RING ENLARGEMENT OF 1-BORAINDANE AND 1-BORATETRALINE DERIVATIVES VIA 1,1-ORGANOBORATION OF 1-ALKYNYL-TRIMETHYLTIN COMPOUNDS

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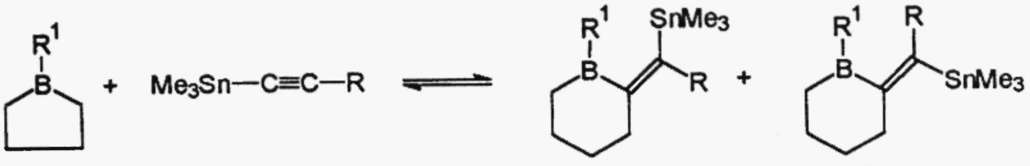
Abstract –

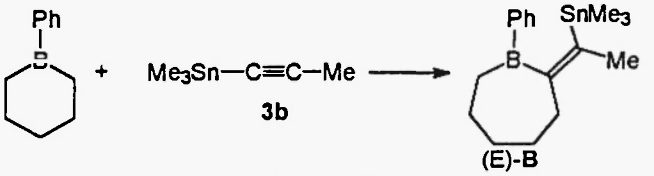
1-Propyl-1-boraindane (**1**) and 1-propyl-1-boratetraline (**2**) react with 1-alkynyl-trimethyltin compounds **3** [$Me_3Sn-C{\equiv}CR$; R = H(**a**), Me (**b**), *t*Bu (**c**), Ph (**d**), $SiMe_3$ (**e**), $SnMe_3$ (**f**)] via 1,1-organoboration either via insertion into the B-Ar or $B-CH_2$(ring) bond to give the new heterocycles **4** and **5** (starting from **1**), and **6** and **7** (starting from **2**), in which the boron containing ring is enlarged by one olefinic carbon atom. There is no indication of insertion into the exocyclic B-*n*Pr bond. For comparison, the reaction between trimethyl-1-propynylsilane (**3b**(Si)) and **1** was studied: In addition to **4b**(Si) and **5b**(Si), compound **6b**(Si) is formed, the product resulting from insertion into the B-*n*Pr bond. In all cases, except when **1e** is used, the (E)-isomers are formed with the Me_3Sn group and the boron atom in *cis*- positions at the new C=C bond. The product distribution **4/5** and **6/7** depends mainly on steric interactions between the substituents at the new C=C bond and the other groups in **4** and **5** or **6** and **7.**

INTRODUCTION

1,1-Organoboration of 1-alkynyltin compounds is a powerful method for the synthesis of organometallic-substituted alkenes [1]. In most cases, this reaction is stereoselective, and alkenes are obtained in high yield with the boryl and the stannyl group in *cis*-positions at the C=C bond. Mixtures of (Z/E)-isomers were observed if another organometallic group such as $SiMe_3$ is attached to the C≡C bond [1,2] as in $Me_3SnC{\equiv}CSiMe_3$ (**3e**). The stereoselectivity may also be lost if cyclic organoboranes are used in 1,1-organoborations [3]. If there are different organyl groups attached to boron, e.g. in RBR^1_2, R_2BR^1 or $R(R^1)BR^2$, a further problem arises, as to which of the B-R, $B-R^1$ or $B-R^2$ bonds is more reactive. Previously it was found that 1-organo-1-boracyclopentanes react with 1-alkynyl(trimethyl)tin compounds **3** by enlargement of the ring to give a mixture of (Z/E)-isomers **A** [eq. (1)], and it was shown that the 1,1-organoboration is readily reversible in these cases [3].

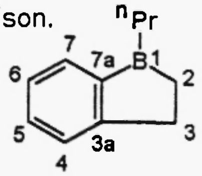


In the case of 1-phenyl-1-bora-cyclohexane, the reaction with **3b** affords selectively the enlarged ring system (E)-**B**, with the Me_3Sn group and the boron atom in *cis*-positions [eq. (2)], and it was found that this reaction was not readily reversible [4].

