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From bis(silylamino)tin dichlorides via di(1-alkynyl)-bis(silylamino)tin to new heterocycles by 1,1-organoboration

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Abstract

Bis(silylamino)tin dichlorides **1** [X_2SnCl_2 with X = $N(Me_3Si)_2$ (**a**), N(9-BBN)$SiMe_3$ (**b**), N(^{t}Bu)$SiMe_3$ (**c**), and $N(SiMe_2CH_2)_2$ (**d**)] were prepared from the reaction of two equivalents of the respective lithium amides (**Li-a**–**d**) with tin tetrachloride, $SnCl_4$, or from the 1:1 reaction of the respective bis(amino)stannylene with $SnCl_4$. The compounds **1** react with two equivalents of lithium alkynides LiC≡C–R^1 to give the di(1-alkynyl)-bis(silylamino)tin compounds $X_2Sn(C≡C–R^1)_2$, **2** (R^1 = Me), **3** (R^1 = ^{t}Bu), and **4** (R^1 = $SiMe_3$). Problems were encountered, mainly with LiC≡C–^{t}Bu as well as with **1b**, since side reactions also led to the formation of 1-alkynyl-bis(silylamino)tin chlorides **5**–**7** and tri(1-alkynyl)(silylamino)tin compounds **8** and **9**. 1,1-Ethylboration of compounds **2**–**4** led to stannoles **10**, **11**, and in the case of propynides, also to 1,4-stannabora-2,5-cyclohexadiene derivatives **12**. The molecular structure of the stannole **11b** (R^1 = $SiMe_3$) was determined by X-ray analysis. The reaction of **2a** and **d** with triallylborane afforded novel heterocycles, the 1,3-stannabora-2-ethylidene-4-cyclopentenes **14**. These reactions proceed via intermolecular 1,1-allylboration, followed by an intramolecular 1,2-allylboration to give **14**, and a second intramolecular 1,2-allylboration leads to the bicyclic compounds **15**. © 2002 Published by Elsevier Science B.V.

Keywords: Tin; Amides; Alkynes; Alkylboration; Allylboration; NMR; X-ray

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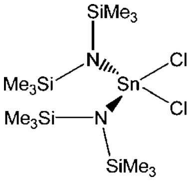
1. Introduction

The use of bis(amino)tin dihalides, e.g. X_2SnCl_2 (X = amino group), in synthesis is not straightforward, since these compounds tend to exchange amino and halogeno substituents if there are no bulky substituents at the amino nitrogen atoms. Thus, the presence of at least one *N*-silyl group offers a twofold advantage, i.e. the basicity of the amino groups is reduced and steric hindrance prevents adduct formation which is a prerequisite for the exchange reactions. Only one of such tin compounds of type **1** has been described in the literature [1] (**1a**), and we report now on the synthesis of three other derivatives.



1a

In the case of cyclic bis(amino)tin dichlorides [2], it was shown that the Cl-substitution by alknyl groups can be achieved to give di(1-alkynyl)tin compounds [3], and that these derivatives can be further converted by 1,1-organoboration into stannoles [4]. Such stannoles, like other metalloles [5], bearing functional groups at the tin atom, are attractive reagents, since the diene system and the Sn–N bonds are reactive centres for studying further transformations. In the present paper we report on the reactions of non-cyclic di(1-alkynyl)-bis(silylamino)tin compounds with triethylborane, BEt_3, and triallylborane, $BAll_3$, in order to explore

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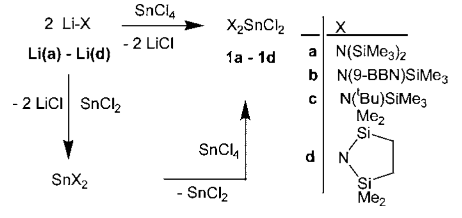
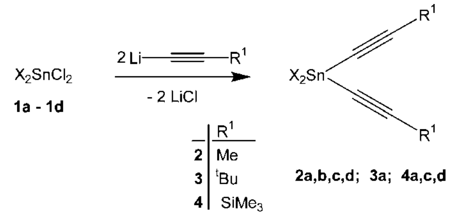


Scheme 1.



Scheme 2.

routes to new stannoles or other heterocycles. The presence of silylamino groups may lead to different results when compared with the known 1,3,2-diazastanna-cyclohexane derivatives [4].

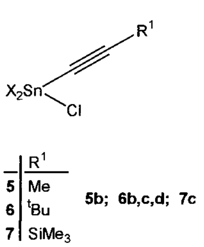
2. Results and discussion

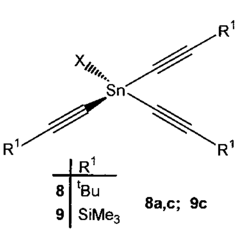
2.1. Synthesis of the bis(silylamino)tin dichlorides X_2SnCl_2 **1a–d**

Scheme 1 shows the most useful synthetic routes leading to the bis(silylamino)tin dichlorides **1a**–**d**. The respective lithium amides served as starting materials. These are readily available from *N*-silylamines which are commercial products except of 9-(*N*-trimethylsilylamino)-9-borabicyclo[3.3.1]nonane [6,7]. The salt elimination reaction (Scheme 1a), using Li-**a**, **b**, **d** proved to be the most straightforward route to **1a**, **b**, **d**. An excess of $SnCl_4$ led to mixtures of the respective dichloride and trichloride [8]. The alternative route via the corresponding bis(amino)stannylene [9] and its reaction with $SnCl_4$ (Scheme 1b) gave better results for **1c**. Again, an excess of $SnCl_4$ afforded mixtures of the dichloride and the trichloride [8]. The products are colourless, crystalline (**1a**) or waxy, moisture-sensitive solids (**1b**–**d**). They were characterised by their NMR data (see Table 1 and Section 4).

2.2. Synthesis of the di(1-alkynyl)-bis(silylamino)tin compounds $X_2Sn(C{\equiv}C{-}R^1)_2$ **2–4**

Treatment of the bis(*N*-silylamino)tin dichlorides **1a**–**d** with various alkynyllithium reagents $LiC{\equiv}C{-}R^1$ (Scheme 2) afforded the di(1-alkynyl)-bis(*N*-silylamino)tin compounds **2**–**4** [R^1 = Me (**2**), ^{t}Bu (**3**), $SiMe_3$ (**4**)] (see Table 2 and Section 4). Surprisingly, these apparently straightforward reactions were not always successful. In some cases, in particular with R^1 = ^{t}Bu and X = N(^{t}Bu)SiMe$_3$ (**c**), the desired products were formed only in low yield along with other products such as 1-alkynyl-bis(silylamino)tin chlorides **5**–**7** or tri(1-alkynyl)-silylaminotin compounds **8** and **9** (see Table 3 for some NMR data of these compounds which were frequently obtained only in mixtures).





2.3. Reactions of the di(1-alkynyl)-bis(silylamino)tin compounds **2–4** with triethylborane BEt_3

The compounds **2a**–**d** and **4a**, **b**, **d** react with BEt_3 in BEt_3 as a solvent to give the stannoles **10a**–**d** and **11a**, **b**, **d** (NMR data in Table 4 and Section 4). In the cases of the propynides **2b** and **2d**, mixtures of stannoles **10b** and **10d** with 1,4-stannabora-2,5-cyclohexadienes **12c** and **12d** (NMR data in Table 5), respectively, were obtained, and the ratio was found to depend, at least in the case of **10d**/**12d**, on the reaction conditions. This observation is in agreement with previous results for 1,1-organoboration of diorganotin propynides, where the 1,4-stannabora-2,5-cyclohexadienes were also the preferred product, sometimes even formed selectively

Table 1
^{119}Sn-, ^{29}Si-, ^{15}N-, ^{13}C- and ^{11}B-NMR data [a] of bis(silylamino)tin dichlorides **1a**–**1d**

	δ^{119}Sn	δ^{29}Si	δ^{15}N	δ^{13}C (NSiMe)	δ^{13}C (NR)
1a	−145.6	9.6 [20.4]	−317.4 [39.6] (4.5)	5.2 [18.3] (56.3)	–
1b [b]	−205.1	11.2 [19.9]	−250.8	4.5 [14.1] (57.9)	30.2 (br) 22.9 33.5
1c	−174.0	6.7 [24.7]	−279.1 [75.0] (7.7)	6.6 [14.0] (56.2)	35.2 [41.5] (1.9); 59.4 [25.1]
1d	−91.3	20.8 [1.6]	−323.7 [70.3] (4.9)	2.7 [<8] (54.3)	9.7 [53.7] (56.7)

[a] In C_6D_6 at 23 °C. All coupling constants to ^{119}Sn [±0.2 Hz] are given in brackets, and to ^{29}Si (±0.1 Hz) in parentheses; (br) denotes broad signals due to partially relaxed ^{13}C–$^{10/11}$B coupling.

[b] $\delta^{11}B = 58.5$.

