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 arylythyn-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 \( \text{C}\equiv\text{C} \) 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-silaboracyclohept-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 \( ^1\text{H}, ^{11}\text{B}, ^{13}\text{C} \) and \( ^{29}\text{Si} \) NMR data.

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

Introduction

Triallylborane, \( \text{B(CH-CH=CH}_2\text{)}_3 \) 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 successfully 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 \( \text{C}\equiv\text{C} \) 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.
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)methylsilane [11] with LiAlH₄ afforded the dihydride 3a, and the analogous reaction of the alkyn-1-yl-trichlorosilanes [12] gave the trihydrides 4a, b (Scheme 2).

![Scheme 2. Reduction of alkyn-1-yl(chloro)silanes with LiAlH₄.](image)

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 triallylboration**

The alkyn-1-ylsilanes 2a, b, c react readily with triallylboration 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.

![Scheme 3. Allylboration of alkyn-1-yl(hydrido)silanes.](image)
Table 3. Selected NMR data<sup>a</sup> for the alkenes 5a,b, 9a and 13a.

<table>
<thead>
<tr>
<th>δ&lt;sup&gt;29&lt;/sup&gt;Si</th>
<th>δ&lt;sup&gt;11&lt;/sup&gt;B</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(2)&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(C−2)&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(C−5)&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(C−6)&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(C−7)&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a &lt;sup&gt;a&lt;/sup&gt;</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = n-Bu</td>
<td>−2.3 (−73.0)</td>
<td>67.6</td>
<td>3.26 [160.5]</td>
<td>135.3 [64.4]</td>
<td>160.2 br</td>
</tr>
<tr>
<td>6b</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = Ph</td>
<td>−9.5 (−49.4)</td>
<td>57.3</td>
<td>3.71 [168.8]</td>
<td>138.4 [66.7]</td>
<td>161.4 br</td>
</tr>
<tr>
<td>9a</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = n-Bu</td>
<td>−33.7 (−29.1)</td>
<td>78.4</td>
<td>3.99 [184.0]</td>
<td>133.0 [68.1]</td>
<td>161.3 br</td>
</tr>
<tr>
<td>13a</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = n-Bu</td>
<td>−63.2 (9.9)</td>
<td>79.2</td>
<td>3.76 [n. o.]</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub> at RT; coupling constants in Hz; isotope-induced chemical shifts<sup>2</sup>Δ<sup>10−11</sup>B(29Si) in p.p.m. 

Table 4. Selected NMR data<sup>a</sup> for the alkenes 6a–c, 10a and 14a,b (1,2-allylboration products).

<table>
<thead>
<tr>
<th>δ&lt;sup&gt;29&lt;/sup&gt;Si</th>
<th>δ&lt;sup&gt;11&lt;/sup&gt;B</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(2)&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(C−2)&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(C−5)&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = n-Bu</td>
<td>−32.3</td>
<td>81.3</td>
<td>4.25 [194.7]</td>
</tr>
<tr>
<td>6b</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = Ph</td>
<td>−30.6</td>
<td>81.0</td>
<td>3.92 [194.4]</td>
</tr>
<tr>
<td>6c</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = p-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;OMe</td>
<td>−30.8</td>
<td>80.9</td>
<td>3.92 [193.8]</td>
</tr>
<tr>
<td>7a</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = n-Bu</td>
<td>−53.3</td>
<td>78.9</td>
<td>4.18 [191.4]</td>
</tr>
<tr>
<td>7b</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; = Ph</td>
<td>−79.0</td>
<td>81.2</td>
<td>3.80 [198.7]</td>
</tr>
<tr>
<td>14a,b</td>
<td>—</td>
<td>−75.4</td>
<td>81.2</td>
<td>3.79 [201.8]</td>
</tr>
</tbody>
</table>

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub> at RT; coupling constants in Hz; <sup>13</sup>C resonances are not assigned due to low concentration; br indicates broadening due to partially relaxed<sup>13</sup>C<sup>−</sup>11B spin-spin coupling; <sup>13</sup>C NMR: δ = −2.9 [51.5] (SiMe<sub>2</sub>); 36.0 (br), 113.7, 136.7 (AlbB); 47.4 [7.6], 118.3, 134.8 (Alb); 127.7, 128.2, 128.6, 144.8 [5.1] (Ph); other<sup>13</sup>C NMR: δ = −2.9 [51.5] (SiMe<sub>2</sub>); 35.9 (br), 113.5, 136.7 (AlbB); 47.5 [7.6], 118.0, 134.8 (Alb); 55.0 (MeO); 113.0, 129.3, 137.3, 158.4 (C<sub>6</sub>H<sub>4</sub>).