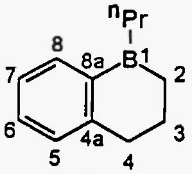


(2)

It was shown that di-*tert*-butyl(methyl)borane reacts with **3b** to give a non-statistical product distribution of (E)-isomers (≈ 1:1), resulting from insertion into the B-*t*Bu and the B-Me bond, respectively [3]. Mixtures of (E)-isomers were also obtained from the reaction between ferrocenyl(diphenyl)borane or various dialkyl(ferrocenyl)boranes and **3b** due to insertion into the B-ferrocenyl or B-Ph, B-ferrocenyl or B-alkyl bond [5]. In analogy to the other cyclic boranes, 9-alkyl-9-borabicyclo[3.3.1]nonanes react with 1-alkynyltin compounds via enlargement of the bicyclic system as the result of a kinetically controlled reaction [6]. The title compounds, 1-propyl-1-boraindane **1** and 1-propyl-1-bora-tetraline **2**, are particularly attractive for studying 1,1-organoboration reactions of 1-alkynyl-(trimethyl)tin compounds **3**, since there are three different B-C bonds. It is well known that 1-alkynylsilanes react in the same way as the corresponding tin compounds [1a,7], and therefore, the reaction of **1** with trimethyl-1-propynylsilane (**3b**(Si)) was studied for comparison.



1



2

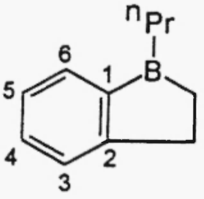
$Me_3Sn—C≡C—R$

3	a	b	c	d	e	f
R	H	Me	*t*Bu	Ph	$SiMe_3$	$SnMe_3$

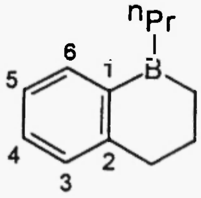
RESULTS AND DISCUSSION

The boranes **1** and **2** can be obtained in an elegant way, in high purity, from the reaction between tripropylborane and styrene or allylbenzene, respectively [8,9]. They were characterized by their ^1H (see experimental part), ^{11}B and ^{13}C NMR data (Table 1). The assignment is based on 2D $^1H/^1H$ COSY, 2D $^{13}C/^1H$ heteronuclear shift correlations (HETCOR), and on the broad ^{13}C NMR signals of carbon atoms attached directly to boron, as a result of partially relaxed scalar ^{13}C-^{11}B coupling [10,11b]. There is a noticeable magnetic deshielding of ^{13}C nuclei in ortho- and para-positions with respect to the boron atom, if one compares with $\delta^{13}C$ of the parent hydrocarbons [12]. This can be attributed to potential BC(pp)π interactions as in other phenylboranes and related systems [13]. The $\delta^{11}B$ values for **1** (δ 82.7) and **2** (δ 76.8) are found in the typical range [11]. They differ because of the ring size, the ^{11}B nucleus in the five-membered ring being typically deshielded (e.g., 1-phenyl-1-boracyclopentane: $\delta^{11}B$ 84.5 [11a], and 1-phenyl-1-boracyclohexane: $\delta^{11}B$ 77.5 [11a].

Table 1. ^{11}B and ^{13}C NMR data[a,b] of 1-propyl-1-boraindane (**1**) and 1-propyl-1-boratetraline (**2**)



