1,1- and 1,2-Allylboration of Alkyn-1-ylsilanes Bearing Si-H Functions. Electron-Deficient Si-H-B Bridges, and Intramolecular Hydrosilylation

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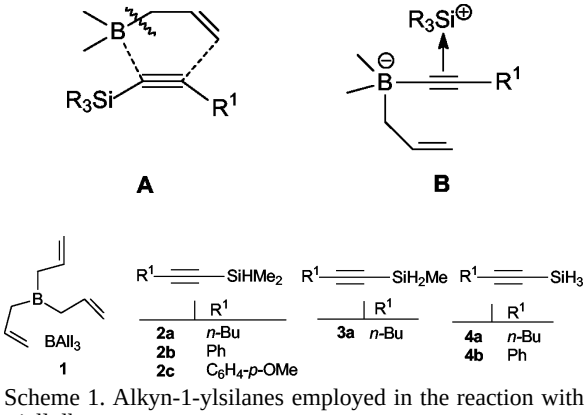
The reactions of *n*-hexyn-1-ylsilanes or arylethyn-1-ylsilanes, bearing methyl groups and one (**2**), two (**3**) or three hydride functions (**4**) at the silicon atom, with triallylborane **1** lead primarily to products of 1,1- or 1,2-allylboration. In the alkenes (**5**, **9**, **13**) formed by stereoselective 1,1-allylboration, with the silyl and the diallylboryl groups in *cis*-positions at the C=C bond an electron-deficient Si-H-B bridge is present. The activation of the Si-H bond in these alkenes induces intramolecular hydrosilylation under very mild reaction conditions to give 1,4-silabora-cyclohept-2-enes (**7** and **11**). The products of 1,2-allylboration (**6**, **10**, **14**) are further transformed into 1-boracyclohex-2-enes (**8**, **12**, **15**) and 7-borabicyclo[3.3.1]non-2-enes (**16**, **17**) by intramolecular 1,2-allylboration reactions. The proposed structures are based on consistent sets of ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR data.

Key words: Silanes, Alkynes, Triallylborane, Organoboration, Heterocycles, NMR

Introduction

Triallylborane, B(CH-CH=CH_2)$_3$ **1**, well known for its permanent allylic rearrangement [1], possesses unusual reactivity, unparalleled by other triorganoboranes [2]. Among numerous useful applications, 1,2-allylboration of various alkynes has opened the way to many new organoboranes [2]. 1,2-Allylboration of alkynes can be explained by proposing the transition state **A**, in which the boron and one terminal olefinic carbon atom are close to the alkynyl carbon atoms. If the alkyne bears one or two organometallic substituents, *e.g.* silyl groups, 1,1-allylboration (intermediate **B**) may compete succesfully with 1,2-allylboration, as has been observed for alkyn-1-ylsilanes, -germanes and -stannanes [3 – 5]. Such organometallically substituted alkynes undergo preferably or even exclusively 1,1-allylboration, as has been found in the case of bis(silyl)ethynes [6]. Intermediates of type **B**, short-lived in the case of alkyn-1-ylsilanes, have been firmly established by NMR spectroscopy and X-ray structural analysis in the course of 1,1-organoboration reactions of alkyn-1-yltin and -lead compounds [7, 8].

We have reported that 1,1-allylboration also works with some alkyn-1-ylsilanes bearing the Si-H function [5, 6], leading to alkenes containing an electron-deficient Si-H-B bridge, as shown by a consistent set of NMR data [5, 6, 9]. This can be understood as a boron-induced activation of the Si-H bond causing intramolecular hydrosilylation to take place under mild conditions without a catalyst. The present work aimed to find out about the influence of an alkyl or aryl substituent at the C≡C bond, in addition to the silyl group (Scheme 1). This should help to compare 1,1- with 1,2-allylboration, and prove the general applicability of combining 1,1-allylboration and intramolecular hydrosilylation. Furthermore, the influence of the presence of two (**3**) or three Si-H functions (**4**) has been studied (Scheme 1). This work was directed more towards mechanistic aspects and exploring potential re-



Scheme 1. Alkyn-1-ylsilanes employed in the reaction with triallylborane.

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Table 1. Selected ^{1}H, ^{13}C and ^{29}Si NMR data[a] of the alkyn-1-ylsilanes **2**, **3** and **4**.

	δ^{29}Si	δ^{1}H	δ^{13}C(≡C-Si)	δ^{13}C(≡C-R^1)
		[^1J(^{29}Si,^{1}H)]	[^1J(^{29}Si,^{13}C)]	[^2J(^{29}Si,^{13}C)]
2c[b]	−37.5	4.37	89.3	106.5
R^1 = *p*-MeO-C$_6$H$_4$		[201.1]	[87.0]	[16.9]
3a[c]	−61.8	3.97	77.0	110.6
R^1 = *n*-Bu		[206.8]	[92.0]	[17.7]
4a[d]	−87.7	3.81	72.1	112.8
R^1 = *n*-Bu		[214.0]	[97.9]	[19.2]
4b[e]	−85.9	4.09	81.5	108.9
R^1 = Ph		[223.3]	[94.9]	[18.1]

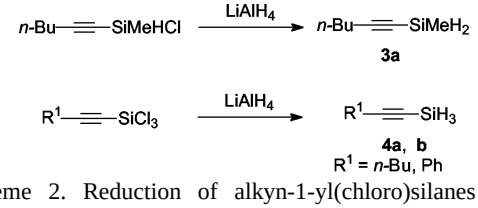
[a] In C_6D_6 at RT; coupling constants in Hz; [b] other ^{13}C NMR data: $\delta = -2.9$ [56.0] ($SiMe_2$); 55.0 (MeO); 113.5, 133.4, 134.8, 159.9 (Ph); [c] other ^{13}C NMR data: $\delta = -6.9$ [56.2] (SiMe); 13.5, 19.6, 21.9, 30.4 (*n*-Bu); [d] other ^{13}C NMR data: $\delta = 13.9$, 20.2, 22.5, 30.9 (*n*-Bu); [e] other ^{13}C NMR data: $\delta = 122.2$ [11.5], 128.3, 129.2, 132.0 (Ph).

arrangements rather than to optimisation of conditions in order to obtain single products in high yield.

Results and Discussion

Synthesis of the alkyn-1-ylsilanes **2** – **4**

The alkyn-1-ylsilanes **2a,b,c** were obtained from the reaction of chloro(diorgano)silanes with the respective lithium alkynide as reported [10]. The reaction of hexyn-1-yl-chloro(methyl)silane [11] with $LiAlH_4$ afforded the dihydride **3a**, and the analogous reaction of the alkyn1-yl-trichlorosilanes [12] gave the trihydrides **4a,b** (Scheme 2).



