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Spirocyclic stannole derivatives by 1,1-organoboration of 2,2-bis(1-alkynyl)-1,3-di-tert-butyl-1,3,2-diazastannacyclohexanes

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Abstract

With the exception of **1c**, the 2,2-bis(1-alkynyl)-1,3-di-tert-butyl-1,3,2-diazastannacyclohexanes (**1**) [C≡C–R^1: R^1 = Me (**a**), Bu (**b**), ^{t}Bu (**c**), Ph (**d**), SiMe$_3$ (**e**), CH$_2$NMe$_2$ (**f**), CH$_2$OMe (**g**)] react with triethylborane, Et$_3$B (**2**), to give the spirocyclic stannole derivatives **4a**,**b**,**d**,**e**,**f**,**g** by intermolecular 1,1-ethylboration, followed by intramolecular 1,1-vinylboration. In the cases of **1f** and **1g**, zwitterionic intermediates **7f**,**g**, in which the tin atom is coordinated to an alkynylborate C≡C bond, were detected by NMR spectroscopy. In the case of the reaction of **1e** with triphenylborane, Ph$_3$B (**3**), exchange reactions involving the Sn–N bonds compete with 1,1-organoboration, and the spirocyclic stannole derivative **5e** is only part of a complex reaction mixture. In the reaction of **1e** with Et$_3$B, an intermediate **8e** with the wrong stereochemistry for ring closure was detected by NMR spectroscopy. Owing to the reversibility of 1,1-organoboration, the spirocyclic stannole **4e** is finally formed. Products and intermediates were characterised by ^{1}H, ^{11}B, ^{13}C, ^{15}N, ^{29}Si and ^{119}Sn NMR spectroscopy. Several absolute signs of coupling constants in **4e** were determined. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkynes; Organotin compounds; Heterocycles; Organoboranes

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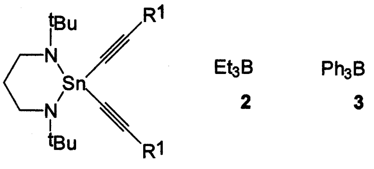
1. Introduction

The reactivity of alkynyltin compounds towards triorganoboranes has been studied in some detail [1,2]. In general, the 1-alkynyltin compound reacts by cleavage of the Sn–C≡ bond, followed by 1,1-organoboration. Such reactions become particularly attractive for the synthesis of heterocycles such as stannoles which are difficult to prepare by other methods [3,4]. There are numerous examples in which bis(1-alkynyl)diorganotin compounds are starting materials [5], including a stannacyclohexane derivative [5h]. In many cases it was found that stannoles can be obtained selectively in high yield. Little work has focused on alkynyltin compounds in which the tin atoms do not bear any organic group in addition to the alkynyl substituent. So far only two compounds of type **1**, namely **1a**,**b**, have been studied with respect to their reactivity towards trialkylboranes. Again it was observed that 1,1-organoboration is the preferred course of the reaction, leading first to zwitterionic intermediates and finally to spirocyclic stannoles [6]. We have now extended this investigation in order to include a greater variety of alkynyl groups (Scheme 1), some of which bear functional groups such as **1e**,**f**,**g**. All alkynes **1** were treated with triethylborane, Et$_3$B (**2**). Compound **1e** was also treated with triphenylborane, Ph$_3$B (**3**). The application of multinuclear magnetic resonance measurements was found extremely useful in



1	a	b	c	d	e	f	g
R1	Me	Bu	tBu	Ph	Me3Si	CH2NMe2	CH2OMe

Scheme 1.

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Table 1
^{13}C, ^{15}N and ^{119}Sn NMR data [a] of 1,2-bis(1-alkynyl)-1,3-di-tert-butyl-1,3,2-diazastannacyclohexanes **1a**–**g**