Table 5. Selected NMR data<sup>a</sup> of 1-bora-4-silacyclohept-2-enes 7a,b and 11a.

<table>
<thead>
<tr>
<th>δ&lt;sup&gt;29&lt;/sup&gt;Si</th>
<th>δ&lt;sup&gt;11&lt;/sup&gt;B</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(2)&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(C−2)&lt;/sub&gt;</th>
<th>δ&lt;sup&gt;13&lt;/sup&gt;C&lt;sub&gt;(C−5)&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>R = Me, R&lt;sup&gt;1&lt;/sup&gt; = n-Bu</td>
<td>−4.6</td>
<td>81.3</td>
<td>148.2 [63.7]</td>
</tr>
<tr>
<td>7b</td>
<td>R = Me, R&lt;sup&gt;1&lt;/sup&gt; = Ph</td>
<td>−4.9</td>
<td>81.3</td>
<td>151.1 [61.5]</td>
</tr>
<tr>
<td>11a</td>
<td>R = H, R&lt;sup&gt;1&lt;/sup&gt; = n-Bu</td>
<td>−17.6</td>
<td>81.2</td>
<td>146.2 [64.4]</td>
</tr>
</tbody>
</table>

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub> at RT; coupling constants in Hz; br indicates broadening due to partially relaxed<sup>13</sup>C<sup>−</sup>11B spin-spin coupling; <sup>13</sup>C NMR: δ = −0.3 [51.5] (SiMe<sub>2</sub>); 34.4 (br), 114.2, 137.6 (AlbB); 37.6 [6.7], 114.8, 135.8 (Alb); 127.0, 127.6, 127.9, 144.3 (Ph); other<sup>13</sup>C NMR: δ = −2.1 [49.4] (SiMe); 14.3, 23.8, 33.4, 35.9 (n-Bu); 35.8 (br), 114.6, 138.2 (AlbB); 41.4 [10.3], 116.4, 136.8 (Alb).

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<sup>11</sup>B nuclear shielding when compared with similar triorganoboranes [13], a decrease in<sup>29</sup>Si nuclear shielding relative to similar alkylsilanes [14], and the magnitude of<sup>13</sup>C<sub>(2)</sub> is reduced, typical of the Si-H-B bridge [5, 6, 9]. Furthermore, the isoce-o-induced chemical shift<sup>2</sup>Δ<sup>10−11</sup>B(29Si), 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<sup>13</sup>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{\textsuperscript{1}H} 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{\textsuperscript{1}H} 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 dataa for 1-bora-cyclohex-2-enes 8b, 12a and 15a.b.

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

a In C₆D₆ at RT; coupling constants in Hz; br indicates broadening due to partially relaxed^{29}Si-{^{13}C} spin-spin coupling; b other ^{13}C NMR signals: δ = -2.1 [51.0], -1.2 [50.5] (SiMe₂); 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{^{1}H} 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 alkyne1-yl(dihydrido)silanes.
(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 alkyne-1-yl(trihydrido)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.

**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.

**Conclusions**

In the title reaction, there is competition between 1,1- and 1,2-allylboration, and the latter dominates for R1 = Ph and p-MeO-C6H4, 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 R¹, and in all these cases electron-deficient Si-H-B bridges are present. The boryl-induced Si-H-activation leads to intramolecular hydroisilylation under exceptionally mild reaction conditions. The combination of 1,1-allylaboration and hydroisilylation 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 by using carefully dried solvents. Starting materials such as triallylborane I [20] and silicon monohydrides 2 were prepared according to literature procedures. NMR measurements: Bruker ARX 250 and DRX 500 NMR spectrometers (¹H, ¹³C, ²⁹Si NMR (refocused INEPT [21] based on ¹J(²⁹Si,¹H)H = 7 or ¹J(²⁹Si,¹H)H = 200 Hz)). The NMR spectra were measured for solutions (5–10%) in C₅D₆ at 23 °C, if not noted otherwise. Chemical shifts are given with respect to Me₄Si [noted otherwise. Chemical shifts are given with respect to Me₄Si]. Ξ(¹H,¹H) = 3.2 Hz; 0.70, 1.00–1.20, 2.23 (t, m, m, 3H, 4H, 2H, n-Bu); 4.90 (q, 1H, SiH, 2H, n-Bu); 2.3 (m, 3H, 4H, 2H, n-Bu); 5.80–6.20 (m, 3H, BAll 2, All); 7.30–7.60 (m, 5H, Ph).