1

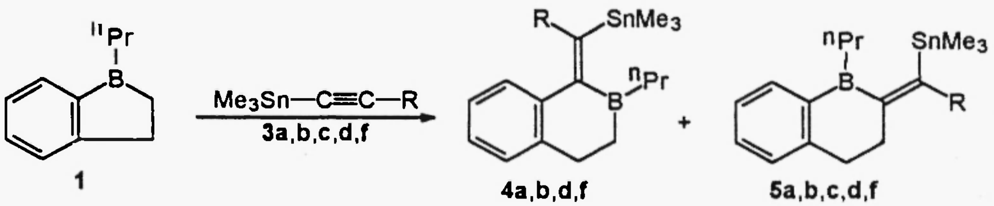


2

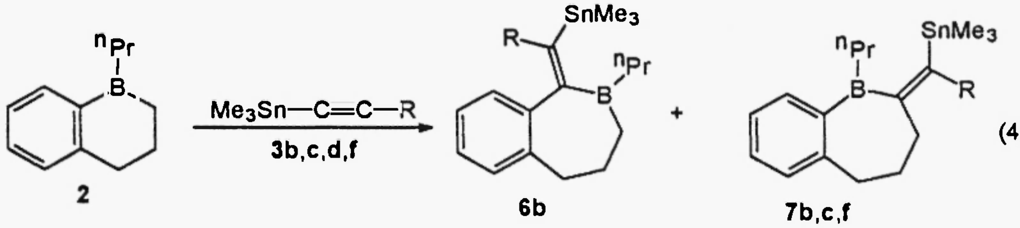
δ^{13}C	B-CH$_2$	Ar-CH$_2$	CH$_2$	1	2	3	4	5	6	B-*n*Pr
1	25.2 (br)	32.8	-	144.3 (br)	164.9	125.5	132.9	125.2	131.9	24.5 (br) 19.3 17.4
2	27.0 (br)	34.1	23.3	136.9 (br)	150.1	128.3	132.7	125.4	134.1	24.7 (br) 18.7 17.1

[a] In CDCl$_3$ at 25 ± 1 °C (≈ 20 %); (br) denotes a broad ^{13}C NMR signal of a boron-bonded carbon atom; the numbering in the formula does not correspond to nomenclature, but has been selected in order to enable the straightforward comparison with ^{13}C NMR data from Tables 2 and 3. [b] δ^{11}B 82.7 (**1**), 76.8 (**2**).

All 1,1-organoboration reactions are complete after warming the 1:1 mixture of **1** or **2** with the respective 1-alkynyltin compound from -78°C to room temperature. The reactions were monitored by ^{119}Sn NMR, but no intermediates were detected. The compounds **1** and **2** behave in a similar way as shown in eqs. (3) and (4). Enlargement of the boron-containing ring is always observed as found for boracyclopentanes and 1-phenyl-1-boracyclohexane [eqs. (1, 2)], but, in contrast to the boracyclopentanes [eq. (1)], the reactions proceed stereoselectively to give exclusively the E-isomers.

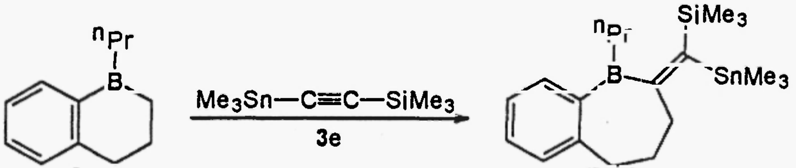


(3)



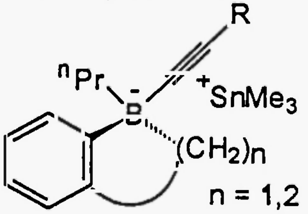
(4)

The reaction between **2** and **3e** (R = $SiMe_3$) is selective (> 95 %) and affords the product (Z)-**7e**, with the Me_3Si group and the boron atom in *cis*-positions [eq. (5)]. A similar result was observed for the 1,1-organoboration of **3e** using triethylborane [2].

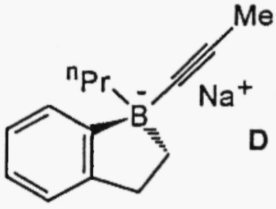


2 (Z)-**7e** (5)

Those compounds **4** or **6** which would result from inserton into the B-aryl bond of **1** or **2** are not formed at all or only in minor quantity if the group R in **3** is fairly bulky (R = *t*Bu, $SiMe_3$, $SnMe_3$). This can be explained considering the energetically unfavourable steric interactions between R and the adjacent aromatic ring. It appears that the cyclic systems in both of the isomers **5** and **7** are more flexible in order to minimize steric interactions. If the steric requirements of the groups R become less demanding, a mixture of **4**/**5** and **6**/**7** is formed in each case. Although not detected here, it can be assumed that borate-like intermediates [1,14] such as **C** play an important role. The synthesis of the corresponding alkynylborate **D** with R = Me was reported [15] but reactions with electrophiles were not carried out. Apparently, the preferred rearrangement of **C** to the products **4** or **5** (n = 1) and **6** or **7** (n = 2) is governed by the minimum of steric hindrance in the final products.



