution.

### **Experimental Section**

General: All preparative work, as well as handling of the samples, was carried out observing precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. Diphenyltin, di-n-butyltin, and di-n-octyltin dichlorides, trimethylsilylethyne, and triethylborane were commercially available and used as received. 1,1-Dibromo-1-stannacyclohexane was prepared as described in the literature.<sup>[34]</sup> <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F, <sup>29</sup>Si, and <sup>119</sup>Sn NMR spectra were recorded in CDCl<sub>3</sub>, C<sub>6</sub>D<sub>6</sub>, and [D<sub>8</sub>]toluene (concentration ca. 5-10%) with samples in 5 mm tubes at  $23 \pm 1$  °C by using Varian Inova 300 and 400 MHz spectrometers; chemical shifts are given relative to Me<sub>4</sub>Si [ $\delta_{\rm H}$ ]  $(CHCl_3) = 7.24, \delta_C (CDCl_3) = 77.0, \delta_H (C_6HD_5) = 7.15, \delta_C (C_6D_6)$ = 128.0,  $\delta_{\rm H}$  (C<sub>6</sub>D<sub>5</sub>CHD<sub>2</sub>) = 2.03,  $\delta_{\rm C}$  (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>) = 20.4,  $\delta_{\rm Si}$  = 0 ppm], external Me<sub>4</sub>Sn [ $\delta_{Sn} = 0$  ppm for  $\Xi$ (<sup>119</sup>Sn) = 37.290665 MHz], external CFCl<sub>3</sub> [ $\delta_{\rm F}$  = 0 ppm for  $\Xi$ (<sup>19</sup>F) = 94.094003 MHz], and external BF<sub>3</sub>·OEt<sub>2</sub> [ $\delta_B = 0$  ppm for  $\Xi(^{11}B) =$ 32.083971 MHz]. Chemical shifts are given to  $\pm 0.1$  ppm for  $\delta_{\rm C}$ ,  $\delta_{\rm F}$ ,  $\delta_{\rm Si}$ , and  $\delta_{\rm Sn}$ , and to  $\pm 0.4$  ppm for  $\delta_{\rm B}$ ; coupling constants are given to  $\pm 0.4$  Hz for  $J(^{119}\text{Sn},^{13}\text{C})$ . <sup>13</sup>C NMR signals were assigned by the usual 2D methods (1H-13C HSQC and HMBC[35]). 19F NMR spectra were assigned by <sup>19</sup>F-<sup>19</sup>F COSY experiments.<sup>[35] 29</sup>Si NMR spectra were recorded by using the refocused INEPT pulse sequence,<sup>[11]</sup> based on  ${}^{2}J({}^{29}\text{Si},{}^{1}\text{H}_{\text{Me}}) = 7$  Hz.  ${}^{119}\text{Sn}$  NMR spectra were recorded directly by single pulse methods or also by the refocused INEPT pulse sequence<sup>[11]</sup> based on  ${}^{2}J({}^{119}Sn,{}^{1}H)$  (50–100 Hz) after optimizing the delay times in the pulse sequence. EI mass spectra (70 eV) were recorded by using a Finnigan MAT 8500 spectrometer with a direct inlet or solutions (1H, 11B, 12C, 19F, 28Si, 120Sn). IR spectra were recorded with a Perkin-Elmer Spectrum 100 FTIR spectrometer equipped with an ATR unit. Melting points were determined by using a Büchi 510 melting point apparatus. Elemental analyses (C, H) were performed with a Vario Elementar EL III instrument. All quantum chemical calculations were carried out by using the Gaussian 09 program package.[36]

**Typical Procedure for the Synthesis of Bis(trimethylsilylethynyl)tin Compounds 3a–d:** A freshly prepared suspension of trimethylsilylethynyllithium [30 mmol; from trimethylsilylethyne and *n*BuLi (1.6 M) in hexane] was cooled to -78 °C, and the respective diorganotin dihalide (15 mmol) was added in one portion. The mixture was stirred, warmed to room temp., and heated at reflux for 10 min. Insoluble materials were removed by filtration and volatile materials were removed under vacuum (10<sup>-2</sup> Torr). The colorless residues consisted of the pure compounds **3a–d** (yields 80–95%). Crystals of **3a** were grown from concentrated solutions in hexane.