1g	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	
R^1	Me	Bu [b]	^{t}Bu	Ph [c]	$SiMe_3$ [d]	CH_2Nme_2	CH_2OMe
Sn–C≡	86.3 [1009.3]	86.9 [1006.5]	84.9 [998.2]	96.7 [924.0]	115.7 [870.2]	91.7 [975.6]	93.2 [956.9]
R^1–C≡	105.1 [206.0]	109.5 [200.6]	117.7 [191.0]	108.3 [192.3]	116.7 [137.8]	104.1 [188.0]	104.9 [194.1]
R^1	4.6 [17.4]	19.9 [15.8] 30.9 [24.5]	30.7 [7.9] 28.3 [14.8]	123.1 [20.3] 132.2 (*o*)	−0.4 −18.5 (δ^{29}Si)	48.7 [13.8] 43.8	64.5 [33.5]
N^{t}Bu	55.7 [6.5] 30.1 [25.1]	55.7 [7.1] 30.1 [25.1]	55.7 [6.9] 30.1 [25.6]	55.9 [9.3] 30.2 [24.6]	55.9 [6.9] 30.2 [24.6]	55.7 [6.9] 30.1 [25.6]	55.8 [7.9] 30.1 [25.6]
NCH_2	47.9 [6.5]	47.9 [6.5]	47.8 [7.9]	47.9 [8.7]	47.7 [5.9]	47.7 [5.9]	47.8 [7.9]
CH_2	34.3 [29.4]	34.3 [28.9]	34.2 [30.2]	34.2 [31.6]	34.1 [29.5]	34.2 [29.5]	34.1 [30.5]
δ^{15}N	−321.4 [100.1]	−321.8 [99.8]	−320.3 [97.4]	n.m.	−319.5 [95.2]	−320.0 [e] [100.3]	−320.5 [100.3]
δ^{119}Sn	−265.4	−264.1	−260.0	−260.3	−280.5	−268.9	−268.5

[a] In C_6D_6 (10–15%) at 25 ± 1°C; coupling constants $J(^{119}Sn,^{13}C)$ and $J(^{119}Sn,^{15}N)$ are given in brackets (±0.5 Hz); n.m. = not measured. Data for **1a**,**b** from Ref. [7].

[b] Other δ^{13}C (R^1): 22.1, 13.7.

[c] Other δ^{13}C (R^1): 128.7 (*m*), 128.4 (*p*).

[d] $^3J(^{119}Sn,^{29}Si) = 6.0$ Hz.

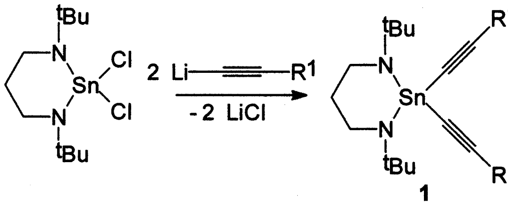
[e] $\delta^{15}N(NMe_2) = -360.2$.

the characterisation of the products and in the elucidation of the nature of intermediates.

2. Results and discussion

2.1. Synthesis of the 2,2-bis(1-alkynyl)-1,3,2-diazastannacyclohexanes (1)

The alkynyltin compounds **1** were prepared as described previously [7], taking advantage of the readily available 2,2-dichloro-1,3-di-tert-butyl-1,3,2-diazastannacyclohexane [8]. The reaction of the latter compound (Eq. (1)) with two equivalents of the lithiated alkynes LiC≡CR^1 afforded the desired compounds **1** in 70–90% yield as colourless, moisture-sensitive solids (**1c**,**d**,**e**) or as yellow oils (**1f**,**g**). The ^{13}C, ^{15}N and ^{119}Sn NMR data of compounds **1**, including those of **1a**,**b** [7] for comparison, are given in Table 1.

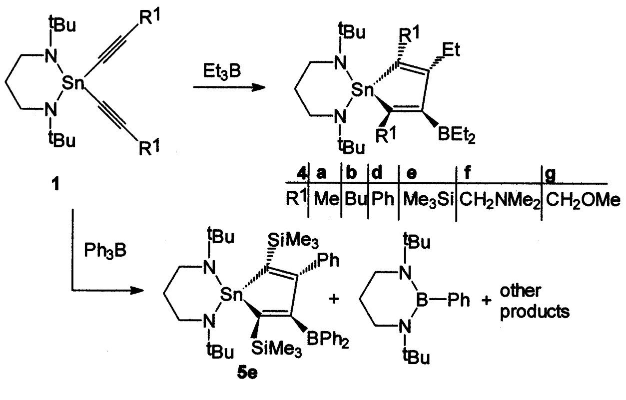


(1)

All ^{13}C NMR data of the alkynyl carbon atoms [9], including the magnitude of coupling constants $J(^{119}Sn,^{13}C)$ [10], are in the expected range. The ^{13}C and ^{15}N NMR data of the 1,3,2-diazastannacyclohexane moiety are almost independent of the nature of R^1, indicating negligible changes of the bonding situation in the six-membered ring. The greatest variations are observed for the δ^{119}Sn data (20 ppm) with changes, analogous to the bis(1-alkynyl)dimethyltin compounds [11,12].