C

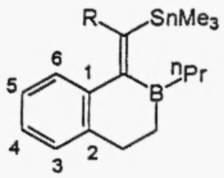


D

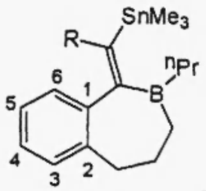
Trimethyl-1-propynylsilane (**3b**(Si)) reacts with **1** after 24 h in boiling toluene to give a 1:0.6:1 mixture [eq. (6)] consisting of the expected compounds **4b**(Si) and **5b**(Si), in addition to **8b**(Si). The latter product is the result of insertion into the exocyclic B-*n*Pr bond which was never observed in the case of the 1-alkynyltin compounds. Considering the rather harsh reaction conditions, compound **8b**(Si) could be the result of thermodynamic control. The structure of **8b**(Si) follows from a consistent set of ^{13}C NMR data (Table 4) in comparison with that of **1** (Table 1) and of (E)-3-diethylboryl-2-trimethylsilyl-2-butene [7b]. The $^{13}C(=C-Si)$ nuclei in **4b**(Si) and **5b**(Si) are markedly better shielded than $^{13}C(Sn-C=)$ in the corresponding tin compounds **4b** and **5b**. This is not only due to the influence of the silicon atom but is also the result of a more pronounced twisting of the C=C-B plane against the C-B-C= plane [16]. The steric repulsion between the B-*n*Pr and the $SiMe_3$ group **4b**(Si) and **5b**(Si) appears to be stronger than between the B-*n*Pr and the $SnMe_3$ group in **4b** and **5b**

^{13}C and ^{119}Sn NMR data of the compounds **4** and **6** are collected in Table 2, and Table 3 contains ^{13}C and ^{119}Sn NMR data of **5** and **7.** The structural assignment of the respective products is straightforward since in **4** and **6** the ^{13}C(B-aryl) NMR signal is absent, whereas in **5** and **7** the ^{13}C(B-CH$_2$-ring) NMR signal is missing. Together with other ^{13}C NMR data as well as ^{1}H and ^{119}Sn NMR data, the approximate ratio of **4/5** (**4a/5a** 1.4 : 1; **4b/5b** 2 : 1; **4c/5c** 0 : 1; **4d/5d** 0.6 : 1; **4f/5f** 0.4 : 1) and **6/7** (**6b/7b** 1 : 1) can be obtained.

Table 2. ^{13}C and ^{119}Sn NMR data[a] of the 1,1-organoboration products 4 and 6



4



6

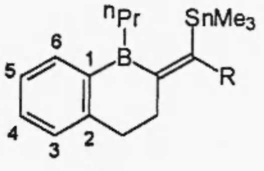
	a	b	c	d	e	f
R=	H	Me	*t*Bu	Ph	SiMe$_3$	SnMe$_3$

	4a	4b	6b	4d	4f
R	-	23.2 [59.8]	21.5 [62.7]	146.2 [37.4] 126.2 [18.3] 129.4 [7.3] 127.8	-5.0 [319.3, 6.1]
Sn-C=	147.2 [463.8]	147.1 [501.8]	136.5 [519.5]	153.6 [462.0]	157.3 [317.4, 286.9]
B-C=	167.4 (br)	160.2 (br)	165.1 (br)	160.0 (br)	182.7 (br)
B-CH$_2$	29.9 (br)	31.3 (br)	33.7 (br)	31.7 (br)	30.2 (br)
CH$_2$	-	-	27.3	-	-
Ar-CH$_2$	28.3	29.4	35.2	29.4	28.7
1	143.4 [84.8]	138.6 [85.9]	138.9 [89.4]	138.7 [78.2]	145.4 [61.1, 74.5]
2	139.8	142.8	141.0 [3.3]	142.7	142.5
3 [b]	127.1	128.7 [7.1]	129.1 [3.3]	128.3	126.9
4 [b]	126.4	125.7	126.0	125.5	126.3
5 [b]	125.0	125.3	126.9	124.7	126.2
6 [b]	126.8	127.2	129.2	126.8	129.7
SnMe$_3$	-7.0 [350.3]	-6.5 [330.2]	-8.3 [324.8]	-6.0 [338.1]	-4.3 [286.9, 6.7]
*n*Pr	24.5 (br) 18.7, 17.4	25.7 (br) 18.9, 17.4	29.1 (br) 18.4, 17.4	25.7 (br) 18.8, 17.5	24.6 (br) 18.6, 17.5
δ^{119}Sn	-57.0	-42.6	-39.0	-41.4	-39.5 [849.7] -43.8 (R)

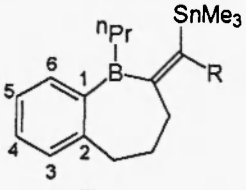
[a] In CDCl$_3$ at 25 ± 1 °C (≈ 10 - 20 %); coupling constants [Hz] J(^{119}SnX) (X = ^{13}C, ^{117}Sn) are given in square brackets; (br) denotes a broad ^{13}C NMR signal for a boron-bonded carbon atom. The numbering scheme is used for simplicity.