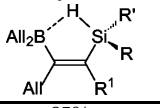
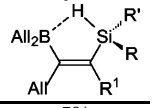
Scheme 2. Reduction of alkyn-1-yl(chloro)silanes with $LiAlH_4$.

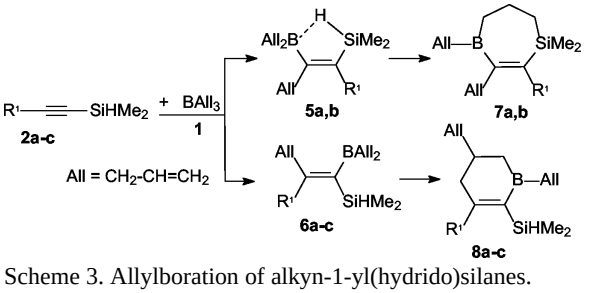
The alkyn-1-ylsilanes **2** – **4** are colourless liquids which could be used either without further purification or after distillation. They have been characterised by their NMR data (Table 1 and Experimental Section).

Reactions of the alkyn-1-yl-hydrido(dimethyl)silanes **2a**, **b**, **c** *with triallylborane* **1**

The alkyn-1-ylsilanes **2a,b,c** react readily with triallylborane **1** (Scheme 3). In the cases of **2a** and **2b**, mixtures (see Table 2 for the product distribution) of the products of 1,1-allylboration (**5a,b**) and 1,2-allylboration (**6a,b**) are formed in the beginning. In the case of **2c**, however, the 1,2-allylboration product is formed selectively. Relevant NMR data of **5** and **6** are given in the Tables 3 and 4, respectively.

Table 2. Product distribution after the reaction of the alkyn-1-ylsilanes **2a** – **c**, **3a**, and **4a,b** with triallylborane **1**.

Starting Alkyn-1-ylsilane	1,1-Allylboration 	1,2-Allylboration 
2a (R^1 = *n*-Bu, R = R' = Me)	95%	5%
2b (R^1 = Ph, R = R' = Me)	25%	75%
2c (R^1 = *p*-C$_6$H$_4$OMe, R = R' = Me)	< 3%	> 97%
3a (R^1 = *n*-Bu, R = Me, R' = H)	50%	50%
4a (R^1 = *n*-Bu, R = R' =H)	5%	95%
4b (R^1 = Ph, R = R' = H)	< 3%	> 97%



Scheme 3. Allylboration of alkyn-1-yl(hydrido)silanes.

Apparently there is competition between 1,1- and 1,2-allylboration. The selective 1,2-allylboration which takes place in the case of **2c** sheds some light on the mechanism. Considering the extreme structures **A** (1,2-allylboration) and **B** (1,1-allylboration), a zwitterionic structure **C**, related to both **A** and **B**, is also conceivable. If R^1 can help to delocalise the positive charge in **C**, cleavage of the Si-C≡ bond (required for 1,1-allylboration) might be suppressed to some extent or even may not take place at all, and this would prevent 1,1-allyboration. For R^1 = Ph, the positive charge in **C** can be delocalised and therefore, 1,2-allylboration is more likely to be observed for R^1 = Ph than for R^1 = *n*-Bu. The delocalisation of positive charge in **C** should be even more favourable for R^1 = C$_6$H$_4$-*p*-OMe. This is confirmed by the observation of selective 1,2-allylboration to give **6c** starting from **2c**. The clean formation of **6c** is evident from the ^{13}C NMR spectrum (Fig. 1).

Table 3. Selected NMR data[a] for the alkenes **5a,b**, **9a** and **13a**.

		δ^{29}Si $\{^2\Delta\}^{10/11}$B(^{29}Si)	δ^{11}B	δ^1H [$^1J(^{29}$Si,^{1}H)]	$\delta^{13}C_{(=C-Si)}$ [$^1J(^{13}$C,^{29}Si)]	$\delta^{13}C_{(=C-B)}$
5a[b]	$R^1 = n$-Bu	−2.3 {−73.0}	67.6	3.26 [160.5]	135.3 [64.4]	160.2 br
5b[c]	R^1 = Ph	−9.5 {−49.4}	57.3	3.71 [168.8]	138.4 [66.7]	161.4 br
9a[d]	$R^1 = n$-Bu	−33.7 {−29.1}	78.4	3.99 [184.0]	133.0 [68.1]	161.3 br
13a[e]	$R^1 = n$-Bu	−63.2 {9.9}	79.2	3.76 [n. o.]	–	–

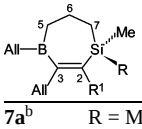
[a] In C_6D_6 at RT; coupling constants in Hz; isotope-induced chemical shifts $^2\Delta^{10/11}$B(^{29}Si) in ppb. [b] other ^{13}C NMR: $\delta = -2.4$ [49.4] ($SiMe_2$); 14.0, 23.0, 29.3, 32.6 (*n*-Bu); 34.6 (br), 112.8, 137.7 (All_2B); 34.9, 115.5 136.2 (All); [c] other ^{13}C NMR: $\delta = -3.6$ [51.3] ($SiMe_2$); 35.7 (br), 114.2, 136.8 (All_2B); 47.6 [7.9], 115.9, 135.1 (All); 126.9, 128.0, 128.1, 141.7 [5.2] (Ph); [d] other ^{13}C NMR: $\delta = -2.1$ [49.4] (MeSi); 14.7, 23.7, 31.1, 32.8 (*n*-Bu); 36.5 (br), 114.2, 137.7 (AllB); 44.5 [7.8], 115.8, 136.8 (All); [e] ^{13}C resonances were not assigned due to low concentration.

Table 4. Selected NMR data[a] for the alkenes **6a – c**, **10a** and **14a,b** (1,2-allylboration products).

