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An efficient route to substituted 1-silacyclopent-2-enes and 1-silacyclohex-2-enes via consecutive 1,2-hydroboration and 1,1-organoboration

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday.

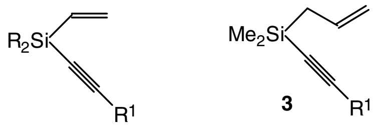
Abstract

The reaction of alkyn-1-yl(vinyl)silanes $R_2Si(C{\equiv}CR^1)CH{=}CH_2$ [R = Me (**1**), Ph (**2**); R^1 = ^{t}Bu (**a**), Ph (**b**), $SiMe_3$ (**c**)] with 9-borabicyclo[3.3.1]nonane in a 1:1 ratio affords the 1-silacyclopent-2-ene derivatives **4a**–**c** (R = Me) and **5a**–**c** (R = Ph) as a result of selective intermolecular 1,2-hydroboration of the vinyl group, followed by intramolecular 1,1-organoboration of the alkynyl substituent. The analogous reaction sequence converts the alkyn-1-yl(allyl)dimethylsilanes **3a**,**c** into the 1-silacyclohex-2-ene derivatives **7a**,**c**. All reactions were monitored by ^{29}Si NMR spectroscopy and the structural assignment of the final products was based on multinuclear magnetic resonance data (^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR). The molecular structure of **6a** was determined by X-ray analysis.

Keywords: Silanes; Heterocycles; Hydroboration; Organoboration; NMR – multinuclear; X-Ray

1. Introduction

Alkyn-1-ylsilanes bearing a second functional group at the silicon atom are attractive starting materials for organometallic syntheses [1]. The second functionality can be another alkyn-1-yl substituent [2], an amino group [3], or an Si–Cl function [4] to name just a few examples. For combining 1,2-hydroboration [5] and 1,1-organoboration [6], a vinyl group is of particular interest in this context. We show that such alkyn-1-yl(vinyl)silanes (e.g., **1**, **2**) are readily accessible by the reaction of chloro(diorgano)(vinyl)silanes, some of which are commercially available, with lithium alkynides. The regioselective intermolecular 1,2-hydroboration of the C=C bond should proceed much faster than that of the internal C≡C bond [5,7]. It can be expected that this 1,2-hydroboration will be followed by an intramolecular 1,1-organoboration via cleavage of the Si–C≡ bond to give 1-silacyclopent-2-enes [2,6,8] Therefore, we have studied the reaction of the silanes **1**–**3** with 9-borabicyclo[3.3.1]nonane (9-BBN). Although, 1-silacyclopentenes have attracted some interest [9,10], there is no convenient synthetic route available, in particular for the isomer with the C=C bond in 2-position.



1, 2 **a, b, c**
R = Me, Ph R^1 = ^{t}Bu, Ph, $SiMe_3$

Formulae 1-3

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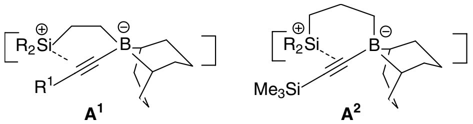
2. Results and discussion

2.1. *Hydroboration/organoboration of the alkenyl(alkyn-1-yl)silanes **1–3** with 9-BBBN*

The 1:1 reaction of **1** and **2** with 9-BBN (Scheme 1) affords selectively the 1-silacyclopent-2-enes **4** and **5**, which could be isolated as colourless oils or a crystalline solid (**5a**). The proposed intermediates **6** were not observed.

In the same way, the reaction of **3** with 9-BBN proceeds to give the 1-silacyclohex-2-enes **7** without side products (Scheme 2). In this case, the intermediate **8a** was detected by NMR measurements (vide infra) prior to its intramolecular rearrangement into **7**.

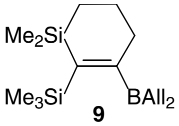
The initial 1,2-hydroboration works in the expected way [5,7] to give selectively the proposed intermediates **6** and **8**, respectively. The assumed intramolecular activation of the Si–C bonds by the electron-deficient boron atom is indicated by dashed lines (Schemes 1 and 2). As in other 1,1-organoboration reactions [8], cleavage of the Si–C≡ bond leads to alkynylborate-like intermediates **A^1** and **A^2**, where the positively charged silicon atom is side-on coordinated to the C≡C bond. Zwitterionic intermediates comparable with **A^1** or **A^2** have been isolated and structurally characterised, when the silicon is replaced by a tin [11] or lead atom [12,13] Finally, the shift of an organyl group from boron to carbon together with formation of the new Si–C= bonds leads to the heterocycles **4**, **5** and **7**.