[b] Assignment can be reversed.

Table 3. ^{13}C and ^{119}Sn NMR data[a] of the 1,1-organoboration products **5** and **7**



5

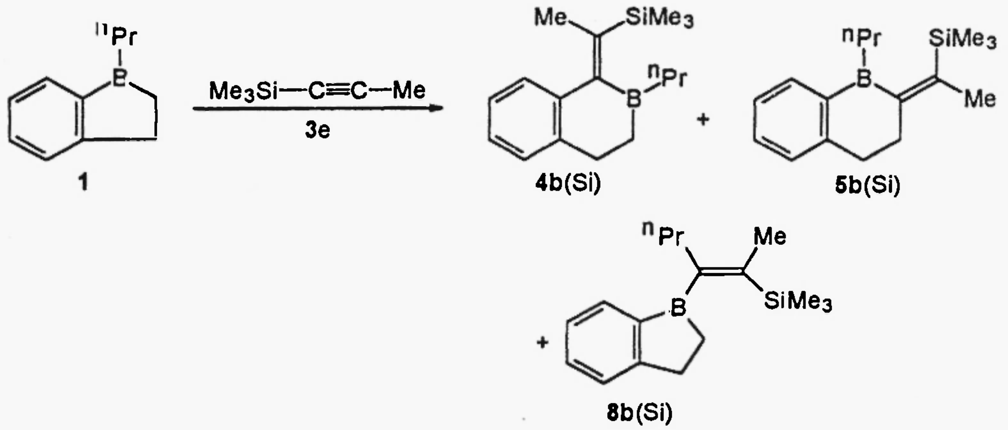


7

	a	b	c	d	e	f
R=	H	Me	*t*Bu	Ph	SiMe$_3$	SnMe$_3$

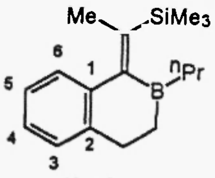
	5a	5b	5c	7c	5d	7e	5f	7f
R [b]	-	22.2 [65.9]	35.5 [9.1] 32.7 [26.3]	33.2 [25.6] 40.3 [58.6]	146.9 [41.5] 126.2 [18.3] 127.9 [6.1] 128.1	-2.1 [11.6]	-5.6 [306.4, 8.0]	-5.3 [302.7, 10.7]
Sn-C=	145.0 [474.9]	152.2 [513.6]	165.5 [535.3]	154.8 [541.4]	156.1 [467.5]	144.1 [302.7]	154.9 [293.0, 339.4]	144.2 [292.4, 344.2]
B-C=	164.6 (br)	159.5 (br)	161.4 (br)	159.8 (br)	159.5 (br)	179.2 (br)	181.7 (br)	182.2 (br)
=-CH$_2$	44.6 [88.5]	31.6 [72.0]	39.6 [54.9]	37.3 [98.9]	34.8 [67.1]	46.4 [112.3]	46.6 [129.4, 105.6]	48.3 [111.1, 131.8]
CH$_2$	-	-	-	31.5 [6.1]	-	23.8 [8.5]	-	23.9 [8.5, n.o]
CH$_2$-Ar	35.6	34.5 [6.7]	37.3	33.8	35.9	33.9	36.5	33.8
1	138.0 (br)	139.3 (br)	139.1 (br)	137.6 (br)	144.0 (br)	136.5 (br)	132.7 (br)	136.7 (br)
2	150.5	150.3	150.1	150.2	150.5	150.5	150.2	150.7
3	128.1	127.9	127.7	127.5	128.1	128.4	128.1	128.4
4	132.8	132.2	131.9	132.8	132.8	133.1	134.8	125.5
5	125.4	125.5	125.7	125.4	125.2	125.6	125.6	133.4
6	135.5	134.4	134.4	136.8	135.7	137.2	132.7	125.5
SnMe$_3$	-7.3 [346.1]	-6.5 [330.2]	-2.6 [316.8]	-2.7 [310.1]	-6.4 [336.9]	-4.7 [301.5]	-5.2 [314.9, 8.0]	-6.1 [311.2, 10.4]
*n*Pr	24.5 (br) 19.9 17.8	25.7 (br) 19.7 17.9	30.1 (br) 19.6 18.0	26.0 (br) 23.7 15.2	26.6 (br) 19.7 17.9	26.7 (br) 23.9 14.9	28.6 (br) 19.3 17.7	26.0 (br) 23.7 14.7
δ^{119}Sn	- 60.5	-46.5	-54.5	-59.1	-47.4	-66.1	-42.9 [889.9] -54.6 (R)	-44.9 [905.7] -54.0 (R)