		δ^{29}Si	δ^{11}B	δ^1H [$^1J(^{29}$Si,^{1}H)]	$\delta^{13}C_{(B,Si)}$	$\delta^{13}C_{(All)}$
6a[b]	$R^1 = n$-Bu	−32.3	81.3	4.25 [194.7]	[b]	[b]
6b[c]	R^1 = Ph	−30.6	81.0	3.92 [194.4]	148.6 br	150.1
6c[d]	$R^1 = p$-C_6H_4OMe	−30.8	80.9	3.92 [193.8]	148.4 br	149.7
10a[e]	$R^1 = n$-Bu	−53.3	78.9	4.18 [191.4]	141.2 br	152.5 n. o
14a[f]	$R^1 = n$-Bu	−79.0	81.2	3.80 [198.7]	135.0 br	154.4
14b[g]	R^1 = Ph	−75.4	81.2	3.79 [201.8]	139.8 br	154.6

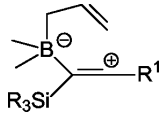
[a] In C_6D_6 at RT; coupling constants in Hz; [b] ^{13}C resonances are not assigned due to low concentration; br indicates broadening due to partially relaxed ^{13}C-^{11}B spin-spin coupling. [c] other ^{13}C NMR signals: $\delta = -2.9$ [51.5] ($SiMe_2$); 36.0 (br), 113.7, 136.7 (All_2B); 47.4 [7.6], 118.3, 134.8 (All); 127.7, 128.2, 128.6, 144.8 [5.1] (Ph); [d] other ^{13}C NMR: $\delta = -2.9$ [51.5] ($SiMe_2$); 35.9 (br), 113.5, 136.7 (All_2B); 47.5 [7.6], 118.0, 134.8 (All); 55.0 (MeO); 113.0, 129.3, 137.3, 158.4 (C_6H_4); [e] other ^{13}C NMR signals: $\delta = -6.0$ [51.1] (SiMe); 14.8, 23.8, 31.9, 33.4 (*n*-Bu); 36.5 (br), 114.6, 137.7 (All_2B); 38.5 [8.4], 119.9, 135.6 (All); [f] other ^{13}C NMR signals: $\delta = 14.8$, 23.5, 31.6, 38.9 [8.4] (*n*-Bu); 36.1 (br), 114.4, 137.5 (All_2B); 44.3 [8.4], 120.7, 137.4 (All); [g] other ^{13}C NMR signals: $\delta = 36.1$ (br), 114.7, 137.2 (All_2B); 46.8 [8.2], 121.0, 136.6 (All); 128.4, 128.9, 129.0, 145.3 [5.6] (Ph).

Table 5. Selected NMR data[a] of 1-bora-4-silacyclohept-2-enes **7a,b** and **11a**.



		δ^{29}Si	δ^{11}B	$\delta^{13}C_{(C-2)}$ [$^1J(^{13}$C,^{29}Si)]	$\delta^{13}C_{(C-3)}$	$\delta^{13}C_{(C-5)}$ [$^1J(^{13}$C,^{29}Si)]	$\delta^{13}C_{(C-6)}$	$\delta^{13}C_{(C-7)}$ [$^1J(^{13}$C,^{29}Si)]
7a[b]	R = Me, $R^1 = n$-Bu	−4.6	81.3	148.2 [63.7]	156.7 br	31.6 br	19.4	18.2 [51.3]
7b[c]	R = Me, R^1 = Ph	−4.9	81.3	151.1 [61.5]	158.4 br	31.8 br	19.1	17.8 [51.3]
11a[d]	R = H, $R^1 = n$-Bu	−17.6	81.2	146.2 [64.4]	158.7 br	30.9 br	20.3	15.5 [51.1]

[a] In C_6D_6 at RT; coupling constants in Hz; br indicates broadening due to partially relaxed ^{13}C-^{11}B spin-spin coupling; [b] other ^{13}C NMR signals: $\delta = 0.8$ [50.1] ($SiMe_2$); 14.1, 23.1, 31.7, 32.9 (*n*-Bu); 35.1 [7.2], 114.9, 136.5 (All); 35.4 (br), 113.5, 137.7 (AllB); [c] other ^{13}C NMR signals: $\delta = 0.23$ [51.5] ($SiMe_2$); 34.4 (br), 114.2, 137.6 (AllB); 37.6 [6.7], 114.8, 135.8 (All); 127.0, 127.6, 127.9, 144.3 (Ph); [d] other ^{13}C NMR signals: $\delta = -2.1$ [49.4] (SiMe); 14.3, 23.8, 33.4, 35.9 (*n*-Bu); 35.8 (br), 114.6, 138.2 (AllB); 41.4 [10.3], 116.4, 136.8 (All).



C

NMR spectroscopic data (Table 3) provide firm evidence for the presence of the electron-deficient Si-H-B bridge in the compounds **5a,b**. There is an increase in ^{11}B nuclear shielding when compared with similar triorganoboranes [13], a decrease in ^{29}Si nuclear shielding relative to similar alkenylsilanes [14], and the magnitude of $|^1J(^{29}\text{Si},^1\text{H})|$ is reduced, typical of the Si-H-B bridge [5, 6, 9]. Furthermore, the isotope-induced chemical shift $^2\Delta^{10/11}$B(^{29}Si), transmitted through the Si-H-B bridge, is characteristic [5, 6, 9]. The boron-induced Si-H activation in the alkenes **5a,b** accelerates intramolecular hydrosilylation [15, 16] under very mild conditions to give the seven-member heterocycles **7a,b**. The structures proposed for **7** are supported by a consistent set of NMR data (see Fig. 2 for the ^{13}C NMR spectrum of **7a** and Table 5 for relevant NMR data).

The alkenes **6a,b,c**, products of 1,2-allylboration, rearrange into substituted 1-boracyclohex-2-enes **8** (relevant NMR data are given in Table 6) by a second (intramolecular) 1,2-allylboration. This process is

