APPLIED ORGANOMETALLIC CHEMISTRY
*Appl. Organometal. Chem.* 2004; **18**: 43–50

# 1,1-Allylboration of bis(silyl)ethynes: electron-deficient Si–H–B bridges and novel heterocycles via intramolecular hydrosilylation

**Bernd Wrackmeyer[1]*, Oleg L. Tok[1] and Yuri N. Bubnov[2]**

[1]Laboratorium für Anorganische Chemie der Universität Bayreuth, D-95440 Bayreuth, Germany
[2]Nesmeyanow Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str. 28, 117813 Moscow, Russia

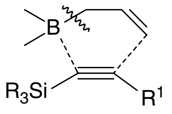
Received 8 August 2003; Revised 25 August 2003; Accepted 10 September 2003

**The reaction of bis(silyl)ethynes 2–4, bearing one, two and three hydrides at one of the silicon atoms, with triallylborane 1 leads primarily to alkenes 5, 8 and 11 respectively by 1,1-allylboration. In these alkenes, the diallylboryl and the silyl group bearing one or more Si–H functions are in cis-positions at the C= C bond, giving rise to the formation of an electron-deficient Si–H–B bridge. This follows unambiguously from the consistent set of NMR data, in particular from the observation of isotope-induced chemical shifts $^{2}\Delta^{10/11}B(^{29}Si)$. The activation of the Si–H bond in 5, 8 and 11 induces intramolecular hydrosilylation under very mild reaction conditions to give 1,4-silabora-cyclo-2-heptenes 7, 10 and 13 respectively. Upon heating, these seven-membered heterocycles undergo ring contraction by 1,1-deallylboration to give the 1-sila-cyclo-2-hexenes 14–16, and bear an exocyclic diallylboryl group in 3-position. All proposed structures are based on consistent $^{1}H$, $^{11}B$, $^{13}C$ and $^{29}Si$NMR data. Copyright © 2004 John Wiley & Sons, Ltd.**

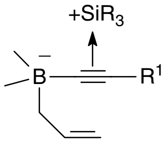
**KEYWORDS:** allylboration; boranes; heterocycles; hydrosilylation; silanes; NMR

## INTRODUCTION

Triallylborane ($BAll_3$, **1**) is a unique triorganoborane,[1,2] and much of its unusual reactivity appears to be related to the permanent allylic rearrangement.[3] 1,2-Allylboration of various alkynes provides an important route to numerous new organoboranes,[1,2] and it has been suggested that the mechanism involves a six-membered transition state **A**, with the boron and one terminal olefinic carbon in close contact to the alkyne carbon atoms. More recently, it was observed that alkyn-1-yl-silanes, -germanes and -stannanes undergo preferably 1,1-allylboration,[4–7] following the well-established mechanism of 1,1-organoboration.[8] The latter involves cleavage of the M–C≡ bond (e.g. M = Si, Ge, Sn), formation of an alkyn-1-ylborate-like intermediate **B**, where the fragment containing M is coordinated side-on to the C≡C bond.[9–13]



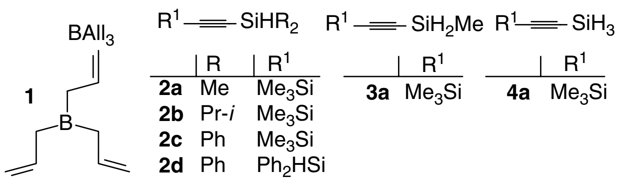
A



B

In a preliminary note we reported that 1,1-allylboration also works with some alkyn-1-ylsilanes bearing the Si–H function.[7] This finding was accompanied by two intriguing observations: (i) the presence of an electron-deficient Si–H–B bridge, strongly supported by a conclusive set of NMR data; (ii) the Si–H bond, activated by the neighbourhood to the electron-deficient boron atom, undergoes hydrosilylation under mild conditions without a catalyst. The present work intends to mark out the general applicability of the approach to combine 1,1-allylboration of bis(silyl)ethynes (Scheme 1) with intramolecular hydrosilylation. In order to explore the reactivity of the alkynes, monitor the complex reactions, and identify the intermediates and final products, an extensive NMR spectroscopic study was necessary.

*Correspondence to: Bernd Wrackmeyer, Anorganische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany.
E-mail: b.wrack@uni-bayreuth.de
Contract/grant sponsor: Volkswagen-Stiftung.
Contract/grant sponsor: Deutsche Forschungsgemeinschaft.
Contract/grant sponsor: Fonds der Chemischen Industrie.



**Scheme 1.**

## RESULTS AND DISCUSSION

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

The alkyn-1-ylsilanes **2a**–**d** were obtained from the reaction of chloro(diorgano)silanes with the respective lithium alkynide as reported.[14] The reduction of dichloro(trimethylsilylethynyl)methylsilane[15] with $LiAlH_4$ afforded the dihydride **3a**, and the analogous reaction of trichloro(trimethylsilylethynyl) silane[16,17] gave the trihydride **4a** (Scheme 2).

The bis(silyl)ethynes **2**–**4** are colourless liquids or a solid (**2d**)[18] and could be used either without further purification or after distillation or recrystallization. They are characterized by their NMR data (Table 1).

### Reactions of the bis(silyl)ethynes 2a–d with triallylborane 1

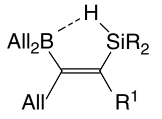
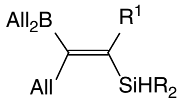
The bis(silyl)ethynes **2a**–**d** react readily with triallylborane **1** (Scheme 3). For the selected substituents $R^1$, all reactions proceed via 1,1-allylboration (see structure **B** for the proposed intermediate), and in some cases mixtures of isomers were obtained (see Table 2 for the product distribution, and see Table 3 for NMR data).

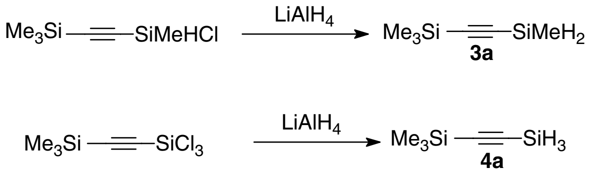
**Table 1.** $^1H$, $^{13}C$, and $^{29}Si$ NMR data[a] of the bis(silyl)ethynes **2**, **3** and **4**

| | $\delta^{29}Si$ (SiH, $SiH_2$, $SiH_3$) | $\delta^1H$(Si–H) [$^1J(^{29}Si, ^1H)$] | $\delta^{13}C$(≡C–Si) [$^1J(^{29}Si, ^{13}C)$] | $\delta^{13}C$(≡C–$R^1$) [$^2J(^{29}Si, ^{13}C)$] |
|---|---|---|---|---|
| **2a** | −38.8 | 4.12 | 110.3 | 115.5 |
| | | [201.3] | [79.3, 12.2] | [76.2, 12.6] |
| **2b** | −16.5 | 3.77 | 108.2 | 118.3 |
| | | [195.8] | [75.1, 11.9] | [76.3, 14.5] |
| **2c**[b] | −41.2 | 5.64 | 106.2 | 119.7 |
| | | [213.0] | [86.6, 12.2] | [74.6, 13.4] |
| **2d** | −40.9 | 5.36 | 112.0 | 112.0 |
| | | [215.6] | [83.9, 13.1] | [83.9, 13.1] |
| **3a**[c] | −62.0 | 3.97 | 106.0 | 117.7 |
| | | [208.7] | [82.1, 12.4] | [75.1, 13.2] |
| **4a**[d] | −88.9 | 3.79 | 101.3 | 120.7 |
| | | [216.9] | [87.0, 12.2] | [75.1, 13.8] |

