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Reactivity of 1-boraadamantanes towards bis(trialkylstannyl)ethynes. First examples of 3-boratricyclo[5.3.1.1^{3,9}]dodecanes, and the molecular structure of a tetraalkyldiboroxane

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Abstract

1-Boraadamantane (**1**) and 2-ethyl-1-boraadamantane (**1**(2-Et)) react with bis(trialkylstannyl)ethynes (**3**), $R_3Sn–C\equiv C–SnR_3$ with R = Me (**a**), Et (**b**), in a 1:1 molar ratio by 1,1-organoboration under very mild conditions to give the 4-methylene-3-borahomoadamantane derivatives **4a,b** and **7a,b**, respectively, which are dynamic at room temperature with respect to deorganoboration. The compounds **4a,b** react further with **3a,b** by 1,1-organoboration to the tricyclic butadiene derivatives **5a,b**. Attempts to crystallise **4a** afforded the product of hydrolysis, the diboroxane **6a** which was characterised by X-ray structural analysis. All products were characterised in solution by ^{1}H-, ^{11}B-, ^{13}C- and ^{119}Sn-NMR spectroscopy.
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1. Introduction

The unique structure of 1-boraadamantane (**1**) [1] invites for studying its reactivity towards nucleophiles [1,2]. The boron atom in **1** occupies a position ideally suited for pyramidal surroundings, in contrast to most other triorganoboranes. Therefore, the Lewis acidity of **1** is high, the tricyclic system is strained, and may be readily enlarged if suitable reagents are offered. Thus, the borane **1** is an attractive candidate for 1,1-organoboration reactions [3], in which alkyn-1-ylmetal derivatives react with triorganoboranes BR$_3$. Cleavage of the M–C≡ bond leads to a zwitterionic alkyn-1-ylborate-like intermediate **A** which then rearranges into the organometallic-substituted alkene **B**. In most cases, the boron and the fragment containing M end up in *cis*-positions at the C=C bond (Scheme 1). The intermediate **A** indicates that there is some resemblance to the reaction of alkyn-1-yl(trialkyl)borates with electrophiles [4].

We have already shown that **1** reacts readily with various alkyn-1-ylsilicon [5–7], -germanium [5], and -tin compounds [5,7] by 1,1-organoboration. The first products obtained were in general 4-methylene-3-borahomoadamantane derivatives, corresponding to **B** in Scheme 1. It has been found that **1** reacts under mild conditions even with those alkyn-1-ylsilanes which proved to be inert towards triethylborane during prolonged heating at 100 °C. As indicated in Scheme 1, the 1,1-organoboration is a reversible process [3,5], and the equilibrium between organo- and deorganoboration depends on the substituents at boron and, in particular on M and the nature of R^1. For **B** with R = Et, M = Si and R^1 = SiMe$_3$, it has been reported that deorganoboration takes place at > 150 °C to give back Et$_3$B and Me$_3$Si–C≡C–SiMe$_3$ [8]. The analogous process has been observed, just above room temperature, in the case of **B** for R = Et, M = Sn and R^1 = SnMe$_3$, where, in contrast to M = Si, the alkyne Me$_3$Sn–C≡C–SnMe$_3$ reacts immediately with the alkene derivative **B** to give an allene [9]. In the case of the compound **2**,

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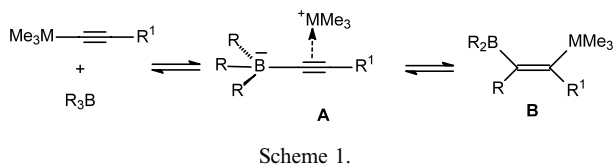
Scheme 1.

Scheme 3.

formed by the reaction of **1** with Me₃Si–C≡C–SiMe₃, the 1,1-organoboration is also readily reversible as shown by the reaction of **2** with pyridine (Scheme 2) [5].

In this work, we report on the reactions of 1-boraadamantane (**1**) and 2-ethyl-1-boraadamantane (**1**(2-Et)) with bis(trimethylstannyl)ethyne (**3a**) and bis(triethylstannyl)ethyne (**3b**), using mainly NMR spectroscopy for monitoring the reactions and investigating the reactivity and the dynamic behaviour of the products.

2. Results and discussion

2.1. Reactions of 1-boraadamantane (1) with the bis(trialkylstannyl)ethynes (3)

As shown in Scheme 3, the equimolar reaction of **1** with the bis(trialkyl-stannyl)ethynes **3a,b** is complete already at $-30\,^{\circ}$C, leading to the 4-methylene-3-bora-homoadamantane derivatives **4a,b** which, under these conditions, appear to possess a rigid structure as compared to the NMR time scale (Figs. 1 and 2). The presence of two (in **4a,b**) or four different tin atoms (in **5a,b**) in the molecule means that the $^{117/119}$Sn satellite signals in the ^{119}Sn-NMR spectra are particularly informative (Fig. 2). Typically for the geminal positions of triorganostannyl groups at olefinic carbon atoms, the magnitude of the coupling constants $|^{2}J(\mathrm{Sn,Sn})|$ is large [10]. At room temperature all NMR spectra (Table 1 and Section 4; ^{1}H-, ^{13}C- and ^{119}Sn-NMR; see Figs. 1 and 3) indicate a dynamic process, by which the trialkyl-stannyl groups exchange positions. Since the $^{117/119}$Sn satellites of the ^{13}C(Sn₂C=) signal are still visible (Fig. 3), this exchange process must be intramolecular, and the structure **C** (corresponding to **A** in Scheme 1) is a likely candidate to explain this. On average, the structures of **4a,b** are maintained during this process.
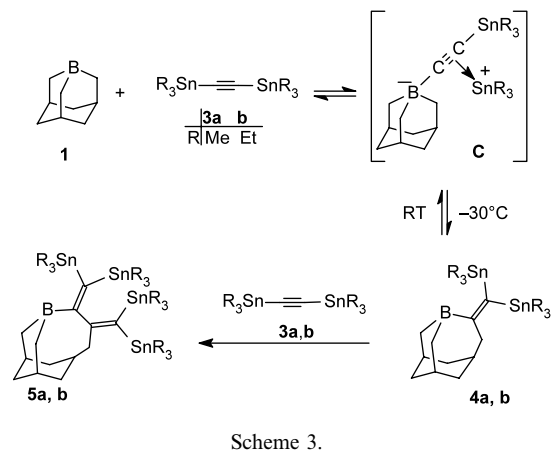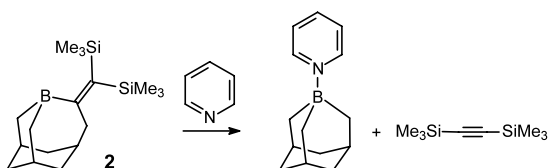
There are only slight changes in the ^{13}C chemical shifts. The ^{119}Sn-NMR signal at high frequency changes its position towards lower frequency by a few ppm when compared with the spectrum at $-30\,^{\circ}$C.