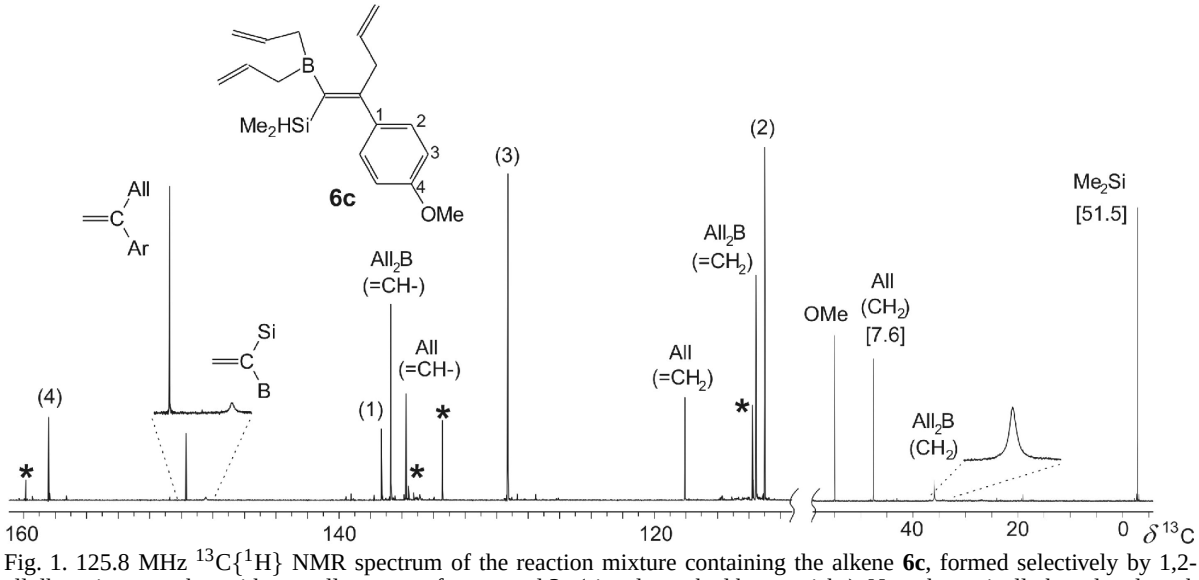


Fig. 1. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture containing the alkene **6c**, formed selectively by 1,2-allylboration, together with a small amount of unreacted **3c** (signals marked by asterisks). Note the typically broad and weak ^{13}C NMR signals for the carbon atoms linked to boron [18] and the satellites owing to $J(^{29}Si,^{13}C)$ (data in Hz given in brackets).

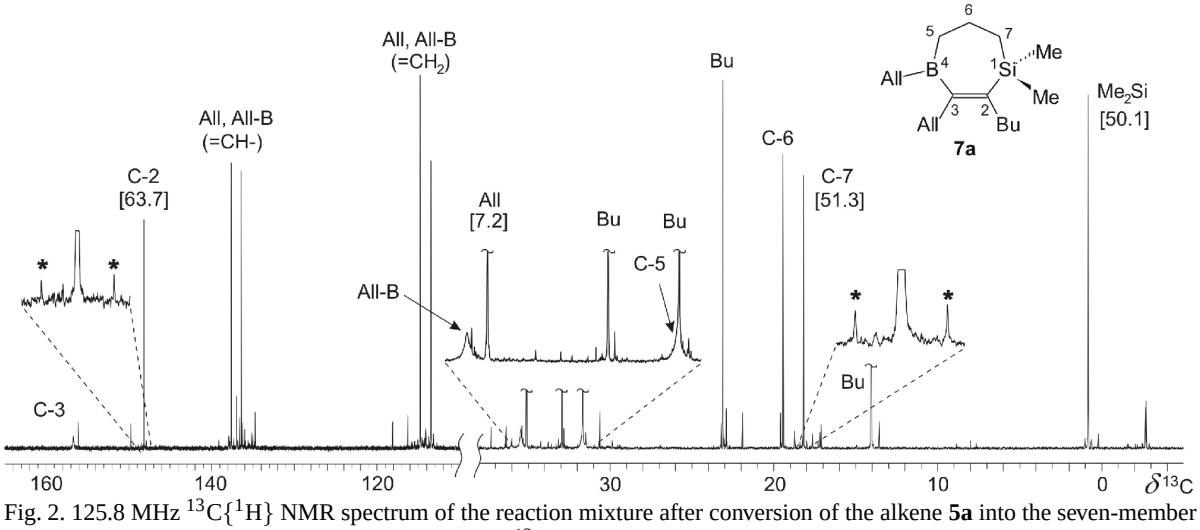


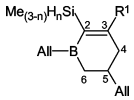
Fig. 2. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture after conversion of the alkene **5a** into the seven-member heterocycle **7a**. Note the typically broad and weak ^{13}C NMR signals for the carbon atoms linked to boron [18] and the satellites owing to $J(^{29}Si,^{13}C)$ (data in Hz given in brackets).

well documented in the chemistry of allylboranes, for example as one of the key steps on the route to 1-boraadamantane [2, 17].

Reaction of n-hexyn-1-yl-dihydrido(methyl)silane **3a** *with triallylborane* **1**

Will the Si-H-B bridge become stronger or weaker if there are two hydrogen atoms linked to silicon as in **3a**? The results of the reaction of **3a** with **1** (Scheme 4) correspond in principle to the findings for the monohydrides. The ^{13}C NMR spectra (see Fig. 3) are readily analysed, showing the presence of the products of 1,1- and 1,2-allylboration. ^{29}Si NMR spectra (see Fig. 4) clearly indicate the presence of the Si-H-B bridge in **9a**, which is absent in the isomer **10a**. However, NMR spectroscopic measurements at variable temper-

Table 6. Selected NMR data[a] for 1-bora-cyclohex-2-enes **8b**, **12a** and **15a,b**.



			δ^{29}Si	δ^{11}B	δ^{1}H	δ^{13}C(2)	δ^{13}C(3)	δ^{13}C(4)	δ^{13}C(5)	δ^{13}C(6)
8b[b]	R^1 = Ph (n = 1)		−28.6	77.9	4.43 [191.7]	139.6 br	178.4	44.9 [5.3]	33.9	30.4 br
12a[c]	−50.4	R^1 = n-Bu (n = 2)		78.9	4.28 [190.6], 4.30 [194.4]	132.3	184.3 [8.2]	42.4 [7.6]	35.1	30.9 br
15a[d]	R^1 = n-Bu (n = 3)		−77.3	78.1	3.81 [198.7]	125.6	185.5	41.9 br	38.1	29.9 br
15b[e]	R^1 = Ph (n = 3)		−72.8	77.1	4.07 [195.3]	130.4 br	182.7 [3.0]	44.9 [5.6]	35.1	30.9 br

[a] In C_6D_6 at RT; coupling constants in Hz; br indicates broadening due to partially relaxed ^{13}C-^{11}B spin-spin coupling; [b] other ^{13}C NMR signals: δ = −2.1 [51.0], −1.2 [50.5] ($SiMe_2$); 34.9 (br), 115.0, 139.1 (AllB); 43.9, 115.8, 137.2 (All); 127.3, 127.8 128.2. 147.2 [4.5] (Ph); [c] other ^{13}C NMR signals: δ = −5.0 [50.0] (SiMe); 14.7, 23.8, 31.9, 34.9 (Bu); 35.1 (br), 114.7, 138.0 (AllB); 43.6, 115.8, 137.1 (All); [d] other ^{13}C NMR: δ = 14.0, 22.9, 30.7 34.0 (Bu); 35.2 (br), 113.5, 136.8 (AllB); 42.7, 115.7, 136.2 (All); [e] other ^{13}C NMR signals: δ = 35.4 (br), 115.2, 137.7 (AllB); 43.5, 116.7, 136.5 (All); 127.4, 128.9, 129.0, 147.0 [5.6] (Ph).