**3a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H} = 0.16$  (s, 18 H, SiMe<sub>3</sub>), 1.31 [t, <sup>2</sup>*J*(<sup>119</sup>Sn,<sup>1</sup>H) = 67.7 Hz, 6.7 Hz, 4 H, CH<sub>2</sub>], 1.36–1.49 (m, 2 H, CH<sub>2</sub>), 1.84 [m, <sup>3</sup>*J*(<sup>119</sup>Sn,<sup>1</sup>H) = 105.5 Hz, 4 H, CH<sub>2</sub>] ppm. IR (ATR, hexane):  $\tilde{v} = 2013$  [v(C=C)] cm<sup>-1</sup>. C<sub>15</sub>H<sub>28</sub>Si<sub>2</sub>Sn (382.9): calcd. C 47.01, H 7.37; found C 46.8, H 7.3.

**3b**: B.p. 83–87 °C/10<sup>-3</sup> Torr, colorless oil. <sup>1</sup>H NMR ([D<sub>8</sub>]toluene):  $\delta_{\rm H} = 0.0$  (s, 18 H, SiMe<sub>3</sub>), 0.74 (t, 7.3 Hz, 6 H, CH<sub>3</sub>), 0.89 [t, J = 7.9 Hz, <sup>2</sup>J(<sup>119</sup>Sn,<sup>1</sup>H) = 60.9 Hz, 4 H, CH<sub>2</sub>-Sn], 1.18 (4 H, CH<sub>2</sub>), 1.48 [m, <sup>3</sup>J(<sup>119</sup>Sn,<sup>1</sup>H) = 77.0 Hz, 4 H] ppm. IR (ATR, hexane):  $\tilde{v} = 2089$  [v(C=C)] cm<sup>-1</sup>. MS (EI): m/z (%) = 370 (100) [M – Bu]<sup>+</sup>, 314 (8) [Sn(CCSiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 216 (12) [Sn(CCSiMe<sub>3</sub>)]<sup>+</sup>, 97 (7) [CCSiMe<sub>3</sub>]<sup>+</sup>, 73 (7) [SiMe<sub>3</sub>]<sup>+</sup>.



**3c:** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 399.81 MHz, 296 K):  $\delta_{\rm H} = 0.14$  (s, 18 H, SiMe<sub>3</sub>), 0.89 (t, 6.7 Hz, 6 H, Me), 1.07 [m, <sup>2</sup>J(<sup>119</sup>Sn,<sup>1</sup>H) = 61.0 Hz, 4 H, CH<sub>2</sub>], 1.18–1.38 (m, 16 H), 1.67 [m, <sup>3</sup>J(<sup>119</sup>Sn,<sup>1</sup>H) = 78.1 Hz, 4 H, CH<sub>2</sub>] ppm. IR (ATR, hexane):  $\tilde{v} = 2084 [v(C=C)] \text{ cm}^{-1}$ . MS (EI): m/z (%) = 525 (2) [M - Me]<sup>+</sup>, 427 (100) [OctSn-(CCSiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 314 (8) [Sn(CCSiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 217 (19) [Sn(CCSiMe<sub>3</sub>)]<sup>+</sup>, 97 (9) [CCSiMe<sub>3</sub>]<sup>+</sup>, 73 (8) [SiMe<sub>3</sub>]<sup>+</sup>, 43 (17) [SiMe]<sup>+</sup>.

**3d**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H} = 0.10$  (s, 18 H, SiMe<sub>3</sub>), 7.07 (m, 6 H, *m/p*-C<sub>6</sub>H<sub>5</sub>), 7.70 [m, <sup>3</sup>*J*(<sup>119</sup>Sn,<sup>1</sup>H) = 66.3 Hz, 4 H, *o*-C<sub>6</sub>H<sub>5</sub>] ppm. C<sub>22</sub>H<sub>28</sub>Si<sub>2</sub>Sn (466.9): calcd. C 56.55, H 6.04; found C 56.8, H 6.1.

Typical Procedure for the Ethyl- and Phenylboration of Bis(trimethylsilylethynyl)tin Compounds to Yield 7a–d(Et, Ph): A stirred solution of the alkynyltin compound (0.7 mmol) in hexane (20 mL) was cooled to -78 °C and an equimolar amount of triethylborane (or triphenylborane as a solution in toluene) was added through a syringe. After 1 h, the yellowish mixture was warmed to room temperature, and after 3 d (BEt<sub>3</sub>) or 1 h (BPh<sub>3</sub>), all volatile materials were removed under vacuum ( $10^{-2}$  Torr). Monitoring the reaction by <sup>29</sup>Si NMR spectroscopy showed for BEt<sub>3</sub> the presence of intermediates of the type 4(Et) (see Figure 1), which rearranged completely into the stannoles 7(Et). The stannoles were left as light-yellow oils or a waxy solid 7d(Et) and 7d(Ph) (>97% pure according to NMR spectroscopy).