Similar to compound **2** (Scheme 2), the tricyclic borane **4a** reacts with tmeda by 1,1-deorganoboration to give the 1-boraadamantane-tmeda adduct (δ^{11}B 0.3) together with **3a** (δ^{119}Sn -81.0).

The reactivity of the compounds **4a,b** becomes apparent by the ease of their further reaction with an excess of **3a,b**. Again, 1,1-organoboration takes place, and the butadiene derivatives **5a,b** are formed almost
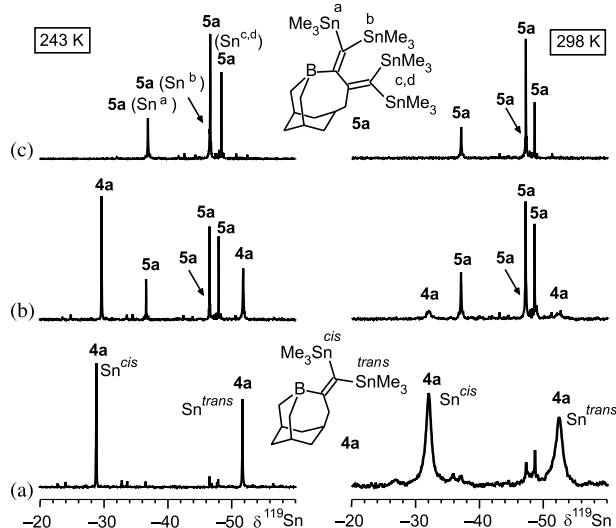

Fig. 1. Monitoring of the progress of the 1,1-organoboration of **3a** with **1** by 93.3 MHz ^{119}Sn{^{1}H}-NMR spectroscopy (refocused INEPT [27]). (A) After mixing the compounds **1** and **3a** (molar ratio 1:1) and 0.5 h at $-30\,^{\circ}$C. (B) After adding a further 0.5 equivalents of **3a** to the reaction mixture of (A), and keeping the mixture for 10 min. at $-30\,^{\circ}$C. (C) After mixing the compounds **1** and **3a** (molar ratio 1:2), and keeping the mixture for 0.5 h at $-30\,^{\circ}$C.
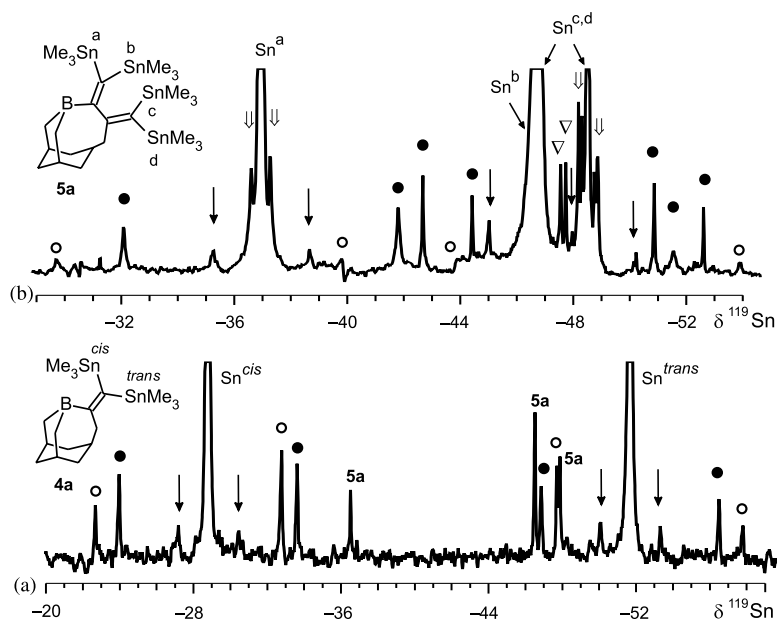

Scheme 2.

Fig. 2. 93.3 MHz $^{119}Sn\{^1H\}$-NMR spectra (refocused INEPT [27]) of **4a** and **5a** (in CDCl$_3$), recorded at 243 K. The Sn-satellite pattern corresponds to AX spin systems (for $^2J(^{119}Sn,^{117}Sn)$) (marked by filled circles), to AB spin systems (for $^2J(^{119}Sn,^{119}Sn)$) (marked by open circles), and to an AB spin system ($^{119}Sn,^{119}Sn$) of which only the inner lines (marked by $\triangledown$) are observed. The $^{117/119}Sn$ satellites for $^5J(^{119}Sn,^{117/119}Sn)$ are marked by $\Downarrow$. The ^{13}C satellites for $^1J(^{119}Sn,^{13}C_{Me})$ are marked by arrows. (A) After mixing the compounds **1** and **3a** (molar ratio 1:1) and 0.5 h at −30 °C. (B) After mixing the compounds **1** and **3a** (molar ratio 1:2) and 0.5 h at −30 °C.

quantitatively along with some unidentified side products. The latter species become dominant if the reaction solutions are kept for some days at room temperature. The molecular structure of **5a,b** follows from a consistent set of NMR data (Table 2), and both ^{13}C and ^{119}Sn spectra with their $^{117/119}Sn$ satellite patterns as a result of four different tin atoms are particularly informative (see Figs. 2 and 4).

2.2. Hydrolysis of the 4-methylene-3-borahomoadamantane derivatives (4)

The compounds **4** are extremely sensitive towards oxidation and traces of moisture. We have failed to isolate them in pure state. Repeated handling of the solutions containing **4a** produced crystalline material which, however, turned out to be **6a** the product of hydrolysis. The same happened with **4b** when attempts were made to purify it by chromatography. (Scheme 4; see Table 3 for ^{11}B-, ^{13}C-, ^{119}Sn-NMR data). The ^{13}C-NMR spectrum of **6a** (Fig. 5) reveals the absence of ^{13}C resonance signals for olefinic carbon atoms, and it shows the presence of an aliphatic carbon atom bearing two stannyl groups. There are also two different broad ^{13}C-NMR signals which are typical of B−C bonds. One of these signals belongs to a quaternary carbon atom.

