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Novel organotin halides. Organometallic substituted stannoles and alkene derivatives with tin–chlorine and tin–bromine bonds—exceptionally small magnitude of coupling constants $|^1J(^{119}Sn, ^{13}C)|$

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Abstract

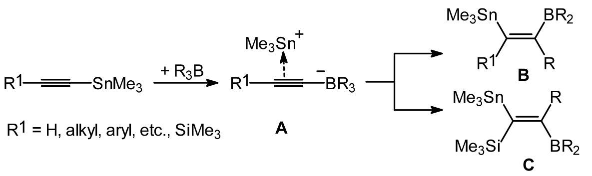
Exchange reactions of spirocyclic stannoles with boron, tin and phosphorus halides lead to stannoles **4**, **5** and **6**, **7**, in which the tin atoms bear two chloro or two bromo ligands. The same stannoles **4** and **5** were prepared by 1,1-ethylboration of bis(trimethylsilylethynyl)tin dichloride (**8**) or -dibromide (**9**), prepared in situ from tetrakis(trimethylsilylethynyl)tin and tin tetrachlodide or -tetrabromide. Alkenes with a similar pattern of substituents at the C=C bond were prepared either by 1,1-ethylboration of the trimethylsilylethynyltin trihalides (**10**, **11**, leading to **12**, **13**) or by exchange reactions of organotin substituted alkenes with tin tetrachloride (leading to **14**). All compounds, in which a trimethylsilyl and an SnX_2 moiety (in the stannoles **4**, **5**) or an SnX_3 group (in the alkenes **12**, **13**) are in geminal positions at the olefinic carbon atoms, decompose already at room temperature by elimination of SnX_2 ($X = Cl$, Br). Exceptionally small coupling constants $|^1J(^{119}Sn, ^{13}C)|$ are observed for these compounds. The comparable derivatives, in which the trimethylsilyl groups are replaced by propyl (stannoles **6**, **7**, and the alkene **14**), are much more stable, and the magnitude of $|^1J(^{119}Sn, ^{13}C)|$ is found in the expected range. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkynes; Organotin; Aminotin compounds; Heterocycles; Organoboranes; 1,1-Organoboration; NMR; Multinuclear

1. Introduction

1-Alkynyltin compounds react with triorganoboranes by 1,1-organoboration [1,2] to give novel organometallic-substituted alkenes, various types of heterocycles, and many other useful organometallic compounds as starting materials for further transformations. The 1,1-organoboration starts by cleavage of the Sn–C≡ bond (Scheme 1), leading to a borate-like intermediate **A**, in which one organyl group is then transferred from boron to the adjacent carbon atom, and the stannyl and boryl groups end up in *cis*-positions at the C=C bond (**B**). If there is another organometallic group involved, e.g. a silyl group, the stereochemistry may be different [3], and the boryl and stannyl groups may end up in *trans*-positions at the C=C bond (**C**), or mixtures of (*E*/*Z*)-isomers are obtained, depending on reaction conditions, since the 1,1-organoboration is a reversible reaction [1,2].

Stannoles are important examples of heterocycles [4,5]. 1,1-Organoboration provides a particularly convenient synthetic route to stannoles bearing different substituents at the carbon atoms. Usually bis(1-alkynyl)-diorganotin compounds serve as starting materials [6],



Scheme 1.

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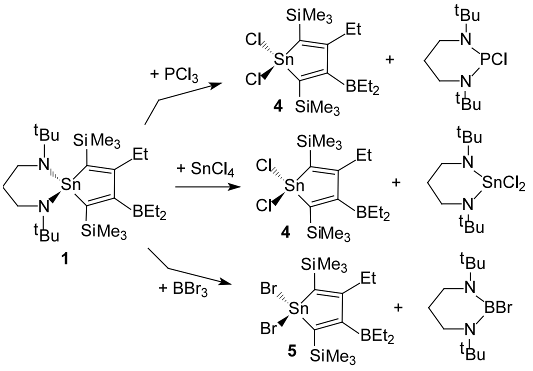
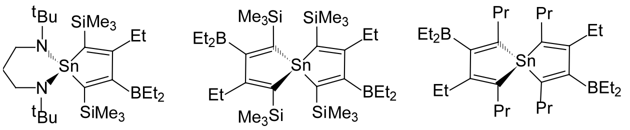


Scheme 2.

including a stannacyclohexane derivative [6g]. The presence of functional groups at the tin atom would be highly desirable for further development of this chemistry. In this context, we have recently reported that the spirocyclic stannole **1** can be prepared in high yield [7]. On the other hand, previous work on the 1,1-organoboration of tetrakis(1-alkynyl)tin has opened the route to the spiro-bistannoles **2** [8] and **3** [9]. If the compounds **1**–**3** undergo exchange reactions with various electrophiles such as BBr_3, $SnCl_4$, or PCl_3, this should eventually lead to stannoles with Sn–Cl or Sn–Br bonds. The reactions of **3** with an excess of BCl_3 or BBr_3 have already been shown to give carboranes, and stannoles with $SnCl_2$ or $SnBr_2$ fragments have been proposed as intermediates [9]. In order to understand the NMR data of such stannoles, we have also tried to prepare alkenes of type **B** or **C** in which the Me_3Sn is replaced by a $SnCl_3$ or $SnBr_3$ group. The present study was performed in order to explore the access to the virtually unknown area of stannoles bearing halogen substituents at the tin atom, taking advantage of multinuclear magnetic resonance for monitoring reactions and analysing complex mixtures.