2.2. 1,1-Organoboration of the alkynyltin compounds 1

The reactions of **1a**,**b** with Et_3B (**2**) have been described [6]. They proceed under relatively mild conditions, and zwitterionic intermediates (vide infra) could be detected by NMR spectroscopy. In contrast, **1c** does not react with **2**, even after prolonged heating at 80°C. The compounds **1d**,**f**,**g** react with **2** under similar conditions as **1a**,**b**, in hexane between −20 and +25°C for several hours or days (**1f**), to give the stannoles **4d**,**f**,**g**. In the case of **1e**, the reaction was rather slow at room temperature and heating at 90°C for several hours was required to obtain the stannole **4e** as the final product (Scheme 2). Triphenylborane **3** reacts slowly with **1e** at room temperature to give a mixture of products which



Scheme 2.

Table 2
^{13}C, and ^{119}Sn NMR data [a] of the spirocyclic stannoles **4a**,**b** (for comparison) and **4d**,**e**,**f**,**g**

	4a	**4b**	**4d**	**4e**	**4f**	**4g**
R^1	Me	Bu	Ph	SiMe$_3$ [h]	CH$_2$NMe$_2$ [i]	CH$_2$OMe [j]
C(1)	138.3 [541.7]	144.2 [529.3]	149.9 [536.8]	147.1 [281.2]	136.2 [485.6]	137.7 [569.1]
C(2)	160.5 (br)	159.1 (br)	161.1 (br)	176.0 (br)	173.7 (br)	165.3 (br)
C(3)	147.3 [186.4]	145.7 [189.2]	148.8 [175.0]	161.0 [162.5]	151.5 [136.9]	146.4 [130.2]
C(4)	133.4 [621.3]	140.8 [611.2]	142.6 [591.5]	137.7 [321.3]	141.6 [694.8]	142.3 [599.6]
N^{t}Bu	55.3 [5.4]	55.5 [8.7]	56.0 [8.3]	55.8 [10.8]	55.6 [7.0]	55.4 [$<$6.0]
	30.2 [20.7]	29.6 [20.5]	30.3 [21.5]	29.5 [21.0]	30.3 [20.1]	29.8 [23.6]
NCH$_2$	50.0 [7.8]	48.2 [5.7]	48.1 [6.3]	48.0 [7.2]	48.9 [14.4]	48.2 [10.8}
CH$_2$	36.5 [25.1]	38.3 [17.9]	36.5 [27.0]	35.5 [13.5]	34.9 [31.4]	35.0 [n.o.]
3-Et	26.7 [74.1]	27.5 [76.8]	26.4 [70.0]	32.8 [123.0]	25.2 [77.2] 14.9 [13.0]	25.7 [73.6] 13.0 [12.6]
	13.0 [10.9]	13.0 [11.0]	13.9 [10.8]	14.8 [10.8]		
BEt$_2$	22.9 (br), 9.2	22.7 (br), 9.2	23.0 (br), 9.9	23.2 (br), 9.6	12.5 (br), 11.0	15.8 (br), 10.8
1-R^1, 4-R^1 [b]	16.2, 19.4	[c]	143.4 [66.4]	2.7 [12.5] [e]	71.7 [121.2]	86.0 [147.8]
			143.0 [77.2] [d]		61.1 [61.0] [f]	73.0 [46.0] [g]
δ^{119}Sn	−87.1	−93.8	−93.9	−13.9	−111.0	−104.5

[a] In C_6D_6 (10–15%) at 25 ± 1°C; coupling constants $J(^{119}Sn,^{13}C)$, $^1J(^{119}Sn,^{15}N)$ and $^2J(^{119}Sn,^{29}Si)$ are given in brackets (± 0.5 Hz); n.m. = not measured; n.o. = not observed; (br) denotes broad ^{13}C NMR signals owing to partially relaxed scalar ^{13}C–^{11}B coupling. δ^{11}B values are at 85 ± 1 (broad signals $h_{1/2} > 600$ Hz). Data for **4a**,**b** from Ref. [6].

[b] Assignment uncertain.

[c] Numerous overlapping signals; no assignment: δ^{13}C 31.0, 23.4, 14.2.

[d] Other δ^{13}C values (without assignment): 128.6, 128.4, 126.3, 125.4.