The molecular structure of **6a** was confirmed by X-ray analysis (vide infra). A similar behaviour has been noted in the reaction of **2** with methanol [5], and frequently

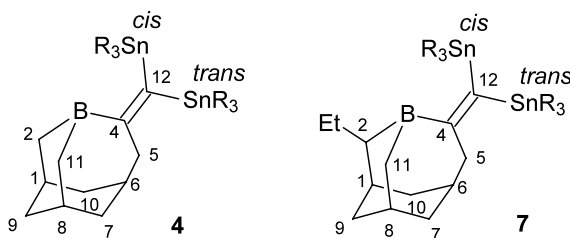also in the reactions of alkenes of type **B** with protic reagents [11,12].

2.2.1. Reactions of 2-ethyl-1-boraadamantane (1(2-Et)) with the bis(trialkylstannyl)ethynes (3)

In the case of 2-ethyl-1-boraadamantane (**1**(2-Et)) [13], the equimolar reaction with **3a,b** can give in principle two products **7** and **8** (Scheme 5). Most likely for steric reasons, the insertion into one of the B−CH$_2$ bond is preferred, and the compounds **7a,b** are formed. A small amount of **8a** (about 5%) is also present. However, the further reactions of **7** with an excess of **3a,b** are no longer selective. A complex mixture is obtained, containing more than three different products, and this mixture was not investigated in detail. The structure of **7** follows conclusively from the consistent set of NMR data (Table 1). The compounds **7** show dynamic properties comparable with those of **4** (Fig. 6).

2.3. Crystal structure analysis of the diboroxane (6a)

Although tetraorganodiboroxanes have been known for a long time [14,15], direct structural information on the solid state is scarce. In fact, the structure determined here for **6a** (Fig. 7) appears to represent the first example of a monomeric tetraalkyldiboroxane studied in the solid state. Tetraethyldiboroxane is a liquid [16], and tetramethyldiboroxane is a bent monomer in the gas phase [17], and crystallises as a dimer [18]. Other known

Table 1
^{13}C-, ^{119}Sn- and ^{11}B-NMR data [a] of the tricyclic compounds **4** and **7**

Compound	4a: R = Me		4b: R = Et		7a: R = Me		7b: R = Et
T (K)	243	298 [b]	243	298 [b]	243 [c]	298 [d]	243 [e]
Sn−C=	133.7 [348.2] [306.5]	134.6 (br) [346] [307]	130.8 [285.6] [237.2]	132 (br)	133.9 [355.1] [302.8]	134.8 (br)	131.5 [292.8] [235.6]
B−C=	187.4 [39.3] [23.8]	187.3 [br]	189.2 [37.9] [20.5]	188 [br]	185.0 [40.8] [24.5]	184.9 [br]	186.7 [38.4] [21.4]
C-5	43.2 [134.5] [114.4]	44.1 (br)	43.9 [123.4] [102.2]	44.5 (br)	42.5 [135.8] [116.6]	43.1 (br)	43.0 [124.9] [104.0]
C-6	30.1	30.9 (br)	30.1	31.4 (br)	30.1	30.7 (br)	30.2
C-7,10	36.5	37.2 (br)	36.5	36.6 (br)	31.5 36.1 37.8	32.0 36.6 38.4	31.9 35.8 37.8
C-9	36.8		36.7				
C-2	36.0	36.7 [br]	36.2	37.7 (br)	45.8	46.6 [br]	45.8
C-11					36.3	37.0 [br]	37.0
C-1,8	34.2	35.0 (br)	34.3	34.9 (br)	34.2 37.4	34.5 (br) 38.2	34.2 37.9
R-Sn (cis)	− 7.1 [305.4] [10.0]	− 6.6 [303] (br)	CH$_2$: 1.9 [306.9] [9.6] CH$_3$: 11.2 [h] [41.2]	CH$_2$: 3.4 [307] (br) CH$_3$: 11.1 [21.8]	− 7.1 [306.5] [10.2]	− 6.7 [300] (br)	CH$_2$: 2.11 [307.6] CH$_3$: 11.22 [l] [21.4]
R-Sn (trans)	− 6.7 [301.7] [11.1]		CH$_2$: 2.2 [303.0] [9.8] CH$_3$: 11.1 [h] [43.2]		− 6.8 [300.6] [11.1]		CH$_2$: 2.13 [303.0] CH$_3$: 11.17 [l] [22.2]
δ^{119}Sn (cis)	− 28.8 [134.0] [305.7] [348.7] (901.9) {942.9}	− 32.4 [f] (br) (940)	− 21.5 [123.1] [285.2] [306.2] (697.9) {729.3}	− 23.4 (br)	− 31.5 [i] [135.4] [307.1] [354.8] (915.5) {955.6}	− 33.3 [j] (br) (927)	− 23.8 [22.7] [125.9] [291.8] [307.1] (701.9) {735.2}
δ^{119}Sn (trans)	− 51.7 [114.7] [301.2] (900.8) {942.9}	− 52.3 [g] (br) (940)	− 41.3 [103.1] [236.8] [302.0] (698.8) {731.4}	− 40.7 (br)	− 53.4 [i] [299.7] (915.5) {951.8}	− 53.7 [k] (br)	− 39.6 [104.9] [236.0] [301.4] (701.9) {734.3}
δ ^{11}B	79.4		79.2		80.0		80.0