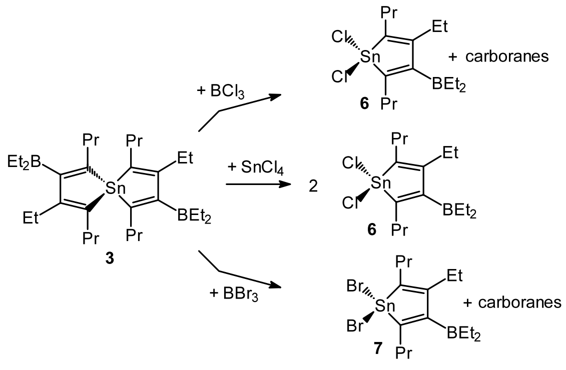
1 **2** **3**

(Formulas 1, 2, 3)

2. Results and discussion

2.1. Exchange reactions of the spirocyclic compounds *1*–*3* with electrophiles

The spirocyclic tin compounds **1**–**3** were prepared as described previously [7–9]. It turned out that the compound **2** is inert against $SnCl_4$, PCl_3 and BBr_3. In the latter case, slow decomposition occurs after prolonged heating in boiling BBr_3, probably as a result of electrophilic attack at the peripheral Me–Si and Et–B bonds.



Scheme 3.

In contrast, compound **1** reacts with $SnCl_4$, PCl_3 and BBr_3 under mild conditions at the Sn–N bonds to give the desired stannoles **4** and **5** together with the respective amino-element derivatives (Scheme 2). In the case of the reaction of **1** with an excess of $SnCl_4$, neither the stannole ring nor the cyclic tin amide undergo fast ring-opening, whereas an excess of PCl_3 or BBr_3 causes opening of the cyclic amide. An excess of BBr_3 also causes decomposition of **5**.

In all cases of the exchange reactions shown in Scheme 1, the reaction solutions became readily cloudy and dark, and a colourless precipitate, identified as $SnCl_2$ or $SnBr_2$, was formed. The ^{13}C-NMR data sets of **4** and **5** were rather surprising when compared with other stannoles of the same type (see Table 1). Therefore, in order to establish the identity of **4** and **5**, another route to these compounds was explored (Section 2.2).

Compound **3** did not react with PCl_3. These reactions are rather sluggish if only Sn–C bonds are present [10]. In contrast, the reaction of **3** with $SnCl_4$ gave **6**. Compound **6** as well as **7** could be identified in the complex reaction solutions which were obtained when only one equivalent of BCl_3 and BBr_3, respectively, was offered to react with **3** [9] (Scheme 3).

The ^{13}C-NMR data of the stannoles **6** and **7** were in the expected range when compared with data for other stannoles with the same substitution pattern at the carbon atoms in positions 2–5 (see Table 2).

2.2. 1,1-Organonoration of equilibrated mixtures containing $Cl_2Sn(C\equiv C–SiMe_3)_2$ (*8*) and $Br_2Sn(C\equiv C–SiMe_3)_2$ (*9*)

Since it was not possible to isolate the stannoles **4** or **5** from the reactions mixtures (Scheme 2), an independent route to such stannoles was explored. 1,1-Ethylboration of $Cl_2Sn(C\equiv C–SiMe_3)_2$ (**8**) and $Br_2Sn(C\equiv C–SiMe_3)_2$ (**9**), in analogy to other bis(1-alkynyl)tin com-

Table 1
^{13}C-, ^{29}Si-, ^{119}Sn-NMR data [a] of stannoles with Me_3Si and Et_2B groups in 2, 5and 3 positions [b]

X_2	**4** Cl/Cl		**5** Br/Br		Me/Me		**2** Spiro		**1** [c] $N^{t}Bu(CH_2)_3N^{t}Bu$	
C(2)	132.6 [d] [110.1] (63.6)		133.9 [93.4] (63.5)		145.0 [194.2] (65.0)		144.1 [121.0] (64.4)		147.1 [281.2]	
C(3)	181.8 (br)		180.6 (br)		181.1 (br)		182.3 (br)		176.0 (br)	
C(4)	161.9 [254.0]		161.6 [245.9]		166.7 [94.8] (11.6)		168.3 [85.9] (11.3)		161.0 [162.5]	
(C5)	125.8 [244.0] (62.0)		127.8 [220.1] (62.8)		139.1 [260.4] (63.8)		138.1 [183.7] (63.4)		137.7 [321.3]	
X_2	–		–				See C(2)–C(5)		55.8 [10.8]	29.5 ($N^{t}Bu$) [21.0]
3-Et	32.1 [172.0]	15.4 [14.0]	31.9 [165.0]	15.6 [13.8]			32.1 [87.0]	15.7	32.8 [123.0]	14.8 [10.8]
BEt_2									23.2 (br) 9.6	
$SiMe_3$							2.2 [11.3]	2.2 [10.7]	2.7 [12.5] [e]	
$\delta^{29}Si$	−5.1 (5-Si) [123.2]	−6.2 (2-Si) [122.1]	−4.8 [123.0]	−5.8 [122.1]	−8.2 [98.2]	−9.7 [97.4]	−8.9 [96.1]	−7.3 [98.1]	−8.1 [118.4]	−9.6 [112.0]
$\delta^{119}Sn$	+74.8		−11.8		+133.5		+222.1		−13.9	

[a] Coupling constants $J(^{119}Sn, ^{13}C)$ and $J(^{119}Sn, ^{29}Si)$ are given in brackets, $J(^{29}Si, ^{13}C)$ in parentheses; (br) denotes a broad signal owing to partially relaxed ^{13}C–^{11}B scalar coupling.