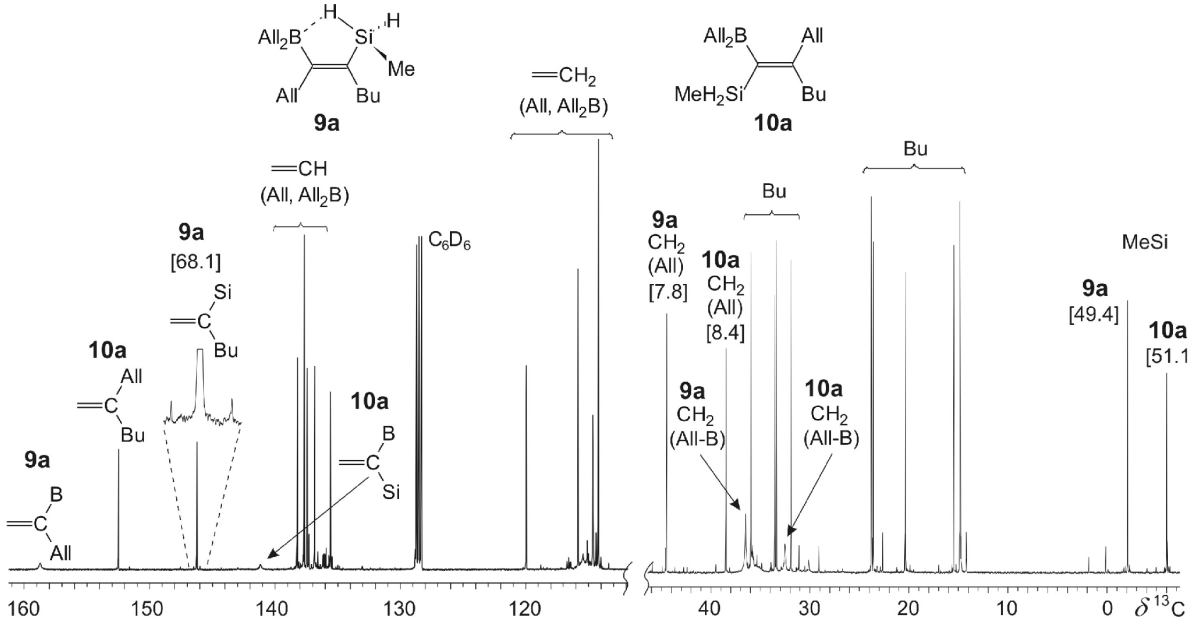
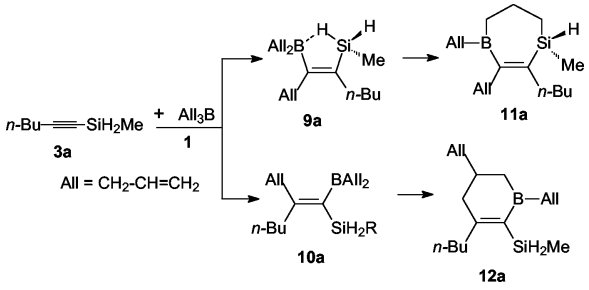


Fig. 3. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture containing the alkenes **9a** and **10a** formed by 1,1- and 1,2-allylboration, respectively, of the alkyne **3a**. A small amount of an excess of triallylborane is still present. Note the typically broad and weak ^{13}C NMR signals for the carbon atoms linked to boron [18] and the satellites owing to $J(^{29}Si,^{13}C)$ (data in Hz given in brackets).



Scheme 4. Allylboration of alkyn1-yl(dihydrido)silanes.

ature did not allow distinguishing between the hydrogen atoms in the bridging and terminal positions. All observed NMR data sets for **9a** (shifts to higher frequencies, compared with monohydrides, of ^{1}H and ^{11}B resonances and to lower frequencies of ^{29}Si resonances, together with the magnitude of $^1J(^{29}Si,^1H)$) indicate fast exchange of terminal and bridging positions of the hydrogen atoms. It appears that the bridge is weaker when compared with the monohydrides.

The formation of the seven-member ring in **11a** *via* intramolecular hydrosilylation again proceeds readily

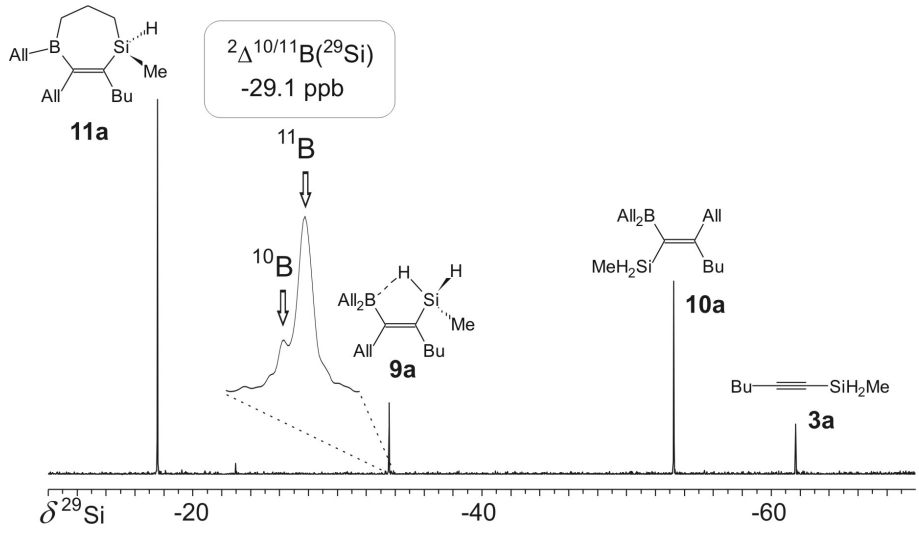
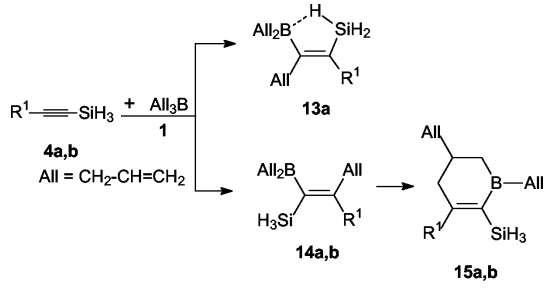


Fig. 4. 99.6 MHz ^{29}Si{^{1}H} NMR spectrum of the reaction mixture containing a small amount of the starting alkyne **3a**, the products of 1,1- and 1,2-allylboration **9a** and **10a**, respectively, as well as the seven-member heterocycle **11a**, formed by intramolecular hydrosilylation of **9a**. The isotope-induced chemical shift $^{2}\Delta^{10/11}$B(^{29}Si), is typical of the Si-H-B bridge in **9a**.