[e] Two signals overlap; δ^{29}Si −8.1 [118.4], −9.6 [112.0].

[f] Other δ^{13}C values (without assignment): 49.9 [14.4], 48.9 [14.4] (NMe$_2$).

[g] Other δ^{13}C values (without assignment): 57.7, 55.5 (OMe).

[h] $\delta^{15}N = -318.7$ [70.5]; cf. **4a** [6] $\delta^{15}N = -317.2$ [27.5].

[i] δ^{11}B 6.4.

[j] δ^{11}B 46.9.

contains the stannole **5e**. Exchange reactions at the Sn–N bonds compete with 1,1-organoboration. The final complex reaction mixture contains the desired stannole **5e** among other unidentified products which could not be separated. All stannoles **4a**–**g** are colourless or yellowish, air-sensitive oils which can be stored in the fridge for several months. We could not purify these compounds by chromatography, and attempts to crystallise them from pentane solutions at low temperature failed. ^{13}C and ^{119}Sn NMR data of the spirocyclic stannoles are given in Table 2.

All NMR data prove the formation of the five-membered stannole ring, and the 1,3,2-diazastannacyclohexane ring remains unchanged. The typical pattern of the ^{13}C NMR signals for the olefinic carbon atoms, three sharp signals with $^{117/119}$Sn satellites according to $^1J(^{119}Sn,^{13}C)$ and $^2J(^{119}Sn,^{13}C)$, and one broad signal for the boron-bonded carbon atom, is observed (Fig. 1). The assignment of the sharp signals is based on their differences in chemical shifts and on the different magnitude of the coupling constants, in analogy to the known dimethyltin derivatives [12]. The trend of the δ^{119}Sn values for compounds **4** is also very similar to that of the dimethyltin analogues [12].

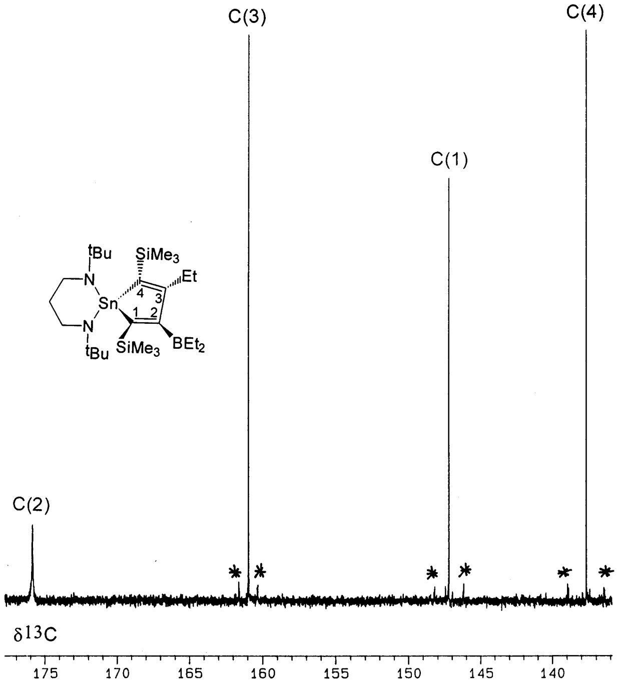


Fig. 1. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of **4e** in C_6D_6 (10%) at 25°C showing the region for olefinic carbon atoms (see text). The assignment is indicated, and $^{117/119}$Sn satellites are marked by asterisks.

The presence of the Me$_3$Si groups in 1,4-positions in **4e** takes influence in particular on the ^{119}Sn nuclear shielding (deshielding by > 70 ppm) and on the magnitude of the coupling constants $^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ and $^{1}J(^{119}\mathrm{Sn},^{15}\mathrm{N})$. The magnitude of $|^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})|$ is much smaller than in the other compounds **4**. The absolute signs of $^{1}J(^{29}\mathrm{Si},^{13}\mathrm{C})$ (< 0), $^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})$ (< 0) (reduced coupling constants $^{1}K(^{119}\mathrm{Sn},^{13}\mathrm{C})$, $^{1}K(^{29}\mathrm{Si},^{13}\mathrm{C}) > 0$, as expected [10]), and $^{2}J(^{119}\mathrm{Sn},^{29}\mathrm{Si})$ (> 0) ($^{2}K(^{119}\mathrm{Sn},^{29}\mathrm{Si}) > 0$) in **4e** were determined by a series of 2D $^{13}\mathrm{C}/^{1}\mathrm{H}$ (one example is given in Fig. 2) and $^{29}\mathrm{Si}/^{1}\mathrm{H}$ HETCOR experiments as described previously for similar compounds [13]. There are also negative contributions to the $^{119}\mathrm{Sn}{-}^{15}\mathrm{N}$ scalar interactions owing to the SiMe$_3$ groups in 1,4-positions. The larger absolute value $|^{1}J(^{119}\mathrm{Sn},^{15}\mathrm{N})| = 70.5$ Hz for **4e** as compared to 27.5 Hz for **4a** indicates a negative sign of $^{1}J(^{119}\mathrm{Sn},^{15}\mathrm{N})$ in **4e**.