[a] In CDCl$_3$; coupling constants $^{n}J(^{119}$Sn,^{13}C) are given in brackets; $^{2}J(^{119}$Sn,^{119}Sn) in braces, $^{2}J(^{119}$Sn,^{117}Sn) are given in parentheses; [br] denotes broad ^{13}C resonances of boron-bonded carbon atoms [28]; (br) denotes broad ^{13}C or ^{119}Sn resonances due to dynamic effects.
[b] δ^{13}C data in toluene-d_8.
[c] Other δ^{13}C data: 13.5 (Me), 22.9 (CH$_2$−Me).
[d] Other δ^{13}C data: 13.6 (Me), 23.2 (CH$_2$−Me).
[e] Other δ^{13}C data: 13.6 (Me), 23.2 (CH$_2$−Me).
[f] $h_{1/2} = \sim 80$ Hz.
[g] $h_{1/2} = \sim 110$ Hz.
[h] Assignment might be reversed.
[i] At 263 K.
[j] $h_{1/2} = 45.8$ Hz.
[k] $h_{1/2} = 77.7$ Hz.
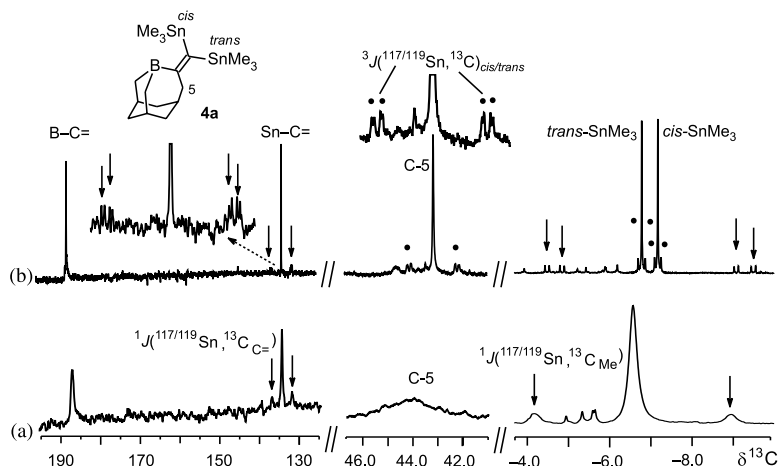[l] Assignment might be reversed.

Fig. 3. 75.5 MHz ^{13}C{^{1}H}-NMR spectrum (in CDCl$_3$) of **4a** (high field region of the ^{13}C$_{Me}$, ^{13}C$_{C-5}$, and the regions of the quaternary olefinic ^{13}C resonance signals). (A) At 298 K. The $^{117/119}$Sn satellites for $^1J(^{117/119}$Sn,^{13}C) (not resolved) are marked by arrows. (B) At 243 K. The $^{117/119}$Sn satellites for $^1J(^{117/119}$Sn,^{13}C) are marked by arrows, the $^{117/119}$Sn satellites for $^3J(^{117/119}$Sn,^{13}C) are marked by filled cycles.

structures are those of tetraphenyldiboroxane [19], tetramesityldiboroxane [20], bis(4-dibenzoborepinyl)-ether [21], and of a ferrocene derivative [22]. The parent compound H$_2$B–O–BH$_2$ has been the subject of theoretical studies [23] which assign the bent arrangement to be energetically slightly more favourable than the linear structure with D_{2d} symmetry. So far, all known solid tetraorganyldiboroxanes possess a bent structure. This is also true for **6a**, although the bond angle BOB (171.8(6)°) is more close to 180° than for all other known examples. There is no symmetry in the molecular structure of **6a**; however, the two halves of the molecule are almost identical. The B–O distances (135.3(11), 135.2(11) pm) are in the range for which partial BO double bond character can be assumed. Both boron atoms possess trigonal planar surroundings (within the experimental error). The planes around the two boron atoms are twisted aginst each other by 86.2°, close to the angle of 90° corresponding to (R$_2$B)$_2$O for a linear B–O–B arrangement with molecular D_{2d} symmetry.

3. Conclusions

The behaviour of cyclic triorganoboranes in the 1,1-organoboration of alkyn-1-ylmetal compounds is difficult to predict. The reactions of bis(trimethylstannyl)-ethyne **3a** with various five-membered cyclic boranes in a 1:1 molar ratio has been reported to proceed by ring-expansion in most cases [24], and in some cases, using an excess of **3**, to allenes [9d]. The analogous reaction of **3a** with 9-ethyl-9-borabicyclo[3.3.1]nonane stops at a dynamic equilibrium [25] which indicates the presence of starting materials and an intermediate corresponding to
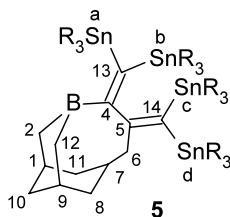
C. In the present work, it was shown that the equimolar reaction of **3** with the tricyclic 1-boraadamantane **1** proceeds beyond **C** towards reversible ring expansion to give fluxional 4-methylene-3-borahomoadamantane derivatives **4**, and in the presence of an excess of **3**, the equilibrium is shifted towards less dynamic products, by further selective ring expansion, to the tricyclic butadiene derivatives **5**.

4. Experimental

4.1. General

The preparation and handling of all compounds were carried out in an atmosphere of dry argon, and carefully dried solvents were used throughout. Starting materials were prepared as described (1-boraadamantane, **1** [1b], 2-Et-1-boraadamantane, **1**(2-Et) were obtained from the adduct **1**(2-Et)–NMe$_3$ by treatment with Et$_2$O–BF$_3$ [1,13], and alkyne derivatives **3** [26]). NMR measurements: Bruker ARX 250: ^{1}H-, ^{11}B-, ^{13}C-, ^{119}Sn-NMR (refocused INEPT [27] based on $^2J(^{119}$Sn,^{1}H) ca. 50 Hz); chemical shifts are given with respect to Me$_4$Si [δ^1H (CHCl$_3$–CDCl$_3$) = 7.24; δ^{13}C(CDCl$_3$) = 77.0]; external Me$_4$Sn [δ^{119}Sn = 0 for $\Xi(^{119}$Sn) = 37.290665 MHz]; external BF$_3$–OEt$_2$ [δ^{11}B = 0 for $\Xi(^{11}$B) = 32.083971 MHz]. EIMS (70 eV): Finnigan MAT 8500 with direct inlet; the m/z data refer to the isotopes ^{1}H, ^{12}C, ^{11}B, and ^{120}Sn. Melting points (uncorrected): Büchi 510 melting point apparatus.

