Reactivity of Triethylborane towards Di(alkyn-1-yl)(chloro)silanes. 
Competition between 1,1-Organoboration and 1,2-Hydroboration

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

Reactions of di(alkyn-1-yl)(chloro)silanes, HSi(Cl)(C≡C-R)₂, R¹Si(Cl)(C≡C-R)₂ or HSi(Cl)-(C≡C-R)C≡C-R’, with an excess of triethylborane, BEt₃, proceed slowly (several days) at 100 – 120 °C. Twofold 1,1-organoboration of HSi(Cl)(C≡C-R)₂ or HSi(Cl)(C≡C-R)C≡C-R’ leads to siloles, independent of R = ’Bu, ’Bu, SiMe₃. This provides the most straightforward way to siloles bearing both a hydrogen and a chlorine at the silicon atom. However, in the cases of R = Ph, BEt₃ acts as 1,2-hydroborating reagent in the intermolecular first step of the reaction, leading to 1-silacyclobuten derivatives. All siloles and 1-silacyclobuten derivatives were characterized by multinuclear NMR spectroscopy (¹H, ¹¹B, ¹³C and ²⁹Si). Comparable 1-silacyclobutene derivatives were formed using 9-borabicyclo[3.3.1]nonane, 9-BBN, as a well established 1,2- hydroborating reagent.

Key words: Triethylborane, Siloles, Silacyclobutene, Hydroboration, Organoboration, NMR

Introduction

Triethylborane, BEt₃, is a commercial reagent and has found widespread applications [1]. In our studies on 1,1-organoboration [2], BEt₃ has been extensively used for 1,1-ethylboration reactions of alkyn-1-yl metal derivatives to form new C–C bonds, both for the synthesis of non-cyclic and cyclic compounds. Among the latter, a variety of siloles [2 – 6] became readily accessible [Scheme 1(a)], circumventing other much more tedious synthetic procedures. These particular 1,1-organoboration reactions require prolonged periods (several days) of heating at elevated temperature (100 – 120 °C) and proceed in two steps. The first step involves intermolecular 1,1-ethylboration, followed in the second step by intramolecular 1,1-vinylboration. Triethylborane, BEt₃, has been considered as thermally stable [7 – 12], and 1,2-dehydroboration, leading to the in situ formation of Et₃BH and elimination of ethene, has never been observed, in contrast with many other trialkylboranes [7, 11, 12]. Recently we have explored the influence of Si–Cl functions in alkyn-1-yl(chloro)silanes on the course of 1,1-ethylboration reactions. It has been shown that reactions of BEt₃ with some alkyn-1-yl(trichloro)silanes [13] and alkyn-1-yl(dichloro)silanes [14] afford exclusively alkenes via 1,2-dehydroboration instead of alkenes expected for 1,1-ethylboration. Moreover, di(alkyn-1-yl)(dichloro)silanes react with BEt₃ to give 1-silacyclobutene derivatives [13] as the result of consecutive 1,2-hydroboration and intramolecular 1,1-vinylboration [Scheme 1(b)].

In this work, we report on the reactivity of di(alkyn-1-yl)(chloro) silanes (Scheme 2) towards BEt₃ to study the potential competition between 1,1-ethylboration and 1,2-hydroboration. This study was expected to open the way to silole derivatives with hitherto unknown substituent patterns, and also to shed some light on mechanistic implications. The potential 1,2-hydroboration activity of BEt₃ was confirmed by compar-

Scheme 1. Formation of silole (a) or 1-silacyclobutene derivatives (b) using BEt₃.
Scheme 2. Syntheses of di(alkyn-1-yl)(chloro)silanes as starting materials.

Results and Discussion

Synthesis of di(alkyn-1-yl)(chloro)silanes 1 – 6

The di(alkyn-1-yl)(chloro)silanes bearing identical [1 – 3; Scheme 2(a)] or different C=C-R groups [4 – 6; Scheme 2(b)] were prepared by the reactions of the respective trichlorosilane R15SiCl3 with the alkynyl lithium reagents following the literature procedure [15]. Pure samples of silanes 1 – 6 were obtained by fractional distillation. Although some of the di(alkyn-1-yl)(chloro)silanes have already been described [16], fairly complete NMR data sets were missing. Therefore, the NMR data of 1 – 6 were collected (Table 1 and Experimental Section).

Formation of siloles: Reactions of di(alkyn-1-yl)(chloro)silanes 1a – 6c with BEt3

The reaction of the silane 1a with BEt3, carried out at 110 – 120 °C, affords selectively the silole 7a. The analogous products (7b and 7c) are observed for R = 'Bu and SiMe3 (Scheme 3). The reaction of 1d with BEt3 gives a mixture of products. The NMR data (Tables 2 and 3) indicate the presence of the silole 7d and a 1-silacyclobutene (vide infra) as major components (40 – 45 % each) along with several unidentified side products (ca. 15 %). The same reactions were carried out under identical reaction conditions with 2a and 3a. The NMR spectra of the reaction solutions (Table 2 and 3) indicate the presence of siloles with different ratios of the di(alkyn-1-yl)(chloro)silane and BEt3.

and e.g. Fig. 2) revealed the formation of the siloles 8a and 9a.