**7a(Et):** <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H} = 0.10$  (s, 9 H, SiMe<sub>3</sub>), 0.21 (s, 9 H, SiMe<sub>3</sub>), 1.36, 0.94 (qt, 10 H, BEt<sub>2</sub>), 2.20 1.01 (qt, 5 H, 4-Et), 1.31 (t, 4 H, CH<sub>2</sub>), 1.42–1.62 (m, 6 H, CH<sub>2</sub>), 1.82 (m, 4 H, CH<sub>2</sub>) ppm.

**7b**(Et): <sup>1</sup>H NMR ([D<sub>8</sub>]toluene):  $\delta_{\rm H} = 0.10$  (s, 9 H, SiMe<sub>3</sub>), 0.20 (s, 9 H, SiMe<sub>3</sub>), 2.17 (q, 2 H, 4-CH<sub>2</sub>) ppm; no assignment of other <sup>1</sup>H NMR signals because of severe overlap.

7c(Et): <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta_H = 0.19$  (s, 9 H, SiMe<sub>3</sub>), 0.29 (s, 9 H, SiMe<sub>3</sub>), 1.79 (q, 4 H, CH<sub>2</sub>, BEt<sub>2</sub>), 1.82 (m, 4 H, CH<sub>2</sub>), 2.08 (q, 2 H, 4-CH<sub>2</sub>) ppm; no assignment of other <sup>1</sup>H NMR signals because of severe overlap.

**7d**(Et): <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H} = -0.22$  (s, 9 H, SiMe<sub>3</sub>), -0.10 (s, 9 H, SiMe<sub>3</sub>), 1.30, 0.87 (qt, 10 H, BEt<sub>2</sub>), 2.16, 0.93 (qt, 5 H, 4-Et), 7.10–7.21 (m, 6 H, Ph), 7.43 (m, 2 H, Ph). C<sub>28</sub>H<sub>43</sub>BSi<sub>2</sub>Sn (565.3): calcd. C 59.49, H 7.67; found C 59.3, H 7.4.

**7a**(Ph): <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H} = 0.09$  (s, 9 H, SiMe<sub>3</sub>), 0.11 (s, 9 H, SiMe<sub>3</sub>), 1.51–1.72 (m, 6 H, CH<sub>2</sub>), 2.02–2.12 (m, 4 H, CH<sub>2</sub>), 6.63–6.91 (m, 3 H, Ph), 7.02–7.26 (m, 5 H, Ph), 7.70 (m, 2 H, Ph) ppm.

**7b**(Ph): <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\rm H} = -0.03$  (s, 9 H, SiMe<sub>3</sub>), -0.01 (s, 9 H, SiMe<sub>3</sub>), 1.01 (t, 6 H, CH<sub>3</sub>), 1.38 (m, 4 H, CH<sub>2</sub>), 1.46 (m, 4 H, CH<sub>2</sub>), 1.82 (m, 4 H, CH<sub>2</sub>), 6.55–6.81 (m. 3 H, Ph), 7.07–7.22 (m, 5 H, Ph), 7.66 (m, 2 H, Ph) ppm.

Typical Procedure for the 1,1-Carboboration of Bis(trimethylsilylethynyl)tin Compounds with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>: A stirred solution of the respective bis(trimethylsilylethynyl)tin compound (0.4 mmol) in hexane (15 mL) was cooled to -78 °C and a solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene (0.096 M, 4.2 mL) was added. The mixture was stirred for 30 min, warmed to room temp., and after 15 min volatile materials were removed under vacuum (10<sup>-2</sup> Torr). The residue was taken up in C<sub>6</sub>D<sub>6</sub>, in which the intermediates 6(C<sub>6</sub>F<sub>5</sub>) are less soluble than the stannoles 7(C<sub>6</sub>F<sub>5</sub>). This enabled us to isolate pure samples of 6(C<sub>6</sub>F<sub>5</sub>). Crystals of 6a(C<sub>6</sub>F<sub>5</sub>) were grown from concentrated solutions in toluene at -26 °C. In solution at room temp., the derivatives 6(C<sub>6</sub>F<sub>5</sub>) rearranged completely after several days into the stannoles 7(C<sub>6</sub>F<sub>5</sub>).

**6a**(C<sub>6</sub>F<sub>5</sub>): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H} = -0.14$  (s, 9 H, SiMe<sub>3</sub>), -0.02 (s, 9 H, SiMe<sub>3</sub>), 0.75-1.88 (m,10 H, CH<sub>2</sub>) ppm.