Table 2
^{13}C-, ^{119}Sn- and ^{11}B-NMR data [a] of the tricyclic compounds **5**

	5a: R = Me		**5b**: R = Et	
T (K)	243	298	243	298 [b]
B–C=	193.7 [74.3] [39.7] $^{2,3}J$	194.5 [br] [70.0] [40.5]	196.0 [66.3] [37.1]	197.0 [br]
=C(5)	173.3 [123.6] [83.7] ^{3}J [23.8] [14.6] ^{2}J	173.4 [124.9] [83.4] [23.8] [14.8]	173.2 [116.0] [76.5] [24.0] [14.0]	173.7 [76.6] [14.1]
=C(13)	147.2 [329.1] [306.9] ^{1}J [9.6] [7.2] ^{4}J	147.9 [325.7] [306.6] [9.5] [7.6]	148.1 [254.8] [231.7] [9.8] [7.2]	149.5 [7.3]
=C(14)	137.8 [342.5] [301.3] ^{1}J [10.0] ^{4}J	139.5 [342.4] [294.2] [10.0]	140.2 [267.0] [221.5] [9.6]	141.9 [223.6] [9.7]
C-6	54.1 [88.9] [63.0] ^{3}J [17.0] ^{4}J	54.2 [92.0] [67.7] [8.6]	55.1 [82.0] [62.0] [16.0]	55.6 [60.7]
C-7	27.1 [7.0] $^{4,5}J$	27.8 [7.6]	27.3	28.2 [6.7]
C-1,9	34.8, 36.7	35.1, 37.1	34.7, 36.7	35.3, 37.4
C-8,11	30.2, 36.1	30.9, 36.7	30.3, 36.1	31.1, 36.7
C-10	40.0	40.6	40.1	40.7
C-2,12	32.6, 37.0	33.2 [br], 37.7 [br]	32.7, 37.3	33.5 [br], 38.2 [br]
R-Sn(a)	− 5.80 [308.5] ^{1}J [8.9] ^{3}J	− 5.3 [309.5] [9.5]	CH$_2$: 3.4 [307.1] [8.3] CH$_3$: 11.3 [f] [17.9]	CH$_2$: 4.6 [306.9] [8.2] CH$_3$: 11.58 [f]
R-Sn(b)	− 5.78 [311.5] ^{1}J [9.2] ^{3}J	− 5.57 [f] [312.3] [8.6]	CH$_2$: 3.9 [310.2] [8.0] CH$_3$: 11.4 [f] [22.2]	CH$_2$: 4.9 [309.9] [8.5] CH$_3$: 11.6 [f]
R-Sn(c)	− 6.1 [311.3] ^{1}J [7.9] ^{3}J	− 5.6 [f] [312.8] [8.6]	CH$_2$: 3.0 [311.5] [6.8] CH$_3$: 11.2 [f] [22.7]	CH$_2$: 4.2 [311.9] CH$_3$: 11.5 [f]
R-Sn(d)	− 3.8 [324.1] ^{1}J [6.3] ^{3}J	− 3.6 [325.2] [6.7]	CH$_2$: 5.1 [320.4] CH$_3$: 11.5 [f] [23.1]	CH$_2$: 6.2 [320.4] [6.5] CH$_3$: 11.7 [f]
δ ^{119}Sn(a)	− 36.3 [d] [328.7] [308.3] (901) ^{2}J (61.6) (16.8) ^{5}J	− 37.0 [326.1] [309.2] (908.2) (62.0) (20.5)	− 37.0 [g] [306.8] [254.7] (703) (58.4) (16.8)	− 37.4 [i] [308.0] (706.1) (62.4) (19.4)
δ ^{119}Sn(b)	− 46.3 [e] (901.3) ^{2}J	− 47.1	− 41.5 [h] [309.3] (703) (33.3)	− 43.2 [j] (705.7) (35.0)
δ ^{119}Sn(c) [c]	− 47.5 [312.0] (759.1) ^{2}J (62.1) (41.6) ^{5}J	− 48.5 [313.2] (765.6) (63.1) (41.6)	− 45.3 [311.5] [222.0] (585.6) (58.4) (33.7)	− 45.7 [312.1] (586.8) (61.0) (34.0)
δ ^{119}Sn(d) [c]	− 46.4 [324.2] (759.1) ^{2}J (17.0) ^{5}J	− 47.2 [324.8] (765.2) (21.0) (7.6)	− 49.8 [320.4] [266.2] (586.0) (16.8) (7.0)	− 50.1 [319.1] (586.8) (20.5) (11.0)
δ ^{11}B	81.0		79.0	

[a] In CDCl$_3$; coupling constants $^{n}J(^{119}$Sn,^{13}C) are given in brackets; coupling constants $^{2}J(^{119}$Sn,^{117}Sn) are given in parentheses; [br] denotes broad ^{13}C resonances of boron-bonden carbon atoms [28].

[b] δ^{13}C data in toluene-d_8.

[c] Assignment might be reversed.

[d] $h_{1/2} = 2.6$ Hz.

[e] $h_{1/2} = 4.7$ Hz.

[f] Assignment might be reversed.

[g] $h_{1/2} = 1.6$ Hz.

[h] $h_{1/2} = 7.4$ Hz.

[i] $h_{1/2} = 2.8$ Hz.

[j] $h_{1/2} = 8.3$ Hz.

4.2. 3-Boratricyclo[4.3.1.1^{3,8}]undecane 4 and 7; general procedure

The equimolar amount of **3** dissolved in CH$_2$Cl$_2$ (**3a**) or pentane (**3b**) (2–4 ml) was added to a solution of **1** or **1**(2-Et) (1–2 mmol) in pentane (2 ml) at − 50 °C. After stirring the solution for 0.5–1 h at 0 °C, the solvent was removed in vacuo (0.1 Torr) to give the products as pure (> 95% according to ^{1}H-NMR), colourless or yellowish

oils. The compounds **4** were not stable at room temperature (r.t.). Attempted distillation led to decomposition. The oily residues were analyzed by NMR spectroscopy.