n-Hexyl-1-yl-trichlorosilane: b. p. 40–42 °C/10⁻³ Torr. ¹H NMR (500 MHz; CDCl₃; 23 °C): δ = 0.95, 1.46, 1.60, 2.38 (t, m, m, m, 3H, 2H, 2H, n-Bu); ¹³C NMR (125.8 MHz; CDCl₃; 23 °C; [J(²⁹Si,¹³C)]) = 13.4; 19.5; 21.9; 29.5 (n-Bu); 77.4 [177.1] (≡C-Si); 113.6 [35.3] (≡C-n-Bu). ²⁹Si NMR (99.6 MHz, CDCl₃): δ = −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 LiAlH₄ in Et₂O at 0 °C. After 1 h the reaction mixture was quenched with aqueous HCl (10%), and extracted with Et₂O, and the organic layer was washed twice with water and dried with Na₂SO₄. The purity of the silanes was checked, and the silanes were purified, if necessary, by fractional distillation.

2c: ¹H NMR: δ = 0.40 (d, 6H, Me₂Si; ³J(H,H) = 3.8 Hz); 3.85 (s, 3H, MeO); 7.49 (m, 2H, C₆H₄). ¹³C NMR: δ = 0.25 (t, 3H, Me₂Si; ³J(H,H) = 4.2 Hz). Ξ(¹H,¹H) = 0.90, 1.20–1.40, 2.23 (t, m, m, 4H, 2H, n-Bu). IR: ν(Si-H) = 2151 cm⁻¹, ν(C≡C) = 2180 cm⁻¹.

4a: ¹H NMR: δ = 0.69, 1.00–1.20, 1.89 (t, m, m, 3H, 4H, 2H, n-Bu) [22]. IR: ν(Si-H) = 2171 cm⁻¹. ¹³C NMR: δ = 7.3–7.6 (m, 5H, Ph).

Reaction of the alkyn-1-ylsilanes 2, 3 and 4 with trialllylorane I. General procedure: To a solution of the alkyn-1-ylsilane (1–2 mmol) in CDCl₃ or C₅D₆ (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 ¹H and ²⁹Si NMR spectroscopy.

5a: ¹H NMR: δ = 0.26 (d, 6H, Me₂Si; ³J(H,H) = 3.4 Hz); 1.32, 1.40, 2.23 (t, m, m, 3H, 2H, 2H, n-Bu); 2.12 (d, 4H, BAll₂); 2.93 (dt, 2H, All); 4.9–5.1 (m, 6H, BAll₂, All); 5.76 (ddt, 1H, All). ¹³C NMR: δ = 7.6 (s, 3H, All); 13.6 (m, 3H, 2H, n-Bu); 21.9 (t, 3H, MeSi, 3;J(H,H) = 3.4 Hz); 2.37 (d, 4H, BAll₂); 2.91 (dt, 2H, All); 5.00–5.20 (m, 6H, BAll₂, All); 5.80–6.20 (m, 3H, BAll₂, All); 7.30–7.60 (m, 5H, Ph).

5b: ¹H NMR: δ = 0.24 (d, 6H, Me₂Si; ³J(H,H) = 3.4 Hz); 2.37 (d, 4H, BAll₂); 2.91 (dt, 2H, All); 5.00–5.20 (m, 6H, BAll₂, All); 5.80–6.20 (m, 3H, BAll₂, All); 7.30–7.60 (m, 5H, Ph).