The silanes 4 – 6 containing different alkynyl-1-yl groups [R ≠ R'; Scheme 2(b)] were treated with BEt3 at 110 – 120 °C. In the case of 4a, 1,1-ethyloboration of the Si–C=C='Bu group occurs more readily than of the Si–C=C='Ph unit (Fig. 3), and in the cases of 5c and 6c, 1,1-ethyloboration of the Si–C=C–SiMe3 units is preferred over C=C='Bu or C=C-Ph groups (Scheme 4). This finding is supported by additional NMR data sets which can be assigned to siloles 13a', 14c' and 15c', present in minor quantities. In addition to the mixture of of di(alkyn-1-yl)(chloro)silanes 1 – 6.

Table 1. 13C and 29Si NMR data of di(alkyn-1-yl)(chloro)silanes 1 – 6.

<table>
<thead>
<tr>
<th>13C (C≡C)</th>
<th>13C (Si–C≡C)</th>
<th>29Si</th>
<th>120.3 [20.0]</th>
<th>111.6, 16.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a*</td>
<td>112.5 [25.9]</td>
<td>77.4</td>
<td>[125.8]</td>
<td>−57.5</td>
</tr>
<tr>
<td>1b*</td>
<td>120.1 [25.1]</td>
<td>75.6</td>
<td>[125.4]</td>
<td>−56.5</td>
</tr>
<tr>
<td>1c*</td>
<td>120.4 [20.0]</td>
<td>103.3</td>
<td>[114.0]</td>
<td>[111.5]</td>
</tr>
<tr>
<td>1d*</td>
<td>109.5 [25.5]</td>
<td>85.5</td>
<td>[124.3]</td>
<td>−55.4</td>
</tr>
<tr>
<td>2a*</td>
<td>110.8 [24.9]</td>
<td>80.1</td>
<td>[122.8]</td>
<td>−34.9</td>
</tr>
<tr>
<td>2b*</td>
<td>108.1 [24.5]</td>
<td>88.3</td>
<td>[121.3]</td>
<td>−32.7</td>
</tr>
<tr>
<td>3a*</td>
<td>109.6 [25.2]</td>
<td>87.2</td>
<td>[126.1]</td>
<td>−42.0</td>
</tr>
<tr>
<td>4a*</td>
<td>112.6 [26.3]</td>
<td>77.4</td>
<td>[126.3, α]</td>
<td>−57.1</td>
</tr>
<tr>
<td>4b*</td>
<td>119.8 [24.7, β]</td>
<td>75.5</td>
<td>[125.2, α]</td>
<td>−57.1</td>
</tr>
<tr>
<td>4c*</td>
<td>113.4 [26.1, β]</td>
<td>76.7</td>
<td>[126.8, α]</td>
<td>−58.8, −16.4</td>
</tr>
<tr>
<td>5a*</td>
<td>119.4 [19.7]</td>
<td>104.2</td>
<td>[114.7]</td>
<td>[111.6, α]</td>
</tr>
<tr>
<td>5b*</td>
<td>85.2</td>
<td>[124.2, α]</td>
<td>103.4</td>
<td>−58.0, −16.3</td>
</tr>
</tbody>
</table>
| a Measured in C6D6: coupling constants J(13C,29Si) [±0.4 Hz] are given in square brackets; * other 13C data: δ = 30.1, 22.1, 19.7, 13.6 ("Bu); " other 13C data: δ = 30.1, 28.3 ("Bu); # other 13C data: δ [J(13C,29Si)] = −1.0 [56.6, SiMe3]; * other 13C data: δ = 121.3, 128.5, 132.6, 130.1 (i, o, m, p, Ph); ‡ other 13C data: δ [J(13C,29Si)] = 5.1 [73.7, Si-Me], 30.2, 22.1, 19.6, 13.6 ("Bu); § other 13C data: δ [J(13C,29Si)] = 4.6 [74.8, Si-Me], 121.8, 132.6, 128.5, 129.8 (i, o, m, p, Ph); ¶ other 13C data: δ [J(13C,29Si)] = 132.6 [99.7], 134.4, 128.7, 131.8 (i, o, m, p, Si-Ph), 121.5, 132.7, 128.5, 130.0 (i, o, m, p, Ph); † other 13C data: δ = 13.6, 19.6, 22.0, 29.9 ("Bu), 28.4, 30.1 ("Bu); ‡ other 13C data: δ [J(31P,13C)] = −0.9 [56.6, SiMe3], 13.5, 19.6, 22.0, 29.8 ("Bu); § other 13C data: δ = −0.9 [56.6, SiMe3], 121.2, 128.5, 132.6, 130.1 (i, o, m, p, Ph); † J(29Si, 29Si).
The siloles bearing identical (7a–d, 8a, 9a) or different (13a, 14c, 15c) substituents at 2 and 5 positions are oily, air and moisture sensitive compounds, and their structures were proposed on the basis of consistent sets of NMR data (Table 2 and Figs. 1, 2, 3).

**Formation of 1-silacyclobutene derivatives: Reactions of di(alkyn-1-yl)(chloro)silanes**

The reaction of 1d with BEt3 gives the silole 7d together with a second major compound, subsequently identified as the 1-silacyclobutene derivative 16d. This result shows that 1,1-ethylboration can be accompanied by competitive reactions which, depending on various substituents, may become dominant, offering an attractive route to novel heterocycles, such as 1-silacyclobutene derivatives. Therefore, the reactions of 2d and 3d with BEt3 are of interest (Scheme 5). NMR spectra of the reaction solutions indicate almost quantitative formation of 1-silacyclobutene derivatives (> 90 %) instead of siloles. In the light of our previous

The siloles, small amounts of the side products 10–12 (Scheme 4) are formed. These products are unsuitable to undergo ring closure via intramolecular 1,1-vinylation. The desired siloles (13–15) are the main components in the reaction mixtures, identified unambiguously by their distinct NMR data.