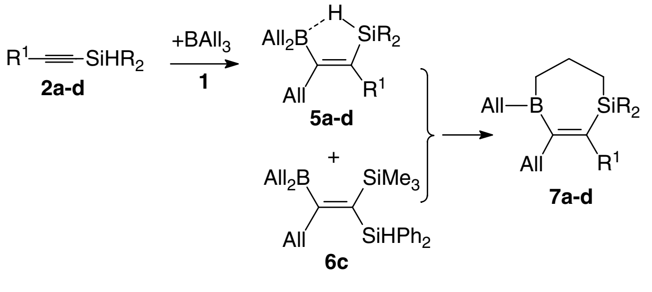
[a] In $C_6D_6$ at room temperature; coupling constants involving $^{29}Si$ are given in brackets (±0.2 Hz). Other NMR data of **2a**, **2b**, and **2d** are listed in Ref. 18.
[b] Other $^{13}C$ NMR data: $\delta = -0.3$ [56.3] ($Me_3Si$); 127.4 (Ph); 130.1 (Ph); 131.5 [76.3] (Ph); 135.1 (Ph). Other $^{29}Si$ NMR data: $\delta = -17.3$ [1.8] ($Me_3Si$).
[c] Other $^{13}C$ NMR data: $\delta = -7.2$ [56.1] (MeSi); −0.4 [56.3] ($Me_3Si$). Other $^{29}Si$ NMR data: $\delta = -18.1$ [1.7] ($Me_3Si$).
[d] Other $^{13}C$ NMR data: $\delta = -0.1$ [56.3] ($Me_3Si$). Other $^{29}Si$ NMR data: $\delta = -17.8$ [1.9] ($Me_3Si$).

**Table 2.** Product distribution after the reaction of the bis(silyl)ethynes **2a**–**d**, **3a**, and **4a** with triallylborane **1**

| | Distribution (%) | |
|---|---|---|
| Starting bis(silyl)ethyne |  |  |
| **2a** | 100 | — |
| **2b** | 100 | — |
| **2c** | 55 | 45 |
| **2d** | 100 | — |
| **3a** | 33 | 67 |
| **4a** | 15 | 85 |



**Scheme 2.**



**Scheme 3.**

NMR spectroscopic data (Table 3) provide convincing evidence for the electron-deficient Si–H–B bridge in in the compounds **5a**–**d**. The increase in $^{11}B$ nuclear shielding when compared with similar triorganoboranes, the decrease in $^{29}Si$ nuclear shielding when compared with similar alkenylsilanes, and the reduced magnitude of $^1J(^{29}Si, ^1H)$ are typical of the Si–H–B bridge.[7,18,19] Another intriguing effect is the observation of isotope-induced chemical shifts $^2\Delta^{10/11}B(^{29}Si)$, which are transmitted through the bridge.[7,18,19] Since Si–H–B bridging is not possible in the alkene **6c**, its NMR data set (Table 3) is ideally suited to demonstrate the unusual bonding situation in the alkenes **5**. The broad absorption band assigned to the Si–H stretching vibration

**Table 3.** NMR data[a] of the olefins **5a–d, 6c, 8a, 9a, 11a** and **12a**

| | $\delta^{29}$Si ($^2\Delta^{10/11}$B($^{29}$Si)) | $\delta^{11}$B | $\delta^1$H [$^1J$($^{29}$Si, $^1$H)] | $\delta^{13}$C$_{(=C-Si)}$ [$^1J$($^{29}$Si, $^{13}$C)] | $\delta^{13}$ C$_{(=C=B)}$ |
|---|---|---|---|---|---|
| **5a**[b] | 12.6<br>(−46.0) | 51.6 | 2.76<br>[129.1] | 136.6<br>[56.5] | 186.5<br>br |
| **5b**[c] | 30.9<br>(−46.0) | 55.6 | 2.73<br>[131.0] | 135.1<br>[57.7] | 191.6<br>br |
| **5c**[d] | −9.0<br>(−45.6) | 54.0 | 4.50<br>[156.6] | 129.2<br>[57.2] | 191.2<br>br |
| **5d**[e] | −12.4<br>(−37.0) | 76.2 | 5.10<br>[198.6] | — | — |
| **6c**[f] | −32.1 | 81.1 | 5.51<br>[189.8] | 132.8<br>[57.2] | 181.5<br>br |
| **8a**[g] | −28.9<br>(−48.9) | 79.5 | 3.78<br>[179.0] | 123.8<br>[53.9] | 184.7<br>br |
| **9a**[h] | −52.9 | 81.3 | 4.16<br>[187.8] | 135.5<br>[55.4, 52.4] | 178.7<br>br |
| **11a**[i] | −63.0<br>(−14.3) | — | 3.96<br>[191.9] | — | — |
| **12a**[j] | −80.8 | 81.1 | 4.17<br>[194.5] | 130.4<br>[55.8, 52.7] | 181.6<br>br |

[a] In $C_6D_6$ at room temperature; coupling constants involving $^{29}$Si are given in brackets (±0.2 Hz); br denotes the signal of a $^{13}$C nucleus linked to boron; isotope-induced chemical shifts $\Delta^{10/11}$B($^{29}$Si) are given in ppb with a negative sign if the resonance signal of the heavier isotopomer is shifted to lower frequencies.

[b] Other $^1$H, $^{13}$C and $^{29}$Si NMR data: Ref. 7.

[c] Other $^{13}$C NMR signals: $\delta = 2.2$ [50.8] ($Me_3Si$); 14.5 [51.0] (SiCH); 20.0 ($CH_3$); 20.5 ($CH_3$); 34.9 (br, $CH_2B$); 44.2 [13.6, 6.9] ($CH_2$); 114.0 (=$CH_2$); 117.1 (=$CH_2$); 137.0 (=CH); 139.1 (=CH). Other $^{29}$Si NMR signal: $\delta = -13.1$ [10.3] ($Me_3Si$, $^{3/4}\Delta^{10/11}$B($^{29}$Si) = +4.0 ppb).

[d] Other $^{13}$C NMR signals: $\delta = 1.7$ [50.5] ($Me_3Si$); 34.1 (br, $CH_2B$); 43.5 [14.8, 7.6] ($CH_2$); 113.9 (=$CH_2$); 116.8 (=$CH_2$); 128.0 (Ph); 130.0 (Ph); 131.9 (76.3) (Ph); 134.9 (=CH); 135.1 (Ph); 136.1 (=CH). Other $^{29}$Si NMR signal: $\delta = -10.8$ [9.4] ($Me_3Si$, $^{3/4}\Delta^{10/11}$B($^{29}$Si) = +5.7 ppb).

[e] $^{13}$C resonances are not assigned due to fast formation of **7d**. Other $^{29}$Si NMR signal: $\delta = -31.4$ [9.1] ($Ph_2HSi$).

[f] Other $^{13}$C NMR signals: $\delta = 0.7$ [51.5] ($Me_3Si$); 36.6 (br, $CH_2B$); 45.2 [11.0] ($CH_2$); 114.3 (=$CH_2$); 116.7 (=$CH_2$); 127.9 (Ph); 127.9 (Ph); 133.1 (76.7) (Ph); 135.6 (=CH); 135.7 (=CH); 136.0 (Ph). Other $^{29}$Si NMR signal: $\delta = -4.8$ [8.4] ($Me_3Si$).