7a(C<sub>6</sub>F<sub>5</sub>): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H}$  = -0.07 (s, 9 H, SiMe<sub>3</sub>), 0.01 (s, 9 H, SiMe<sub>3</sub>), 1.25-1.49 (m, 6 H, CH<sub>2</sub>), 1.77-1.93 (m, 4 H, CH<sub>2</sub>) ppm.

**6b**(C<sub>6</sub>F<sub>5</sub>): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H} = -0.12$  (s, 9 H, SiMe<sub>3</sub>), -0.05 (s, 9 H, SiMe<sub>3</sub>), 0.9 (t, 6 H, CH<sub>3</sub>), 1.21-1.67 (m, 12 H, CH<sub>2</sub>) ppm.

**7b**(C<sub>6</sub>F<sub>5</sub>): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H} = -0.09$  (s, 9 H, SiMe<sub>3</sub>), -0.03 (s, 9 H, SiMe<sub>3</sub>), 0.95 (t, 6 H, CH<sub>3</sub>), 1.21–1.37 (m, 8 H, CH<sub>2</sub>), 1.56–1.68 (m, 4 H, CH<sub>2</sub>) ppm.

**6d**(C<sub>6</sub>F<sub>5</sub>): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H} = -0.12$  (s, 9 H, SiMe<sub>3</sub>), 0.02 (s, 9 H, SiMe<sub>3</sub>), 7.30–7.48 (m, 6 H, Ph), 7.93 (m, 4 H, Ph) ppm.

**7d**(C<sub>6</sub>F<sub>5</sub>): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\rm H}$  = −0.14 (s, 9 H, SiMe<sub>3</sub>), 0.00 (s, 9 H, SiMe<sub>3</sub>), 7.30–7.46 (m, 6 H, Ph), 7.91 (m, 4 H, Ph) ppm.

**Crystal Structure Determinations of 3a and 6a(C\_6F\_5):** Details pertinent to the crystal structure determinations are listed in Table 5.<sup>[37]</sup> Crystals of appropriate size were selected (in perfluorinated oil at tom temperature)<sup>[38]</sup> and the data collections were carried out at 133 K using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit. Structure solutions and refinements were accomplished by using SIR97,<sup>[39]</sup> SHELXL-97,<sup>[40]</sup> and WinGX.<sup>[41]</sup>)

Table 5. Crystallographic data<sup>[a]</sup> of 1,1-bis(trimethylsilylethynyl)-1-stannacyclohexane (**3a**) and the zwitterionic intermediate **6a**( $C_6F_5$ ).

Parameters	3a	<b>6a</b> (R = $C_6F_5$ )
Formula	C <sub>15</sub> H <sub>28</sub> Si <sub>2</sub> Sn	C <sub>33</sub> H <sub>28</sub> BF <sub>15</sub> Si <sub>2</sub> Sn
M [g/mol]	383.24	895.23
Crystal shape	Colorless plate	Colorless plate
Crystal size [mm <sup>3</sup> ]	$0.33 \times 0.32 \times 0.28$	$0.33 \times 0.07 \times 0.06$
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	ΡĪ
Lattice parameters		
a [pm]	1825.7(1)	1090.8(3)
<i>b</i> [pm]	906.8(1)	1126.3(3)
<i>c</i> [pm]	1238.4(1)	1682.3(5)
a [°]	90	93.078(20)
β [°]	108.336(3)	108.074(19)
γ [°]	90	109.428(19)
Z	4	2
$\rho_{\text{calcd.}} [\text{g/cm}^3]$	1.308	1.630
F(000)	784	888
$\theta$ range [°]	1.73-26.08	1.67-25.615
$\mu \text{ [mm^{-1}]}$	1.422	0.867
T [K]	133(2)	133(2)
Reflections collected	7042	23275
Independent reflec-	3199	4299
tions $[I \ge 2\sigma(I)]$		
Absorption correction	numerical	_[b]
Refined parameters	163	469
$wR_2/R1 \ [I \ge 2\sigma(I)]$	0.0162/0.0384	0.0427/0.0760
Max./min. residual	0.482/-0.229	1.047/-0.443
electron density		
$[10^{-6} \mathrm{epm^{-3}}]$		

<sup>[</sup>a] Diffractometer: STOE IPDS II, Mo- $K_a$ ,  $\lambda = 71.073$  pm, graphite monochromator. [b] Absorption corrections did not improve the parameter set.

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