[b] In the case, of spiro compounds, the numbering was changed to that of the stannoles.

[c] $\delta\,^{13}C$ 48.0 [7.2] 35.5 [13.5] $(CH_2)_3$.

[d] $^{1}J(^{13}C(2), ^{13}C(3)) = 48.4$ Hz.

Table 2
^{13}C- and ^{119}Sn-NMR data [a] of stannoles with propyl and Et_2B groups in 2, 5 and 3 positions [b]

X,X =	**6** Cl,Cl				**7** Br,Br				Me,Me		**3** Spiro [b]	
C(2)	130.9 [641.9]				131.1 [590.6]				141.4 [424.0]		140.7 [380.9]	
C(3)	160.5 (br)				158.3 (br) [104.5]				164.8 (br)		145.2 (br) [50.0]	
C(4)	149.1 [275.2]				147.0 [259.8]				151.7 [117.2]		152.5 [112.3]	
(C5)	131.9 [809.0]				131.5 [698.8]				140.3 [475.2]		140.0 [432.2]	
X_2	–				–				−8.1 [292.1]		See C(2)–C(5)	
3-Et	28.3 [102.1]	13.9 [11.6]			27.4 [105.5]	14.2 [n.o.]			[55.6]	14.1 [n.o.]	26.6[53.4]	14.2 [9.6]
BEt_2	22.8 (br) 9.3				22.2 (br) 8.9				22.2 (br) 9.0		22.2 (br) 9.0	
2,5-Pr_2	35.6 [95.8]	32.3 [95.2]	26.0 [19.5]	25.1[17.4]	[98.9]	31.7 [85.8]	26.0 [17.2]	25.8 [n.o.]	37.6 [70.8]	34.0 [63.2]	38.2 [71.4]	34.6 [63.8]
$\delta^{119}Sn$	+13.1				−31.7				−3.5		−13.7	

[a] Coupling constants $J(^{119}Sn, ^{13}C)$ and $J(^{119}Sn, ^{29}Si)$ are given in brackets, $J(^{29}Si, ^{13}C)$ in parentheses; (br) denotes a broad signal owing to partially relaxed ^{13}C–^{11}B scalar coupling; n.o. means not observed.

[b] In the case, of spiro compounds, the numbering was changed to that of the stannoles.

Table 3
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data [a] of the bis(1-alkynyl) **8**, **9** and mono(1-alkynyl)tin compounds **10**, **11** and the tris(1-alkynyl)tin compounds for comparison

	8 [b]	**9**	**10** [b]	**11**	$ClSn(C{\equiv}CSiMe_3)_3$ [b]	$BrSn(C{\equiv}CSiMe_3)_3$
Sn–C≡	101.6 [1319.9] (9.8)	101.3 [1169.0] (9.9)	99.6 [1496.8] (n.o.)	101.1 [1184.7] (9.3)	102.8 [1160.6] (10.3)	101.8 [n.o.] (9.8)
Si–C≡	123.7 [212.0] (n.o.)	122.65 [c] [187.7] (68.6)	125.6 [228.9] (n.o.)	122.63 [d] [183.4] (66.6)	121.9 [191.2] (70.5)	121.7 [182.5] (70.7)
MeSi	−0.8 [2.9] (56.7)	−0.8 [2.9] (56.7)	−0.9 [n.o.] (57.2)	−0.9 [2.9] (57.0)	−0.6 [2.9] (56.5)	−0.6 [2.9] (56.3)
$\delta^{29}Si$	−15.0 [19.7]	−15.8 [18.7]	−13.7 [20.5]	−14.7 [17.5]	−16.2 [19.0]	−16.5 [19.0]
$\delta^{119}Sn$	−210.4	−353.6	−161.6	−437.0	−286.7	−350.0

[a] In C_6D_6 at 25 °C; coupling constants $J(^{119}Sn, ^{13}C)$ and $J(^{119}Sn, ^{29}Si)$ in brackets and $J(^{29}Si, ^{13}C)$ in parentheses; n.o. means not observed.

[b] Data taken from B. Wrackmeyer, G. Kehr, Main Group Met. Chem. 16 (1993) 305.

[c] $^1J(^{13}C{\equiv}^{13}C) = 101.7$ Hz.