Table 2
^{119}Sn-, ^{29}Si-, ^{15}N-, ^{13}C-, and ^{11}B-NMR data [a] of di(1-alkynyl)-bis(silylamino)stannanes **2**–**4**

	δ^{119}Sn	δ^{29}Si	δ^{15}N	δ^{13}C (N)		δ^{13}C (Sn–C≡C–R^1)		
				SiMe$_x$	NR^2	Sn–C≡	≡C–R1	R^1
2a ≡C–Me	−228.8	7.0 [8.0]	−344.3 [67.9], (6.3)	5.6 [13.5] (55.7)	–	86.0 [1061.7]	107.3 [217.7]	4.4 [18.0]
2b [b] ≡C–Me	−276.7	8.2 [25.3]	n.m.	4.9 [10.9] (56.1)	30.2 (br), 33.6, 23.2	86.2 [1047.0]	106.4 [214.9]	4.7 [17.8]
2c ≡C–Me	−260.1	3.9 [33.4]	−313.1 [118.4] (10.0)	7.0 [9.6] (55.6)	57.3 [12.4]; 35.4 [29.5]	89.3 [945.1]	105.2 [194.7]	4.9 [16.5]
2d ≡C–Me	−200.6	18.8 [6.6]	−346.0 [90.2] (6.6)	3.1 (53.8)	10.3 [37.3] (56.1)	82.5 [1084.0]	107.9 [223.9]	4.4 [18.3]
3a ≡C–^{t}Bu	−223.6	66.9 [8.0]	−343.9 [65.8] (6.4)	5.6 [13.7] (55.7)	–	84.4 [1053.3]	119.2 [201.8]	28.3 [15.6]; 30.5 [7.5]
3b ≡C–^{t}Bu	−274.0	8.2 [25.8]	n.m.	5.0 [10.9] (56.3)	29.8 (br), 33.6, 23.2	84.9 [1036.8]	118.4 [198.8]	28.5 [15.9]; 30.4 [7.6]
3d ≡C–^{t}Bu	−196.5	18.8 [6.6]	−345.5 [88.4] (6.6)	3.2 (53.8)	10.3 [37.1] (56.1)	81.2 [1079.1]	119.8 [208.7]	28.4 [15.5], 30.5 [7.7]
4a ≡C–SiMe$_3$	−248.2	7.6 [9.0], −18.2 [16.5]	−343.1 [62.2] (6.1)	5.6 [14.2] (55.8)	–	115.2 [912.8] (10.4)	119.1 [146.1] (73.9)	−0.6 (56.0)
4b [c] ≡C–SiMe$_3$	−298.6	8.9 [25.5]; −18.4 [16.2]	−271.7 [85.0] (10.2)	4.9 [11.4] (56.3)	30.2 (br), 33.6, 23.2	115.0 [894.1] (10.8)	118.3 [142.2] (74.5)	−0.5 (56.3)
4c ≡C–SiMe$_3$	−279.7	4.6 [32.3], −18.9 [14.9]	−311.0 [112.8] (9.6)	6.9 [10.1] (55.8)	57.6 [13.3]; 35.4 [n.m.]	119.3 [803.4] (10.6)	117.2 [127.8] (75.2)	−0.4 (56.1)
4d ≡C–SiMe$_3$	−217.2	19.4 [6.1]; −18.1 [17.4]	−345.2 [85.6] (6.4)	3.1 (53.8)	10.2 [38.0] (56.2)	111.4 [938.9] (10.5)	120.1 [153.3] (73.6)	−0.7 (56.0)

[a] In C_6D_6 at 23 °C. All coupling constants to ^{119}Sn [±0.2 Hz] are given in brackets, and to ^{29}Si (±0.1 Hz) in parentheses; (br) denotes broad signals due to partially relaxed ^{13}C–$^{10/11}$B coupling; n.m. means not measured.

[b] $\delta^{11}B = 54.6$.

[c] $\delta^{11}B = 55.8$.

Table 3
^{119}Sn-, ^{29}Si-, ^{15}N-, and ^{13}C-NMR data [a] of 1-alkynyl-bis(silylamino)tin chlorides **5**–**7**, and tri(1-alkynyl)-(silylamino)stannanes **8**–**9**

	δ^{119}Sn	δ^{29}Si	δ^{15}N	δ^{13}C (N)		δ^{13}C (Sn–C≡C–R^1)		
				SiMe$_x$	NR	Sn–C≡	≡C–R^1	R^1
5c ≡C–Me	−197.1	5.1 [30.1]	−297.8 [103.8] (8.9)	6.9 [11.0] (55.8)	58.2 [17.4]; 35.4 [29.8]	90.5 [1000.3]	106.2 [211.1]	4.8 [16.9]
6b ≡C–^{t}Bu	−222.2	9.7 [23.5]	n.m.	4.8 [12.1] (56.5)	29.8 (br), 33.6 23.1	85.4 [1122.6]	119.0 [217.3]	28.5 [13.1], 30.6 [7.7]
6c ≡C=^{t}Bu	−193.7	5.3 [30.3]	−297.5 [102.8](8.2)	6.8 [11.4], (55.9)	58.2 [17.3]; 35.3 [n.m.]	89.6 [984.0]	118.5 [192.1]	28.4 [n.m.]; 30.4 [7.2]
6d ≡C=^{t}Bu	−123.7	19.6 [4.0]	−335.1 [84.1], (5.7)	2.9 (53.5); 3.0 (53.9)	10.0 [44.4] (56.0)	82.1 [1158.7]	120.8 [225.8]	28.4 [16.3], 30.2 [8.3]
7c ≡C=SiMe$_3$	−208.3	5.5 [30.4], −18.0 [14.8]	−296.6 [98.9] (8.9)	6.8 [11.4] (55.8)	58.3 [18.0]; 35.4 [n.m.]	119.7 [844.6] (n.m.)	117.3 [n.m.] (n.m.)	−0.5 (56.1)
8a ≡C=^{t}Bu	−275.8	5.9 [8.1]	n.m.	5.8 [11.8]	–	80.1 [n.m]	114.4 [n.m.]	28.5 [n.m.]; 30.5 [n.m.]
8c ≡C=^{t}Bu	−293.5	4 [30.6]	−318.1 [133.7] (10.3)	6.6 [n.m.]	56.3 [11.5]; 35.2 [n.m.]	81.8 [1074.2]	118.8 [206.6]	28.4 [15.7]; 30.6 [7.8]
9c ≡C=SiMe$_3$	−329.1	5.1 [29.5]; −18.2 [17.2]	−316.3 [129.6] (9.9)	6.3 [11.7] (55.8)	56.5 [12.5]; 35.2 [31.5]	111.1 [949.3] (10.9)	118.5 [153.9] (74.7)	0.4 (56.2)

[a] In C_6D_6 at 23 °C. All coupling constants to ^{119}Sn [± 0.2 Hz] are given in brackets, and to ^{29}Si (± 0.1 Hz) in parentheses; (br) denotes broad signals due to partially relaxed ^{13}C–$^{10/11}$B coupling; n.m. means not measured.

Table 4
^{119}Sn-, ^{29}Si-, ^{15} N-, ^{13}C-, and ^{11}B-NMR data [a] of the stannoles **10a–d** (2,5-Me$_2$), **11a**, **b** and **d** (2,5-(SiMe$_3$)$_2$)

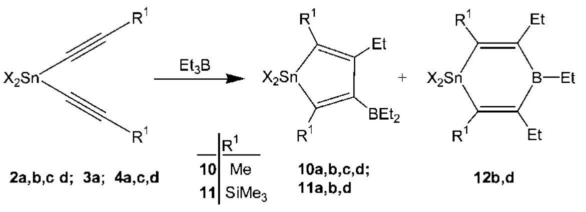
	10a	**10b**	**10c**	**10d**	**11a**	**11b**	**11d**
δ^{13}C(2)	134.2 [576.2]	134.6 [568.8]	138.6 [551.9]	129.8 [597.2]	146.4 [284.5] (n.m.)	143.4 [266.3] (n.m.)	143.6 [283.1] (63.6)
δ^{13}C(3)	163.0 (br)	161.3 (br)	160.6 (br)	164.8 [85.0 ± 4] (br)	175.9 (br)	175.5 (br)	178.2 (br)
δ^{13}C(4)	150.5 [201.1]	150.0 [199.0]	148.0 [190.5]	151.7 [189.1]	163.1 [182.1]	163.7 [n.m.]	164.6 [170.6]
δ^{13}C(5)	132.4 [655.8]	132.2 [641.8]	136.3 [623.2]	128.5 [673.0]	139.3 [373.6]	140.9 [360.8]	136.1 [375.4]
δ^{13}C(2,5-Me$_2$/2, 5-(SiMe$_3$)$_2$)	16.5 [80.8]; 19.7 [92.0]	16.4 [82.1]; 19.7 [93.4]	16.1 [79.3]; 19.3 [86.7]	17.3 [82.7]; 20.6 [93.2]	3.9 [12.6] (51.8); 4.0 [11.0] (52.3)	3.6 [13.3] (51.6); 4.2 [10.8] (52.4)	3.6 [13.0] (52.1); 3.7 [11.3] (52.1)
δ^{13}C(BEt$_2$)	22.5 (br) 9.3	22.6 (br) 9.4	22.7 (br) 9.3	22.5 (br) 9.4	23.2 (br) 9.8	22.9 (br)/23.4 (br) 9.6/9.7	23.3 (br) 9.9
δ^{13}(4-Et)	26.7 [78.0]; 13.0 [10.7]	26.5 [76.2]; 13.4 [11.2]	26.7 [78.0]; 12.7 [10.5]	26.5 [75.5]; 13.0 [11.2]	32.5 [134.8]; 15.6 [13.0]	32.7 [129.2]; 16.2 [12.4]	32.6 [130.5]; 15.5 [12.2]
δ^{13}C(NR)	SiMe$_3$ 5.4 [9.3] (55.2)	SiMe$_3$ 4.68 [7.7] (55.6); 4.69 [7.7] (55.6). 9-BBN 29–32 (br) 33.5–34.0; 23–24 (br)	SiMe$_3$ 6.9/7.0 ^{t}Bu 56.3 35.1/35.2	SiMe$_2$ 3.39 (53.4); 3.40 (53.4). Si–CH$_2$ 10.6 [21.5] (56.1)	*N*-SiMe$_3$ 7.1 [9.4] (55.3)	*N*–SiMe$_3$ 6.0 [8.0] (56.0); 7.1 [5.4] (56.1). 9-BBN 30.0 (br)/30.3 (br) 34.1 23.4	*N*–SiMe$_3$ 4.3 [3.2] (53.5); 4.4 [3.2] (53.5). SiCH$_2$ 11.0 [16.3]
δ^{119}Sn	−38.9	−79.7	−56.8	−40.1	10.2	−22.6	28.7
δ^{29}Si(NSi); δ^{29}Si(CSi)	4.4 [8.1]	5.4 [15.4]	0.5/0.6	16.5	4.4 [5.7]; −6.3 [132.5]; −8.0 [140.2]	4.6/4.8; −6.3 [128.3]; −6.6 [148.4]	16.3; −7.1 [127.7]; −8.6 [132.3]
δ^{15}N	−342.9 [82.0] (6.5)	n.m.	−312.77 [30.6]; −312.81 [29.0]	−344.2 [63.0] (6.7)	−337.7 [135.2] (5.3)	−262.7	−341.3 [111.0] (5.3)
δ^{11}B	90 ± 1	87 ± 1/55 ± 1	89 ± 1	88 ± 1	87 ± 1	85 ± 1/55 ± 1	90 ± 1