[g] Other $^{13}$C NMR signals: $\delta = -4.7$ [49.1] (MeSi); 1.3 [50.9] ($Me_3Si$); 35.1 (br, $CH_2B$); 43.0 [8.2] ($CH_2$); 113.4 (=$CH_2$); 116.7 (=$CH_2$); 135.6 (=CH); 136.8 (=CH). Other $^{29}$Si NMR signal: $\delta = -10.5$ [9.4] ($Me_3Si$,$^{3/4}$ $\Delta^{10/11}$B($^{29}$Si) = +3.7 ppb).

[h] Other $^{13}$C NMR signals: $\delta = -5.7$ [50.2] (MeSi); 0.6 [50.9] ($Me_3Si$); 36.0 (br, $CH_2B$); 41.7 [12.9, 11.0] ($CH_2$); 114.2 (=$CH_2$); 116.8 (=$CH_2$); 135.5 (=CH); 135.9 (=CH). Other $^{29}$Si NMR signal: $\delta = -5.4$ [8.3] ($Me_3Si$).

[i] $^{11}$B and $^{13}$C resonances are not assigned due to fast formation of **13a**. Other $^{29}$Si NMR signal: $\delta = -8.7$ [8.0] ($Me_3Si$).

[j] Other $^{13}$C NMR signals: $\delta = 0.9$ [51.3] ($Me_3Si$); 36.6 (br, $CH_2B$); 42.4 [13.8, 10.3] ($CH_2$); 115.1 (=$CH_2$); 117.8 (=$CH_2$); 135.6 (=CH); 136.5 (=CH). Other $^{29}$Si NMR signal: $\delta = -4.5$ [8.5] ($Me_3Si$).

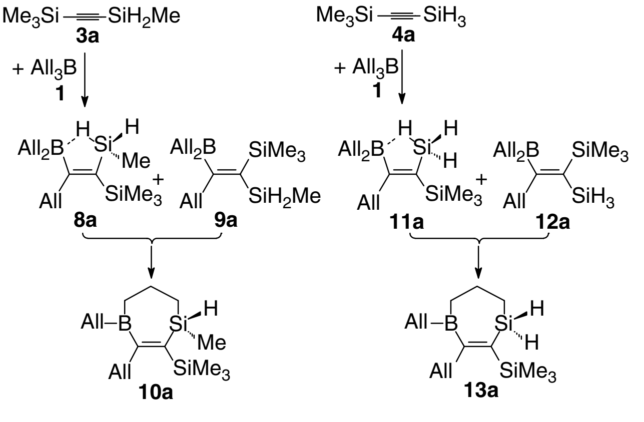
($\nu$(Si–H) = 1870 ± 30 cm$^{-1}$) in the IR spectra of **5** is shifted markedly to lower wavenumbers when compared with that for the starting bis(silyl)ethynes **2** (2140 ± 20 cm$^{-1}$).

Most interestingly, the alkenes **5**, containing the Si–H–B bridge, undergo intramolecular hydrosilylation[20–26] under very mild conditions without a catalyst to give the seven-membered heterocycles **7** (see Table 4 for relevant NMR data). It should be noted that **6c** is also converted into **7c**, typical of an equilibrium between **6c** and **5c** via 1,1-deallylboration.[8] We ascribe the ease of the hydrosilylation to the boron-induced intramolecular Si–H activation in **5**.

## Reactions of the silicon di- (3a) and tri-hydride (4a) with triallylborane (1)

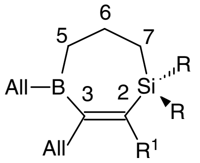
Will the Si–H–B bridge become stronger or weaker if there are two or three hydrogen atoms linked to silicon, as in **3a** and **4a** respectively? The results of the reaction of **3a** and **4a** with **1** are summarized in Scheme 4, and they correspond in principle to the findings for the monohydrides. $^{29}$Si NMR spectra (Fig. 1) clearly indicate the presence of the Si–H–B bridge in **8a**, which is absent in the isomer **9a**. However, NMR spectroscopic measurements at variable temperature (298–183 K) did not enable us to distinguish between the hydrogen atoms in the bridging and terminal positions. The experimental NMR data set for **8a** [shifts to higher frequencies, compared with monohydrides, of $^1$H and $^{11}$B resonances and to lower frequencies of $^{29}$Si resonances, together with a relative increase in the magnitude of $^1J$($^{29}$Si, $^1$H)] indicates fast exchange of hydrogen atoms in terminal and bridging positions. IR spectra do not give more insight into the dynamic process, since there is only a broad absorption for $\nu$(Si–H), shifted slightly (<30 cm$^{-1}$) to lower wavenumbers relative to undisturbed Si–H stretching modes. It appears that the Si–H–B bridge for the dihydride and the trihydride is weaker when compared with the monohydrides. This assumption is supported by quantum chemical calculations (density functional theory and *ab initio* methods) of related model compounds.[31]

The formation of the seven-membered rings in **10a** and **13a** via hydrosilylation again proceeds readily, corresponding to the finding for **7**; it does not even require heating of the reaction solutions. The fact that both **8a** and **9a** and both **11a**



**Scheme 4.**

**Table 4.** NMR data[a] of 1,4-silabora-cyclo-2-heptenes **7a**, **c**, **d**, **10a** and **13a**



| | $\delta^{29}$Si<br>[$^2J(^{29}$Si, $^{29}$Si)] | $\delta^{11}$B | $\delta^{13}$C$_{(C-2)}$<br>[$^1J(^{29}$Si, $^{13}$C)] | $\delta^{13}$C$_{(C-3)}$ | $\delta^{13}$C$_{(C-5)}$ | $\delta^{13}$C$_{(C-6)}$ | $\delta^{13}$C$_{(C-7)}$<br>[$^1J(^{29}$Si, $^{13}$C)] |
|---|---|---|---|---|---|---|---|
| **7a**[b] | −4.3 | 80.5 | 154.9 | 179.8 | 29.6 | 18.2 | 19.5 |
| R = Me | [8.2] | | | br | br | | [49.8] |
| $R^1$ = SiMe$_3$ | | | | | | | |
| **7c**[c] | −11.4 | 81.4 | 141.5 | 185.5 | 29.6 | 18.5 | 17.6 |
| R = Ph | [7.6] | | [54.6, 52.7] | br | br | | [52.2] |
| $R^1$ = SiMe$_3$ | | | | | | | |
| **7d**[d] | −29.6 | 81.3 | 137.2 | 188.6 | 30.8 | 19.7 | 15.1 |
| R = Ph | [6.3] | | [66.3] | br | br | | [52.9] |
| $R^1$ = SiPh$_2$H | | | | | | | |
| **10a**[e] | −12.2 | 71.5 | 139.8 | 181.8 | 28.6 | 19.6 | 14.3 |
| R = H, Me | Δ = −91.4 | | [55.0, 50.7] | br | br | | [50.0] |
| $R^1$ = SiMe$_3$ | [8.7] | | | | | | |
| **13a**[f] | −44.2 | 81.1 | 136.1 | 183.2 | 31.2 | 20.2 | 10.9 |
| R = H | Δ = −8.6 | | [54.7, 49.1] | br | br | | [50.2] |
| $R^1$ = SiMe$_3$ | [8.0] | | | | | | |

[a] In $C_6D_6$ at room temperature; coupling constants involving $^{29}$Si are given in brackets (±0.2 Hz); br denotes the broad signal of a $^{13}$C nucleus linked to boron; Δ denotes isotope-induced chemical shifts $^2\Delta^{10/11}$B($^{29}$Si), given in ppb with a negative sign if the resonance signal of the heavier isotopomer is shifted to lower frequencies.