In the presence of Lewis bases such as in **4f** and **4g**, coordinative interactions with the boryl groups as well as with the tin atom must be considered as shown by the proposed structure of **4f** (Scheme 3). The coordinative N–B or O–B bonds are clearly evident from the increase in ^{11}B nuclear shielding [14], the O–B bond in **4g** (δ^{11}B 46.9) being considerably weaker than the N–B bond in **4f** (δ^{11}B 6.4). The ^{119}Sn nuclear shielding is slightly higher than in the stannoles without such substituents, indicating fairly weak coordinative N–Sn or O–Sn bonds. However, there are marked changes in the magnitude of coupling constants $|^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})|$, as expected for carbon atoms being preferably in axial or equatorial positions of trigonal bipyramidal surroundings of a penta-coordinate tin atom [12,15,16]. In **4f**, the coupling constant $|^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C(1)})|$ has the smallest value in the series of alkyl substituents in 1,4-positions, whereas $|^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C(4)})|$ has the largest value (Scheme 3). Since the N–B coordination in **4f** follows unambiguously from the δ^{11}B value, the N–Sn coordination must be exerted by the NMe$_2$ group of R^1 in 4-position. This requires that C(4) prefers on average in equatorial position, whereas C(1) is in axial position, in agreement with the observed trends in the coupling constants. Of course, these molecules are fluxional and therefore, the differences in the magnitude of the coupling constants are much less pronounced when compared with more rigid structures [15,16].

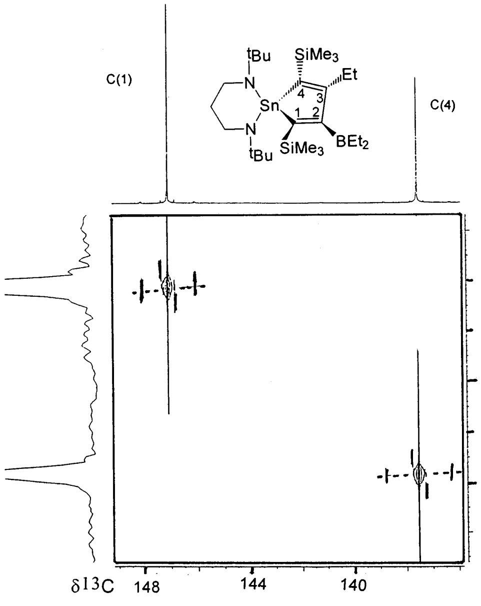
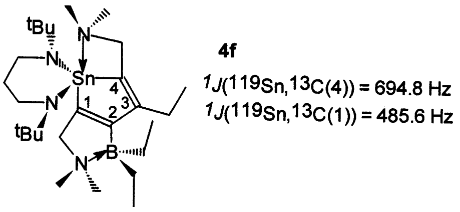
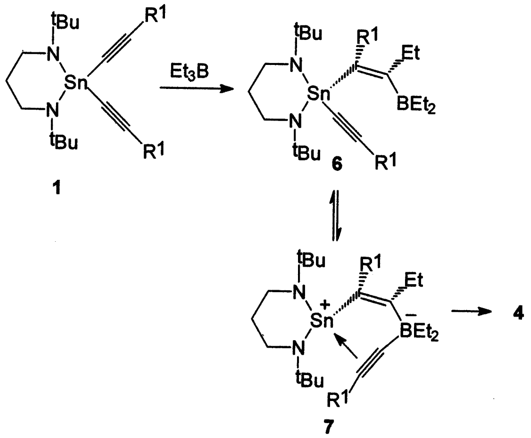