### Table 2. 11B, 13C and 29Si NMR data of siloles 7 – 9 and 13 – 15.

<table>
<thead>
<tr>
<th></th>
<th>11B</th>
<th>13C (C-2)</th>
<th>13C (C-3)</th>
<th>13C (C-4)</th>
<th>13C (C-5)</th>
<th>29Si</th>
<th>31B</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>135.3 [73.1]</td>
<td>169.1 (br)</td>
<td>157.2 [15.7]</td>
<td>131.7 [78.8]</td>
<td>-7.0</td>
<td>89.7</td>
<td></td>
</tr>
<tr>
<td>7b</td>
<td>145.7 [84.1]</td>
<td>166.4 (br)</td>
<td>156.7 [16.9]</td>
<td>139.3 [76.9]</td>
<td>-5.8</td>
<td>87.5</td>
<td></td>
</tr>
<tr>
<td>7c</td>
<td>139.9 [48.3] [63.3]</td>
<td>186.9 (br)</td>
<td>173.3 [10.2] [12.7]</td>
<td>132.3 [55.6] [61.9]</td>
<td>9.8, -10.2, -9.8</td>
<td>87.1</td>
<td></td>
</tr>
<tr>
<td>7d</td>
<td>141.9 [79.5]</td>
<td>172.1 (br)</td>
<td>159.7 [n. m.]</td>
<td>136.2 [n. m.]</td>
<td>-6.6</td>
<td>86.7</td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>136.6 [72.5]</td>
<td>167.1 (br)</td>
<td>155.4 [15.1]</td>
<td>132.5 [78.1]</td>
<td>16.7</td>
<td>86.1</td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td>136.6 [73.6]</td>
<td>169.0 (br)</td>
<td>157.2 [15.0]</td>
<td>132.7 [79.4]</td>
<td>5.3</td>
<td>86.8</td>
<td></td>
</tr>
<tr>
<td>13a</td>
<td>145.7 [72.0]</td>
<td>164.4 (br)</td>
<td>155.3 [16.9]</td>
<td>132.2 [79.1]</td>
<td>-7.4</td>
<td>89.0</td>
<td></td>
</tr>
<tr>
<td>13b</td>
<td>135.5</td>
<td>168.8 (br)</td>
<td>157.7</td>
<td>139.3</td>
<td>-5.6</td>
<td>89.0</td>
<td></td>
</tr>
<tr>
<td>14a</td>
<td>143.4 [69.2]</td>
<td>169.3 (br)</td>
<td>174.6 [10.7]</td>
<td>126.6 [63.7]</td>
<td>0.8</td>
<td>88.3</td>
<td></td>
</tr>
<tr>
<td>15b</td>
<td>144.3 [70.2]</td>
<td>170.7 (br)</td>
<td>174.5 [11.4] [10.1]</td>
<td>138.7 [57.4] [60.7]</td>
<td>0.9</td>
<td>88.5</td>
<td></td>
</tr>
</tbody>
</table>

* Measured in C6D6, coupling constants corresponding to J(13C,29Si) and J(13C,29Si) are given in square brackets, n. m. means not measured, (br) indicates a broad 13C resonance signal of carbon linked to boron atom owing to partially relaxed 11B–13C spin-spin scalar coupling [21].

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**Scheme 4. Reactions of di(alkyn-1-yl)(chloro)silanes**

H(C=C-R)Si(C=C-R)=C=C-R′ 4–6 (R ≠ R′) with BEt3 to afford mixtures of the respective siloles.
Table 3. 11B, 13C and 29Si NMR data\textsuperscript{a} of alkenyl(alkyn-1-yl)silanes 19 and 20.

<table>
<thead>
<tr>
<th></th>
<th>δ\textsuperscript{11B}</th>
<th>δ\textsuperscript{13C} (BC=)</th>
<th>δ\textsuperscript{13C} (=C)</th>
<th>δ\textsuperscript{13C} (Si–C≡)</th>
<th>δ\textsuperscript{11B}</th>
<th>δ\textsuperscript{29Si}</th>
</tr>
</thead>
<tbody>
<tr>
<td>19\textsuperscript{a,b}</td>
<td>144.0 [73.4, br]</td>
<td>162.2</td>
<td>82.9 [104.9]</td>
<td>110.7 [21.1]</td>
<td>81.9</td>
<td>-15.6</td>
</tr>
<tr>
<td>19\textsuperscript{c}</td>
<td>147.7 [73.7, br]</td>
<td>156.3</td>
<td>91.8 [103.9]</td>
<td>108.2 [20.5]</td>
<td>83.6</td>
<td>-14.6</td>
</tr>
<tr>
<td>20\textsuperscript{d}</td>
<td>144.1 [75.5, br]</td>
<td>158.7</td>
<td>90.2 [109.0]</td>
<td>109.3 [21.3]</td>
<td>84.6</td>
<td>-23.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measured in C\textsubscript{6}D\textsubscript{6}, coupling constants \(J(13C,29Si)\) [±0.4 Hz] are given in square brackets, (br) denotes a broad 13C resonance signal as the result of partially relaxed scalar 11B–13C spin-spin coupling [21].