[a] In C$_6$D$_6$ at 23 °C. All coupling constants to ^{119}Sn [±0.2 Hz] are given in brackets, and to ^{29}Si (±0.1 Hz) in parentheses; (br) denotes broad signals due to partially relaxed ^{13}C–$^{10/11}$B coupling; n.m. means not measured.

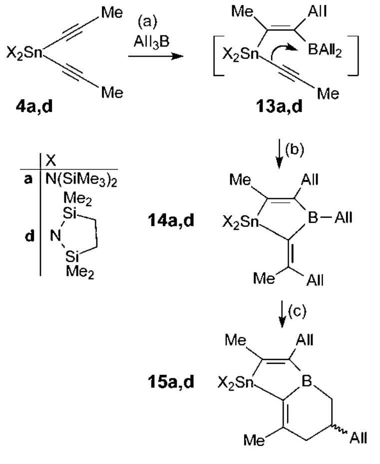
Table 5
^{119}Sn-, ^{29}Si-, ^{15}N-, ^{13}C-, and ^{11}B-NMR data [a] of 1,4-stannabora-2,5-cyclohexadienes **12b** and **12d**

	12b	**12d**
δ^{13}C(2,6)	150.4 (br)	148.9 (br) [651.2]
δ^{13}C(3,5)	165.3 (br)	166.7 (br) [65.0 ± 4]
δ^{13}C(2,6-Me)	20.1 [59.3]	20.8 [56.5]
δ^{13}C(3,5-Et)	24.4 [94.3], 14.2 [13.4]	24.2 [91.4], 14.5 [13.0]
δ^{13}C(B-Et)	18.8 (br) 9.4	17.9 (br) 9.2
δ^{13}C(R)	5.1 [7.7] (55.6); 9-BBN 29–32 (br) 33.5–34.0, 23–24 (br)	$SiMe_2$ 3.7 [1.6] (53.4). $SiCH_2$ 10.8 [21.0] (56.5)
δ^{119}Sn	−190.5	−149.5
δ^{29}Si	5.5 [15.9]	16.2
δ^{15}N	n.m.	−349.7 [50.0] (6.5)
δ^{11}B	n.m.	68 ± 2

[a] In C_6D_6 at 23 °C. All coupling constants to ^{119}Sn [± 0.2 Hz] are given in brackets, and to ^{29}Si (± 0.1 Hz) in parentheses; (br) denotes broad signals due to partially relaxed ^{13}C–$^{10/11}$B coupling; n.m. means not measured.



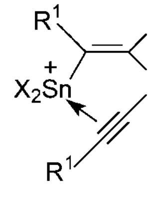
Scheme 3.



Scheme 4.

[10,11]. Treatment of the alkyne derivatives **3** (R^1 = ^{t}Bu) with BEt_3 did not lead to any defined products, since 1,1-ethylboration did not take place, even under pressure at 160 °C in BEt_3; only extensive decomposition of the compounds **3** was observed (Scheme 3).

The formation of the heterocycles **10**–**12** is consistent with the mechanism proposed previously [10], in which a zwitterionic species **A** plays the decisive role. Starting from **A**, intramolecular 1,1-vinylboration leads to stannoles, and alternatively intramolecular 1,1-ethylboration can lead to 1,4-stannabora-2,5-cyclohexadienes (**12**). According to AM1 calculations [12] on **12b**, the bond angles at the tin atom (CSnC ≈ 100° and NSnN ≈ 118°) are much wider than those determined experimentally and calculated for **11b** (vide infra). Intermediates of type **A** have been isolated and structurally characterised [13]. In the present study, the reaction conditions were too harsh for the isolation of intermediates like **A**. The intermolecular 1,1-ethylboration of the sterically congested alkynyltin compounds **2**–**4** requires a fairly high activation energy, and therefore, any intermediate of type **A** formed in the initial steps of the 1,1-organoboration reactions are short-lived, being converted rapidly into the respective final product.



A

2.4. Reaction of *2a*, *d* with triallylborane, BAll$_3$; combination of 1,1-organoboration and 1,2-allylboration

Triallylborane, $BAll_3$, is well known as a rather special triorganoborane due to permanent allylic rearrangement [14], and it was found that it reacts with many alkynes by 1,2-allylboration for which a six-membered transition state has been proposed [15]. Recently it was shown that 1-alkynylsilicon, -germanium and -tin compounds may react with $BAll_3$ either by 1,1- or 1,2-allylboration, and that the 1,1-allylboration is the preferred route in many cases [16,17]. The reactions of **2a** and **2b** with $BAll_3$ were studied, and surprisingly, they lead neither to stannoles nor to 1,4-stannabora-2,5-cyclohexadienes. Instead, the novel 1,3-stannabora-2-ethylidene-4-cyclopentene derivatives **14a** and **14d**, respectively, were formed (Scheme 4, NMR data in Table 6 and Section 4). It is proposed that these reactions proceed as shown in Scheme 4(a) via the intermediates **13a**, **d** which are in equilibrium with the zwitterionic intermediates of type **A**, when the intermolecular 1,1-allylboration is followed by an intramolecular transfer of the second alkynyl group from tin to boron. The next step shown in Scheme 4(b) can be understood as an intramolecular 1,2 allylboration leading to **14a** and **14d**. If 1,2-allylboration would be the first step followed by 1,1-allylboration, the same products could result. However, the preference [16,17] of intermolecular 1,1-allylboration indicates that this reaction most likely dominates in the beginning. These

Table 6
^{119}Sn-, ^{15}N-, ^{11}B-, ^{29}Si- and ^{13}C-NMR data [a] of 2-ethylidene-1,3-stannabora-4-cyclopentenes **14a**, **d** and 1-bora-7-stannabicyclo[4.3.0]nona-5,8-dienes **15a**, **d**

	14a [b]	**14d** [c]	**15a** [d]	**15d** [e]
δ^{119}Sn	−96.7	−72.3	−60.5	−49.8
δ^{15}N	−341.4	−344.4	−342.3, −343.7	−346.6, −345.6
δ^{11}B	68.6	64.6	61.0	61.1
δ^{29}Si	4.9 [7.6]	16.4 [<2]	4.0 [6.9], 4.1 [6.0]	16.2, 16.3 [<2]
δ^{13}C(1)	160.6 [134.9] br	164.1 [127.2] br	156.6 [153.1] br	158.5 [145.9] br
δ^{13}C(2)	175.3 [628.5]	171.3 [612.8]	177.4 [660.4]	175.6 [658.0]
δ^{13}C(3)	157.7 [396.2] br	154.2 [403.2] br	145.1 [518.3] br	142.2 [541.6] br
δ^{13}C(4)	155.3 [15.6]	157.9 [11.0]	172.4	171.8
δ^{13}C(5)	–	–	34.8 [85.8]	34.5 [82.8]
δ^{13}C(6)	–	–	35.0 [10.0]	35.3 [9.3]
δ^{13}C(7)	–	–	26.8 [73.2] br	26.7 [68.0] br

[a] In CDCl$_3$ at 23 °C. All coupling constants to ^{119}Sn [±0.2 Hz] are given in brackets, and to ^{29}Si (±0.1 Hz) in parentheses; br denotes broad signals due to partially relaxed ^{13}C–$^{10/11}$B coupling. See Fig. 6 for numbering of the carbon atoms.

[b] Other ^{13}C-NMR data: 5.8 (Me$_3$Si, (55.6), 10.1); 21.5 (Me, 61.5); 31.4 (CH$_2$, 66.2); 31.6 (CH$_2$B); 34.3 (Me, 97.4); 46.3 (CH$_2$, 115.5); 114.8 (=CH$_2$); 114.9 (=CH$_2$); 116.6 (=CH$_2$); 136.3 (=CH–); 136.4 (=CH–); 136.7 (=CH–).