[b] Other $^1$H, $^{13}$C and $^{29}$Si NMR data see Ref. 7.

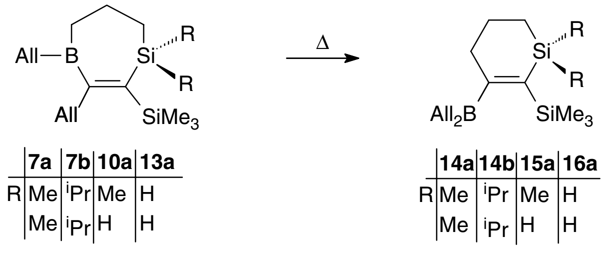
[c] Other $^{13}$C NMR signals: $\delta = 2.7$ [50.8] (Me$_3$Si); 35.4 (br, CH$_2$B); 43.5 [10.9] (CH$_2$); 113.8 (=CH$_2$); 114.2 (=CH$_2$); 127.6 (Ph); 128.9 (Ph); 132.4 (Ph, 70.1); 135.5 (Ph); 135.8 (=CH); 138.3 (=CH). Other $^{29}$Si NMR signal: $\delta = -8.5$ [7.6] (Me$_3$Si).

[d] Other $^{13}$C NMR signals: $\delta = 34.8$ (br, CH$_2$B); 45.8 (10.3) (CH$_2$); 113.8 (=CH$_2$); 117.0 (=CH$_2$); 127.6 (Ph); 127.8 (Ph); 129.1 (Ph); 129.1 (Ph); 134.9 [54.0] (Ph); 134.9 [54.4] (Ph); 135.0 (–CH=); 135.5 (Ph); 135.8 (Ph); 136.0 (=CH). Other $^{29}$Si NMR signal: $\delta = -40.9$ [6.3] (Ph$_2$HSi).

[e] Other $^{13}$C NMR signals: $\delta = -1.8$ [47.9] (MeSi); 1.9 [50.4] (Me$_3$Si); 33.4 (br, CH$_2$B); 42.9 [12.1] (CH$_2$); 113.3 (=CH$_2$); 116.1 (=CH$_2$); 136.4 (=CH); 137.0 (=CH). Other $^{29}$Si NMR signal: $\delta = -9.6$ [8.7] (Me$_3$Si, $^{3/4}\Delta^{10/11}$B($^{29}$Si) = +8.9 ppb).

[f] Other $^{13}$C NMR signals: $\delta = 2.2$ [50.9] (Me$_3$Si); 34.8 (br, CH$_2$B); 43.8 [10.1] (CH$_2$); 114.8 (=CH$_2$); 117.1 (=CH$_2$); 136.6 (=CH); 136.8 (=CH). Other $^{29}$Si NMR signal: $\delta = -8.7$ [8.0] (Me$_3$Si).

and **12a** are consumed in the course of the hydrosilylation indicates that the 1,1-allylboration is reversible, like other 1,1-organoborations,[8] and the equilibrium is being shifted towards **10a** via **8a** and towards **13a** via **11a**. The $^{13}$C NMR spectra of **7**, **10a** and **13a** with characteristic broad (B–C)[32–34] and sharp signals, together with $^{29}$Si satellites corresponding to $J(^{29}$Si, $^{13}$C) and $^{13}$C satellites (for some signals) corresponding to $^1J(^{13}$C, $^{13}$C) (see Fig. 2 for **10a**), shows the clean and quantitative formation of most of these products. The $^{29}$Si NMR spectra of **10a** and **13a** indicate that there is also an Si–H–B bridge (see Fig. 3 for **10a**). However, attempts to induce further hydrosilylation of the remaining B-allyl group by prolonged heating of samples of **10a** or **13a** were not successful (*vide infra*).



**Scheme 5.**

## Further rearrangement of the 1,4-silabora-cyclo-2-heptenes 7, 10a and 13a

Since the heterocycles **7**, **10a** and **13a** contain reactive and labile element–hydrogen and element–carbon bonds, their behaviour with respect to potential further rearrangements is of interest. As shown in Scheme 5, heating (not required in the case of **7b**) of these heterocycles induces a 1,1-deallylboration leading to ring contraction from seven- to six-membered rings. Compound **14b** is formed already in the reaction solution when **5b** is hydrosilylated to give **7b**. The 1-sila-cyclo-2-hexenes **14a**,**b** **15a** and **16a**, bearing the diallylboryl group in 3-position (see Table 5 for relevant NMR data), were formed, in agreement with previous observations.[7] This

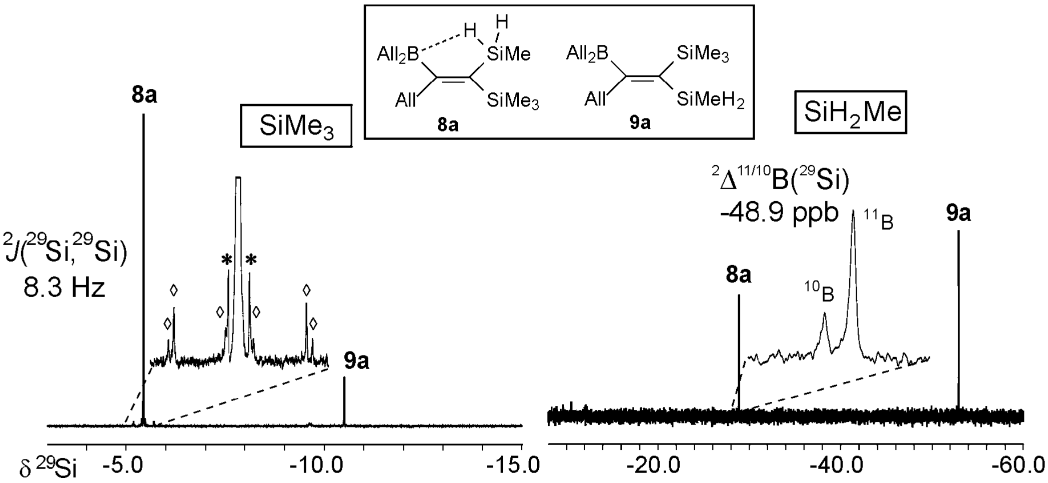


**Figure 1.** The 99.6 MHz $^{29}$Si{$^{1}$H} NMR spectrum of a mixture containing the isomers **8a** and **9a**, recorded using the refocused INEPT pulse sequence[27–30] based on $^{2}J(^{29}Si, ^{1}H_{Me})$ ($SiMe_3$ groups) and $^{1}J(^{29}Si, ^{1}H)$ ($SiH_2$ groups). The expansion of the $^{29}Si(SiMe_3)$ signal of **9a** shows $^{13}C$ satellites (rhombus) and $^{29}Si$ satellites (asterisks). Characteristic of the electron-defibient Si–H–B bridge is the isotope-induced chemical shift $^{2}\Delta^{10/11}B(^{29}Si)$ as indicated. This is readily identified by the 1 : 4 ratio of the respective signal intensities.