\textsuperscript{b} other 13C data: \(\delta [J(13C,29Si)] = 6.2\) [64.6, Si-Me], 35.2, 31.7, 22.2, 14.3 (=C-Bu), 30.5, 22.9, 19.9, 13.7 (=C-Bu), 34.4, 34.5, 31.3 (br), 23.6 (9-BBN);

\textsuperscript{c} other 13C data: \(\delta [J(13C,29Si)] = 5.1\) [65.9, Si-Me], 34.7, 34.7, 31.7 (br), 23.7 (9-BBN), 140.0, 132.5, 129.9, 129.5, 129.4, 128.6, 128.5, 122.5 (Ph);

\textsuperscript{d} other 13C data: \(\delta = 34.7, 34.6, 31.9\) (br), 23.6 (9-BBN), 139.1, 135.5, 134.5, 134.3, 132.6, 132.4, 130.7, 130.3, 129.4, 129.0, 128.7, 122.3 (Ph, Si-Ph).

Fig. 1. 100.5 MHz 13C\{1H\} and 79.6 MHz 29Si\{1H\} (inserted) NMR spectra of 7c. In the 13C NMR spectrum, the 29Si satellites, marked by asterisks, correspond to \(J(13C,29Si)\) and \(nJ(13C,29Si), n \geq 2\). Note the typically broad signal belonging to the carbon atom bonded to boron [21]. In the 29Si NMR spectrum, the respective 13C satellites are marked by asterisks and diamonds, while 29Si satellites, marked by arrows, correspond to \(2J(29Si,29Si)\). The 29SiMe\textsubscript{3} nuclei 2′ and 5′ are precisely assigned based on these NMR data.

Fig. 2. Part of the 100.5 MHz 13C\{1H\} NMR spectrum of a crude reaction mixture mainly containing 8a. Only 13C signals belonging to the silole ring are shown. The 29Si satellites, marked by asterisks, represent \(J(13C,29Si)\) and \(2J(13C,29Si)\). Note the typically broad signal belonging to the carbon atom bonded to boron [21].
Table 4. $^{11}$B, $^{13}$C and $^{29}$Si NMR data	extsuperscript{a} of 1-silacyclobutene derivatives 16–18, 21 and 22.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{11}$B</th>
<th>$^{13}$C (C-1)</th>
<th>$^{13}$C (C-2)</th>
<th>$^{13}$C (C-3)</th>
<th>$^{13}$C (C-4)</th>
<th>$^{29}$Si</th>
<th>$^{29}$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>16d	extsuperscript{b}</td>
<td>n.a.</td>
<td>141.9 [n.o.]</td>
<td>173.3 (br)</td>
<td>159.4 [n.o.]</td>
<td>−16.4</td>
<td>86.7</td>
<td></td>
</tr>
<tr>
<td>17d	extsuperscript{c}</td>
<td>130.1</td>
<td>147.2 [58.0]</td>
<td>179.9 (br)</td>
<td>157.2 [63.8]</td>
<td>10.7</td>
<td>85.7</td>
<td></td>
</tr>
<tr>
<td>18d	extsuperscript{d}</td>
<td>134.4</td>
<td>146.2 [58.8]</td>
<td>182.8 (br)</td>
<td>156.3 [63.6]</td>
<td>−1.2</td>
<td>86.9</td>
<td></td>
</tr>
<tr>
<td>21a	extsuperscript{e}</td>
<td>128.9 [12.2]</td>
<td>147.1 [58.4]</td>
<td>175.9 (br)</td>
<td>165.3 [58.7]</td>
<td>11.7</td>
<td>84.2</td>
<td></td>
</tr>
<tr>
<td>21d	extsuperscript{f}</td>
<td>131.0</td>
<td>147.8 [57.9]</td>
<td>177.8 (br)</td>
<td>161.0 [61.1]</td>
<td>11.0</td>
<td>86.8</td>
<td></td>
</tr>
<tr>
<td>22d	extsuperscript{g}</td>
<td>132.6</td>
<td>146.9 [58.8]</td>
<td>180.6 (br)</td>
<td>160.2 [62.4]</td>
<td>−1.8</td>
<td>84.6</td>
<td></td>
</tr>
</tbody>
</table>

	extsuperscript{a} Measured in C$_6$D$_6$, coupling constants $^1J$(13C,$^{29}$Si) and $^2J$(13C,$^{29}$Si) are given in square brackets [±0.4 Hz]. (br) denotes a broad $^{13}$C resonance signal as the result of partially relaxed scalar $^{11}$B–$^{13}$C coupling [21]. $^b$ Other carbons were not assigned, as silole accompanied by some other unknown side products are present; $^c$ Other $^{13}$C data: $^\delta$ $[J^{(13C,^{29}Si)}]$ = 21.7 (br), 9.3 (BEt$_2$), 138.4 [4.6], 136.9 [5.3], 134.3, 132.7, 132.5, 130.3, 129.3, 129.1, 128.9, 128.1, 127.9 (Ph); $^d$ Other $^{13}$C data: $^\delta$ $[J^{(13C,^{29}Si)}]$ = 21.7 (br), 9.3 (BEt$_2$), 138.4 [4.6], 136.9 [5.3], 134.3, 132.7, 132.5, 130.3, 129.3, 129.1, 128.9, 128.1, 127.9 (Ph); $^e$ Other $^{13}$C data: $^\delta$ $[J^{(13C,^{29}Si)}]$ = 21.7 (br), 9.3 (BEt$_2$), 138.4 [4.6], 136.9 [5.3], 134.3, 132.7, 132.5, 130.3, 129.3, 129.1, 128.9, 128.1, 127.9 (Ph); $^f$ Other $^{13}$C data: $^\delta$ $[J^{(13C,^{29}Si)}]$ = 21.7 (br), 9.3 (BEt$_2$), 138.4 [4.6], 136.9 [5.3], 134.3, 132.7, 132.5, 130.3, 129.3, 129.1, 128.9, 128.1, 127.9 (Ph); $^g$ Other $^{13}$C data: $^\delta$ $[J^{(13C,^{29}Si)}]$ = 21.7 (br), 9.3 (BEt$_2$), 138.4 [4.6], 136.9 [5.3], 134.3, 132.7, 132.5, 130.3, 129.3, 129.1, 128.9, 128.1, 127.9 (Ph).
Fig. 4. Monitoring of the reaction of 3d with BEt₃ by 59.6 MHz ²⁹Si NMR spectroscopy (A) after 3 d; (B) after 9 d; (C) after 15 d. The reaction mixture contains only the starting silane 3d and the 1-silacyclobutene derivative 18d (ca. 9 : 1). No intermediate analogous to 19 and 20 were detected.