[c] Other ^{13}C-NMR data: 3.2 (Me$_2$Si, (53.4), 29.4); 10.3 (CH$_2$Si, (56.0), 21.7); 21.3 (Me, 60.7); 31.3 (CH$_2$B); 33.5 (CH$_2$, 64.5); 34.3 (Me, 97.4); 45.5 (CH$_2$, 110.0); 114.7 (=CH$_2$); 114.8 (=CH$_2$); 116.6 (=CH$_2$); 135.8 (=CH–); 136.2 (=CH–); 136.7 (=CH–).

[d] Other ^{13}C-NMR data: 5.5 (Me$_3$Si, (55.3), 9.1); 5.6 (Me$_3$Si, (55.3), 10.0); 21.2 (Me, 72.5); 32.8 (Me, 62.7); 42.7 (CH$_2$, 7.6); 43.6 (CH$_2$, 87.5); 114.4 (=CH$_2$); 115.7 (=CH$_2$); 136.3 (=CH–); 137.6 (=CH–).

[e] Other ^{13}C-NMR data: 3.1 (MeSi, (53.6)); 3.2 (MeSi, (53.2)); 3.2 (MeSi, (53.2)); 3.3 (MeSi, (53.2)); 10.4 (CH$_2$Si, (55.6), 21.1); 10.4 (CH$_2$Si, (55.6), 20.7); 21.3 (Me, 71.8); 34.3 (Me, 61.3); 43.0 (CH$_2$, 7.5); 43.1 (CH$_2$, 86.6); 114.3 (=CH$_2$); 115.7 (=CH$_2$); 136.3 (=CH–); 137.6 (=CH–).

reactions of **2a**, **d** with BAll$_3$ take place at room temperature and are complete after 3–4 h. The formation of the compounds **14** is the first example of combining 1,1- and 1,2-allylboration. Heating of the reaction solutions induces a further intramolecular 1,2-allylboration [Scheme 4(c)] which leads to **15a** or **15d**. The latter type of reaction is well known in allylborane chemistry [15].

2.5. NMR spectroscopic results

2.5.1. General

All NMR spectroscopic data in the Tables 1–6 and in Section 4 support the proposed structures. ^{119}Sn-NMR signals were measured by single pulse techniques [18], and in some cases it was also possible to use polarisation transfer (INEPT [19]), based on scalar ^{119}Sn–^{1}H coupling across three bonds. ^{29}Si-NMR spectra [20] were readily recorded with a high signal-to-noise ratio (Fig. 1) by using the INEPT pulse sequence [19], based on $^{2}J(^{29}\mathrm{Si},^{1}\mathrm{H}_{\mathrm{Me}}) \approx 7$ Hz. In many cases, it proved possible to record ^{15}N-NMR spectra at natural abundance with a signal-to-noise ratio that allowed to detect $^{117/119}$Sn and ^{29}Si satellites according to the coupling constants $^{1}J(^{119}\mathrm{Sn},^{15}\mathrm{N})$ and $^{1}J(^{29}\mathrm{Si},^{15}\mathrm{N})$ [21] (see Figs. 2 and 3). Again INEPT, based on $^{3}J(^{15}\mathrm{N},^{1}\mathrm{H}_{\mathrm{SiMe}}) \approx 1.5$ Hz, proved useful for this purpose. In most cases, the ^{13}C-NMR spectra could be recorded with $^{117/119}$Sn satellites, even for ^{13}C resonances of quaternary carbon atoms which helped greatly for the assignment of the ^{13}C-NMR signals (Figs. 4 and 5). In the ^{13}C-NMR spectra, the observation of broad signals indicates, in general, the presence of carbon atoms linked to the quadrupolar $^{10/11}$B nuclei [22], although there are some examples (e.g. in the case of the 1,4-stannabora-cyclohexa-2,5-dienes (**12**)), where intramolecular dynamic processes cause broadening of ^{13}C-NMR signals. The ^{11}B-NMR signals were found in the range typical of three-coordinate boron atoms as very broad signals, a consequence of the unsymmetrical charge distribution at the site of the boron nuclei and the fairly large molecular mass [23].

2.5.2. Chemical shifts δ^{13}C,δ^{15}N,δ^{29}Si, δ^{119}Sn

All chemical shifts in the bis(silylamino)tin dichlorides **1a**–**1d** change in the same way as in the corresponding siliylaminotin trichlorides [8]. The range of

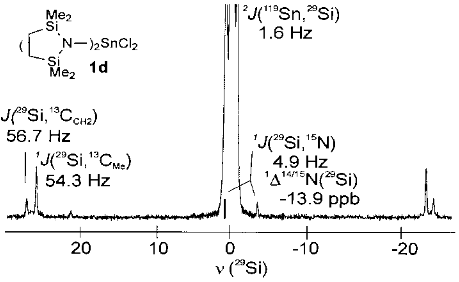


Fig. 1. 99.6 MHz ^{29}Si-NMR spectrum of **1d** in C$_6$D$_6$ (23 ± 1 °C), recorded by using the refocused INEPT pulse sequence (based on $^{3}J(^{15}\mathrm{N},^{1}\mathrm{H}_{tert\text{-}\mathrm{Bu}}) = 2.5$ Hz) with ^{1}H decoupling. The $^{117/119}$Sn satellites ($^{2}J(\mathrm{Sn},^{29}\mathrm{Si}) = 1.6$ Hz), ^{13}C satellites, and ^{15}N satellites are shown. Because of the isotope-induced chemical shift $^{1}\Delta^{14/15}\mathrm{N}(^{29}\mathrm{Si})$ [20,34] only one of the ^{15}N satellites is visible (the position of the second one is indicated). The magnitude of $^{1}J(^{29}\mathrm{Si},^{15}\mathrm{N})$ was determined from the ^{15}N-NMR spectrum.

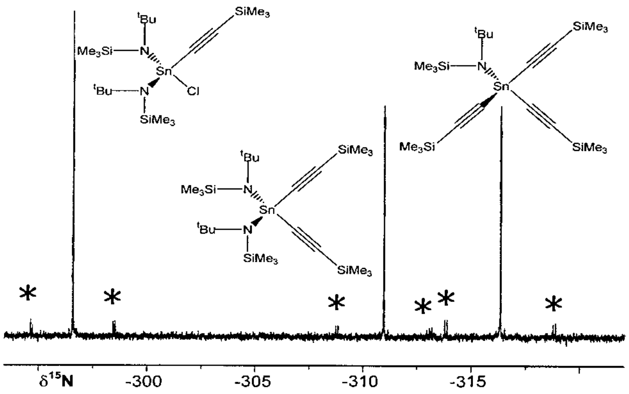


Fig. 2. 50.5 MHz ^{15}N-NMR spectrum of a mixture containing the tin amides **4c**, **7c** and **9c** in C_6D_6 (23 ± 1 °C), measured by using the refocused INEPT pulse sequence with ^{1}H decoupling. The $^{117/119}$Sn satellites are clearly visible (**4c**: $^1J(^{119}Sn,^{15}N) = 112.8$ Hz; **7c**: $^1J(^{119}Sn,^{15}N) = 98.9$ Hz; **9c**: $^1J(^{119}Sn,^{15}N) = 129.6$ Hz.

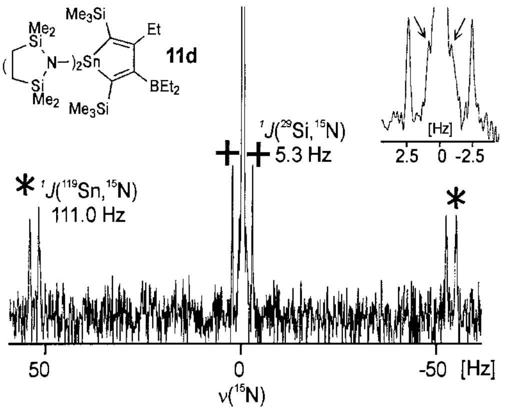


Fig. 3. 25.2 MHz ^{15}N-NMR spectrum of the stannole **11d** (in C_6D_6, 23 ± 1 °C), recorded by using the INEPT pulse sequence, based on $^3J(^{15}N,^1H_{SiMe}) = 1.5$ Hz; showing $^{117/119}$Sn (asterisks) and ^{29}Si satellites (+). The expansion shows ^{13}C satellites due to $^2J(^{15}N,^{13}C)$ (arrows).

the δ^{119}Sn values for the apparently similar compounds **1** is large (> 100 ppm), and the lowest ^{119}Sn nuclear shielding is observed for **1d**, in which the tin atom is linked to nitrogen atoms which are part of five-membered rings. The highest ^{119}Sn nuclear shielding is caused by the 9-BBN substituent at the nitrogen atoms in **1b**. The trends in the δ^{119}Sn values observed for **1a**–**d** are also evident for all other derivatives studied here, except of the stannoles **10a**–**d**, where the trends are less pronounced. In stannoles other electronic effects become competitive and the explanation of the δ^{119}Sn data is less straightforward. Thus, the deshielding influence of $SiMe_3$ groups (compare the data for **11** with those for **10**) is obvious, as was also found for stannoles with other substituents at the tin atom [24]. The ^{119}Sn nuclear shielding in 1,4-stannabora-2,5-cyclohexadienes (**12**) is significantly increased with respect to the stannoles, typical of the influence of a six-membered as compared to a five-membered ring.