Compound **4a**: 4-bis(trimethylstannyl)methylene-3-boratricyclo[4.3.1.1^{3,8}]undecane: colourless oil. EIMS: m/z (%) = 487 (12) [M^{+} − H], 323 (29) [M^{+} − Me$_3$Sn], 165 (100) [Me$_3$Sn^{+}]. ^{1}H-NMR (toluene-d_8, 298 K): 0.19 (br) (s, 18H, Me$_3$Sn), 1.20–2.05 (m), 2.30 (m, 3H).
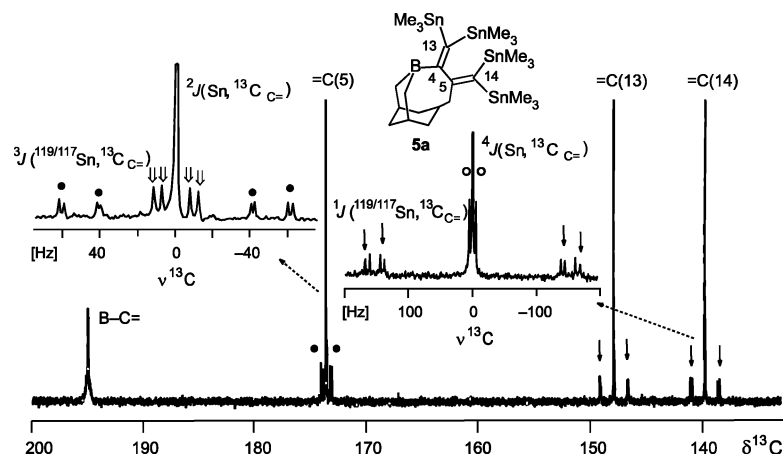
Fig. 4. 125.8 MHz $^{13}C\{^1H\}$-NMR spectrum of **5a** showing the regions of the quaternary olefinic ^{13}C resonance signals (in CDCl$_3$, 25 ± 1 °C). (The assignments are based on the $^{117/119}$Sn satellites and the weak and broad ^{13}C-NMR signal, typical of the linkage to an ^{11}B nucleus [28]) The $^{117/119}$Sn satellites for $^1J(^{117/119}Sn,^{13}C_=)$ are marked by arrows. The $^{117/119}$Sn satellites for $^2J(^{117/119}Sn,^{13}C_=)$ (not resolved) are marked by ⇓. The $^{117/119}$Sn satellites for $^3J(^{117/119}Sn,^{13}C_=)$ are marked by filled cycles. The $^{117/119}$Sn satellites for $^4J(^{117/119}Sn,^{13}C_=)$ (not resolved) are marked by open cycles.

Compound **4b**: 4-bis(triethylstannyl)methylene-3-boratricyclo[4.3.1.1^{3,8}]undecane: yellowish oil. EIMS: m/z (%) = 571 (31) [M$^+$ − H], 407 (100) [C$_{12}$H$_{23}$Sn$_2^+$]. ^{1}H-NMR (toluene-d_8, 298 K, J/Hz): δ [$^nJ(^{119}Sn,^1H)$] = 0.92 (br) (m, 12H, SnCH$_2$), 1.25 [71.1] (t, 18H, CH$_3$, 7.9 Hz), 1.35–2.05 (m, 12 H), 2.33 (m, 3H).

Compound **7a**: 2-ethyl-4-bis(trimethylstannyl)methylene-3-boratricyclo[4.3.1.1^{3,8}]undecane; colourless oil; ^{1}H-NMR (CDCl$_3$, 298 K, J/Hz): δ = 0.1 (m, 18H, Me$_3$Sn), 0.83 (t, 3H, *CH$_3$*CH$_2$, 7.3 Hz), 0.85–1.0 (m), 1.2–1.7 (m), 1.75–1.9 (m), 2.05–2.4 (m).

Compound **7b**: 2-ethyl-4-bis(triethylstannyl)methylene-3-boratricyclo[4.3.1.1^{3,8}]undecane; yellow oil; ^{1}H-NMR (CDCl$_3$, 298 K, J/Hz): δ = 0.82 (t, 3H, *CH$_3$*CH$_2$C, 7.2 Hz), 0.88 (m, 12H, SnCH$_2$), 0.95–1.05 (m), 1.18 (t, 18H, *CH$_3$*CH$_2$Sn, 7.85 Hz), 1.25–1.35 (m), 1.4–1.7 (m), 1.75–2.05 (m), 2.2 (m), 2.25–2.4 (m).

4.3. 3-Boratricyclo[5.3.1.1^{3,9}]dodecane 5; general procedure:

A solution of **1** (1 mmol) in pentane (2 ml) was cooled to − 50 °C and **3** (2 mmol) dissolved in pentane (2 ml) was added dropwise. After stirring the solution for 0.5 h

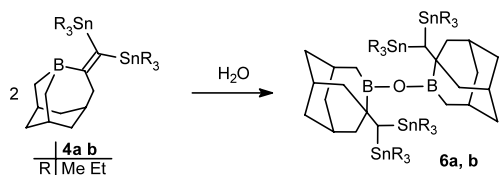(for **5a**) or 2 weeks (for **5b**) at 0 °C, the solvent was removed in vacuo (8–9 Torr).

Compound **5a**: 4,5-bis(bis(trimethylstannyl)methylene)-3-boratricyclo[5.3.1.1^{3,9}]dodecane: yellow oil (> 95% according to ^{1}H-NMR). EIMS: m/z (%) = 631 (17) [M$^+$ − (Me$_3$Sn + H + 3 Me)], 487 (21) [M$^+$ − (Me$_3$SnCCSnMe$_3$ + H)], 165 (100) [Me$_3$Sn$^+$]. ^{1}H-NMR (CDCl$_3$, 298 K, J/Hz): δ [$^nJ(^{119}Sn,^1H)$] = 0.095 [51.9] (s, 9H, Me$_3$Sn), 0.099 [50.6] (s, 9H, Me$_3$Sn), 0.12 [51.4] (s, 9H, Me$_3$Sn), 0.18 [50.7] (s, 9H, Me$_3$Sn), 0.80–2.40 (m), 2.5 (m, 2H).

Compound **5b**: 4,5-bis(bis(triethylstannyl)methylene)-3-boratricyclo[5.3.1.1^{3,9}]dodecane; yellow oil (∼ 70%; according to ^{1}H-NMR, contains **4b** (25–30%)).

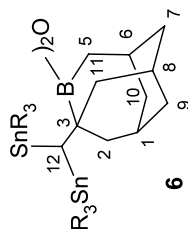### 4.4. Synthesis of the diboroxanes 6

4.4.1. 4,4′-Oxybis[3-(1,1-bistrimethylstannyl)methyl-4-boratricyclo[4.3.1^{3,8}]undecane] (6a)

A solution of **3a** (2 mmol) in CH$_2$Cl$_2$ (2 ml) was added dropwise to a solution of **1** (1 mmol) in CH$_2$Cl$_2$ (2 ml) at 20 °C. After stirring the solution for 0.5 h, the solvent was removed in vacuo (0.1 Torr) and the residue was dissolved in pentane. After 1 day at r.t. the solution was filtered, the solvent removed in vacuo (0.1 Torr). Crystalisation from CDCl$_3$ took 2–5 days and gave crystals of **6a**, m.p. 216–219 °C. EIMS: m/z (%) = 829 (18) [M$^+$ − Me$_3$Sn], 651 (22) [M$^+$ − (Me$_3$Sn)$_2$CH], 309 (85) [M$^+$ − (Me$_3$Sn)$_2$CH − (Me$_3$Sn)$_2$C], 165 (100) [Me$_3$Sn$^+$]. ^{1}H-NMR (CDCl$_3$, 298 K, J/Hz): δ [$^nJ(^{119}Sn,^1H)$] = 0.10 [49.5] (s, 36H, SnMe$_3$), 1.19 (d, 4H, BCH$_2$, 4.5 Hz), 1.40–1.63 (m, 12 H), 1.74 (s, 2H, SnCHSn), 1.78–2.15 (m, 14H).