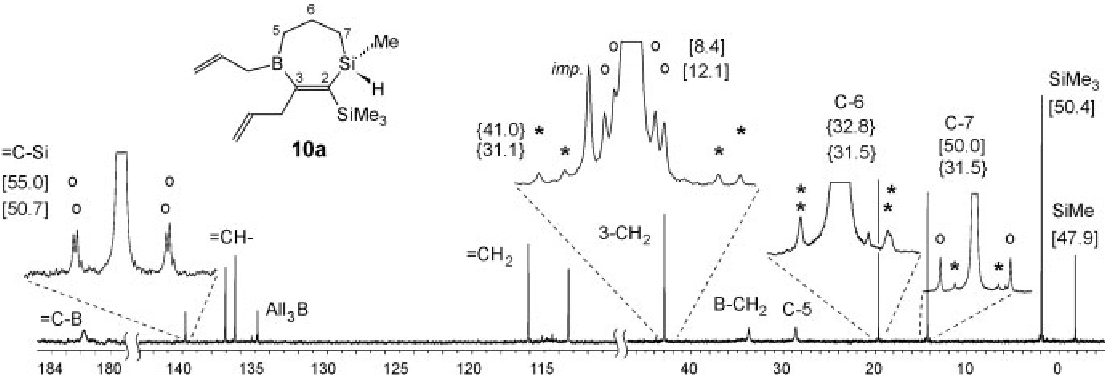


**Figure 2.** The 125.8 MHz $^{13}$C{$^{1}$H} NMR spectrum of the 1,4-silabora-2-cycloheptene **10a** (*ca* 10% in $CDCl_3$ at 23 °C), obtained without further purification from consecutive 1,1-allylboration and intramolecular hydrosilylation starting from **3a** via **8a.** The typically broad NMR signals of the $^{13}C$ nuclei attached to boron[32–34] are readily identified, and many of the sharp signals are accompanied by $^{29}Si$ satellites (coupling constants $J(^{29}Si, ^{13}C)$ in Hertz given in brackets), and in some cases also by $^{13}C$ satellites for $^{1}J(^{13}C, ^{13}C)$ (in hertz given in braces).

rearrangement can be monitored by $^{29}Si$ NMR (Fig. 3), where the characteristic $^{29}Si$ NMR signals of the seven-membered ring decrease in intensity with respect to the new growing signals of the six-membered ring.

## CONCLUSIONS

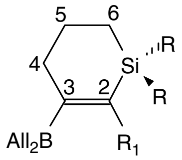
Bis(silyl)ethynes react with triallylborane predominantly by 1,1-allylboration (in contrast to the well-documented 1,2-allylboration known for many other alkynes), leading to numerous new alkenes with diallylboryl and silyl groups in cis-positions at the C=C bond. If the silyl group contains an Si–H function then an electron-deficient Si–H–B bridge is formed. This can be understood as a boryl-induced Si–H bond activation, leading to intramolecular hydrosilylation under exceptionally mild reaction conditions, by which novel seven-membered heterocycles (**7**, **10a**, **13a**) are obtained in high yield and high purity. These rearrange upon heating selectively into six-membered heterocycles (**14**–**16**). The combination of 1,1-allylboration and intramolecular hydrosilylation is a new concept for the syntheses of heterocyclic compounds.

## EXPERIMENTAL

### General and starting materials

All compounds were prepared and handled under dry argon, observing all necessary conditions to exclude air and

**Table 5.** NMR data[a] of 1-sila-cyclo-2-hexenes **14a,b, 15a** and **16a**



| | $\delta^{29}Si$ $[^2J(^{29}Si, ^{29}Si)]$ | $\delta^{11}B$ | $\delta^{13}C_{(C-2)}$ $[^1J(^{29}Si, ^{13}C)]$ | $\delta^{13}C_{(C-3)}$ | $\delta^{13}C_{(C-4)}$ | $\delta^{13}C_{(C-5)}$ | $\delta^{13}C_{(C-6)}$ $[^1J(^{29}Si, ^{13}C)]$ |
|---|---|---|---|---|---|---|---|
| **14a**[b] | −6.0 | 76.9 | 145.1 | 181.7 | 31.4 | 21.1 | 13.6 |
| R = Me | [7.0] | | [51.9, 51.9] | br | [12.6, 11.0] | | [50.4] |
| $R^1 = SiMe_3$ | | | | | | | |
| **14b**[c] | −6.3 | 81.5 | 150.2 | 185.2 | 31.4 | 21.7 | 4.7 |
| $R = {}^iPr$ | [7.1] | | [52.0, 48.9] | br | [10.5, 10.5] | | [47.7] |
| $R^1 = SiMe_3$ | | | | | | | |
| **15a**[d] | −33.8 | 77.5 | 131.9 | 182.8 | 31.3 | 20.6 | 9.8 |
| R = H, Me | [6.7] | | [57.6, 49.4] | br | [12.3, 9.9] | | [50.2] |
| $R^1 = SiMe_3$ | | | | | | | |
| **16a**[e] | −56.1 | 79.0 | 128.1 | 185.1 | 31.8 | 21.5 | 5.7 |
| R = H | [6.6] | | [58.2, 49.1] | br | [12.7, 9.7] | | [50.2] |
| $R^1 = SiMe_3$ | | | | | | | |

[a] In $C_6D_6$ at room temperature; coupling constants involving $^{29}Si$ are given in brackets (±0.2 Hz); br denotes the broad signal of a $^{13}C$ nucleus linked to boron.

[b] Other $^1H$, $^{13}C$ and $^{29}Si$ NMR data see Ref. 7.

[c] Other $^{13}C$ NMR signals: $\delta = 1.8$ [46.3] ($Me_3Si$); 13.8 [51.0] (SiCH); 18.2 (1.9) ($CH_3$); 18.4 (1.9) ($CH_3$); 34.5 (br, $CH_2B$); 113.9 (=$CH_2$); 134.8 (=CH). Other $^{29}Si$ NMR signal: $\delta = -11.5$ ($Me_3Si$).

[d] Other $^{13}C$ NMR signals: $\delta = -2.2$ [49.8] (MeSi); 0.9 [50.2] ($Me_3Si$); 34.3 (br, $CH_2B$); 114.1 (=$CH_2$); 135.7 (=CH). Other $^{29}Si$ NMR signal: $\delta = -6.4$ ($Me_3Si$).