Substitution of the chloro ligands in **1** by other functions leads to a slight increase in ^{29}Si(N) nuclear shielding. There is no particular influence of the stannole ring in **10** or **11**, or from the novel heterocyclic ring system in **14** or **15** on ^{29}Si(N) nuclear shielding.

The ^{15}N nuclear shielding increases markedly if the chloro ligands in **1** are replaced by alkynyl groups (see also Fig. 2). The organoboration products **10**–**12** have δ^{15}N values in the same range as the alkynyl derivatives **2**–**4**.

^{13}C chemical shifts are all in the typical range expected for the type of compounds studied here. A detailed discussion of ^{13}C-NMR data of organometallic-substituted alkynes (see Ref. [25] for a compilation of data) will be presented elsewhere [26]). The ^{13}C-NMR data of the stannoles **10**, **11**, 1,4-stannabora-2,5-cyclohexadienes (**12**), and of the 2-ethylidene-1,3-stannabora-4-cyclopentenes (**14a**, **d**) and 1-bora-7-stanna-bicyclo[4.3.0]nona-5,8-dienes (**15a**, **d**) are conclusive with respect to the proposed structures (see also Section 2.5.3), which is most conveniently recognised by looking at the pattern and number of ^{13}C-NMR signals for olefinic carbon atoms (see also Figs. 4 and 5).

2.5.3. Coupling constants $J(^{119}Sn,^{13}C)$, $^1J(^{29}Si,^{15}N)$, $^1J(^{119}Sn,^{15}N)$, $^2J(^{119}Sn,^{29}Si)$

The appearance of satellites in ^{13}C-, ^{15}N- or ^{29}Si-NMR spectra as a result of coupling with other rare spin-1/2 nuclei is important for structural assignments as well as (in particular for ^{15}N) for collecting new data in the field of coupling constants. The compounds studied in this work are interesting candidates for such studies as is evident from the spectra in Figs. 1–5. All coupling constants $^1J(^{29}Si,^{15}N)$ are likely to possess a positive sign [20,21], in contrast with $^1J(^{119}Sn,^{15}N)$. The sign of the latter coupling constant is positive in **1**, **2**–**9** and most likely negative in **10** and **11**, as indicated by the comparison with data for aminotin trichlorides [8] and amino(trimethyl)tin compounds [8,21], where the sign is known.

The differences in the magnitude of the coupling constants $^3J(^{119}Sn,N,Si,^{13}C)$ are related in the usual way to the respective dihedral angles, as can be seen from the large values $|^3J(^{119}Sn,^{13}C_{CH2})|$, measured in all bis(2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1yl) derivatives (**d**). According to AM1 calculations [12], the dihedral angles $SnNSiCH_2$ are either close to 0 or 180°, in contrast to those for SiMe carbon atoms. The changes in the magnitude of $^2J(^{119}Sn,^{29}Si)$ across nitrogen or sp^2-hybridised carbon atoms follow other rules. All values $^2J(^{119}Sn,N,^{29}Si)$ in bis(2,2,5,5-tetramethyl-1,2,5-azadisila-cyclopent-1yl) derivatives are small and can be resolved only in favourable cases (e.g. Fig. 1). The other data $^2J(^{119}Sn,N,^{29}Si)$ can be of either sign,

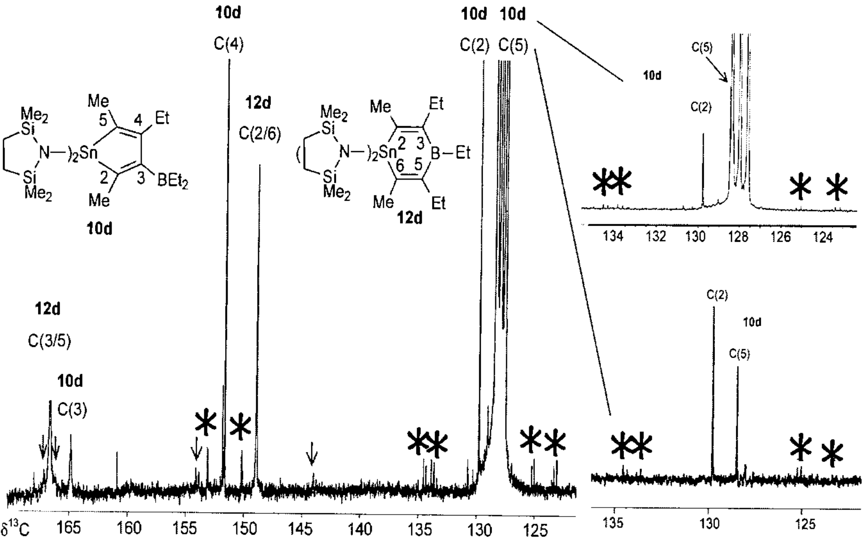


Fig. 4. 62.9 MHz $^{13}C\{^{1}H\}$-NMR spectra of a mixture containing the stannole **10d** and the 1,4-stannabora-2,5-cyclohexadiene (**12d**) in C_6D_6 (23 ± 1 °C) showing the region for olefinic carbon atoms. Note the broad lines for $^{13}C(3)$ in **10d** and $^{13}C(3,5)$ in **12d** for the ^{13}C nuclei linked to boron. One of the ^{13}C resonances of **10d** is close to the solvent resonances. The INEPT experiment based on $^{3}J(^{13}C(2,5),^{1}H_{SiMe})$ confirms readily that the assignment is correct.

and they are larger than in corresponding amino(trimethyl)tin compounds [8]. The magnitude of $^{2}J(^{119}Sn,^{29}Si)$ in the 2,5-bis(trimethylsilyl)-substituted stannoles **11** are rather large, in agreement with findings for comparable stannoles [24].

The magnitude of the coupling constants $^{1}J(^{119}Sn,^{13}C)$ measured in this work covers a fairly large range from 266 to 1159 Hz. The largest values are found for the 1-alkynyltin derivatives, where the effects of amino and alkynyl groups are similar, and the influence of chloro ligands leads to the largest values of $|^{1}J(^{119}Sn,^{13}C\equiv)|$. The smallest values of $|^{1}J(^{119}Sn,^{13}C\equiv)|$ are always found if a trimethylsilyl group is in geminal position to tin at the olefinic carbon atoms in the stannoles **11**. The same trend is observed for comparable stannoles [24] or alkenes [27]. In the cases of 2-ethylidene-1,3-stannabora-4-cyclopentenes (**14a**, **d**) and 1-bora-7-stanna-bicyclo[4.3.0]nona-5,8-dienes (**15a**, **d**), we notice rather large changes in the $^{1}J(^{119}Sn,^{13}C)$ values (see also Fig. 5), in particular, for the carbon atom which bears tin and boron (e.g. there is an increase of 34.3% on going from **14d** to **15d**). This indicates changes in the bond angles at the tin atom as well as at the respective carbon atom. The calculated (AM1 [12]) gas phase structures of **14d** and **15d** show that the bond angles SnC3C4 (129°) and SnC3B (99°) (**14d**) change to 136 and 103°, respectively, in **15d**.

Changes in the magnitude of coupling constants $^{2}J(^{119}Sn,\equiv^{13}C)$ in the 1-alkynyltin compounds follow the trends of $^{1}J(^{119}Sn,^{13}C\equiv)$ values. In the stannoles, the values of $^{2}J(^{119}Sn,^{13}C(4))$ reflect two coupling pathways, across two and three bonds. The latter contribution is much larger and, very often, of opposite sign when compared with the former.

2.6. X-ray structural analysis of the stannole **11b**

The molecular structure of **11b** is shown in Fig. 6. The five-membered ring is almost planar with a typically [28–30] acute endocyclic bond angle CSnC 86.0(1)°. In contrast, the exocyclic NSnN bond angle is wider (108.9(1)°), enforced by the bulky amino groups.

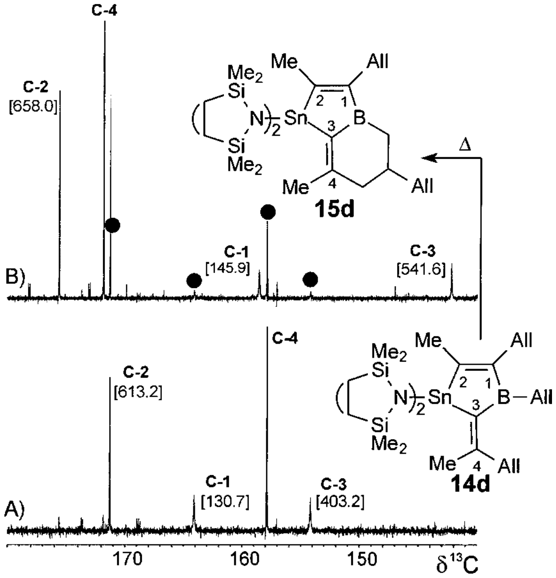


Fig. 5. 125.8 MHz $^{13}C\{^{1}H\}$-NMR spectra of the reaction mixture of **2d** and triallylborane in $CDCl_3$ at 23 ± 1 °C (coupling constants $^{1}J(^{119}Sn,^{13}C)$ are given in brackets). Note the broad signals for ^{13}C nuclei linked to boron; their assignment is clear because of the different magnitude of $^{1}J(^{119}Sn,^{13}C)$ and $^{2}J(^{119}Sn,^{13}C)$. (A) After 3 h at room temperature (**14d**). (B) After heating for 1 h at 80 °C (**15d**, the remaining signals of **14d** are marked by full circles).