Scheme 4.

Table 3
^{13}C-, ^{119}Sn- and ^{11}B-NMR data [a] of the of the diboroxanes 6

6

	δ ^{13}C									δ ^{119}Sn	δ ^{11}B
	SnR_3	C-12	C-3	C-2,11	C-9	C-7,10	C-6	C-5	C-1,8		
6a [b]: R = Me	−5.7 [299.6] [10.6]	24.6 [304.6]	36.6 [br]	44.9 [44.3]	36.1	38.3	26.6	32.0 [br]	29.3 [5.9]	5.7 (104.3)	55.1
6b [c]: R = Et	CH$_2$: 4.5 [303.7] [8.5] CH$_3$: 11.6 [22.3]	24.4 [260.0]	[br] [d]	46.9 [32.6]	36.2	38.4	27.2	31.7 [br]	30.1 [8.2]	7.1.	54.2

[a] Coupling constants $^nJ(^{119}Sn,^{13}C)$ are given in brackets; coupling constants $^2J(^{119}Sn,^{117}Sn)$ are given in parentheses; [br] denotes broad ^{13}C resonances of boron-bonded carbon atoms [28].
[b] In CDCl$_3$.
[c] In C$_6$D$_6$.
[d] Not observed.

4.4.2. 4,4′-Oxybis[3-(1,1-bistriethylstannyl)methyl-4-boratricyclo[4.3.1^{3,8}]undecane] (6b)

Compound **3b** (1 mmol) was added to a solution of **1** (1 mmol) in toluene-d_8 (2 ml) at 20 °C. After 2 months at r.t. column chromatography of the solution on Al$_2$O$_3$ (hexane–CH$_2$Cl$_2$) in an atmosphere of dry argon afforded **6b** (from CH$_2$Cl$_2$) as a yellowish oil. EIMS: m/z (%) = 1117 (22) [M$^+$ − 3Me], 955 (30) [M$^+$ − Et$_3$Sn], 748 (70) [M$^+$ − 2Et$_3$Sn], 735 (40) [M$^{+\bullet}$ − (Et$_3$Sn)$_2$CH], 207 (90) [Et$_3$Sn$^+$], 179 (100) [Et$_2$SnH$^+$]. ^{1}H-NMR (CDCl$_3$, 298 K, J/Hz): δ [$^nJ(^{119}Sn,^1H)$] = 0.9–1.05 (m, 24H, SnCH$_2$), 1.35 (t, 36 H, CH_3CH$_2$Sn, 8.0 Hz), 1.0–1.3 (m), 1.4–1.65 (m), 1.7–2.15 (m).

4.5. Crystal structure determination of the diboroxane 6a

A single crystal of **6a**, recrystallised from CDCl$_3$, was sealed under argon in a Lindemann capillary. The reflection intensities were collected on a Siemens P4 diffractometer (Mo–K$_\alpha$ radiation, λ = 71.073 pm, graphite monochromated). Structure solution and refinement was carried out with the program package SHELXTL-PLUS V.5.1. Measuring temperature for the structure determination was 296 K. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms are on calculated positions. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