A^1 **A^2**

Formulae A^1 and A^2

Compounds of type **7** have already been obtained by a completely different route, using the 1,1-allylboration of bis(silyl)ethyne, which is followed by intramolecular hydrosilylation and thermally induced ring contraction to give 1-silacyclohex-3-enes such as **9** [14].



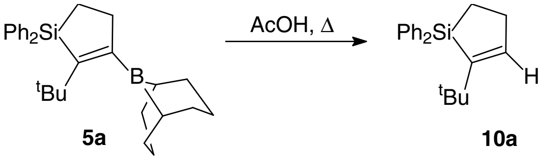
9

Formula 9

The heterocycles **4**, **5** and **7** are fairly stable towards common protodeborylation reactions. There is no reaction with methanol at room temperature or after prolonged periods of heating. Similarly, they do not react with acetic acid at room temperature. Only after heating at 110 °C in toluene, the reaction with acetic acid proceeds slowly to give **10a** as shown for **5a** in Scheme 3.

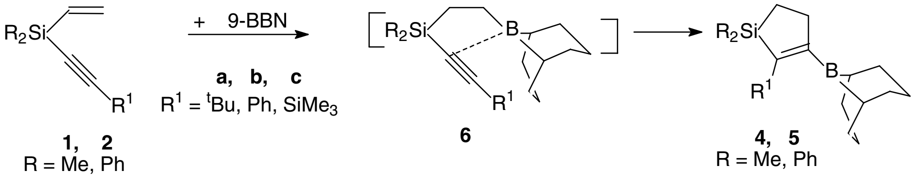
2.2. *NMR spectroscopy*

The proposed structures of the products **4**, **5**, **7** and **10** in solution follow from the consistent set of NMR data (^{1}H, ^{11}B, ^{13}C, ^{29}Si NMR), as listed in Table 1 (see the Section 3 for ^{1}H NMR data).



5a **10a**

Scheme 3.

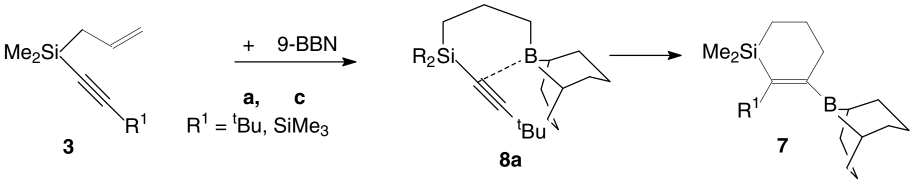


1, 2
R = Me, Ph

6

4, 5
R = Me, Ph

Scheme 1.



3

8a

7

Scheme 2.

Table 1
^{13}C and ^{29}Si NMR data[a]1-silacyclopent-2-enes (**4a**–**c**, **5a**,**c**, **10a**) and 1-silacyclohex-2-enes (**7a**,**c**)

	δ^{29}Si	δ^{13}C$_{(C\text{-}2)}$	δ^{13}C$_{(C\text{-}3)}$	δ^{13}C$_{(C\text{-}4)}$	δ^{13}C$_{(C\text{-}5)}$	δ^{13}C$_{(C\text{-}6)}$
4a[b]	16.7	151.7 [63.5]	166.1 br	35.0	12.1 [53.3]	
4b[c]	19.3	152.6 [60.6]	170.8 br	35.1 [6.7]	12.0 [53.3]	
4c[d]	29.0 (11.4)	142.7 [61.5], [47.4]	187.9 br	40.2 [11.2], [6.8]	10.9 [51.5]	
5a[e]	9.3	149.3 [65.6]	170.8 br	34.9	13.0 [55.1]	
5c[f]	20.7 (9.7)	138.9 [60.8], [49.5]	193.0 br	40.6 [12.1], [8.0]	11.9 [ ]	
7a[g]	−17.7	143.2 [64.0]	163.8 br	32.6	22.9	15.9 [50.9]
7c[h]	−15.6 (6.5)	136.3 [56.9], [50.5]	185.0 br	36.0 [10.6], [4.9]	22.3	15.0 [50.2], [5.0]
10a[i]	7.6	152.8 [64.0]	146.6 [11.2]	30.5	11.5 [55.0]	