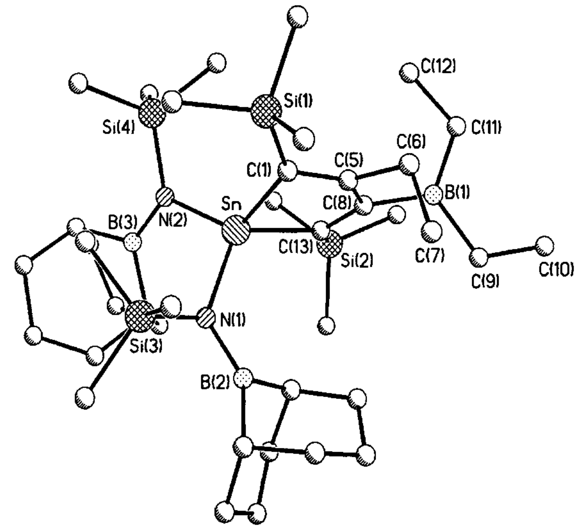


Fig. 6. Molecular structure of **11b**. Selected bond lengths (pm) and angles (°): Sn–N1 209.9(2), Sn–N2 209.0(2), Sn–C1 218.2(3), Sn–C13 217.0(3), C1–C5 134.0(4), C5–C8 152.8(4), C5–C6 152.9(4), C6–C7 153.7(7), C8–C13 135.0(4), C9–C10 149.6(5), C11–C12 150.3(8), Si1–C1 188.6(3), Si2–C13 187.5(3), B1–C8 158.3(5), B1–C9 162.0(7), B1–C11 154.0(7), N1–B2 141.5(4), N2–B3 141.6(4), N1–Si3 176.2(2), N2–Si4 176.8(2); N2SnN1 108.94(8), C1SnC13 86.10(10), N1SnC1 102.50(9), N1SnC13 120.26(9), N2SnC13 112.26(10), Si1C1Sn 136.68(14), Si2C13Sn 128.47(15), B1C9C10 118.0(4), BC11C12 117.5(4), C5C6C7 111.2(3).

Semi-empirical AM1 calculations [12] of **11b** in the gas phase gave the bond angles CSnC = 86.4° and NSnN = 111.7° in reasonable agreement with the solid-state structure. In the hexaphenyl-stannole, $Ph_2SnC_4Ph_4$, the corresponding bond angles C(2)SnC(5) and C(Ph)SnC(Ph) are 84.6(2) and 112.3°, respectively [28], very close to the calculated (AM1) values 84.1 and 111.6° [28]. This has encouraged us to use AM1 calculations for the structural predictions in the case of compounds **12b**, **14d** and **15d** (vide supra). The planes CSnC and NSnN in **11b** form an angle of 76.9°. The angles SnCSi are wide and rather different (136.5° at C1, and 128.3° at C13). The CBC plane of the diethylboryl group lies almost perpendicular (101.0°) to the plane of the ring carbon atoms C5, C8 and C13. The bonding situation within the Et_2B group is somewhat surprising, considering the large difference in the B–CH_2 bond lengths (164.9(7) and 153.6(8) pm; compared, e.g. with Et_3B: 157.2–157.7 pm [31]), the short CH_2–CH_3 bond lengths (147.9(9) and 148.4(9) pm; compared, e.g. with Et_3B: 152.5–155.3 pm [31]), and the wide bond angles BCH_2CH_3 (117.5°; compared, e.g with BEt_3: 118.9° [31]). The latter effect is typical of structures of Et_2B-compounds [31] and may be the result of hyperconjugation, whereas reasons for the changes in the bond lengths of the Et_2B group in **11b**, when compared with Et_3B, are less obvious.

In the *N*-silyl-*N*-boryl groups in **11b**, the surroundings of the boron and nitrogen atoms are trigonal-planar within the experimental error. The planes SnNSi are slightly twisted against the CBC planes (11.4 and 19.2°) which still allows for efficient NB(pp)π interactions, in agreement with B–N bond lengths (142.2(4), 142.5(6) pm) in the range of BN double bonds [32].

3. Conclusions

New stannole derivatives **10** and **11** with two amino groups linked to tin can be prepared by 1,1-ethylboration of the respective di(1-alkynyl)-bis(silylamino)tin compounds. These stannoles deserve attention with regard to further transformations considering, in particular, the well-known reactivity of Sn–N bonds [1,33]. Treatment of di(1-alkynyl)-bis(silylamino)tin compounds with triallylborane affords the 2-ethylidene-1,3-stannabora-4-cyclopentene derivatives **14**, a new heterocyclic system, the unprecedented result of combined 1,1- and 1,2-allylboration.

4. Experimental

4.1. General and starting materials

The synthesis and handling of all compounds were carried out in an atmosphere of dry Ar, and carefully dried solvents were used throughout. Starting materials were prepared as described: 9-H-9-BBN dimer [35], $BAll_3$ [36], Me_3Si(9-BBN)NH [37], Me_3Si(9-BBN)NLi (**Li-c**) [38] or were used as commercial products without further purification (all other silylamines, BuLi (1.6 M in hexane), $SnCl_4$, the alkynes and BEt_3). NMR measurements: Bruker ARX 250 or DRX 500 [^{1}H-, ^{11}B-, ^{13}C-, ^{15}N-, ^{29}Si-, ^{119}Sn-NMR [direct measurement (^{11}B, ^{13}C, ^{119}Sn) or refocused INEPT [19]: ^{15}N (based on $^3J(^{15}N,^1H_{Me})$ 2.8 Hz (^{t}Bu) or 1.5 Hz ($SiMe_3$)), ^{29}Si (based on $^2J(^{29}Si,^1H_{Me}) \approx 7$ Hz) and ^{119}Sn (based on $^3J(^{119}Sn,^1H_{Me}) \approx 55$ Hz)]. Chemical shifts are given with respect to Me_4Si [δ^1H ($CHCl_3/CDCl_3$) = 7.24; $\delta^{13}C$ ($CDCl_3$) = 77.0; $\delta^{29}Si = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz]; external neat $MeNO_2$ [$\delta^{15}N = 0$ for $\Xi(^{15}N) = 10.136767$ MHz], external Me_4Sn [$\delta^{119}Sn = 0$ for $\Xi(^{119}Sn) = 37.290665$ MHz], and external BF_3–OEt_2 [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz].

4.2. Synthesis of the bis(silylamino)tin dichlorides ***1a–d***

4.2.1. Bis(silylamino)tin dichlorides ***1a***, ***1b***, ***1d***

The respective lithiumamide **Li-a**, **Li-b** or **Li-d** (100 mmol) was suspended in pentane (50 ml) and a solution of $SnCl_4$ (50 mmol) in pentane (50 ml) was added dropwise at 0 °C under vigorous stirring. The reaction mixture was allowed to warm up to ambient temperature and then kept stirring for 3 h. All insoluble material was filtered off, and the solvent was removed in vacuo to give the products in a yield of 70–95%. The colourless to yellowish, crystalline (**1a**) or waxy (**1c** and **1d**) solids can be further purified by sublimation.

4.2.2. Bis[(silyl(tert-butyl)amino]tin dichloride ***1c***

The lithiumamide **Li-c** (100 mmol) was suspended Et_2O/pentane (50 ml), and solid $SnCl_2$ (50 mmol) was added at − 78 °C under stirring. The reaction mixture was allowed to warm up to room temperature (r.t.) and then kept stirring for 3 h. After that the mixture was cooled to − 78 °C, and a solution of $SnCl_4$ (48 mmol) in pentane (50 ml) was added under stirring, and the mixture was warmed again to r.t. All insoluble material was filtered off, and the solvent was removed in vacuo to give the product as a colourless, waxy solid in a yield of 90%. It can be purified by sublimation.

Compound **1a**: colourless, crystalline solid; 95%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.34$ (s, 36H, $SiMe_3$).

Compound **1b**: yellowish, waxy solid; 74%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.35$ (s, 18H, $SiMe_3$); 1.57 (s (br), 4H, BCH); 1.30–1.48/1.73–1.98 (m, 24H, $(CH_2)_3$).

Compound **1c**: colourless, waxy solid; 90%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.39$ (s, 18H, $SiMe_3$); 1.45 (s, 18H, ^{t}Bu).

Compound **1d**: colourless, waxy solid; 85%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.28$ (s, 24H, $SiMe_2$); 0.71 (s, 8H, $SiCH_2$).

4.3. Synthesis of the di(1-alkynyl)-bis(silylamino)tin compounds ***2–4***

A suspension of freshly prepared lithium alkynide in hexane was kept stirring at ambient temperature, and a solution of the respective bis(silylamino)tin dichloride **1a–d** (0.45 equivalents) was added dropwise. Depending on the starting materials, the reaction mixtures were kept stirring for 12–24 h at 55–90 °C. Products were either the pure di(1-alkynyl)-bis(*N*-silylamino)tin compounds **2–4** in high yields or mixtures consisting of 1,1-alkynyl-bis(silylamino)tin chlorides **5–7**, tri(1-alkynyl)-silylaminotin compounds **8** and **9** and di(1-alkynyl)-bis(silylamino)tin compounds **2–4** (mainly for R^1 or $R^2 = {}^t$Bu) which could not be separated. The specific reaction conditions and results are given below with the ^{1}H-NMR data.