[e] Other $^{13}C$ NMR signals: $\delta = 1.0$ [50.7] ($Me_3Si$); 35.1 (br, $CH_2B$); 115.0 (=$CH_2$); 136.3 (=CH). Other $^{29}Si$ NMR signal: $\delta = -6.1$ ($Me_3Si$).

moisture, and by using carefully dried solvents. Starting materials such as triallylborane **1**[35,36] and silicon monohydrides **2**[14,18] were prepared according to literature procedures. NMR measurements: Bruker ARX 250 and DRX 500 [$^1H$, $^{11}B$, $^{13}C$, $^{29}Si$ NMR (refocused INEPT[27–30] based on $^2J(^{29}Si, ^1H_{Me}) = 7$ Hz or $^1J(^{29}Si, ^1H) = 200$ Hz)]. Chemical shifts are given relative to $Me_4Si$ [$\delta^1H$ ($CHCl_3/CDCl_3$) = 7.24 or $\delta^1H$ ($C_6D_5H$) = 7.15; $\delta^{13}C$ ($CDCl_3$) = 77.0 or $\delta^{13}C$ ($C_6D_6$) = 128; $\delta^{29}Si = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz], $BF_3$–$Et_2O$ [$\delta^{11}B = 0$; $\Xi(^{11}B) = 32.083971$ MHz]. Assignments in $^1H$ and $^{13}C$ NMR spectra are based on appropriate 2D $^1H/^1H$ COSY, $^1H/^1H$ NOESYTP, $^1H/^{13}C$ and $^1H/^{29}Si$ HETCOR experiments. Mass spectra (EI, 70 eV; Finnigan MAT 8500 with direct inlet) of the 1,1-allylboration products **5**, **6**, **8**, **9**, **11** and **12** and of the heterocycles **7**, **10**, **13**–**16** did not give conclusive results because of the presence of mixtures and/or further rearrangements. IR spectra: Perkin Elmer, Spectrum 2000 FTIR.

## Preparation of silicon di- (3a) and tri-hydrides (4a); general procedure

### *Synthesis of chloromethyl(trimethylsilylethynyl)-, and trichloro(trimethylsilylethynyl)-silanes*

The solution of trimethylsilylethynyl lithium (20–40 mmol) in THF (20 ml), freshly prepared from ethynyl(trimethyl)silane and BuLi, was added slowly to the solution of a five fold molar excess of $MeSiHCl_2$ or $SiCl_4$ in THF (40 ml) at −78 °C. The mixture was allowed to warm to room temperature, and all volatile materials were removed *in vacuo* at room temperature. The residue was taken up in pentane, and insoluble materials were filtered off. The pentane was distilled off first, and then the silanes (yield 60–80%) were purified by fractional distillation.

Chloro(methyl)(trimethylsilylethynyl)silane: b.p. 40–42 °C/15 Torr; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta[^1J(^{29}Si, ^1H)] = 0.05$ (s, 9H, $Me_3Si$); 0.28 (d, 3H, MeSi); 4.90 [249.2] (q, 1H, SiH). $^{13}C$ NMR (125 MHz, $CDCl_3$); $\delta[J(^{29}Si, ^{13}C)] = -0.6$ [56.3] ($Me_3Si$); 1.3 [64.6] (MeSi); 106.4 [96.9, 11.6] (≡C–Si); 119.2 [72.7, 16.6] (≡C–$SiMe_3$). $^{29}Si$ NMR (99.6 MHz, $CDCl_3$): $\delta[^3J(^{29}Si, ^{29}Si)] = -23.3$ [1.8] (MeSi); −17.0 [1.8] ($Me_3Si$).

Trichloro(trimethylsilylethynyl)silane: b.p. 37–38 °C/$10^{-3}$ Torr; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 0.07$ (s, 9H, $Me_3Si$). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta[^1J(^{29}Si, ^{13}C)] = -0.7$ [56.7] ($Me_3Si$); 102.0 [160.7, 11.2] (≡C–$SiCl_3$); 120.5 [68.2, 26.7] (≡ C–$SiMe_3$). $^{29}Si$ NMR (99.6 MHz, $CDCl_3$): $\delta = -33.3$($SiCl_3$); −14.5($Me_3Si$).

## Reduction of the chlorosilanes

The solution of the respective chlorosilane (3–6 mmol) in diethyl ether (15 ml) was added slowly to a suspension of an excess of $LiAlH_4$ in $Et_2O$ (25 ml) at 0 °C. After continued stirring for 1 h, the reaction mixture was quenched with aqueous HCl (10%) and extracted with $Et_2O$; the organic

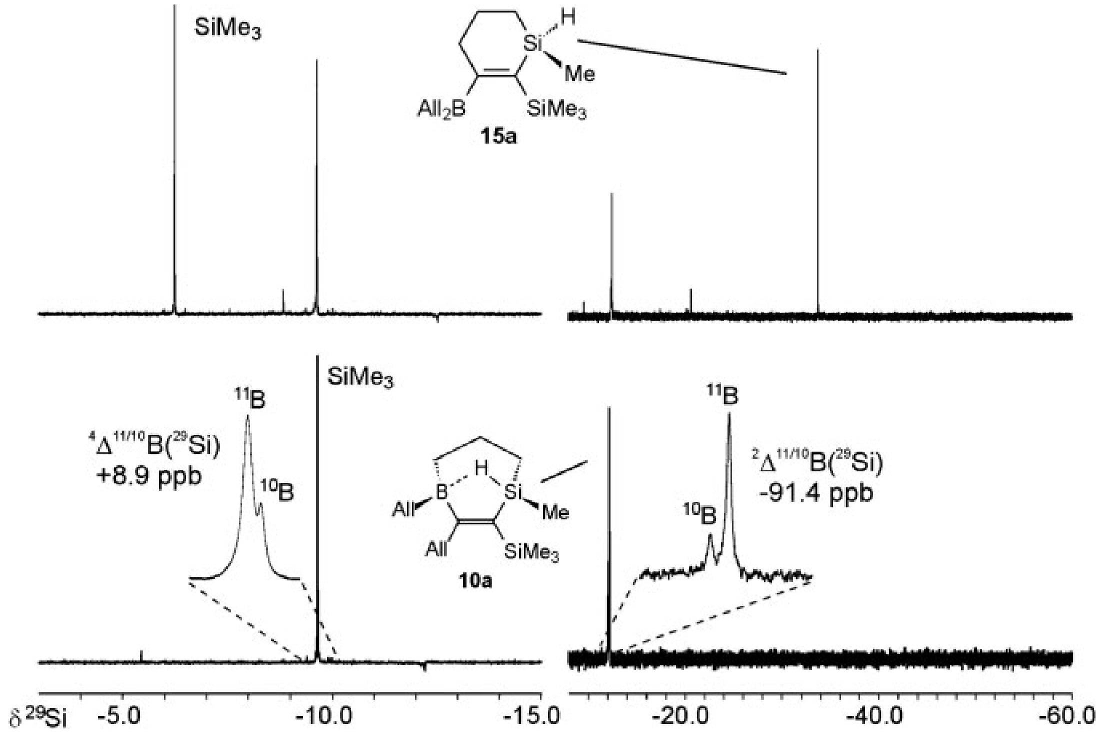


**Figure 3.** The 99.6 MHz $^{29}$Si{$^1$H} NMR spectra of almost pure **10a** (lower trace) and a mixture containing mainly **10a** and **15a** (upper trace; after heating of **10a** at 80 °C for 6 h), recorded by using the refocused INEPT pulse sequence[27–30] based on $^2J(^{29}\text{Si}, ^1\text{H}_{\text{Me}})$ (SiMe$_3$ groups) and $^1J(^{29}\text{Si}, ^1\text{H})$ (SiH$_2$ groups). Heating of **10a** leads to rearrangement into **15a** by 1,1-deallylboration. In the case of **10a**, we note again (see Fig. 1) the isotope-induced chemical shift $^2\Delta^{10/11}\text{B}(^{29}\text{Si})$, typical of the Si–H–B bridge. Furthermore, another long-range isotope-induced shift $^{3,4}\Delta^{10/11}\text{B}(^{29}\text{Si})$ is detected (positive sign!), which is transmitted either through the C=C bond (across three bonds) or via the B–H–Si bridge (across four bonds). This small effect is frequently observed if such a bridge is present, and has not been detected so far in the absence of this bridge. Thus, it is not observed in the case of **15a**.

layer was washed twice with water, dried with Na$_2$SO$_4$ and the silanes were obtained by fractional distillation (see also Table 1 for other NMR data).