Compound 6a: C$_{34}$H$_{68}$B$_2$OSn$_4$, a colourless prism with dimensions $0.26 \times 0.18 \times 0.12$ mm^3 crystallises in the triclinic space group $P\bar{1}$ with the lattice parameters a = 11.399(2), b = 12.262(3), c = 16.494(3) Å, α = 102.59(3)°, β = 98.60(3)°, γ = 107.83(3)°, V = 2083.1(7) 10^6 pm^3, Z = 2, μ = 2.393 mm^{-1}; 5969 reflections collected in the range $3° \leq 2\vartheta \leq 60°$, 4785 reflections independent, 3939 assigned to be observed [$I > 2\sigma(I)$], full-matrix least-squares refinement against F^2 with 371 parameters converged at R_1/wR_2-values of 0.039/0.097; empirical absorption correction (Ψ-scans) resulted in min./max. transmission factors of 0.4813/0.5929, the max./min. residual electron density was $0.83/ − 0.87 \times 10^{-6}$ e pm^{-3}.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 207323 for compound **6a**. 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).
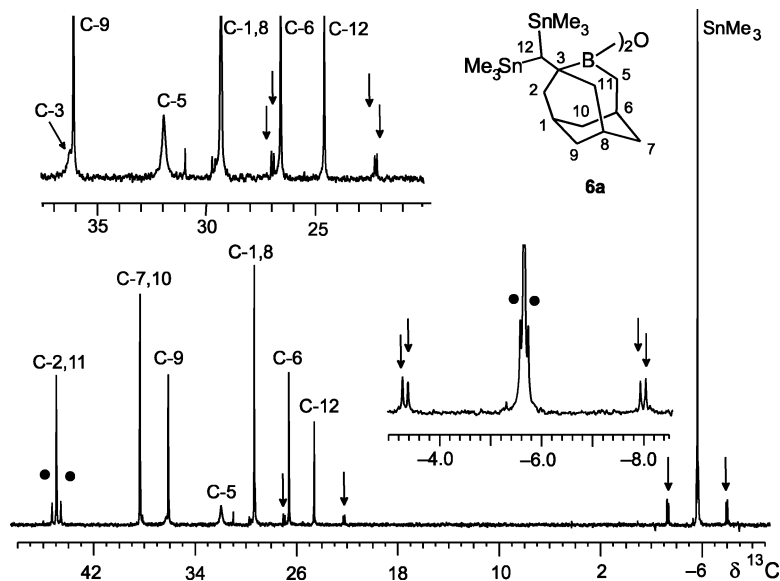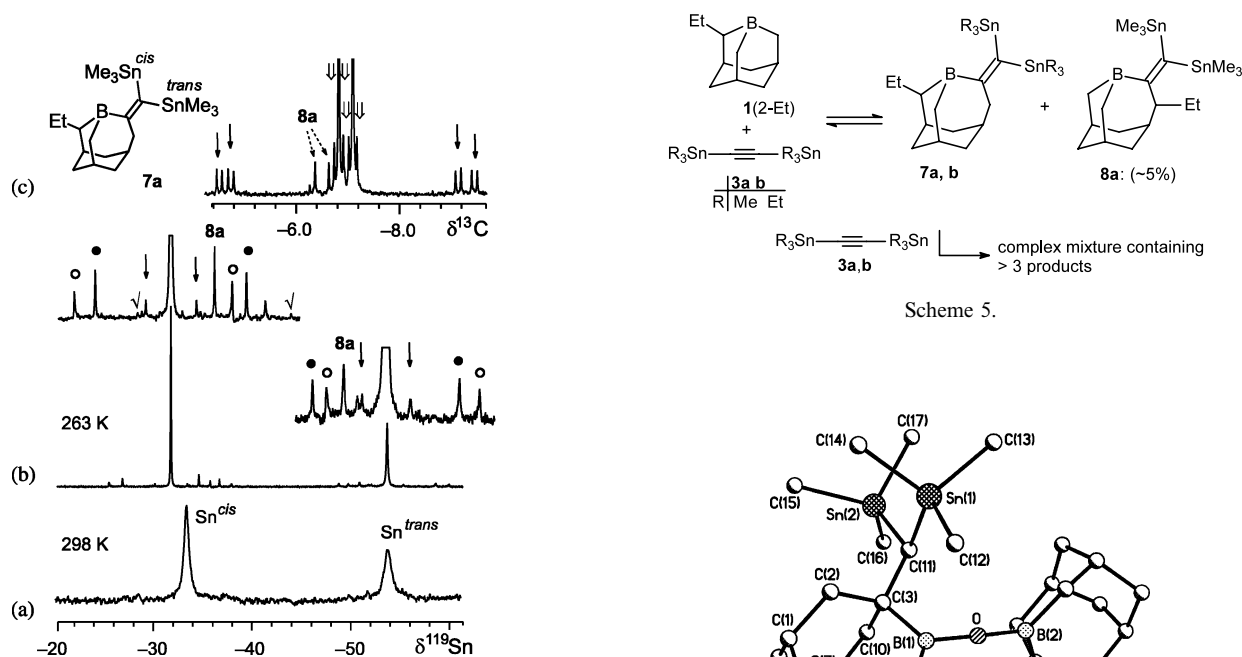
Fig. 5. 62.9 MHz ^{13}C{^{1}H}-NMR spectrum of **6a** (in CDCl$_3$ 25±1 °C). Note the $^{117/119}$Sn satellites and the broad signals typical [28] of the carbon atoms linked to boron. The $^{117/119}$Sn satellites for $^1J(^{117/119}$Sn,^{13}C) are marked by arrows. The $^{117/119}$Sn satellites for $^3J(^{117/119}$Sn,^{13}C$_{\text{C-2,11}}$) (not resolved) are marked by filled cycles.

Fig. 6. ^{119}Sn{^{1}H}- and ^{13}C{^{1}H}-NMR spectra of **7a** obtained from the reaction of **1**(2-Et) with **3a** (molar ratio 1:1, in CDCl$_3$). The side product **8a** (∼ 5%) is detected in the ^{119}Sn (δ − 34.3 and − 50.5) (B), and also in the ^{13}C-NMR spectra (C). (A) 93.3 MHz ^{119}Sn{^{1}H}-NMR spectrum (refocused INEPT [27]) at 298 K. (B) 93.3 MHz ^{119}Sn{^{1}H}-NMR spectrum (refocused INEPT [27]) at 263 K. The $^{117/119}$Sn-satellite pattern corresponds to AX spin systems (two-times ^{119}Sn−^{117}Sn), marked by filled cycles, and to an AB spin system (^{119}Sn−^{119}Sn) (marked by open cycles). The ^{13}C satellites for $^1J(^{119}$Sn,^{13}C$_{\text{Me}}$) are marked by arrows. The $^{117/119}$Sn-satellites pattern of **8a** corresponds to AX spin systems ($^2J(^{119}$Sn,^{117}Sn) = 927 Hz) (marked by ▽). (C) 75.5 MHz ^{13}C{^{1}H}-NMR spectrum at 243 K (high field region of the ^{13}C$_{\text{Me}}$ resonance signals). The $^{117/119}$Sn satellites for $^1J(^{117/119}$Sn,^{13}C$_{\text{Me}}$) are marked by arrows; the $^{117/119}$Sn satellites for $^3J(^{117/119}$Sn,^{13}C$_{\text{Me}}$) (not resolved) are marked by ⇓ .

Scheme 5.
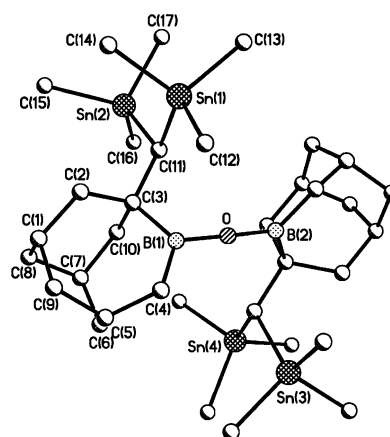

Fig. 7. Molecular structure of the diboroxane **6a**; selected bond lengths (pm) and bond angles (°): B(1)O 135.2(11), B(2)O 135.3(11), B(1)C(3) 159.2(11), B(1)C(4) 155.1(12), C(2)C(3) 155.9(10), C(3)C(10)156.9(10), C(3)C(11) 154.7(12), C(4)C(5) 153.9(11), Sn(1)C(11) 219.0(7), Sn(2)C(11) 218.5(7), Sn(1)C(13) 213.7(8), Sn(2)C(15)216.8(10); B(1)OB(2) 171.8(6), C(3)BC(4) 122.9(8), Sn(1)C(11)Sn(2) 109.7(4), C(3)C(11)Sn(1) 113.4(4), C(3)C(11)Sn(2) 118.7(5).

Acknowledgements

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