[d] $^1J(^{13}C{\equiv}^{13}C) = 101.4$ Hz.

pounds [6,7], should lead to such stannoles. By preparing mixtures of $Sn(C{\equiv}C–SiMe_3)$ with $SnCl_4$ or $SnBr_4$, with the tin tetrahalide in slight excess, one obtains very fast ($SnCl_4$) or after gentle heating ($SnBr_4$) mixtures which contain mainly $Cl_2Sn(C{\equiv}C–SiMe_3)_2$ (**8**) and $Br_2Sn(C{\equiv}C–SiMe_3)_2$ (**9**) together with a small amount of $Cl_3Sn–C{\equiv}C–SiMe_3$ (**10**) and $Br_3Sn–C{\equiv}C–SiMe_3$ (**11**) (see Table 3 for NMR data of **8**–**11**). Treatment of these mixtures with triethylborane, Et_3B (Scheme 4), affords the stannoles **4** and **5** [identified by the same NMR parameters as measured for the products from the exchange reactions (Scheme 2)]. At the same time, the alkenes **12** and **13** were formed by 1,1-ethylboration of **10** and **11**, respectively. By increasing the amount of **10** and **11** in the equilibrated mixtures of the alkynes, after 1,1-ethylboration, the NMR signal intensities of **12** and **13** increased, confirming the correct assignment. Again, slow precipitation of tin(II) halides was observed. The slow decomposition of the stannoles **4**, **5** and also of the alkenes **12** and **13** could be monitored by recording the NMR spectra since numerous new NMR signals were growing.

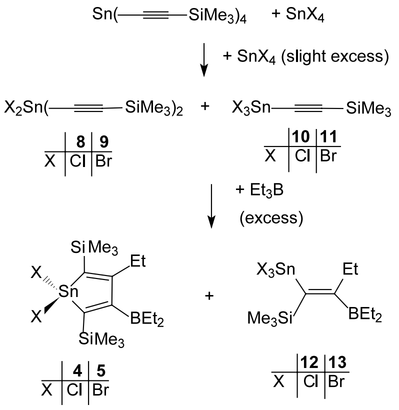
2.3. Exchange reaction of compounds of type *B* with tin tetrachloride

The reaction of **B** (Scheme 1) with tin tetrachloride is straightforward for R^1 = alkyl, aryl. An example is given for R^1 = Pr which gives the alkene **14**. The same compound is also available by treating the zwitterionic compound of type **A** [6f] with an excess of $SnCl_4$ (Scheme 5).

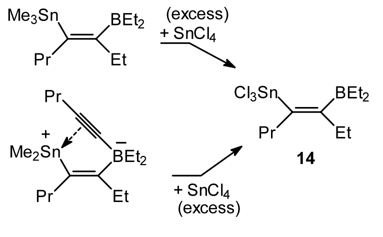
The NMR data of the alkenes **12**–**14** and of some compounds for comparison are listed in Table 4. The data for **12** and **13** are exceptional, indicating a special role of the presence of Me_3Si and SnX_3 groups at the C=C bond.

2.4. Decomposition of the stannoles *4*, *5* and of the alkenes *12*, *13*

The precipitation of tin(II) halides from the solutions containing the stannoles **4**, **5** or the alkenes **12**, **13**, in contrast with the behaviour of **6**, **7**, and **14**, indicates that the Sn–C= bonds in the former compounds are weak, in accordance with the small magnitude of the coupling constants $|^1J(^{119}Sn, ^{13}C)|$. Some of the numerous new NMR signals which slowly grow, when changes in the solutions containing **4** and **12** or **5** and **13** are monitored, can be assigned. Thus, ^{13}C- and



Scheme 4.



Scheme 5.

Table 4
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data [a] of **12**, **13**, **14** and some other organometallic-substituted alkenes for comparison

R^1 =	**12** SiMe$_3$	**3** SiMe$_3$	**C** (R = Et) [b] SiMe$_3$	**14** (R = Et) Pr	**B** (R = Et) Pr
Sn–C=	147.2 [c] [231.7] (58.1)	147.5 [193.4] (58.0)	140.8 [304.6] (59.2)	141.0 [956.9]	139.3 [525.3]
B–C=	174.4 (br)	173.2 (br)	181.8 (br)	171.5 (br)	162.0 (br)
Et	37.1 [227.4], 13.2 [12.2]	36.5 [230.0], 13.1 [n.o.]	34.8 [118.4], 14.4 [18.5]	24.2 [240.9], 12.9 [15.6]	22.9 [83.9], 14.5 [10.4]
BEt$_2$	22.5 (br) 9.1	22.5 (br).9.3	23.0 (br) 9.4	21.0 (br) 9.0	21.7 (br) 9.1
Me$_3$Sn	–	–	−4.9 [302.7]	–	−7.9 [316.1]
R^1	1.4 [17.0] (52.3)	1.7 [16.5] (52.5)	1.6 [11.6] (50.7)	34.7 [149.6] 24.5 [24.0]	35.5 [58.9] 23.8 [12.0]
δ^{29}Si	−3.5 [108.2]	−3.3 [110.8]	−7.1 [92.1]	–	–
δ^{119}Sn	−96.0	−275.0	−66.4	−78.7	−48.5

[a] Coupling constants $J(^{119}\text{Sn}, ^{13}\text{C})$ and $J(^{119}\text{Sn}, ^{29}\text{Si})$ are given in brackets, $J(^{29}\text{Si}, ^{13}\text{C})$ in parentheses; (br) denotes a broad signal owing to partially relaxed ^{13}C–^{11}B scalar coupling; n.o. means not observed.

[b] Data from Ref. [3].

[c] $^1J(^{13}\text{C}{=}^{13}\text{C}) = 48.1$ Hz.