(see Fig. 4), corresponding to the finding for **7**. Attempts to induce a second intramolecular hydrosilylation of the remaining B-allyl group were not successful, indicating that the Si-H bond in **7a** is not activated.

Reaction of the alkyn-1-yl(trihydido)silanes **4a**, **b** *with triallylborane* **1**

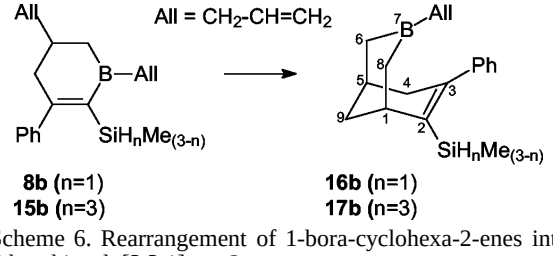
The reaction of the trihydrides **4a,b** with **1** (Scheme 5) leads to the isomers **13** and **14**, analogous to those obtained from the mono- and dihydrides. However, the amount of the isomers **13** containing the Si-H-B bridge is rather low, when compared with the results for dihydrides and monohydrides (Table 2). The presence of the Si-H-B bridge in **13a** follows from the NMR data (Table 3), although it appears to be a rather weak interaction.



Scheme 5. Allylboration of alkyn-1-yl(trihydrido)silanes.

Thermal rearrangement of the products formed by 1,2-allylboration

A thermal rearrangement, well documented in the chemistry of allylboranes [2, 17, 19], takes place in the case of the 1-bora-cyclohex-2-enes, as shown for the products **8b** and **15b** (Scheme 6), leading to the bicyclic boranes **16b** and **17b**, respectively. This rearrangement requires prolonged heating at 80 °C and is accompanied by decomposition.



Scheme 6. Rearrangement of 1-bora-cyclohexa-2-enes into 7-borabicyclo[3.3.1]non-2-enes.

Conclusions

In the title reaction, there is competition between 1,1- and 1,2-allyboration, and the latter dominates for R^1 = Ph and *p*-MeO-C_6H_4, since these substituents can delocalise the positive charge in a zwitterionic intermediate. The 1,1-allylboration affords products with defined stereochemistry (boryl and silyl group

in *cis*-positions) for various organic groups R[1], and in all these cases electron-deficient Si-H-B bridges are present. The boryl-induced Si-H-activation leads to intramolecular hydrosilylation under exceptionally mild reaction conditions. The combination of 1,1-allylboration and hydrosilylation is a useful strategy for the synthesis of novel heterocyclic compounds.

Experimental Section

General and starting materials

All compounds were prepared and handled under dry argon, observing all necessary conditions to exclude air and moisture, and by using carefully dried solvents. Starting materials such as triallylborane **1** [20] and silicon monohydrides **2** were prepared according to literature procedures. NMR measurements: Bruker ARX 250 and DRX 500 NMR spectrometers [^{1}H, ^{11}B, ^{13}C, ^{29}Si NMR (refocused INEPT [21] based on $^2J(^{29}\mathrm{Si},^1\mathrm{H}_{\mathrm{Me}}) = 7$ or $^1J(^{29}\mathrm{Si},^1\mathrm{H}) = 200$ Hz)]. The NMR spectra were measured for solutions (5 – 10%) in C_6D_6 at 23 °C, if not noted otherwise. Chemical shifts are given with respect to Me_4Si [δ^1H ($CHCl_3$/$CDCl_3$) = 7.24; δ^1H (C_6D_5H) = 7.15; δ^{13}C ($CDCl_3$) = 77.0; δ^{13}C (C_6D_6) = 128.0; δ^{29}Si = 0 for $\Xi(^{29}\mathrm{Si})$ = 19.867184 MHz], BF_3-OEt_2 [δ^{11}B = 0; $\Xi(^{11}\mathrm{B})$ = 32.083971 MHz]. Assignments in ^{1}H and ^{13}C NMR spectra are based on appropriate 2D ^{1}H/^{1}H COSY, ^{1}H/^{1}H NOESYTP experiments, and ^{1}H/^{13}C and ^{1}H/^{29}Si heteronuclear shift correlations. IR spectra: Perkin Elmer, Spectrum 2000 FTIR.

Preparation of the silicon di- (**3a**) *and trihydrides* (**4a**, **b**) *via the chlorides hexyn-1-yl-chloro(methyl)silane, hexyn-1-yl-trichlorosilane and phenylethynyl-trichlorosilane*

The solution of the lithium alkynide (20 – 40 mmol) in THF (20 ml), freshly prepared from the respective alkyne and *n*-BuLi, was added slowly to the solution of a 5-fold molar excess of $MeSiHCl_2$ or $SiCl_4$ in THF (40 ml) at −78 °C. The mixture was allowed to warm up to r. t., all volatile materials were removed *in vacuo* at r. t., the residue was taken up in pentane, and insoluble materials were filtered off. Then pentane was distilled off first, and the silanes were purified by fractional distillation.

n-Hexyn-1-yl-chloro(methyl)silane: b. p. 61 – 65 °C/16 Torr. ^{1}H NMR (500 MHz; $CDCl_3$: 23 °C): $\delta = 0.34$ (d, 3H, MeSi, ^3J(H,H) = 3.0 Hz); 0.73, 1.18, 1.23, 1.92 (t, m, m, m, 3H, 2H, 2H, 2H, *n*-Bu); 4.90 (q, 1H, SiH, ^3J(H,H) = 3.0 Hz, $^1J(^{29}\mathrm{Si},^1\mathrm{H})$ = 247.2 Hz). ^{13}C NMR (125.8 MHz; $CDCl_3$; 23 °C; [$J(^{29}\mathrm{Si},^{13}\mathrm{C})$]); $\delta = 1.8$ [64.6] (MeSi); 13.6; 19.6; 22.0; 30.3 (*n*-Bu); 78.9 [108.2] (≡C-Si); 112.4 [22.4] (≡C-*n*-Bu). ^{29}Si NMR (99.6 MHz, $CDCl_3$; 23 °C): $\delta = -22.2$.

Phenylethynyl-trichlorosilane: b. p. 66 – 68 °C/10^{-3} Torr [12b].

n-Hexyn-1-yl-trichlorosilane: b. p. 40 – 42 °C/10^{-3} Torr. ^{1}H NMR (500 MHz; $CDCl_3$; 23 °C): $\delta = 0.95$, 1.46, 1.60, 2.38 (t, m, m, m, 3H, 2H, 2H, 2H, *n*-Bu);. ^{13}C NMR (125.8 MHz; $CDCl_3$; 23 °C; [$J(^{29}\mathrm{Si},^{13}\mathrm{C})$]); $\delta = 13.4$; 19.5; 21.9; 29.5 (*n*-Bu); 77.4 [177.1] (≡C-Si); 113.6 [35.3] (≡C-*n*-Bu). ^{29}Si NMR (99.6 MHz, $CDCl_3$): $\delta = -31.9$.