Fig. 5. 59.6 MHz ²⁹Si{¹H} NMR spectrum (refocused INEPT) of the reaction mixture containing the starting silane 2a and the intermediate 19a. Expansion is given for the signal belonging to 19a, showing ¹³C satellites, owing to ²nJ(¹³C,²⁹Si), n = 1, 2.

via 1,2-hydroboration of one Si–C≡C- bond to give at first the alkenyl(alkyn-1-yl)silanes 19 and 20 as intermediates. These are fairly stable [17, 18] and were fully characterized by multinuclear NMR spectroscopy (Table 4; Fig. 5). On further heating 19 and 20 undergo intramolecular 1,1-vinylboration affording the 1-silacyclobutene derivatives 21 and 22 (Scheme 6; Fig. 6). The NMR data obtained for 21 and 22 compare well with those reported previously for analogous heterocycles [18]. The reactions shown in Scheme

Scheme 6. Reactions of di(alkyn-1-yl)(chloro)silanes 2a, d and 3d with 9-BBN.

6 were carried out to support the data obtained for the four-membered heterocycles 16–18 (Scheme 5),
where BEt₃ served unexpectedly as a hydroborating reagent.

**Reaction mechanism**

The proposed mechanisms for the formation of siloles and 1-silacyclobutene derivatives are summarized in Scheme 7. Clearly, the product distribution depends on the Si–Cl and C≡C-R/R' functions. The silanes bearing R = R' = Ph open the way to 1-silacyclobutene derivatives. We propose a transition state D, containing a six-membered cycle, and suggests the ability of the C≡C-Ph group to delocalize a positive charge plays an important role in its stabilization. Starting from D, the intermediate E is formed by β-hydrogen transfer and elimination of ethene. Intramolecular rearrangement by 1,1-vinylboration, similar to the formation of the siloles (from C), leads from E towards the 1-silacyclobutene derivatives.

**NMR spectroscopic studies**

The ¹¹B, ¹³C and ²⁹Si NMR data for siloles (7–9, 13–15), alkenyl(alkyn-1-yl) silane intermediates (19, 20) and 1-silacyclobutene derivatives (16–18, 21, 22) are summarized in Tables 2–4, respectively. The ¹H NMR data are listed in the Experimental Section. The data sets are in full agreement with the proposed structures. Both siloles and 1-silacyclobutenes can readily be identified by their characteristic NMR...
parameters (for comparison see Figs. 1, 2 and 6). The chemical shifts $\delta^{11}$B for intermediates (i.e. 19 and 20; $\delta = 82 \pm 1$) and all products were observed in the expected range typical of triorganoboranes without significant BC(11B) pi interactions [19,20]. The siloles and 1-silacyclobutenes possess well distinguishable $^{13}$C NMR data. Most $^{13}$C NMR signals could be readily assigned by their $^{29}$Si satellites ($^{1}J^{(29)Si,^{13}C}$ and $^{2}J^{(29)Si,^{13}C}$) or by the typical increase in the line widths owing to partially relaxed one-bond $^{13}$C$-^{11}$B spin-spin coupling [21]. Because of their simplicity (Figs. 3, 4), $^{29}$Si NMR spectra are helpful in monitoring the reactions, and $\delta^{29}$Si data are markedly different for siloles and 1-silacyclobutenol derivatives (Tables 2 and 3). In the $^{1}H$ NMR spectra (e.g. 16d, 17d, 18d), a singlet for an olefinic proton [C=CH(Ph)] and the absence of signals for the ≡C-Et group in the aliphatic region clearly show that ≡C-Hydroborating has taken place.

**Conclusions**

1,1-Ethylboration of di(alkyn-1-yl)(chloro)silanes is an efficient method for the preparation of siloles bearing substituents on the silicon atom such as Si-Cl and Si-H. In comparison to other reported methods [22] this process is fairly straightforward. In particular the H(Cl)Si-group in the new siloles, almost without precedent, is promising for further transformations. The role of the Si-Cl function for the stability of the Si-C≡ bond is evident from a series of reactions where BEt$_3$ acts as hydroborating reagent leading to 1-sila-cyclobutene derivatives. In this context, the influence of the phenyl group at the C≡C bond is striking.