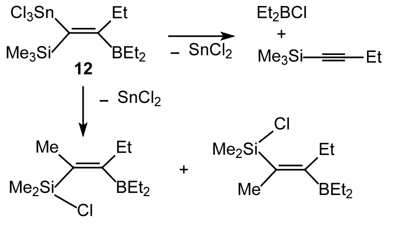
^{29}Si-NMR signals show that Me$_3$Si–C≡C–Et is a major decomposition product of **12**. In ^{11}B-NMR spectra the typical, fairly sharp ^{11}B-NMR signal for Et$_2$BCl ($\delta^{11}\text{B} = 78.0$) can be seen in the beginning of the decomposition. Possible ways of the decomposition of **12** are shown in Scheme 6. These routes also apply to **13**.

The decomposition of **12** suggests that a short-lived ionic intermediate of the type [Me$_3$Si–C=C(Et)BEt$_2$]$^+$ [SnCl$_3$]$^-$ is involved, considering that a Me$_3$Si group has a stabilising influence on carbocations.

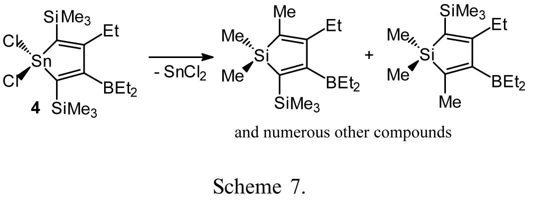
In the cases of the stannoles **4** and **5**, the situation with respect to decomposition pathways is even more complex, and Scheme 7 contains only a fraction of potential routes of the decomposition. However, the ^{29}Si-NMR spectra show signals without $^{117/119}$Sn satellites in the region typical of siloles [11].

2.5. NMR spectroscopic results

Representative data are listed in the Tables 1–4. The ^{29}Si- and ^{13}C-NMR spectra of the equilibrium mixture obtained from Sn(C≡CSiMe$_3$)$_4$ and SnBr$_4$ are shown in the Figs. 1 and 2. The refocused INEPT pulse sequence with ^{1}H-decoupling [12]; based on $^3J(={}^{13}\text{C}, {}^1\text{H(SiMe)})$ [13], is of particular advantage for observing the ^{13}C(2, 5) signals in the cases of **4** and **5** (see Fig. 3). The δ^{13}C data for the stannoles **4**, **5** and of the 2,5-dipropyl-substituted stannoles **6**, **7** show similar trends when compared with the respective SnMe$_2$-derivatives, although the increase in shielding of the ^{13}C(2, 5) nuclei in **4**, **5** is much larger than in **6**, **7**. In the alkenes **12**, **13**, and to a much smaller extend in **14**, the shielding of the ^{13}C nuclei bearing the SnX$_3$ group is reduced with respect to the Me$_3$Sn-derivatives, exactly the opposite trend as in the stannoles. Most noteworthy however, the trend of the values of the coupling constants $^1J(^{119}\text{Sn}, ^{13}\text{C})$ in the stannoles **4**, **5** and in the alkenes **12**, **13** is opposite to that found for **6**, **7** and **14**. If there is a SiMe$_3$ group attached to the olefinic carbon atom bearing a stannyl group, the magnitude of $|^1J(^{119}\text{Sn}, ^{13}\text{C})|$ is always smaller than for the comparable alkyl derivative. However, one would expect that the substitution of methyl groups at the tin atom by chloro or bromo ligands causes a significant increase in the magnitude of $|^1J(^{119}\text{Sn}, ^{13}\text{C})|$. These expectations are fulfilled for pairs such as stannoles **6**, **7**/Me$_2$Sn derivative (Table 2) **14**/Me$_3$Sn derivative (Table 4), MeSnCl$_3$–Me$_4$Sn, PhSnCl$_3$–PhSnMe$_3$ or Me$_3$SnC≡CSiMe$_3$–Cl$_3$SnC≡CSiMe$_3$ (Table 3), in complete agreement with the model of rehybridisation [14]. This model predicts an increased s-character of the Sn–C hybrid orbital if SnMe$_2$ or SnMe$_3$ are replaced by SnX$_2$ or SnX$_3$ (X = Cl, Br), respectively. In contrast, there is even a decrease in $|^1J(^{119}\text{Sn}, ^{13}\text{C})|$ in the stannoles **4**, **5** and the alkenes **12**, **13** when compared with the corresponding dimethyl or trimethyltin compounds. Interestingly, the magnitude of coupling constants across two or three bonds changes in the expected manner, when compared with methyltin derivatives, similar to analogous changes in **6**, **7** or **14**. The small values $|^1J(^{119}\text{Sn}, ^{13}\text{C})|$ indicate weak Sn–C bonds, and reflect the contribution of polar structures (with the extreme of ionic structures) to the



Scheme 6.



and numerous other compounds

Scheme 7.