[a] In C_6D_6, 297 K. Coupling constants $J(^{29}\text{Si},^{13}\text{C})$ are given in brackets, $J(^{29}\text{Si},^{29}\text{Si})$ in parentheses; (br) denotes a broad signal owing to partially relaxed ^{13}C–^{11}B scalar coupling.

[b] Other ^{13}C NMR data: $\delta = 1.7$ {48.0] (Me_2Si); 24.2 (BBN); 33.4 (br, BBN); 34.2 (^{t}Bu); 34.4 (^{t}Bu); 36.1 (BBN). ^{11}B NMR data: $\delta = 85.3$.

[c] Other ^{13}C NMR data: $\delta = -0.6$ [49.2] (Me_2Si); 24.2 (BBN); 33.0 (br, BBN); 34.9 (BBN); 126.6 (Ph); 128.4 (Ph); 128.8 (Ph); 144.4 (Ph). ^{11}B NMR data: $\delta = 85.6$.

[d] Other ^{13}C NMR data: $\delta = 0.9$ {48.0] (Me_2Si); 2.7 [50.4] (Me_3Si); 24.1 (BBN); 33.6 (br, BBN); 35.3 (BBN). ^{11}B NMR data: $\delta = 86.2$. Other ^{29}Si NMR data: $\delta = -10.4$ (11.4) (Me_3Si).

[e] Other ^{13}C NMR data: $\delta = 24.3$ (BBN); 33.5 (BBN); 34.6 (^{t}Bu); 36.1 (BBN); 36.3 (^{t}Bu, 6.2); 128.7 [5.3] (*m*-Ph); 129.9 (*p*-Ph); 136.5 (*o*-Ph); 137.6 [65.5] (*i*-Ph). ^{11}B NMR data: $\delta = 83.2$.

[f] Other ^{13}C NMR data: $\delta = 2.9$ [50.8} (Me_3Si); 24.0 (BBN); 33.7 (br, BBN); 35.4 (BBN); 128.6 [4.7] (*m*-Ph); 130.0 (*p*-Ph); 136.2 [3.4] (*o*-Ph); 137.7 [65.3] (*i*-Ph). ^{11}B NMR data: $\delta = 85.5$. Other ^{29}Si NMR data: $\delta = -8.7$ (9.7) (Me_3Si).

[g] Other ^{13}C NMR data: $\delta = 3.1$ [49.6] (Me_2Si); 24.3 (BBN); 33.0 (br, BBN); 34.4 (^{t}Bu); 36.2 (br, BBN); 38.1 (^{t}Bu, 4.2); 38.5 (br, BBN). ^{11}B NMR data: $\delta = 82.9$.

[h] Other ^{13}C NMR data: $\delta = 1.4$ [50.0] (Me_2Si); 3.3 [49.7] (Me_3Si); 24.0 (BBN); 33.2 (br, BBN); 36.6 (BBN). ^{11}B NMR data: $\delta = 86.6$. Other ^{29}Si NMR data: $\delta = -9.2$ (8.5) (Me_3Si).

[i] Other ^{13}C NMR data: 32.6 (^{t}Bu); 35.7 (^{t}Bu, 4.9); 128.7 [5.1] (*m*-Ph); 130.0 (*p*-Ph); 136.3 [3.9] (*o*-Ph); 137.0 [66.2] (*I*-Ph).

In several cases, ^{13}C NMR spectra were recorded with a signal-to-noise ratio that allowed for the observation of ^{29}Si and ^{13}C satellites corresponding to coupling constants $J(^{29}\text{Si},^{13}\text{C})$ and $J(^{13}\text{C},^{13}\text{C})$, respectively. The latter data are given in Table 2. Representative ^{13}C NMR spectra are shown in Figs. 1 and 3. The ^{29}Si NMR spectra are similarly instructive (Fig. 2). The application of refocused INEPT experiments [15] guarantees high resolution and a signal-to-noise ratio sufficient for the detection of ^{29}Si and ^{13}C satellites. The latter confirm the assignments of $J(^{29}\text{Si},^{13}\text{C})$ values measured from ^{13}C NMR spectra.