**Experimental Section**

All preparative work and handling of air-sensitive chemicals were carried out by observing necessary precautions to exclude traces of oxygen and moisture. Trichlorosilane, trichloro(methyl)silane, trichloro(phenyl)silane, 1-hexyne, 3,3-dimethyl-but-1-yne, ethynylbenzene, trimethylethylene, $\alpha$-butylithium in hexane (1.6 M), triethylborane (BEt$_3$), 9-borabicyclo[3.3.1]nonane (9-BBN) were commercial products and were used without further purification. NMR spectra: Bruker ARX 250 MHz or Varian Inova 300 MHz and 400 MHz spectrometers (23 ± 1 °C), all equipped with multi-nuclear units, using $^{13}$C$_{6}$D$_{5}$ solutions (ca. 15 – 20 % v/v) in 5 mm tubes. Chemical shifts are given with respect to SiMe$_4$ [δH $^{13}$C(C$_6$D$_5$H) = 7.15, δ$^{13}$C(C$_6$D$_5$) = 128.0, δ$^{29}$Si = 0 for SiMe$_4$ with $\Sigma(29)$Si = 19.87/187 MHz], and δ$^{11}$B = 0 for BF$_3$·OEt$_2$ with $\Sigma^{11}B$ = 32.083971 MHz. $^{29}$Si NMR spectra were recorded using the refocused INEPT pulse sequence with $^{1}H$ decoupling [23], based either on $^{1}J^{(29)Si,^{1}H}$ $\approx 280$ Hz, $^{2}J^{(29)Si,C(=C)}$ $\approx 30 – 35$ Hz, $^{3}J^{(29)Si,^{13}H}$($^{1}$SiMe)) or $^{2}J^{(29)Si,^{1}H}(SiPh))$ $\approx 7$ Hz (after optimization of the respective refocusing delays).

**Synthesis of di(alkyn-1-yl)(chloro)silanes 1 – 6**

To a freshly prepared suspension of Li-C≡C-²Bu (61 mmol) in hexane (50 mL), trichlorosilane HSiCl$_3$ (1.9 mL, 19.3 mmol) was added slowly at −78 °C. The reaction mixture was allowed to reach r.t. Insoluble materials were filtered off, and all readily volatile materials were removed under reduced pressure (10⁻² Torr). The oily residue was analyzed to contain a mixture of HCl$_3$Si-C≡C-Ph, HClSiC≡C-Ph$_2$ (1a) and HSi(C≡C-Ph)$_3$, and fractional distillation gave pure 1a as a colorless oil. The same procedure was followed for the syntheses of the analogous silanes 1b – d, 2a, d and 3d. A solution of HCl$_3$Si-C≡C-²Bu (lighter fraction of the mixture containing 1b) in hexane (10 mL) was added to a freshly prepared Li-C≡C-²Bu suspension at −78 °C. The reaction mixture was slowly warmed to r.t. and was stirred for 1 h. The work-up procedure as described above gave the pure silane 4a as a colorless oil (yield 43.1 %). The same procedure was adopted for the synthesis of silanes 5c (yield 49 %) and 6c (yield 37.3 %).

1a: B. p. = 85 °C/2 × 10⁻² Torr. – $^{1}$H NMR data (250 MHz): δ = 0.7, 1.2, 1.9 (t, m, t, 18H, ²Bu), 5.2 (s, 1H, $^{1}J^{(29)Si,^{1}H}$ = 276.1 Hz, Si–H). – IR (C$_6$D$_6$): $\nu$ = 2185 (C=C), 2147 (Si–H) cm⁻¹.

1b: B. p. = 47 °C/1.8 × 10⁻¹ Torr. – $^{1}$H NMR (250 MHz): δ = 1.0 (s, 18H, ²Bu), 5.3 (s, 1H, $^{1}J^{(29)Si,^{1}H}$ = 274.2 Hz, Si–H). – IR (C$_6$D$_6$): $\nu$ = 2158 (C=C), 2128 (Si–H) cm⁻¹.

1c: B. p. = 58 °C/8.3 × 10⁻² Torr. – $^{1}$H NMR (250 MHz): δ = −0.04 (s, 18H, SiMe$_3$), 5.1 (s, 1H, $^{1}J^{(29)Si,^{1}H}$ = 279.0 Hz, Si–H).

1d: B. p. = 112 °C/1.0 × 10⁻³ Torr. – $^{1}$H NMR (250 MHz): δ = 5.4 (s, 1H, $^{1}J^{(29)Si,^{1}H}$ = 280.9 Hz, Si–H), 6.8 – 7.0, 7.2 – 7.3 (m, m, 10H, Ph).

2a: B. p. = 83 – 85 °C/2.8 × 10⁻² Torr. – $^{1}$H NMR (400 MHz): δ = 0.6 (s, 3H, $^{2}J^{(29)Si,^{1}H}$ = 8.2 Hz, Si–Me), 0.5, 1.1, 1.7 (t, m, t, 18H, ²Bu).

2d: B. p. = 145 – 150 °C/9.1 × 10⁻² Torr. – $^{1}$H NMR (400 MHz): δ = 0.5 (s, 3H, $^{2}J^{(29)Si,^{1}H}$ = 8.0 Hz, Si–Me), 6.6, 7.1 (m, m, 10H, Ph).

3d: B. p. = 192 – 196 °C/0.14 Torr. – $^{1}$H NMR (400 MHz): δ = 6.8, 7.2, 8.0 (m, m, 15H, Si–Ph, Ph).