[a] In CDCl$_3$ at 25 ± 1 ^{0}C (≈ 10 - 20 %); coupling constants [Hz] J(^{119}SnX) (X = ^{13}C, ^{29}Si, ^{117}Sn) are given in square brackets; (br) denotes the broad ^{13}C NMR signal for a boron-bonded carbon atom. The numbering scheme is used for simplicity. - [b] δ^{29}Si -6.0.

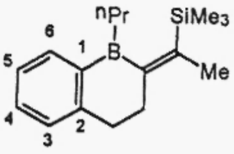


(6)

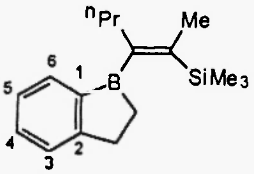
Table 4. ^{13}C and ^{29}Si NMR data[a] of the 1,1-organoboration products **4b**(Si), **5b**(Si) and **8b**(Si)



4b(Si)



5b(Si)



8b(Si)

	4b(Si)	5b(Si)	8b(Si)
R	19.6	17.3	18.3
Si-C=	137.6	140.0	134.9
B-C=	155.8 (br)	159.5 (br)	160.0 (br)
B-CH_2	32.7 (br)	-	25.0 (br)
=-CH_2	-	32.8	-
CH_2-Ar	33.1 [b]	35.2	33.3 [b]
1	138.4	140.0 (br)	145.2 (br)
2	143.9	149.7	164.6
3	129.2 [b]	128.0	126.0 [b]
4	125.4 [b]	131.9	133.2 [b]
5	125.5 [b]	125.6	125.4 [b]
6	127.0 [b]	133.8	132.0 [b]
$SiMe_3$	0.7 [b]	0.5	-0.4 [b]
nPr	17.4 18.7 26.4 (br)	17.4 19.5 29.3 (br)	14.8 22.5 29.7
$\delta^{29}Si$	-4.3 [b]	-4.8	-5.9 [b]

[a] In $CDCl_3$ at 25 ± 1°C (≈20 %); (br) denotes the broad ^{13}C resonance signal for a boron-bonded carbon atom; $^{13}C(Si-C=)$ NMR signals were assigned by refocused INEPT experiments with ^{1}H-decoupling [18], based on long range coupling constants $^{3}J(={}^{13}CSiC^{1}H)$ and $^{2}J(={}^{13}C,{}^{1}H_{Me})$. The numbering scheme is used for simplicity.

[b] Assignment can be reversed.

EXPERIMENTAL

All handling of the compounds and all synthetic work was carried out in an inert atmosphere of Ar or N_2, observing all precautions to exclude traces of oxygen and moisture. The syntheses of the boranes **1** and **2** was described [9a]. The 1-alkynyl(trimethyl)tin compounds **3** were prepared following literature procedures [17].

NMR spectra were measured from samples dissolved in C_6D_6 or $CDCl_3$ in 5 mm (o.d.) tubes, using JEOL FX 90 Q, BRUKER WP 200, ARX 250, AC 300 and AM 500 spectrometers, all equipped with multinuclear units. ^{29}Si NMR spectra were measured by using the refocused INEPT pulse sequence [18] (based on $^2J(^{29}Si^1H_{Me}) \approx 7.0$ Hz) with ^1H decoupling. ^{119}Sn NMR spectra were measured by inverse gated ^1H decoupling and also by using the refocused INEPT pulse sequence [18] (based on $^2J(^{119}Sn,^1H) \approx 55$ Hz) with ^1H decoupling. Routine parameters served for the measurement of all other nuclei. Chemical shifts are given with respect to Me_4Si ($\delta^1H(C_6D_6) = 7.15$; $\delta^{13}C(C_6D_6) = 128.0$; $\delta^{29}Si$ with $\Xi(^{29}Si, Me_4Si) = 19.867184$ MHz), $Et_2O{-}BF_3$ ($\delta^{11}B$ with $\Xi(^{11}B, Et_2O{-}BF_3) = 32.083971$ MHz) and Me_4Sn ($\delta^{119}Sn$ with $\Xi(^{119}Sn, Me_4Sn) = 37.290665$ MHz).