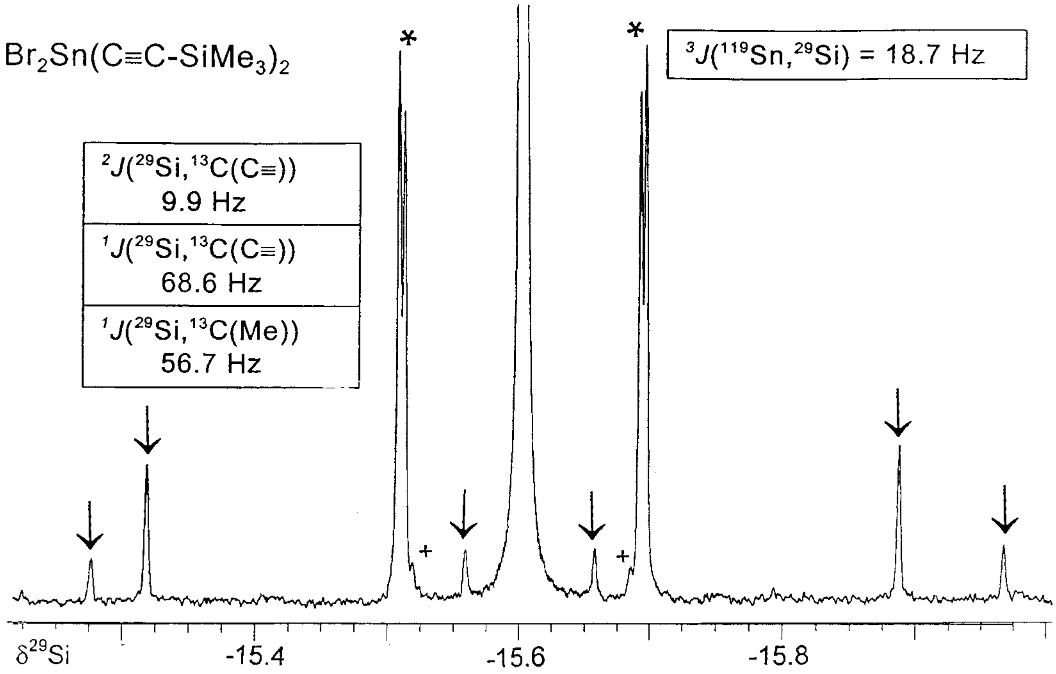


Fig. 1. 99.4 MHz ^{29}Si-NMR spectrum (refocused INEPT with ^{1}H decoupling) of $Br_2Sn(C{\equiv}C–SiMe_3)_2$ (reaction solution in C_6D_6 at 22 ± 1 °C) showing $^{119/117}$Sn (*), ^{115}Sn (+), and ^{13}C satellites (arrows).

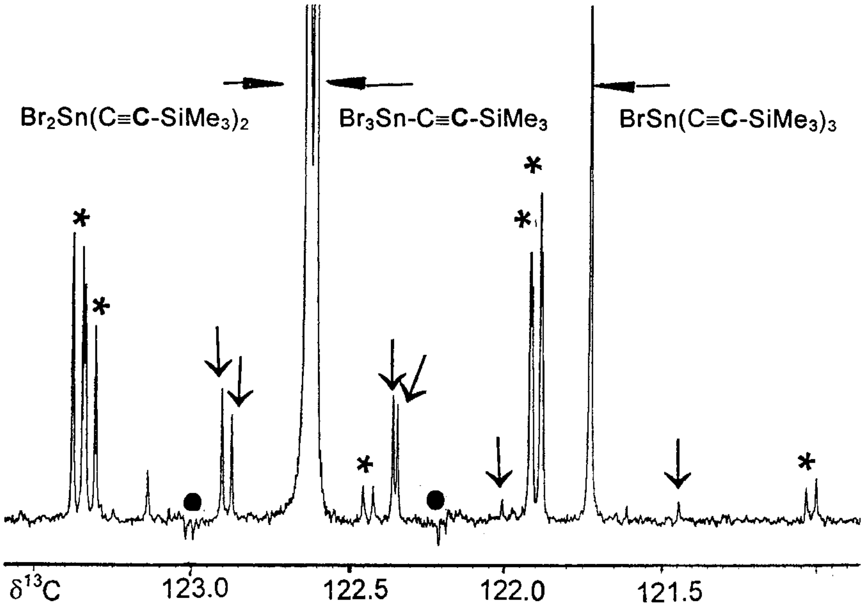


Fig. 2. 125.8 MHz ^{13}C-NMR spectrum (refocused INEPT with ^{1}H decoupling) of the reaction mixture containing all three trimethylsilylethynyltin bromides. The INEPT pulse sequence was based on $^{3}J(\equiv^{13}C, {}^{1}H(SiMe))$ ca. 3 Hz which enables to observe selectively the $^{13}C(\equiv C–Si)$ resonance signals with a high signal-to-noise ratio: the $^{119/117}$Sn (*), ^{29}Si (arrows) and ^{13}C satellites (filled circles) are indicated. Typical of a homonuclear spin pair, the magnetisation due to $^{13}C–^{13}C$ coupling is not refocused in the INEPT pulse sequence, and therefore, the ^{13}C satellite signals are out of phase.

ground state. This must be ascribed to the stabilisation of these polar structures by the Me_3Si group adjacent to the same olefinic carbon atom which is linked to the SnX_2 or SnX_3 fragment.

For monitoring of most of the reactions described here, ^{29}Si-NMR is very useful. The appearance of $^{117/119}$Sn satellites owing to $^{2}J(^{117/119}Sn, {}^{29}Si)$ is diagnostic for the fragment in which a stannyl and a silyl group are in geminal positions linked to an olefinic carbon atom. The decomposition of the respective stannoles and of the alkenes by elimination of tin(II) halide is then indicated by the growing of new ^{29}Si signals without these satellites.