6b: ¹H NMR: δ = −0.04 (d, 6H, Me₂Si; ³J(H,H) = 4.0 Hz); 2.41 (d, 4H, BAll₂); 3.09 (dd, 2H, All); 5.00–5.20 (m, 6H, BAll₂, All); 5.85 (ddt, 1H, All); 6.04 (ddt, 2H, BAll₂); 7.30–7.60 (m, 5H, Ph).

6c: ¹H NMR: δ = −0.05 (d, 6H, Me₂Si; ³J(H,H) = 4.0 Hz); 2.37 (d, 4H, BAll₂); 3.04 (dd, 2H, All); 3.88 (s, 3H, MeO); 5.0–5.1 (m, 6H, BAll₂, All); 5.81 (ddt, 1H, All); 6.12 (ddt, 2H, BAll₂); 6.93 (m, 2H, C₆H₄); 7.20 (m, 2H, C₆H₄).

9a: ¹H NMR: δ = 0.29 (t, 3H, MeSi, ³J(H,H) = 4.0 Hz); 1.0; 1.40–1.60, 2.3 (t, m, m, m, 3H, 4H, 2H, n-Bu); 2.3 (m, 4H, BAll₂); 2.98 (dt, 2H, All); 5.0–5.2 (m, 6H, BAll₂, All); 5.8–6.1 (m, 3H, BAll₂, All).
Constitution of the alkenes 5 and 9 into 1,4-silabicyclohept-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: 1H NMR: δ = 0.05 (s, 6H, MesSi); 0.72 (m, 2H, C5H2); 0.95, 1.20 – 1.40, 2.28 (t, m, m, 3H, 4H, 2H, n-Bu); 1.20 – 1.40 (m, 1H, C5H2, n-Bu); 1.78 (m, 2H, C5H2); 2.20 (dt, 2H, BAll); 3.14 (dt, 2H, All); 4.90 – 5.00 (m, 4H, BAll, All); 5.73, 5.95 (ddt, ddt, 1H, 1H, BAll, All, Ph).

7b: 1H NMR: δ = 0.03 (s, 6H, MesSi); 0.90 (m, 2H, C5H2); 1.39 (m, 2H, C5H2); 1.68 (m, 2H, C5H2); 2.23 (dd, 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: 1H NMR: δ = 0.23 (d, 3H, MesSi, 3J(H,H) = 4.0 Hz); 0.73, 1.10 (m, m, 1H, 1H, C5H2); 1.04, 1.40 – 1.60, 2.43 (t, m, m, 3H, 4H, 2H, n-Bu); 1.40 – 1.60 (m, 2H, C5H2); 1.92 (m, 2H, C5H2); 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-allylboronation 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 CsD6 for 12 h at 70 – 80 °C leads to the formation of 1-boracyclohex-2-enes 8, 12 and 15 together with bicyclic products (vide infra).

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

8b: 1H NMR: δ = 0.15, 0.22 (d, d, 3H,2H MesSi, 3J(H,H) = 3.8 Hz); 0.75, 1.42 (dd, dd, 1H, 1H, C5H2); 2.07 (m, 1H, C5H2); 2.20 (m, 2H, BAll); 2.28, 2.76 (dd, 1H, 1H, C5H2); 2.37 (m, 2H, BAll); 4.30 (sp, 1H, SiH, 3J(H,H) = 3.8 Hz, 1J(29Si,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).

10a: 1H NMR: δ = 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, BAll2); 2.74 (d, 2H, All); 5.00 – 5.20 (m, 6H, BAll2, All); 5.81 (m, 1H, All); 6.06 (m, 2H, BAll).

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

14a: 1H NMR: δ = 1.05, 1.47, 1.56, 2.32 (t, m, m, 3H, 2H, 2H, n-Bu); 2.26 (d, 4H, BAll2); 2.85 (d, 2H, All); 5.00 – 5.20 (m, 6H, BAll2, All); 5.85 (ddd, 1H, All); 5.99 (ddd, 2H, BAll).

14b: 1H NMR: δ = 2.38 (d, 4H, BAll2); 3.1 (d, 2H, All); 3.84 (s, 3H, SiH3, 1J(29Si,1H) = 201.0 Hz); 5.00 – 5.20 (m, 6H, BAll2, All); 5.86 (ddd, 1H, All); 6.16 (ddd, 2H, BAll2); 7.00 – 7.20 (m, 5H, Ph).

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

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