4a: B. p. = 44 °C/1.0 × 10⁻² Torr. – $^{1}$H NMR (250 MHz): δ = 0.7, 1.4, 1.6 (t, m, t, 9H, ²Bu), 1.0 (s, 9H, ²Bu), 5.2 (s, 1H, $^{1}J^{(29)Si,^{1}H}$ = 273.5 Hz, Si–H).

5c: B. p. = 55 °C/1.0 × 10⁻² Torr. – $^{1}$H NMR (250 MHz): δ = 0.00 (s, 9H, SiMe$_3$), 0.6, 1.0 – 1.2, 1.8 (t, m, t, 9H, ²Bu), 5.2 (s, 1H, $^{1}J^{(29)Si,^{1}H}$ = 273.8 Hz, Si–H).
6c: B. p. = 78 °C/1 × 10−2 Torr. – 1H NMR (250 MHz): δ = 0.01 (s, 9H, SiMe3), 6.8–7.0, 7.2 (m, 5H, Ph), 5.2 (s, 1H, 1J(29Si,1H) = 279.1 Hz, Si–H).

11-Ethylboration of silanes I–6, syntheses of siloles 7–9 and 11–15

General procedure: A Schlenk tube was charged with the solution of the respective di(alkyn-1-yl)silane and triethylborane in large excess (as the reagent as well as the solvent). The reaction solution was heated at 100–120 °C (oil bath temperature). The reaction was monitored by 29Si NMR spectroscopy. After it was complete, all volatile materials were removed under reduced pressure, and the remaining brown oily liquids (siloles) were studied by NMR spectroscopy. Except for the reaction time, the experimental procedure was the same for all siloles. Time required for reaction completion was 1 d (7a), 2 d (7b, 8a), 4 h (7c), 10 d (7d) and 20 d (9a).

7a: B. p. = 120 °C/10 × 10−3 Torr. – 1H NMR (250 MHz): δ = 0.8, 0.9, 1.3, 2.3 (t, m, t, 18H, -Bu), 0.9, 2.0 (t, q, 5H, Et), 0.9, 1.6 (t, br, 10H, BEt2), 5.5 (s, 1H, 1J(29Si,1H) = 237.4 Hz, Si–H).

7b: B. p. = 100 °C/10 × 10−3 Torr. – 1H NMR (250 MHz): δ = 1.1, 1.3 (s, s, 18H, -Bu), 1.0, 2.1 (t, q, 5H, Et), 1.1, 1.6 (t, br, 10H, BEt2), 5.4 (s, 1H, 1J(29Si,1H) = 222.6 Hz, Si–H).

7c: 1H NMR (400 MHz): δ = 0.2, 0.3 (s, s, 18H, SiMe3), 0.9, 2.2 (t, q, 5H, Et), 0.9, 1.0, 1.3 (t, m, t, 10H, BEt2), 5.6 (s, 1H, 1J(29Si,1H) = 222.4 Hz, Si–H).

7d: 1H NMR (250 MHz): δ = 0.9, 2.1 (t, q, 5H, Et), 1.1, 1.2–1.5 (t, m, 10H, BEt2), 5.6 (s, 1H, 1J(29Si,1H) = 234.9 Hz, Si–H), 6.8–7.0, 7.1–7.3 (m, 10H, Ph).

8a: 1H NMR (400 MHz): δ = 0.5 (s, 3H, Si-Me), 0.8, 0.8, 1.3, 2.2 (t, m, m, 18H, -Bu), 1.0, 2.3 (t, m, 5H, Et), 0.9, 1.5 (t, m, 10H, BEt2).

9a: 1H NMR (400 MHz): δ = 0.6–1.4, 1.8–2.5 (overlapping multiplets of -Bu, BEt2 and Et groups), 7.1, 7.7 (m, m, 5H, Si–H).

13a: 1H NMR (250 MHz): δ = 0.7, 1.2–1.3, 1.9 (t, m, m, 9H, -Bu), 1.1 (s, 9H, -Bu), 1.1, 2.2 (m, q, 5H, Et), 1.1, 1.2–1.3 (m, m, 10H, BEt2), 5.3 (s, 1H, 1J(29Si,1H) = 221.9 Hz, Si–H).

13a': 1H NMR (250 MHz): δ = 5.3 (s, 1H, Si–H).

14a: 1H NMR (250 MHz): δ = 0.3 (s, 9H, SiMe3), 0.8, 1.0–1.2, 2.2 (t, m, t, 9H, -Bu), 0.9, 2.0–2.1 (t, m, 5H, Et), 1.0, 1.3 (m, m, 10H, BEt2), 5.5 (s, 1H, 1J(29Si,1H) = 222.3 Hz, Si–H).

14a': 1H NMR (250 MHz): δ = 0.2 (s, 9H, SiMe3), 5.5 (s, 1H, Si–H).

15c: 1H NMR (250 MHz): δ = 0.3 (s, 9H, SiMe3), 1.0, 2.4 (t, q, 5H, Et), 0.9, 1.4 (t, q, 10H, BEt2), 5.5 (s, 1H, 1J(29Si,1H) = 226.1 Hz, Si–H), 7.0–7.1, 7.4–7.6 (m, m, 5H, Ph).

15c': 1H NMR (250 MHz): δ = 0.3 (s, 9H, SiMe3), 5.2 (s, 1H, Si–H).

Alkenyl(alkyn-1-yl)silanes 10a, 11c and 12c
Silanes 10a, 11c and 12c were present as side products accompanying the siloles 13–15.