The assignment of the ^{13}C NMR spectra is supported by the typically broad ^{13}C NMR signals for carbon atoms linked to boron, as a result of partially relaxed scalar ^{13}C–^{11}B spin–spin coupling [16,17]. Together with the ^{29}Si and ^{13}C satellites the assignments are unambiguous. The preferred orientation of the 9-BBN fragment with respect to the planes of the rings containing silicon in **4**, **5** or **7** is of interest. For steric reasons, the BC_2 plane of the 9-BBN unit should be orthogonal to the respective ring plane, and rotation about the C(3)–B bond may be hindered. This is not the case, at least at room temperature, for the compounds **4** and **5**, whereas in the case of the six-membered rings **7** the slow rotation about the C(3)–B bond is indicated by the broad and different ^{13}C signals for the four CH_2 groups of the 9-BBN unit as marked for **7c** in Fig. 3. The intermediate **8a** is formed almost quantitatively prior to rearrangement into **7a**, and this is evident from the ^{13}C NMR spectrum shown in Fig. 3. Similar to **4**, **5** and **7**, the same arguments apply for the unequivocal assignment of the ^{13}C NMR signals.

Table 2
Coupling constants ^1J (^{13}C,^{13}C) (in Hz) in 1-silacyclopent-2-enes **4a**–**c**, **10a**, and in the 1-silacyclohex-2-ene **7a**

	$^1J(^{13}\text{C}(2), {}^{13}\text{C}(3))$	$^1J(^{13}\text{C}(3), {}^{13}\text{C}(4))$	$^1J(^{13}\text{C}(4), {}^{13}\text{C}(5))$	$^1J(^{13}\text{C}(5), {}^{13}\text{C}(6))$
4a	42.3	28.1	30.4	
4b	49.8	28.6	29.3	
4c	45.3	29.0	30.7	
10a	55.7	41.6	29.7	
7a	36.9	30.7	33.5	29.5

The ^{11}B NMR signals of the products are rather broad ($h_{1/2} >$ 500 Hz) and are found at high frequencies in the typical range [18] for triorganoboranes. The ^{29}Si chemical shifts serve as a criterion for the assessment of the ring size [19], since the ^{29}Si nuclei in the five-membered rings are significantly deshielded when compared with six-membered rings (see Table 1 and Fig. 2). The influence of phenyl groups in comparison with methyl groups at silicon is the same as usual [19].

Considering the preferred orientation of the boryl group in **4**, **5** and **7**, hyperconjugation [20,21] should be reflected by the magnitude of the coupling constants $^1J(^{13}\text{C},^{13}\text{C})$ (Table 2) for the ring carbon atoms in the positions 2 and 3, and 3 and 4, respectively. Recently, it has been shown that this parameter is sensitive to hyperconjugation [22]. The data in Table 2 show that the presence of the tert-butyl group has a significant influence on the magnitude of $^1J(^{13}\text{C}(2),^{13}\text{C}(3))$ and