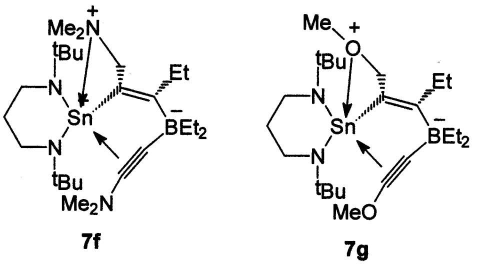
Fig. 2. Contour plot of the 2D 75.5 MHz $^{13}\mathrm{C}{-}^{1}\mathrm{H}$ HETCOR experiment, based on $^{3}J(^{13}\mathrm{C}, \mathrm{Si}, \mathrm{C}, ^{1}\mathrm{H}_{\mathrm{Me}})$, showing the $^{13}\mathrm{C}(1,4)$ resonances of **4e**. The passive spins are ^{29}Si and $^{117/119}$Sn. The negative tilts of the cross peaks [18] for the ^{29}Si satellites prove that the signs of $^{2}K(^{29}\mathrm{Si}, ^{1}\mathrm{H}_{\mathrm{me}})$ and $^{1}K(^{29}\mathrm{Si}, ^{13}\mathrm{C}(1,4))$ are opposite. The former is known to be negative. There is a slight positive tilt of the cross peaks for $^{117/119}$Sn satellites (dashed lines). Therefore, the signs of $^{4}K(^{117/}$119Sn, C, Si, C, $^{1}\mathrm{H}_{\mathrm{Me}})$ and $^{1}K(^{119}\mathrm{Sn}, ^{13}\mathrm{C}(1,4)$ are alike. By a series of similar experiments, it can be shown that $^{4}K(^{117/119}\mathrm{Sn}, \mathrm{C}, \mathrm{Si}, \mathrm{C}, ^{1}\mathrm{H}_{\mathrm{Me}}) > 0$.



Scheme 3.



Scheme 4.



Scheme 5.

2.3. Intermediates in the 1,1-organoboration reactions

There is clear evidence for the stepwise 1,1-organoboration of bis(1-alkynyl)tin compounds [1,2]. In the present cases, it was already shown [6] that the intermolecular 1,1-organoboration leads to intermediates of type **6** which are in equilibrium with **7** (Scheme 4), and from **7** the stannole is formed by intramolecular 1,1-vinylboration.

It is also known [12] that such zwitterionic species are stabilised by coordinative Sn–N or Sn–O interactions which are possible in the case of $R^1 = CH_2NMe_2$ or CH_2OMe (Scheme 5). Indeed, NMR spectra of reaction solutions of the 1,1-organoboration of **1f,g** showed characteristic signals for zwitterionic intermediates even after 24 h at room temperature, and in the case of **7f**, a full set of ^{11}B, ^{13}C and ^{119}Sn NMR data (Table 3) could be obtained.

The reaction of **1e** with triorganoboranes is somewhat more complicated. In general it proved impossible to detect the zwitterionic intermediates if $R^1 = SiMe_3$ since these intermediates are particularly short-lived and, under the reaction conditions (heating is frequently required), rearrange rather fast to the final products or to other more stable intermediates. Recently, a few exceptions have been observed [17]. A further problem arises because the 1,1-organoboration is no longer stereoselective for 1-alkynyltin compounds with $R^1 = SiMe_3$ [1,2]. On the other hand, the latter feature enables one to find such intermediates which do not have the correct stereochemistry for intramolecular 1,1-vinylboration. This is shown by the ^{29}Si NMR spectrum (Fig. 3) of the reaction solution which indicates the presence of starting material **1e**, the final product **4e**, and a large amount of the intermediate **8e** (δ^{29}Si −3.3, $^2J(^{119}\text{Sn},^{29}\text{Si}) = 154.4$ Hz, −20.2, $^3J(^{119}\text{Sn},^{29}\text{Si}) = 6.0$ Hz; δ^{119}Sn −242.4) which cannot rearrange to a heterocycle. The 1,1-organoboration is a reversible reaction [1,2], and therefore, upon heating, **8e** loses Et_3B to give back **1e**. Any time the 1,1-organoboration of **1e** produces the compound **6e** with the correct stereochemistry (Scheme 4), fast rearrangement to **7e** takes place, followed by similarly fast intramolecular 1,1-vinylboration to **4e**.