Reduction of the silicon chlorides

The solution of the respective silicon chloride in diethyl ether was added slowly to a suspension of an excess of $LiAlH_4$ in Et_2O at 0 °C. After 1 h the reaction mixture was quenched with aqueous HCl (10%), and extracted with Et_2O, and the organic layer was washed twice with water and dried with Na_2SO_4. The purity of the silanes was checked, and the silanes were purified, if necessary, by fractional distillation.

2c: ^{1}H NMR: $\delta = 0.40$ (d, 6H, Me_2Si, ^3J(H,H) = 3.8 Hz); 3.85 (s, 3H, MeO); 6.89 (m, 2H, C_6H_4); 7.49 (m, 2H, C_6H_4). **3a**: b. p. 60 – 61 °C/50 Torr. ^{1}H NMR: $\delta = 0.25$ (t, 3H, MeSi, ^3J(H,H) = 4.2 Hz); 0.90, 1.20 – 1.40, 2.23 (t, m, m 3H, 4H, 2H, *n*-Bu). IR: ν(Si-H) = 2155 cm^{-1}, ν(C≡C) = 2180 cm^{-1}. **4a**: ^{1}H NMR: $\delta = 0.69$, 1.00 – 1.20, 1.89 (t, m, m, 3H, 4H, 2H, *n*-Bu) [22]. IR: ν(Si-H) = 2171 cm^{-1}. **4b**: ^{1}H NMR: $\delta = 7.3 - 7.6$ (m, 5H, Ph).

Reaction of the alkyn-1-ylsilanes **2**, **3** *and* **4** *with triallylborane* **1**. General procedure: To a solution of the alkyn-1-ylsilane (1 – 2 mmol) in $CDCl_3$ or C_6D_6 (0.5 ml) the equimolar amount of **1** was added in one portion at r. t. Then the mixture was kept for several hours at r. t., and the progress of the reactions was monitored by ^{1}H and ^{29}Si NMR spectroscopy.

5a: ^{1}H NMR: $\delta = 0.26$ (d, 6H, Me_2Si, ^3J(H,H) = 3.4 Hz); 1.32, 1.40, 2.23 (t, m, m, 3H, 4H, 2H, *n*-Bu); 2.12 (d, 4H, $BAll_2$); 2.93 (dt, 2H, All); 4.9 – 5.1 (m, 6H, $BAll_2$, All); 5.76 (ddt, 1H, All).

5b: ^{1}H NMR: $\delta = 0.24$ (d, 6H, Me_2Si, ^3J(H,H) = 3.4 Hz); 2.37 (d, 4H, $BAll_2$); 2.91 (dt, 2H, All); 5.00 – 5.20 (m, 6H, $BAll_2$, All); 5.80 – 6.20 (m, 3H, $BAll_2$, All); 7.30 – 7.60 (m, 5H, Ph).

6b: ^{1}H NMR: $\delta = -0.04$ (d, 6H, Me_2Si, ^3J(H.H) = 4.0 Hz); 2.41 (d, 4H, $BAll_2$); 3.09 (dt, 2H, All); 5.00 – 5.20 (m, 6H, $BAll_2$); 5.85 (ddt, 1H, All); 6.04 (ddt, 2H, $BAll_2$); 7.30 – 7.60 (m, 5H, Ph).

6c: ^{1}H NMR: $\delta = -0.05$ (d, 6H, Me_2Si, ^3J(H.H) = 4.0 Hz)); 2.37 (d, 4H, $BAll_2$); 3.04 (dt, 2H, All); 3.88 (s, 3H, MeO); 5.0 – 5.1 (m, 6H, $BAll_2$, All); 5.81 (ddt, 1H, All); 6.12 (ddt, 2H, $BAll_2$); 6.93 (m, 2H, C_6H_4); 7.20 (m, 2H, C_6H_4).

9a: ^{1}H NMR: $\delta = 0.29$ (t, 3H, MeSi, ^3J(H,H) = 4.0 Hz); 1.0, 1.40 – 1.60, 2.3 (m, m, m, 3H, 4H, 2H, *n*-Bu); 2.3 (m, 4H, $BAll_2$); 2.98 (dt, 2H, All); 5.0 – 5.2 (m, 6H, $BAll_2$, All); 5.8 – 6.1 (m, 3H, $BAll_2$, All).

10a: ^{1}H NMR: $\delta = 0.30$ (t, 3H, MeSi, ^3J(H,H) = 4.3 Hz); 1.03, 1.40 – 1.60, 2.43 (t, m, m, 3H, 4H, 2H, *n*-Bu); 2.3 (m, 4H, $BAll_2$); 2.74 (d, 2H, All); 5.00 – 5.20 (m, 6H, $BAll_2$, All); 5.81 (m, 1H, All); 6.06 (m, 2H, BAll).

13a: ^{1}H NMR signals were not assigned owing to low concentration and overlap with signals from the other isomer.

14a: ^{1}H NMR: $\delta = 1.05$, 1.47, 1.56, 2.32 (t, m, m, m, 3H, 2H, 2H, 2H, *n*-Bu); 2.26 (d, 4H, $BAll_2$); 2.85 (d, 2H, All_2); 5.00 – 5.20 (m, 6H, $BAll_2$, All); 5.85 (ddt, 1H, All); 5.99 (ddt, 2H, $BAll_2$).

14b: ^{1}H NMR: $\delta = 2.38$ (d, 4H, $BAll_2$); 3.1 (d, 2H, All); 3.84 (s, 3H, SiH_3, $^1J(^{29}Si,^1H)$ = 201.0 Hz); 5.00 – 5.20 (m, 6H, $BAll_2$, All); 5.86 (ddt, 1H, All); 6.16 (ddt, 2H, $BAll_2$); 7.00 – 7.20 (m, 5H, Ph).

Conversion of the alkenes **5** *and* **9** *into 1,4-silaboracyclohept-2-enes* **7** *and* **11**

The complete conversion of **5** into **7** required gentle heating of the solutions at 50 – 60 °C for 2 h. In contrast, the intramolecular hydrosilylation of **9** to **11** took place already at r. t.