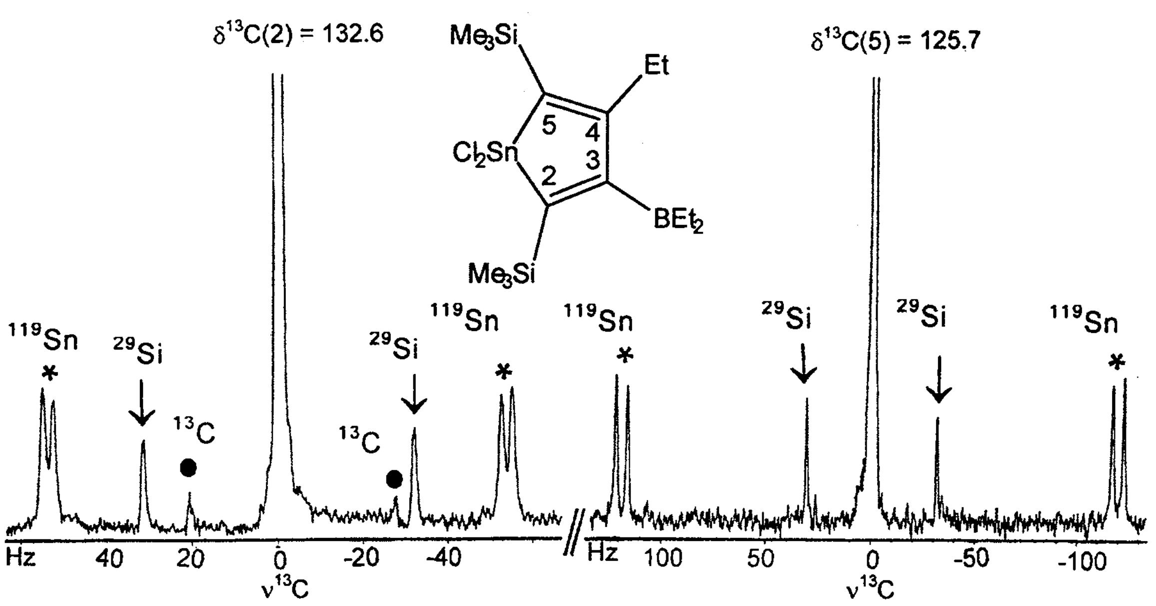


Fig. 3. 125.8 MHz ^{13}C-NMR spectra (refocused INEPT with ^{1}H decoupling) of the stannole **4** (in C_6D_6), showing the ^{13}C(2) and ^{13}C(5) signals. The INEPT pulse sequence was based on ^{3}J(=^{13}C, ^{1}H(SiMe$_3$)) ca. 1.5 Hz, which enables to observe these signals selectively with a high signal-to-noise ratio: the $^{117/119}$Sn (*) [^{1}J(^{119}Sn, C(2)) = 110.1 Hz; ^{1}J(^{119}Sn, C(5)) = 244.0 Hz] and ^{29}Si satellites (arrows) [^{1}J(^{29}Si, ^{13}C(2)) = 63.6 Hz; ^{1}J(^{29}Si, ^{13}C(5)) = 62.0 Hz] are indicated. In the case of ^{13}C(2), the ^{13}C satellites due to ^{1}J(^{13}C(2), ^{13}C(3)) = 48.4 Hz are also observed (filled circles) with a distorted phase (see also Fig. 2).

3. Conclusions

Stannoles (**4**–**7**) with chloro or bromo ligands at the tin atom can be prepared by various routes, including exchange reactions and 1,1-organoboration. However, they decompose readily by elimination of SnX$_2$ if the 2,5-substituents are trimethylsilyl groups. The same is true for alkenes if SiMe$_3$ and SnX$_3$ (X = Cl, Br) groups are in geminal positions at the C=C bond. This is unexpected at a first glance, since Me$_3$Si groups usually exert a stabilizing effect. The low stability of such stannoles and alkenes can be traced to contributions from extreme canonic structures, in which a vinyl cation and the [SnX$_2$R]$^-$ or the [SnX$_3$]$^-$ anions can be postulated in order to explain the weak Sn–C= bonds. In strong contrast to stannoles or alkenes in which the geminal SiMe$_3$ groups are replaced by alkyl groups, unusually small coupling constants $|^{1}J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})|$ are observed, in agreement with weak Sn–C bonds.

4. Experimental

4.1. General: measurements and materials

All preparative work and handling of the compounds was carried out under an inert atmosphere (Ar or N$_2$), using carefully dried glass ware and dry solvents. The element halides and Et$_3$B were commercial products. The spirocyclic compounds **1** [7], **2** [8], and **3** [9], and Sn(C≡CSiMe$_3$)$_4$, and the mixtures **8**/**10** and **9**/**11** [15] were obtained as described.