Compound **2a**: white, crystalline solid; reaction time 20 h at 55 °C, yield 92%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.47$ (s, 36H, $SiMe_3$); 1.40 (s, 6H, ≡C–Me).

Compound **2b**: yellowish, waxy solid; reaction time 20 h at 55 °C; yield 92%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.35$ (s, 18H, $SiMe_3$); 1.50 (s, 6H, ≡C–Me); 1.61 (s (br), 4H, BCH); 1.15–1.40/1.70–1.90 (m, 24H, $(CH_2)_3$).

Compound **2c**: in mixture with **1c** (9%), **5c** (40%) and **8c** (9%); reaction time 20 h at 65 °C; yield 42%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.32$ (s, 18H, $SiMe_3$); 1.44 (s, 18H, ^{t}Bu); 1.57 (s, 6H, ≡C–Me).

Compound **5c**: in mixture with **1c** (9%), **2c** (42%) and **8c** (9%); reaction time 20 h at 65 °C; yield 40%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.33$ (s, 18H, $SiMe_3$); 1.45 (s, 18H, ^{t}Bu); 1.55 (s, 3H, ≡C–Me).

Compound **2d**: colourless, mobile oil; reaction time 20 h at 55 °C; yield 95%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.37$ (s, 24H, $SiMe_2$); 0.81 (s, 8H, $SiCH_2$); 1.41 (s, 6H, ≡C–Me).

Compound **3a**: in mixture with **8a** (5%); reaction time 20 h at 80 °C; yield 95%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.45$ (s, 36H, $SiMe_3$); 1.10 (s,18H, ≡C^{t}Bu).

Compound **8a**: in mixture with **3a** (95%); reaction time 20 h at 80 °C; yield 5%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.32$ (s, 18H, $SiMe_3$); 1.04 (s, 27H, ≡C^{t}Bu).

Compound **6a**: in mixture with **1a** (75%); reaction time 2 h at 90 °C; yield 25%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.41$ (s, 36H, $SiMe_3$); 1.09 (s, 9H, ≡C^{t}Bu).

Compound **3c**: in mixture with **1c** (20%), **6c** (38%) and **8c** (38%); reaction time 24 h at 75 °C; yield 4%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.35$ (s, 18H, $SiMe_3$); 1.01 (s, 18H, ≡C^{t}Bu); 1.40 (s, 18H, N^{t}Bu).

Compound **6c**: in mixture with **1c** (20%), **3c** (4%) and **8c** (38%); reaction time 24 h at 75 °C; yield 38%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.43$ (s, 18H, $SiMe_3$); 1.10 (s, 9H, ≡C^{t}Bu); 1.50 (s, 18H, N^{t}Bu).

Compound **8c**: in mixture with **1c** (20%), **3c** (4%) and **6c** (38%); reaction time 24 h at 75 °C; yield 38%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.50$ (s, 9H, $SiMe_3$); 1.05 (s, 27H, ≡C^{t}Bu); 1.52 (s, 9H, N^{t}Bu).

Compound **3b**: in mixture with **1b** (8%) and **6b** (50%); reaction time 18 h at 80 °C, yield 42%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.40$ (s, 18H, $SiMe_3$); 1.06 (s, 18H, ≡C^{t}Bu); 1.69 (s (br), 4H, BCH); 1.2–1.5/1.7–2.0 (m, 24H, $(CH_2)_3$).

Compound **6b**: in mixture with **1b** (8%) and **3b** (42%); reaction time 18 h at 80 °C; yield 50%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.32$ (s, 18H, $SiMe_3$);1.06 (s, 9H, ≡C^{t}Bu); 1.60 (s (br), 4H, BCH); 1.2–1.5/1.7–2.0 (m, 24H, $(CH_2)_3$).

Compound **3d**: in mixture with **6d** (17%);reaction time 14 h at 65 °C; yield 83%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.44$ (s, 24H, $SiMe_2$); 0.87 (s, 8H, $SiCH_2$); 1.09 (s, 18H, ≡C^{t}Bu).

Compound **6d**: in mixture with **3d** (83%); reaction time 14 h at 65 °C, yield 17%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.36$ (s, 12H, $SiMe_2$); 0.39 (s, 12H, $SiMe_2$) 0.78 (s, 8H, $SiCH_2$); 1.06 (s, 9H, ≡C^{t}Bu).

Compound **4a**: yellowish, crystalline solid; reaction time 12 h at 70 °C, yield 97%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.10$ (s, 18H, ≡C–$SiMe_3$); 0.49 (s, 36H, N–$SiMe_3$).

Compound **4b**: colourless, crystalline solid; reaction time 18 h at 75 °C; yield 92%; ^{1}H-NMR (C_6D_6, 250 MHz): $\delta = 0.06$ (s, 18H, ≡C$SiMe_3$); 0.45 (s, 18H, N–SiMe$_3$); 1.75 (s (br), 4H, BCH); 1.3-1.5/1.8–2.1 (m, 24H, (CH$_2$)$_3$).

Compound **4c**: in mixture with **7c** (29%) and **9c** (54%); reaction time 18 h at 80 °C; yield 17%; ^{1}H-NMR (C$_6$D$_6$, 250 MHz): $\delta = 0.04$ (s, 18H, $\equiv$C–SiMe$_3$); 0.43 (s, 18H, NSiMe$_3$); 1.51 (s, 18H, ^{t}Bu).

Compound **7c**: in mixture with **4c** (17%) and **9c** (54%); reaction time 18 h at 80 °C; yield 29%; ^{1}H-NMR (C$_6$D$_6$, 250 MHz): $\delta = -0.03$ (s, 9H, $\equiv$C–SiMe$_3$); 0.39 (s, 18H, NSiMe$_3$); 1.46 (s, 18H, ^{t}Bu).

Compound **9c**: in mixture with **4c** (17%) and **7c** (29%); reaction time 18 h at 80 °C; yield 54%; ^{1}H-NMR (C$_6$D$_6$, 250 MHz): $\delta = 0.05$ (s, 27H, $\equiv$C–SiMe$_3$); 0.42 (s, 9H, NSiMe$_3$); 1.44 (s, 9H, ^{t}Bu).

Compound **4d**: colourless, crystalline solid; reaction time 12 h at 65 °C; yield 90%; ^{1}H-NMR (C$_6$D$_6$, 250 MHz): $\delta = 0.08$ (s, 18H, $\equiv$SiMe$_3$); 0.45 (s, 24H, SiMe$_2$); 0.84 (s, 8H, SiCH$_2$).

4.4. 1,1-Ethylboration of the di(1-alkynyl)-bis(silylamino)tin compounds

*4.4.1. Di(1-propynyl)-bis(silylamino)tin compounds **2a–d***

The respective di(1-propynyl)-bis(silylamino)tin compound **2a–d** (ca. 200 mg) was dissolved in toluene-d_8 (0.5 ml) in an NMR tube, and BEt$_3$ (0.5 ml) was added in one portion. After 12 h at 45 °C the NMR spectra showed almost quantitative formation of organoboration products. In the cases of **2a** or **2c**, the stannoles **10a** or **10c** are formed selectively. The propynides **2b** or **2d** reacted to give mixtures consisting of a stannole and a 1,4-stannabora-2,5-cyclohexadiene **10b/12b** (molar ratio 2.8:1) **10d/12d** (molar ratio 1:1.7). Under milder reaction conditions (2 days at r.t.), **10b/12b** were obtained in a ratio of 2.6:1, and **10d/12d** in a ratio 1:3.

Compound **10a**: ^{1}H-NMR (C$_6$D$_6$, 250 MHz), δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.35 (s, 36H, SiMe$_3$); 0.91 (t, 3H, CCH$_2$Me); 1.09 (t, 6H, BCH$_2$Me); 1.25–1.45 (m (br), 4H, BCH$_2$);1.90 (q, 2H, CCH$_2$) 1.95 (s, 3H, 2-Me, [61.1]); 2.08 (s, 3H, 5-Me, [63.4]).

Compound **10b**: ^{1}H-NMR (C$_6$D$_6$, 250 MHz), δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.35 (s, 18H, SiMe$_3$); 1.04 (t, 6H, BCH$_2$Me); 1.20–2.00 (m, 28H, 9-BBN); 1.89 (s, 3H, 2-Me, [62.4]); 2.06 (s, 3H, 5-Me, [50.5]); other signals are not assigned due to overlapping with 9-BBN-resonances.

Compound **10c**: ^{1}H-NMR (C$_6$D$_6$, 500 MHz), δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.327 (s, 9H, SiMe$_3$); 0.334 (s, 9H, SiMe$_3$); 1.248 (s, 9H, N^{t}Bu); 1.249 (s, 9H, N^{t}Bu); 1.65–1.75/1.85–1.95 (m, 2H, CCH$_2$); 1.86 (s, 3H, 2-Me, [56.5]); 2.00 (s, 3H, 5-Me, [57.5]); other signals are not assigned due to overlapping multiplets in the range of 0.7–1.3.