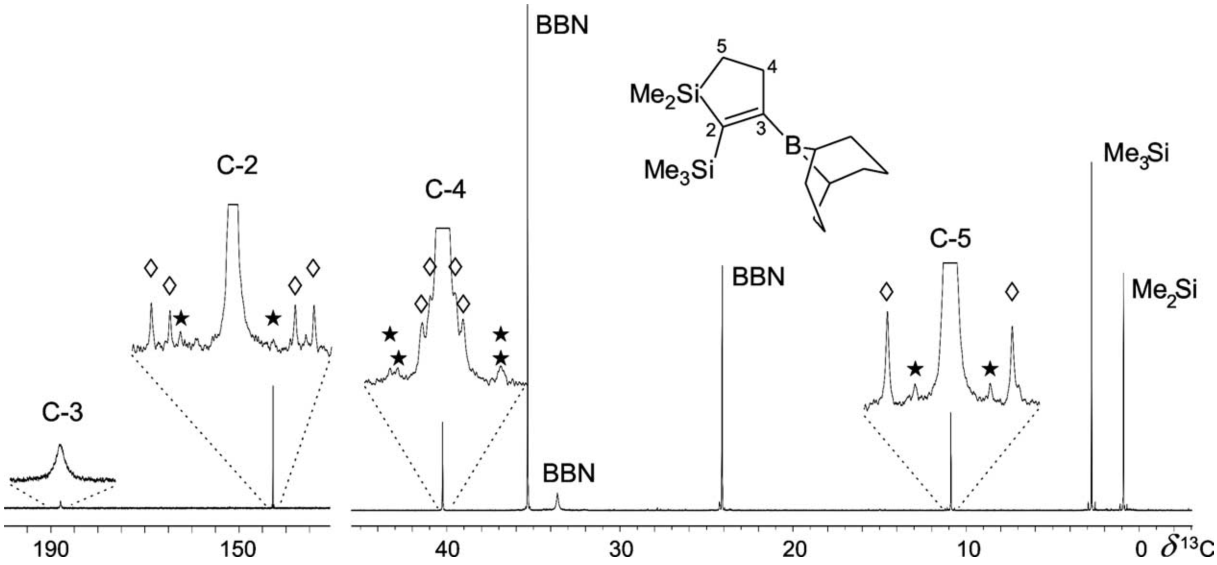


Fig. 1. 125.8 MHz $^{13}C\{^1H\}$NMR spectrum of the 1-silacyclopent-2-ene **4c** in C_6D_6 (10%). Note the broad ^{13}C NMR signals of carbon atoms bonded to boron. ^{29}Si and ^{13}C satellites are marked by rhombus and asterisks, respectively (for coupling constants see Tables 1 and 2).

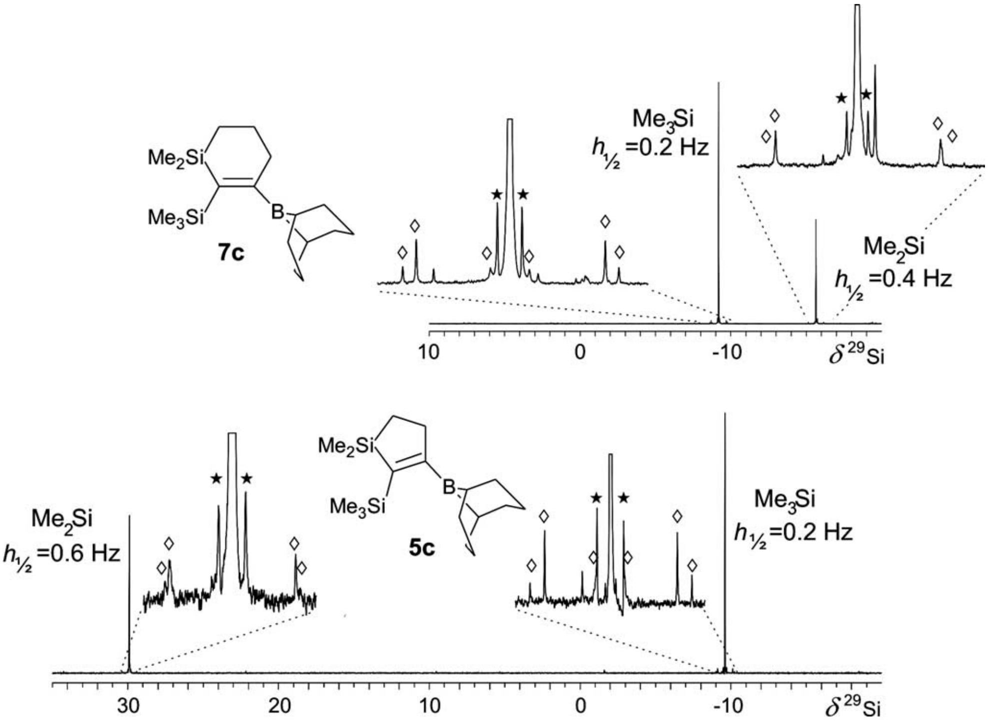


Fig. 2. 99.6 MHz $^{29}Si\{^1H\}$NMR spectra of **4c** (lower trace) and **7c** (upper trace), both recorded using the refocused INEPT pulse sequence [20] with delays based on $^2J(^{29}Si,^1H_{Me}) = 7$ Hz. Note the marked difference in ^{20}Si nuclear shielding for the $SiMe_2$ groups. ^{13}C and ^{29}Si satellites are marked by asterisks and rhombus, respectively (for data see Table 1). The ^{29}Si NMR signals of the $SiMe_2$ groups are slightly broader than those of the $SiMe_3$ groups, since the scalar ^{29}Si–^{11}B coupling is less well averaged for the larger coupling interaction typical for the *trans* positions of the nuclei [16].