**2c**: b.p. 18–120 °C/10$^{-3}$ Torr; $^1$H NMR: $\delta = 0.66$ (s, 9H, Me$_3$Si); 7.8–8.1 (m, 10H, Ph).

**3a**: b.p. 59–60 °C/15 Torr; $^1$H NMR: $\delta = 0.17$ (s, 9H, Me$_3$Si); 0.28 (t, 3H. MeSi). IR: $\nu = 2159$ cm$^{-1}$ (br, Si–H), 2093 cm$^{-1}$ (C≡C).

**4a**: b.p. 30–35 °C/15 Torr; $^1$H NMR: $\delta = 0.11$ (s, 9H, Me$_3$Si). IR: $\nu = 2177$ cm$^{-1}$ (br, Si–H), 2098 cm$^{-1}$ (C≡C).

## Reaction of the bis(silyl)ethynes 2, 3 and 4 with triallylborane 1; general procedure

To a solution of the bis(silyl)ethyne (1–2 mmol) in CDCl$_3$ or C$_6$D$_6$ (0.6 ml) was added an equimolar amount of **1** in one portion at room temperature. Then the mixture was kept at room temperature for 6–10 h, and the progress of the reactions was monitored by $^1$H and $^{29}$Si NMR spectroscopy.

**5b**: $^1$H NMR: $\delta = 0.30$ (s, 9H, Me$_3$Si); 1.07 (m, 2H, CH); 1.16 (d, 6H, CH$_3$); 1.18 (d, 6H; CH$_3$); 2.23 (d, 4H, CH$_2$B); 3.23 (dt, 2H, CH$_2$); 5.0–5.1 (m, 6H, =CH$_2$); 5.81 (ddt, 1H, =CH); 6.19 (ddt, 2H, =CH).

**5c**: $^1$H NMR: $\delta = 0.28$ (s, 9H, Me$_3$Si); 2.21 (dd, 2H, CH$_2$B); 2.31 (dd, 2H, CH$_2$B); 3.46 (d, 2H, CH$_2$); 4.9–5.2 (m, 6H, =CH$_2$); 5.9–6.2 (m, 3H, =CH); 7.5–7.6 (m, 6H, Ph); 7.8–7.9 (m, 4H, Ph).

**5d**: $^1$H NMR: $\delta = 2.31$ (d, 4H, CH$_2$B); 3.33 (dt, 2H, CH$_2$); 5.0–5.2 (m, 6H, =CH$_2$); 5.6–6.0 (m, 3H, =CH); 7.3–7.8 (m, 20H, Ph).

**6c**: $^1$H NMR: $\delta = 0.30$ (s, 9H, Me$_3$Si); 2.08 (d, 4H, CH$_2$B); 3.19 (d, 2H, CH$_2$); 4.9–5.2 (m, 6H, =CH$_2$); 5.9–6.2 (m, 3H, =CH); 7.5–7.6 (m, 6H, Ph); 7.8–7.9 (m, 4H, Ph).

**8a**: $^1$H NMR: $\delta = 0.25$ (s, 9H, Me$_3$Si); 0.28 (t, 3H, MeSi); 2.14 (m, 4H; CH$_2$B), 3.08 (dt, 2H, CH$_2$); 4.9–5.1 (m, 6H, =CH$_2$); 5.7–6.0 (m, 3H, =CH).

**9a**: $^1$H NMR: $\delta = 0.08$ (s, 9H, Me$_3$Si); 0.27 (t, 3H, MeSi); 2.25 (br, 4H, CH$_2$B); 3.12 (dt, 2H, CH$_2$); 4.9–5.1 (m, 6H, =CH$_2$); 5.7–6.0 (m, 3H, =CH).

**11a**: assignment of $^1$H NMR spectra uncertain because of low concentration in mixture with **12a** and fast rearrangement into **13a**.

**12a**: $^1$H NMR: $\delta = 0.22$ (s, 9H, Me$_3$Si); 2.27 (br, 4H, CH$_2$B); 3.10 (d, 2H, CH$_2$); 5.0–5.2 (m, 6H, =CH$_2$); 5.75 (ddt, 1H, =CH); 5.97 (ddt, 2H, =CH).

## Conversion of 5, 8, 11 into the 1,4-silabora-2-cycloheptenes 7, 10 and 13

The complete conversion of **5** into **7** required gentle heating of the reaction solutions at 50–60 °C for 2 h. In contrast, the intramolecular hydrosilylation of **8** or **11** took place already slowly (**8**) or rather fast (**11**) at room temperature.

**7b**: $^1$H NMR signals were not assigned with certainty, since partial rearrangement into **14b** took place.

**7c**: >98% yield; $^1$H NMR: $\delta = 0.22$ (s, 9H, $Me_3Si$); 1.42 (t, 2H, $CH_2Si$); 1.55 (t, 2H, $CH_2B$); 2.06 (m, 2H, $CH_2$); 2.15 (d, 2H, $CH_2B$); 3.69 (d, 2H, $CH_2$); 5.0–5.3 (m, 4H, $=CH_2$); 5.9–6.2 (m, 2H, $=CH$); 7.5–7.9 (m, 10H, Ph).

**7d**: >98% yield; $^1$H NMR: $\delta = 1.54$ (t, 2H, $CH_2Si$); 1.61 (t, 2H, $CH_2B$); 1.92 (d, 2H, $CH_2B$); 2.25 (tt, 2H, $CH_2$); 3.47 (d, 2H, $CH_2$); 4.8–5.2 (m, 4H, $=CH_2$); 5.10 (s, 1H, SiH, $^1J(^{29}Si, ^1H) = 198.6$ Hz); 5.69 (ddt, 1H, $=CH$); 6.12 (ddt, 1H, $=CH$); 7.4–7.9 (m, 20H, Ph).

**10a**: >96% yield (see Fig. 2); $^1$H NMR: $\delta = 0.20$ (d, 3H, MeSi); 0.23 (s, 9H, $Me_3Si$); 0.67 (m, 1H, H-5); 0.82 (m, 1H, H-5); 1.11 (m, 1H, H-7); 1.31 (m, 1H, H-7); 1.73 (m, 1H, H-6); 1.85 (m, 1H, H-6); 2.12 (dd, 1H, $CH_2B$); 2.20 (dd, 1H, $CH_2B$); 3.22 (dt, 2H, $CH_2$); 3.77 (m, 1H, SiH, $^1J(^{29}Si, ^1H) = 164.7$ Hz); 4.92 (m, 2H, $=CH_2$); 4.99 (ddt, 1H, $=CH_2$); 5.04 (ddt, 1H, $=CH_2$); 5.71 (ddt, 1H, $=CH$); 5.96 (m, 1H, $=CH$). IR: $\nu(Si{-}H) = 2121$ cm$^{-1}$ (broad).