7a: ^{1}H NMR: $\delta = 0.05$ (s, 6H, Me_2Si); 0.72 (m, 2H, C^7H_2); 0.95, 1.20 – 1.40, 2.28 (t,m,m, 3H, 4H, 2H, *n*-Bu); 1.20 – 1.40 (m, 1H, C^6H_2, *n*-Bu); 1.78 (m, 2H, C^5H_2); 2.20 (dt, 2H, BAll); 3.14 (dt, 2H, All); 4.90 – 5.00 (m, 4H, BAll, All); 5.75, 5.95 (ddt, ddt, 1H,1H, BAll, All).

7b: ^{1}H NMR: $\delta = 0.03$ (s, 6H, Me_2Si); 0.90 (m, 2H, C^7H_2); 1.39 (m, 2H, C^6H_2); 1.68 (m, 2H, C^5H_2); 2.23 (d, 2H, BAll); 3.04 (dt, 2H, All); 5.00 – 5.20 (m, 4H, BAll, All); 5.80 – 6.20 (m, 2H. BAll, All); 7.20 – 7.50 (m, 5H, Ph).

11a: ^{1}H NMR: $\delta = 0.23$ (d, 3H, MeSi, ^3J(H,H) = 4.0 Hz); 0.73, 1.10 (m, m, 1H, 1H, C^7H_2); 1.04, 1.40 – 1.60, 2.43 (t, m, m, 3H, 4H, 2H, *n*-Bu); 1.40 – 1.60 (m, 2H, C^6H_2); 1.92 (m, 2H, C^5H_2); 2.20 – 2.30 (m, 2H, BAll); 3.18, 3.23 (ddt, ddt, 1H,1H, All); 5.00 – 5.20 (m, 4H, BAll, All); 5.80 – 6.10 (m, 2H, BAll, All).

Conversion of the 1,2-allylboration products **6**, **10** *and* **14** *into the 1-boracyclohex-2-enes* **8**, **12** *and* **15**

Heating of the solutions containing the boranes **6**, **10** or **14** in C_6D_6 for 12 h at 70 – 80 °C leads to the formation of 1-bora-cyclohex-2-enes **8**, **12** and **15** together with bicyclic products (vide infra).

8a: ^{1}H NMR signals were not assigned because of the low concentration of **8a** in the reaction mixture.

8b: ^{1}H NMR: $\delta = 0.15$, 0.22 (d, d 3H,2H Me_2Si, ^3J(H,H) = 3.8 Hz); 0.75, 1.42 (dd, dd, 1H, 1H, C^6H_2); 2.07 (m, 1H, C^5H); 2.20 (m, 2H, BAll); 2.28, 2.76 (dd, dd, 1H, 1H, C^4H_2); 2.37 (m, 2H, All); 4.30 (sp, 1H, SiH, ^3J(H,H) = 3.8 Hz, $^1J(^{29}Si,^1H)$ = 177.9 Hz); 5.00 – 5.10 (m, 4H, BAll, All); 5.7 – 6.2 (m, 2H, BAll, All); 7.20 – 7.50 (m, 5H, Ph).

12a: ^{1}H NMR: $\delta = 0.37$ (q, 3H, MeSi, ^3J(H,H) = 4.3 Hz); 0.77, 1.75 (dd, m, 1H, 1H, C^6H_2); 1.00, 1.40 – 1.60, 2.31 (t, m, m, 3H, 4H, 2H, *n*-Bu); 1.65 (m, 1H, C^5H); 1.94 (m, 2H, BAll); 1.99, 2.14 (m, m, 1H, 1H, C^4H_2); 2.42 (m, 2H, All); 4.50 (m, 2H, SiH_2); 5.00 – 5.20 (m, 4H, BAll, All); 5.80 – 6.10 (m, 2H, BAll, All).

15a: ^{1}H NMR: $\delta = 0.82$, 1.77 (dd, ddd, 1H,1H, C^6H_2); 1.05, 1.48, 1.57, 2.37 (t, m, m, m, 3H, 2H, 2H, 2H, *n*-Bu); 1.64 (m, 1H, C^5H); 1.97, 2.15 (dd, m, 1H,1H, C^4H_2); 2.15 (m, 2H, BAll); 2.51 (m, 2H, All); 4.03 (s, 3H, SiH_3, $^1J(^{29}Si,^1H)$ = 193.0 Hz); 4.90 – 5.20 (m, 4H, BAll, All); 5.8 – 6.1 (m, 2H, BAll, All).

15b: ^{1}H NMR: $\delta = 0.80$, 1.82 (ddd, m, 1H, 1H, C^6H_2); 2.09, 2.70 (m, dd, 1H, 1H. C^4H_2); 2.13 (m, 1H, C^5H); 2.70 (m, 2H, BAll); 2.52 (d, 2H, All); 4.07 (s, 3H, SiH_3, $^1J(^{29}Si,^1H)$ = 195.3 Hz); 5.10 – 5.20 (m, 4H, BAll, All); 5.87, 6.14 (ddt, ddt, 1H, 1H, BAll, All); 7.20 – 7.40 (m, 5H, Ph).

Intramolecular 1,2-allylboration of **8b** *and* **15b** *to the 7-borabicyclo[3.3.1]non-2-enes* **16b** *and* **17b**

Heating of the solution of the monocyclic boranes **8b** or **15b** in C_6D_6 at 70 – 80 °C for 24 – 48 h leads to conversion (35 – 80%) into the bicyclic compounds **16b** and **17b**. Prolonged further heating induces the formation of an increasing amount of decomposition products rather than complete rearrangement.

16b: ^{1}H NMR: No assignment was made owing to severe overlap with signals of **8b**. ^{13}C NMR: $\delta = -2.5$ (MeSi, 51.0); −2.4 (MeSi, 51.3); 19.1 (C-9); 20.6 (br., C-6); 20.7 (br., C-8); 36.3 (br., CH_2B); 37.7 (C-4, 6.4); 43.1 (C-5); 44.0 (C-1, 5.7); 115.9 (=CH_2); 126.9 (Ph); 127.6 (Ph); 127.9 (Ph); 137.2 (=CH-); 146.8 (Ph, 5.2); 175.5 (C-3, 3.8). ^{29}Si NMR (C_6D_6; 23 °C): $\delta = -27.3$.

17b: ^{1}H NMR: No assignment was made owing to severe overlap with signals of **15b**. ^{13}C NMR: $\delta = 18.2$ (C-9); 21.2 (br., C-6); 21.3 (br., C-8); 36.4 (C-4, 7.6); 37.6 (br., CH_2B); 44.0 (C-5); 44.5 (C-1, 6.2); 116.9 (=CH_2); 127.8 (Ph); 128.3 (Ph); 128.9 (Ph); 136.0 (=CH-); 147.0 (Ph, 4.8); 179.7 (C-3, 2.2). ^{29}Si NMR (C_6D_6; 23 °C): $\delta = -73.3$.

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