3. Conclusions

Since various bis(1-alkynyl)-1,3-di-tert-butyl-1,3,2-diazastannacyclohexanes can be readily converted into novel stannoles of type **4** by 1,1-organoboration, these compounds can now be used for further transformations. This can be done by taking advantage of the well-known reactivity of Sn–N, Sn–C or B–C bonds. Thus, the syntheses of other new stannoles as well as of other metalloles seem feasible, if the substitution of the 1,3,2-diazastannacyclohexane moiety can be achieved. Furthermore, reductions of the Sn(IV) to Sn(II) compounds seem feasible by retaining the stannole unit.

Table 3
^{11}B, ^{13}C, ^{119}Sn NMR [a] data of the zwitterionic intermediates **7f** and **7a** [6] for comparison [d]

	7a	**7f**
R^1	Me	CH_2NMe_2
Sn–**C**=	133.2 [984.0]	145.1 [1084.6]
B–**C**=	178.0 (br)	177.5 (br)
B–**C**≡	114.7 (br) [130]	130.9 (br) [n.o.]
R^1–**C**≡	124.2 [82.8]	105.6 [61.6]
=C–**R¹**	18.8 [189.6]	61.2 [134.3], 47.4
≡C–**R¹**	6.2 [<3.0]	55.2 [n.o.], 44.0
BEt₂	17.0 (br), 13.6	15.0 (br), 13.5
N^{t}Bu	56.6 [7.1], 30.5 [22.9]	56.6 [11.6], 30.7 [22.5]
NCH₂	48.2 [16.9]	49.0 [12.1]
CH₂	35.6 [16.9]	35.4 [18.3]
δ^{11}B	−7.1	−9.2 [b]
δ^{119}Sn	−32.8	−125.0 [c]

[a] In CD_2Cl_2 (10–15%) at −10 ± 1°C; coupling constants $J(^{119}\text{Sn},^{13}\text{C})$ are given in brackets (±0.5 Hz); n.o. = not observed; (br) denotes broad ^{13}C NMR signals owing to partially relaxed scalar ^{13}C–^{11}B coupling.

[b] $h_{1/2} = 850$ Hz; δ^{11}B −9.2 (25°C) with $h_{1/2} = 280$ Hz.

[c] $h_{1/2} = 33$ Hz; δ^{119}Sn −115.0 (25°C) with $h_{1/2} = 118$ Hz; δ^{119}Sn −125.0 (−50°C) with $h_{1/2} = 37$ Hz.

[d] For **7g** in toluene, the ^{119}Sn NMR spectrum showed a signal at δ^{119}Sn −64.7 (−15°C).

4. Experimental

The preparative work and all handling of samples was carried out under an inert atmosphere (Ar or N_2), using carefully dried glassware and dry solvents. BuLi (1.6 M) in hexane, Et_3B were commercial products. Triphenylborane was obtained as described [20], 2,2-dichloro-1,3-di-tert-butyl-1,3,2-diazastannacyclohexane was prepared as reported [8] (note that the *N*,*N*′-di-tert-butyl-1,3-diaminopropane has to be purified by distillation prior to use). All bis(1-alkynyl)tin compounds **1** were obtained following the literature procedure [9], and their purity was >95% according to ^{1}H NMR.

NMR spectra were recorded by using Jeol FX90Q, Bruker AC 300, ARX 250 and AMX 500 instruments, all 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^1H (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_2Cl_2) = 52.3] and external references [δ^{11}B ($BF_3{}^-OEt_2$) = 0, Ξ^{11}B = 32.083971 MHz; δ^{15}N ($MeNO_2$, neat) = 0, Ξ^{15}N = 10.136767 MHz; δ^{29}Si (Me_4Si) = 0, Ξ^{29}Si = 19.867184 MHz;