Compound **10d**: ^{1}H-NMR (C$_6$D$_6$, 500 MHz), δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.14 (s, 24H, SiMe$_2$); 0.70 (s, 8H, SiCH$_2$); 0.76 (t, 3H, CCH$_2$Me); 0.77 (t, 6H, BCH$_2$Me); 1.10–1.25 (m (br), 4H, BCH$_2$); 1.75 (q, 2H, CCH$_2$) 1.83 (s, 3H, 2-Me, [59.0]); 1.97 (s, 3H, 5-Me, [57.5]).

Compound **12b**: ^{1}H-NMR (C$_6$D$_6$, 250 MHz), δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.40 (s, 18H, SiMe$_3$); 0.82 (t, 6H, CCH$_2$Me); 1.20–2.00 (m, 28H, 9-BBN); 2.17 (s, 6H, 2,6-Me, [61.3]); 2.25–2.40 (m, 4H, CCH$_2$); other signals are not assigned due to overlapping with 9-BBN-resonances.

Compound **12d**: ^{1}H-NMR (C$_6$D$_6$, 500 MHz), δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.11 (s, 24H, SiMe$_2$); 0.68 (s, 8H, SiCH$_2$); 0.84 (t, 3H, BCH$_2$Me); 0.91 (t, 6H, CCH$_2$Me); 1.20–1.30 (m (br), 2H, BCH$_2$); 2.03 [63.0] (s, 6H, 2,6-Me); 2.26 (q, 4H,3,5-CH$_2$).

4.4.2. Di(3,3-dimethyl-1-butynyl)tin compounds

The mixtures (ca. 500 mg) described in Section 4.3, containing the compounds **3a**, **c**, **d** together with BEt$_3$ (1 ml) were heated in a Schlenk tube under pressure for 18 h, and the reaction solutions were examined by NMR spectroscopy. The temperature was increased stepwise from 110 to 160 °C. Reactions set in at 160 °C, and complex, not identified mixtures of decomposition products and metallic tin were obtained.

*4.4.3. Di(1-trimethylsilylethynyl)-bis(silylamino)tin compounds **4a–d***

A mixture in an NMR tube was prepared consisting of the respective di(1-trimethylsilylethinyl)-bis(silylamino)tin compound **4a–d** (ca. 200 mg) and BEt$_3$ (0.5 ml). After 8 h at 120 °C the complete set of NMR data showed almost quantitative formation of the stannoles **11a**, **b** and **d**. Compound **4c** does not react with BEt$_3$ under these conditions. Single crystals of **11b** suitable for X-ray diffraction analysis were isolated from a solution of **11b** in Et$_3$B.

Compound **11a**: ^{1}H-NMR (C$_6$D$_6$, 250 MHz), δ^1H = 0.31, 0.43 (s, s, 9H, 9H, 2,5-SiMe$_3$); 0.38 (s, 36H, NSiMe$_3$); 0.96 (t, 3H, CCH$_2$Me); 1.03 (t, 6H, BCH$_2$Me); 1.35–1.55 (m (br), 4H, BCH$_2$); 2.22 (q, 2H, CCH$_2$).

Compound **11b**: ^{1}H-NMR (C$_6$D$_6$, 250 MHz), δ^1H = 0.26, 0.43 (s, s, 9H, 9H, 2,5-SiMe$_3$); 0.47 (s, 9H, NSiMe$_3$); 0.52 (s, 9H, NSiMe$_3$); 0.95 (t, 3H, CCH$_2$Me); 1.03 (t, 6H, BCH$_2$Me) 1.30–2.00 (m, 28H, 9-BBN); 1.84 (s (br), 4H, BCH); 2.15–2.30 (m, 2H, CCH$_2$); signals for BCH$_2$ are not assigned due to overlapping with 9-BBN resonances.

Compound **11d**: ^{1}H-NMR (C$_6$D$_6$, 250 MHz), δ^1H = 0.29, 0.32 (s, s, 9H, 9H, 2,5-SiMe$_3$); 0.37 (s, 12H, SiMe$_2$); 0.42 (s, 12H, SiMe$_2$); 0.85 (s, 8H, SiCH$_2$); 0.98 (t, 3H, CCH$_2$Me); 1.04 (t, 6H, BCH$_2$Me); 1.30–1.60 (m (br), 4H, BCH$_2$); 2.20 (q, 2H,CCH$_2$).

4.5. Reaction of the di(1-alkynyl)stannanes **2a**, **d** with triallylborane

To a solution of **2a**, **d** (ca. 1 mmol) in 1 ml of $CDCl_3$ an equimolar amount of $BAll_3$ was added at ambient temperature. After 3 h the complete set of NMR data showed almost quantitative formation of the heterocycles **14a** and **d**. Additional stirring of the solutions for 3 h at 80 °C led to the quantitative formation of the bicyclic compounds **15a** and **d**.

Compound **14a**: ^{1}H-NMR (500.1 MHz; $CDCl_3$): δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.18 (s, 36H, Me_3Si); 2.17 (s, 3H, Me, [12.4]); 2.27 (s, 3H, Me, [65.6]); 2.47 (dt, 2H, All-B, J(H,H) = 7.3, 1.4 Hz); 3.03 (dt, 2H, All, J(H,H) = 7.0, 1.2 Hz); 3.17 (dt, 2H, All, J(H,H) = 5.8, 1.7 Hz); 4.8–5.1 (m, 6H, $=CH_2$); 5.76 (ddt, 1H, =CH–, J(H,H) = 17.0, 10.0, 7.4 Hz); 5.9–6.0 (m, 2H, =CH–).

Compound **14d**: ^{1}H-NMR (500.1 MHz; $CDCl_3$): δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.11 (s, 12H, Me_2Si, [8.2]); 0.14 (s, 12H, Me_2Si, [8.4]); 0.69 (s, 8H, CH_2Si, [13.5]); 2.21 (s, 3H, Me, [12.2]); 2.27 (s, 3H, Me, [61.3]); 2.48 (dt, 2H, All-B, J(H,H) = 7.5, 1.5 Hz); 3.14 (dt, 2H, All, J(H,H) = 6.9, 1.2 Hz); 3.24 (dt, 2H, All, J(H,H) = 5.9, 1.5 Hz); 4.8–5.1 (m, 6H, $=CH_2$); 5.8–6.0 (m, 3H, –CH=).

Compound **15a**: ^{1}H-NMR (500.1 MHz; $CDCl_3$): δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.15 (s, 18H, Me_3Si, [2.8]); 0.16 (s, 18H, Me_3Si, [2.6]); 0.83 (dd, 1H, All, J(H,H) = 17.1, 10.6 Hz); 1.66 (ddd, 1H, All, J(H,H) = 17.3, 4.0, 0.9 Hz); 1.82 (m, 2H, All); 1.88 (s, 3H, Me, [15.9]); 2.08 (m, 2H, All); 2.33 (s, 3H, Me, [58.1]); 2.37 (dd, 1H, All, J(H,H) = 17.4, 3.7 Hz); 3.12 (dt, 2H, All, J(H,H) = 6.2, 1.4 Hz); 4.9–5.1 (m, 4H, $=CH_2$); 5.6–5.9 (m, 2H, =CH–).

Compound **15d**: ^{1}H-NMR (500.1 MHz; $CDCl_3$): δ [$^nJ(^{119}\text{Sn},^1\text{H})$] = 0.11 (s, 6H, MeSi); 0.12 (s, 6H, MeSi); 0.13 (s, 6H, MeSi); 0.15 (s, 6H, MeSi); 0.70 (s, CH_2Si); 0.87 (dd, 1H, J(H,H) = 17.3, 11.2 Hz); 1.71 (dd, 1H, J(H,H) = 17.5, 3.5 Hz); 1.86 (m, 1H); 2.01 (dd, J(H,H) = 17.3, 10.1 Hz); 2.12 (m, 2H, All); 2.24 (s, 3H, Me, [13.1]); 2.33 (s, 3H, Me, [55.3]); 2.42 (dd, 1H, J(H,H) = 17.2, 3.9 Hz); 3.17 (d, 2H, All, J(H,H) = 5.9); 4.8–5.1 (m, 4H, $=CH_2$); 5.7–5.9 (m, 2H, =CH–).

4.6. Crystal structure determination of the stannole **11b**

A single crystal of **11b**, recrystallised from Et_3B, was sealed under Ar in a Lindemann capillary. Intensity data collection was carried out in a Siemens P4 diffractometer with Mo–K$_\alpha$ radiation ($\lambda = 71.073$ pm, graphite monochromator) at r.t. The hydrogen atoms are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

Compound **11b**: $C_{38}H_{72}B_3N_2Si_4Sn$, colourless prism of dimensions 0.35 × 0.20 × 0.15 mm, crystallises in the triclinic space group $P\bar{1}$; $a = 1182.2(2)$, $b = 1263.0(2)$, $c = 1719.7(3)$ pm, $\alpha = 87.43(2)$, $\beta = 86.26(2)$, $\gamma = 65.59(2)°$, $Z = 2$, $\mu = 0.677$ mm^{-1}; 9472 reflections collected in the range 3.0–50.0° in ϑ, 8164 reflections independent ($I > 2\sigma(I)$); full-matrix least-squares refinement with 433 parameters, R_1/wR_2-values 0.0319/0.0883, absorption correction (semi-empirical by Ψ scans), min/max transmission factors 0.6810/0.8139; max/min residual electron density 0.94/ − 0.64 e × 10^{-6} pm^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 169100 for compound **11b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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