1: ^1H NMR ($CDCl_3$, 25 ± 1°C): δ^1H = 7.73 (m, 1H), 7.31 (m, 2H), 7.13 (m, 1H), 2.89 (m, 2H, CH_2-Ar), 1.48 (m, 2H, CH_2-CH_2Ar), 1.63, 1.60, 1.01 (m, m, t, 7H, B-*n*Pr).

2: ^1H NMR ($CDCl_3$, 25 ± 1°C): δ^1H = 7.79 (m, 1H), 7.28 (m, 1H), 7.12 (m, 2H), 2.70 (m, 2H, CH_2-Ar), 1.75 (m, 2H, CH_2-CH_2Ar) 1.47 (m, 2H, CH_2-CH_2CH_2Ar), 1.00, 1.60, 1.00 (m, m, t, 7H, B-*n*Pr)

1,1-Organoboration of trimethyl-1-propynyltin (**3b**) *using 1-phenyl-1-boracyclohexane*:
1-Phenyl-2-[(E)-2′-trimethylstannyl-1′-propylidene]-1-boracycloheptane (E)-**B**
A solution of 0.62 g (3 mmol) of **3b** in 15 ml of hexane was cooled to -78°C and 0.475 g (3 mmol) of 1-phenyl-1-boracyclohexane were added in one portion through a syringe. After warming to room temperature, the solvent was removed in vacuo, and 1.09 g of a colourless oil was left which was identified as pure (> 97 % according to ^1H NMR) (E)-**B**. - ^1H NMR ($CDCl_3$, 25 ± 1°C): δ^1H [$J(^{119}Sn,^1H)$] = -0.25 [52.0] (s, 9H, $SnMe_3$), 0.8 - 2.8 (m, 10 H, $-(CH_2)_5-$), 2.1 [54.0] (s, 3 H, $=CCH_3$), 6.9 - 8.2 (m, 5 H, C_6H_5); the *cis*-positions of Me_3Sn and B-Ph group were evident from $^1H/^1H$ NOE difference spectra [19]. - ^{13}C NMR ($CDCl_3$, 25 ± 1°C): $\delta^{13}C$ [$J(^{119}Sn,^{13}C)$] = -8.1 [324.0] ($SnMe_3$), 140.4 [530.0] (Sn-C=), 162.0 (broad, B-C=), 31.3 [86.6] (=-CH_2-), 30.3, 24.8, 27.7 (CH_2), 20.3 [66.0] (=-Me); Ph: 141.0 (broad, i), 137.0 (o), 127.8 (m), 132.5 (p). - ^{11}B NMR ($CDCl_3$, 25 ± 1°C): $\delta^{11}B$ = 75.0. - ^{119}Sn NMR ($CDCl_3$, 25 ± 1°C): $\delta^{119}Sn$ = -46.9.

1,1-organoboration of the 1-alkynyl-trimethyltin compounds **3** *using the boranes* **1** *and* **2**; *general procedure*: The reactions were carried out in the same way as described for (E)-**B**, except in the case of **3a** where a THF-solution (1 M) was used. In all cases, oily residues were obtained after all volatile material was removed in vacuo. The compounds or the mixture of isomers were pure (> 90 %) according to ^{1}H NMR spectra. For ^{13}C and ^{119}Sn NMR data, see Tables 1 and 2. A complete set of ^{1}H NMR data **4/5** and **6/7** was obtained, and the data are available on request. The ^{11}B NMR spectra show broad ($\Delta\nu_{1/2}$ >800 Hz) signals at δ 74 ± 4.

1,1-Organoboration of trimethyl-1-propynylsilane **3b**(Si) *using the borane* **1**
A mixture of .. g (3 mmol) and 0.475 (3 mmol) of **1** in 15 ml of toluene was heated up to reflux for 24 h. After removing the solvent and other volatile material in vacuo, an oily liquid was left which turned out to be a 1:0.6:1 mixture of the compounds **4b**(Si), **5b**(Si) and **8b**(Si) (see Table 4 for ^{13}C and ^{29}Si NMR data). This composition did not change significantly after distillation (70^{0}C/10^{-3} Torr).

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