NMR spectra were recorded by using Bruker ARX 250 and DRX 500 instruments, equipped with multinuclear units and variable temperature control. If not mentioned otherwise, samples dissolved in C_6D_6 (10–20%) in 5 mm (o.d.) tubes were measured at 25 ± 1 °C. Chemical shifts are given with respect to solvent signals [δ^{1}H (C_6D_5H) = 7.15; ($C_6D_5CD_2H$) = 2.03; (CDHCl$_2$) = 5.33; δ^{13}C (C_6D_6) = 128.0; ($C_6D_5CD_3$) = 20.4; (CD$_2$Cl$_2$) = 52.3] and external references [δ^{11}B (BF$_3$·OEt$_2$) = 0, Ξ^{11}B = 32.083971 MHz; δ^{29}Si (Me$_4$Si) = 0, Ξ^{29}Si = 19.867184 MHz; and δ^{119}Sn (Me$_4$Sn) = 0, Ξ^{119}Sn = 37.290665 MHz]. The ^{13}C-NMR signals of olefinic and alkynyl carbon atoms were best detected by using the refocused INEPT pulse sequence [12] [based on ^{2}J(^{13}C, ^{1}H) (n = 3, 4) [13]] with ^{1}H decoupling. All ^{29}Si-NMR spectra were recorded using the refocused INEPT pulse sequence {based on ^{2}J(^{29}Si, ^{1}H$_{\mathrm{Me}}$)] with ^{1}H decoupling [12]}; ^{119}Sn-NMR spectra were measured by inverse gated ^{1}H decoupling in order to suppress the NOE [16]. The ^{119}Sn-NMR signals are fairly broad owing to partially relaxed scalar ^{119}Sn–$^{10/11}$B and ^{119}Sn–X (X = $^{35/37}$Cl, $^{70/81}$Br) coupling, and therefore, short (< 0.3 s) acquisition times were used.

*4.2. Exchange reactions of **1–3** with element halides. General procedure*

Compound **1** (0.585 g; 1 mmol) was dissolved in toluene (2 ml), the solution was cooled to − 78 °C, and the respective element halide (1 mmol) was injected in one portion. The solution was allowed to reach ambient temperature, and the progress of the reaction was checked by ^{119}Sn-NMR in each case, and by ^{11}B- or ^{31}P-NMR for the reaction with BBr_3 or PCl_3. In all cases, the reaction was complete, leading to the stannoles **4** and **5**, after warming to room temperature (r.t.). Complex **4**: ^{1}H-NMR (250 MHz, [D$_8$]toluene, 25 °C): $\delta^1H = 2.11$ q, 1.01.t, 5H (Et–C=); 1.3–0.83 m, 10H (Et_2B); 0.26 s, 9H·(Me_3Si); 0.18 s, 9H (Me_3Si). Complex **5**: ^{1}H-NMR (250 MHz, [D$_8$]toluene, 25 °C): $\delta^1H =$ 2.22 q, 1.05 t, 5H (Et–C=); 1.35–0.8 m, 10H (Et_2B); 0.30 s, 9H (Me_3Si); 0.22 s, 9H (Me_3Si).

The analogous procedure served for studying the reaction of **2** and **3** with element halides. There was no reaction of **2** with element halides at r.t., and decomposition was observed when a mixture of **2** and BBr_3 was heated at > 80 °C. The 1:1 reaction of **3** with $SnCl_4$, afforded the stannole **6** in quantitative yield (> 95% pure according to ^{1}H-NMR), isolated as a yellowish oil after removing the solvent in vacuo (elemental Anal. $C_{16}H_{29}BCl_2Sn$; C, 45.30; H, 6.75; Cl, 16.58. Calc. C, 45.55; H, 6.94; Cl, 16.80%). Attempts at the distillation of **6** under reduced pressure led to extensive decomposition at > 90 °C/10^{-2} Torr.

*4.3. 1.1-Organoboration of **8**/**10** or **9**/**11** with triethylborane. General procedure*

The equilibrated toluene solutions containing **8**/**10** or **9**/**11** were cooled to −78 °C and an excess of Et_3B was added in one portion through a syringe. After warming these mixtures to r.t., ^{29}Si- and ^{119}Sn-NMR spectra were recorded which indicated that the reactions were complete. Insoluble material (identified as $SnCl_2$) was formed in the solutions as well as in the oily residues which remained after removing the toluene in vacuo. The soluble fractions showed many new ^{29}Si-NMR signals in addition to the signals for the stannoles and the alkene derivatives which were dominant in the beginning. Heating of the solutions for 2 h at 80 °C led to increasing amounts of decomposition products.

*4.4. Synthesis of the alkene **14***

A solution of the zwitterionic intermediate (0.4 mmol), obtained from the 1:1 reaction of $Me_2Sn(C{\equiv}CPr)_2$ with Et_3B [6e], in $CDCl_3$ was cooled to − 78 °C and $SnCl_4$ (0.8 mmol; 98 μl) was injected through a syringe. After removing all volatile material, a yellowish oil was isolated and was identified as pure (> 95% according to ^{1}H-NMR) **14**. Attempted distillation (> 70 °C/10^{-3} Torr) led to decomposition. The same product was obtained from the reaction of (*Z*)-3-diethylboryl-4-trimethylstannyl-hept-3-ene with an excess of $SnCl_4$, carried out in the same way. Complex **14**: elemental analysis: $C_{11}H_{22}BSnCl_3$; C 33.65, H 5.57, Cl 27.40; calc. C 33.85, H 5.68, Cl 27.24%); ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): $\delta^1H = 1.39$ q, 4H, 0.98 t, 6H (Et_2B); 2.26 q, 2H, 1.00 t, 3H (EtC=); 2.60 t, 2H, 1.62 m, 2H, 1.01 t, 3H (PrC=).

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