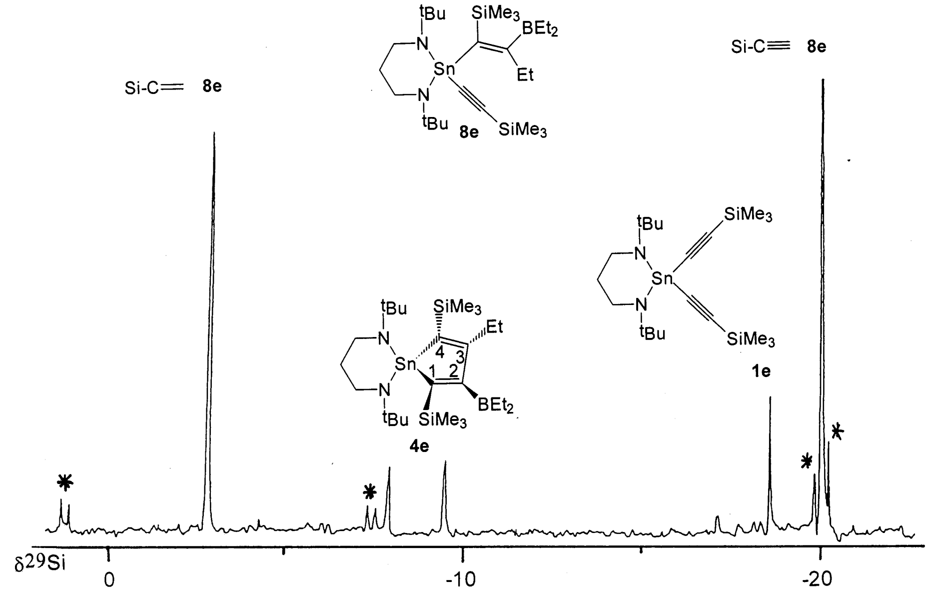


Fig. 3. 17.8 MHz ^{29}Si NMR spectrum (refocused INEPT [19]) of the reaction mixture resulting from the reaction of **1e** with Et_3B (**2**) after 1 h at room temperature. $^{117/119}$Sn satellites are marked by asterisks.

δ^{119}Sn (Me_4Sn) = 0, Ξ^{119}Sn = 37.290665 MHz]. ^{15}N NMR spectra were recorded by the refocused INEPT pulse sequence with ^{1}H decoupling [19], taking advantage of the scalar coupling ^{15}N–^{1}H(^{t}Bu) across three bonds with a magnitude of ca. 2.8 Hz. In most cases it proved possible to detect $^{117/119}$Sn satellites after a few hours of spectrometer time. All ^{29}Si NMR spectra were measured using the same technique, based on $^2J(^{29}\mathrm{Si},^1\mathrm{H}_{\mathrm{Me}})$. ^{119}Sn NMR spectra were measured by inverse gated ^{1}H decoupling in order to suppress the NOE. By using spectrometers at high field strength ($B_0 > 7.1$ T), ^{119}Sn nuclear spin relaxation in the compounds studied is mainly governed by the mechanism of chemical shift anisotropy. This means that pulse angles in the order of 50–60° and fast repetition times (ca. 0.1 s) can be used. The signals are fairly broad owing to partially relaxed scalar ^{119}Sn–^{14}N coupling and therefore, short (0.3 s) acquisition times were used. All 2D experiments were optimised by appropriate 1D polarisation transfer experiments.

*4.1. 1,1-Organoboration of the alkynes **1**. General procedure*

A solution of the alkynes **1** (0.1 g) in toluene (5 ml) was cooled to − 78°C, and an excess of Et_3B (**3**) (0.6 ml) was added in one portion. The mixture was warmed to room temperature, and the progress of the reaction was monitored by ^{119}Sn and ^{29}Si NMR (**1e**), as shown in Fig. 3. After heating for 1–5 h at 80°C, all alkynes, except those of **1c**, were completely converted into the stannoles **4**. The solvent and the excess of Et_3B were removed in vacuo, and the stannoles were left as colourless or slightly yellow oils in quantitative yield (purity > 95% according to ^{1}H NMR). These compounds decompose on silica or Al_2O_3, and all attempts to crystallise them either from pentane or from pentane/ether mixtures at − 78°C failed.

The reaction of **1e** with Ph_3B (**3**) in the molar ratio 1:1 was carried out in the same way as for Et_3B. ^{29}Si NMR spectra showed that starting material was still present although various products, including **5e** (δ^{29}Si − 6.6, − 8.0, $^2J(^{119}\mathrm{Sn},^{29}\mathrm{Si})$ = 111.0 and 112.0 Hz; δ^{119}Sn − 16.9; full assignment of the ^{13}C NMR spectrum was not possible) had already been formed. At least 40% of Ph_3B was consumed in exchange reactions (see Scheme 2). By using a large excess of **3**, all of **1e** was consumed after 2 h at room temperature, giving again a complex mixture of compounds, including **5e**.

In the cases of **1f,g**, the experiments were repeated in CD_2Cl_2 in order to obtain a complete set of ^{13}C NMR data of the intermediates **7f,g**. This was successful for **7f** (Table 3).

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