10a: 1H NMR (250 MHz): δ = 5.6 (s, 1H, 1J(29Si,1H) = 248.6 Hz, Si–H). – 13C NMR: δ = 82.9 (Si–C≡), 119.2 (≡C), 30.4 (6-Bu-Me3). – 29Si NMR: δ = −39.8.

11c: 29Si NMR: δ = −42.6 ppm, 1J(29Si,1H) = 246.6 Hz.

12c: 1H NMR (250 MHz): δ = 0.2 (s, 9H, SiMe3), 5.6 (s, 1H, 1J(29Si,1H) = 244.8 Hz, Si–H). – 13C NMR: δ = 1.3 (SiMe3), 89.9 (Si–C≡), 108.7 (≡C), 139.3 (≡C), 191.6 (br, C≡), 123.6, 128.5, 129.5, 132.3 (Ph). – 29Si NMR: δ = −43.0, −5.1 (29SiMe3).

Hydroboration of di(alkyn-1-yl)(chloro)silanes I–3 using BEt3 as hydroboring reagent
A mixture of the silane MeSiCl(C≡CPh)2, 2d (0.5 g, 1.8 mmol) and BEt3 (1 mL, in slight excess) was sealed in an NMR tube and kept at 100–120 °C in an oil bath. The progress of the reaction was monitored by 29Si NMR spectroscopy, and after 12 d the reaction was found to be complete. The NMR tube was cooled in liquid N2 and opened. Excess of BEt3 and other volatiles were removed under reduced pressure (10−2 Torr), and the oily residue was identified as 17d (ca. 90 % pure according to 1H NMR spectra). The procedure for 18d was identical to 17d, except that heating lasted for 15 d and the reaction was complete only to ca. 90 % (Fig. 4).

17d: 1H NMR (400 MHz): δ = 0.7 (s, 3H, Si-Me), 0.9, 1.4 (t, m, 10H, BEt2), 6.4 (s, 1H, 3J(1H,29Si) = 19.3 Hz, =CH), 6.9–7.4 (m, 10H, Ph–Ph).

18d: 1H NMR (400 MHz): δ = 1.0, 1.5 (t, m, 10H, BEt2), 6.5 (s, 1H, 3J(1H,29Si) = 21.4 Hz, =CH), 6.8–7.4 (m, 15H, Si–Ph, Ph).

Hydroboration of di(alkyn-1-yl)(chloro)silanes 2a, d and 3d using 9-BBN
A solution of silane 2a (0.74 g, 3.1 mmol) in C6D6 (1.5 mL) was mixed with the crystalline 9-BBN dimer (0.387 g, 3.1 mmol). The mixture was heated to 80 °C for 20 min. During this time 9-BBN was completely consumed (monitored by 11B NMR spectroscopy). The NMR data clearly indicated the formation of 19a. The 1,2-hydroboration of the silanes 2d and 3d was carried out in the same way leading to alkenyl(alkyn-1-yl)silanes 19d and 20d.
19a: $^1$H NMR (400 MHz): $\delta = 0.7$ (s, 3H, $^2J(29Si,1H) = 7.4$ Hz, Si-Me), 0.7, 0.9, 1.2–1.3, 2.0, 2.5 (t, t, m, t, m, 18H, $^2$Bu), 1.4, 1.8–2.0 (m, m, 14H, 9-BBN), 7.0 (t, 1H, $^3J(1H,1H) = 7.3$ Hz, $^3J(29Si,1H) = 21.1$ Hz, =CH).

19d: $^1$H NMR (400 MHz): $\delta = 0.3$ (s, 3H, $^2J(29Si,1H) = 7.7$ Hz, Si-Me), 1.2, 1.6–2.1 (m, m, 14H, 9-BBN), 7.3, 7.1, 7.0, 6.7–6.8 (m, m, m, 10H, Ph), 7.9 (s, 1H, $^3J(1H,29Si) = 21.7$ Hz, =CH).

20d: $^1$H NMR (400 MHz): $\delta = 1.4$, 1.9–2.2 (m, m, 14H, 9-BBN), 7.9, 7.6, 6.9–7.3 (m, m, 15H, Si-Ph, Ph), 8.2 (s, 1H, $^3J(29Si,1H) = 21.4$ Hz, =CH).

Syntheses of 1-silacyclobutene derivatives 21a, d and 22d

Compounds 19 and 20 were heated at 80 °C to afford the 1-silacyclobutene derivatives 21a, 21d and 22d upon ring closure. The time required for complete rearrangement via intramolecular 1,1-vinylboration was 7 d (21a), 5 d (21d) and 12 h (22d).

21a: $^1$H NMR (400 MHz): $\delta = 0.8$ (s, 3H, Si-Me), 0.8, 1.3, 2.3 (t, m, m, 18H, $^2$Bu), 1.3, 1.8–1.9 (m, m, 14H, 9-BBN), 5.8 (t, 1H, $^3J(1H,1H) = 6.9$ Hz, $^3J(29Si,1H) = 22.1$ Hz, =CH).

21d: $^1$H NMR (400 MHz): $\delta = 0.4$ (s, 3H, $^2J(29Si,1H) = 7.1$ Hz, Si-Me), 1.2–2.1 (m, 14H, 9-BBN), 6.6–7.2 (m, 11H, Ph, =CH).

22d: $^1$H NMR (400 MHz): $\delta = 1.4–2.0$ (m, 14H, 9-BBN), 6.8–7.2, 7.4, 7.9 (m, m, 16H, Si-Ph, Ph, =CH).

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