**13a**: >96% yield; $^1$H NMR : $\delta = 0.40$ (s, 9H, $Me_3Si$); 0.93 (m, 2H, H-3); 1.42 (m, 2H, H-1); 1.93 (m, 2H, H-2); 2.33 (d, 2H, $CH_2B$); 3.35 (dt, 2H, $CH_2$); 4.28 (t, 2H, $SiH_2$ $^1J(^{29}Si, ^1H) = 186.1$ Hz); 5.0–5.2 (m, 4H, $=CH_2$); 5.7–6.1 (m, 2H, $=CH$).

## 1,1-Deallylboration of 7, 10 and 13 to 3-diallylboryl-1-sila-cyclo-2-hexenes 14–16

Heating of the $C_6D_6$ solutions of 1,4-silabora-2-cycloheptenes **7**, **10** and **13**, at 70–80 °C for 24–36 h (<1 h in the case of **5b**/**7b**), 12–15 h and 6–10 h respectively, gave 50–95% conversion into the 1-sila-cyclo-2-hexenes **14**–**16**.

**14b**: 30 h at 80 °C; conversion >90%; $^1$H NMR : $\delta = 0.08$ (s, 9H, $Me_3Si$); 0.72 (m, 2H, H-6); 1.0–1.3 (m, 14H, $^i$Pr); 1.67 (m, 2H, H-5); 1.75 (m, 2H, H-4); 2.1 (m, 4H, $CH_2B$); 4.9–5.2 (m, 4H, $=CH_2$); 6.02 (m, 2H, $=CH$).

**15a**: 15 h at 70 °C; conversion >90%; $^1$H NMR : $\delta = 0.09$ (s, 9H, $Me_3Si$); 0.22 (d, 3H, MeSi); 0.71 (m, 1H, H-6); 0.97 (m, 1H, H-6); 1.76 (m, 1H, H-5); 1.87 (m, 1H, H-5); 2.2 (m, 4H, $CH_2B$); 2.27 (m, 2H, H-4); 4.18 (m, 1H, SiH, $^1J(^{29}Si, ^1H) = 182.9$ Hz); 4.9–5.1 (m, 4H, $=CH_2$); 5.99 (m, 2H, $=CH$).

**16a**: 8 h at 70 °C; conversion >90%; $^1$H NMR : $\delta = 0.26$ (s, 9H, $Me_3Si$); 0.97 (m, 2H, H-6); 1.75 (m, 2H, H-5); 1.82 (m, 2H, H-4); 2.26 (d, 4H, $CH_2B$); 4.36 (t, 2H, $SiH_2$, $^1J(^{29}Si, ^1H) = 188.3$ Hz); 5.0–5.2 (m, 4H, $=CH_2$); 6.0 (m, 2H, $=CH$).

## Acknowledgements

Support of this work by Volkswagen-Stiftung, Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

## REFERENCES

1. Mikhailov BM, Bubnov YuN. *Organoboron Compounds in Organic Synthesis*. Harwood: Chur, 1984.
2. Bubnov YuN. *Pure Appl. Chem.* 1988; **59**: 895.
3. Bubnov YuN, Gurski ME, Gridnev ID, Ignatenko AV, Ustynyuk YuA, Mstislavsky VI. *J. Organometal. Chem.* 1992; **424**: 127.
4. Wrackmeyer B, Tok OL, Bubnov YuN. *J. Organometal. Chem.* 1999; **580**: 234.
5. Wrackmeyer B, Bhatti MH, Ali S, Tok OL, Bubnov YuN. *J. Organometal. Chem.* 2002; **657**: 146.
6. Wrackmeyer B, Tok OL, Klimkina E, Bubnov YuN. *Inorg. Chim. Acta* 2000; **300–302**: 169.
7. Wrackmeyer B, Tok OL. Bubnov YuN. *Angew. Chem.* 1999; **111**: 214; *Angew. Chem. Int. Ed. Engl.* 1999; **38**: 124.
8. Wrackmeyer B. *Coord. Chem. Rev.* 1995; **145**: 125.
9. Wrackmeyer B, Horchler K, Boese R. *Angew. Chem.* 1989; **101**: 1563; *Angew. Chem. Int. Ed. Engl.* 1989; **28**: 1500.
10. Wrackmeyer B, Kehr G, Boese R. *Angew. Chem.* 1991; **103**: 1374; *Angew. Chem. Int. Ed. Engl.* 1991; **30**: 1370.
11. Wrackmeyer B, Kundler S, Boese R. *Chem. Ber.* 1993; **126**: 1361.
12. Wrackmeyer B, Kundler S, Milius W, Boese R. *Chem. Ber.* 1994; **127**: 333.
13. Wrackmeyer B, Horchler von Locquenghien K, Kundler S. *J. Organometal. Chem.* 1995; **503**: 289.
14. Davidsohn WE, Henry MC. *Chem. Rev.* 1967; **67**: 73.
15. Lang H, Lay U. *Z. Anorg. Allg. Chem.* 1991; **596**: 17.
16. Shergina NL, Sherstyannikova LV, Kuznetsov AL, Yarosh OG, Mirskov RG, Voronkov MG. *Izv. Akad. Nauk SSSR Ser. Khim.* 1985; 2716.
17. Petrov AD, Shchukovskaya LL. *Zhur. Obshch. Khim.* 1955; **25**: 1128.
18. Wrackmeyer B, Milius W, Tok OL. *Chem. Eur. J.* 2003; 4732.
19. Wrackmeyer B, Tok OL. *Magn. Reson. Chem.* 2002; **40**: 406.
20. Marciniec B. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd edition, Cornils B, Herrmann WA (eds). Wiley–VCH: Weinheim, 2002; 491–512.
21. Ojima I. In *Chemistry of Organic Silicon Compounds*, vol. 2 Patai S, Rappaport Z (eds). Wiley: Chichester, 1989; 1479–1536.
22. Kogure T. *Rev. Silicon Germanium Tin Lead Compd.* 1981; **5**: 7.
23. Roesler R, Har BJN, Piers WE. *Organometallics* 2002; **21**: 4300.
24. Rubin M, Schwier T, Gevorgyan V. *J. Org. Chem.* 2002; **67**: 1936.
25. Weinmann M, Kamphowe TW, Schuhmacher J, Mueller K, Aldinger F. *Chem. Mater.* 2000; **12**: 2112.
26. Parks DJ, Piers WE. *J. Am. Chem. Soc.* 1996; **118**: 9440.
27. Morris GA, Freeman R. *J. Am. Chem. Soc.* 1979; **101**: 760.
28. Morris GA. *J. Am. Chem. Soc.* 1980; **102**: 428.
29. Burum DP, Ernst RR. *J. Magn. Reson.* 1980; **39**: 163.
30. Schraml J. In *The Chemistry of Organic Silicon Compounds*, vol. 3 Rappoport Z, Apeloig Y (eds). Wiley: Chichester, 2001; 223–339.
31. Wrackmeyer B, Tok OL. In preparation.
32. Wrackmeyer B. *Prog. NMR Spectrosc.* 1979; **12**: 227.
33. Wrackmeyer B. *Annu. Rep. NMR Spectrosc.* 1988; **20**: 61.
34. Wrackmeyer B. *Polyhedron* 1986; **5**: 1709.
35. Topchiev AV, Prokhorova AA, Paushkin YaM, Kurashev MV. *Izv. Akad. Nauk SSSR Ser. Khim.* 1958; 370.
36. Schroeder VS, Thiele K-H. *Z. Anorg. Allg. Chem.* 1977; **428**: 225.