$^1J(^{13}C(3),^{13}C(4))$, if the data for the 1-silacyclopent-2-ene **10a** serve for comparison. The magnitude of $^1J(^{13}C(4),^{13}C(5))$ is almost identical in **4** and **10a**, whereas the magnitude of $^1J(^{13}C(2),^{13}C(3))$ and $^1J(^{13}C(3),^{13}C(4))$ for **4** is significantly reduced when compared with **10a**.

2.3. Crystal structure of the 1-silacyclopent-2-ene *5a*

The molecular structure of **5a** is shown in Fig. 4. The five-membered ring is almost exactly planar (mean deviation from plane 5.5 pm) and the endocyclic bond angle at the silicon atom is expectedly small (93.66(8)°). The

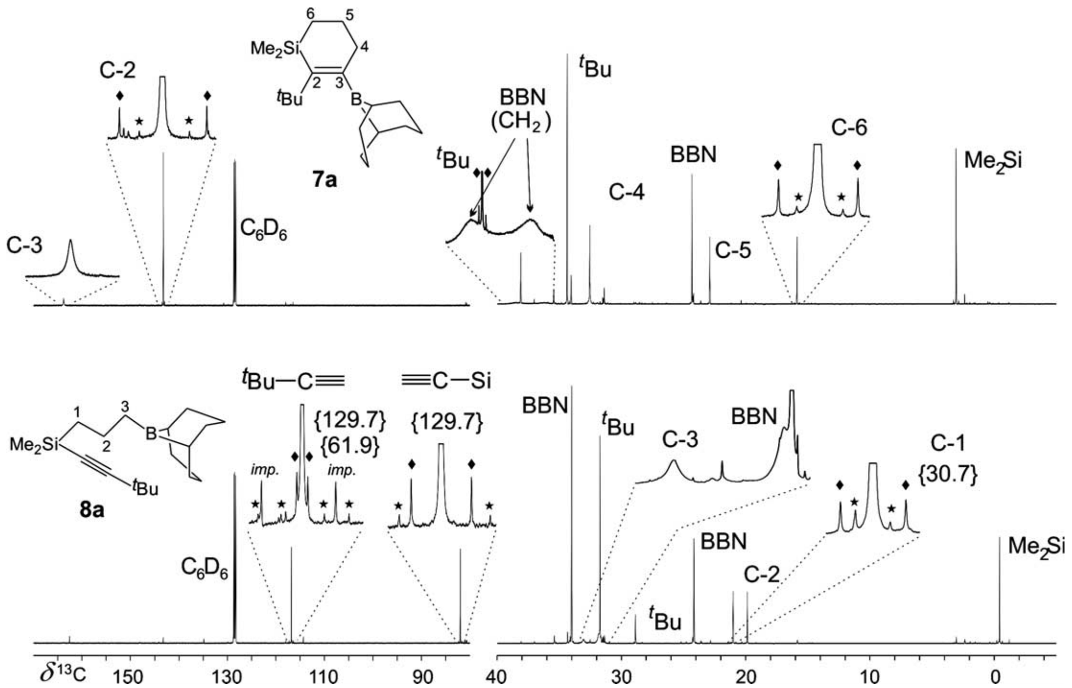


Fig. 3. 125.8 MHz $^{13}C\{^{1}H\}$NMR spectra of the 1-silacyclohex-2-ene **7a** (upper trace) and its precursor, the intermediate **8a** (slower trace). Note the broad ^{13}C NMR signals of carbon atoms bonded to boron. ^{29}Si and ^{13}C satellites are marked by rhombus and asterisks, respectively. The data for $^{1}J(^{13}C,^{13}C)$ for the intermediate **8a** are given in braces.

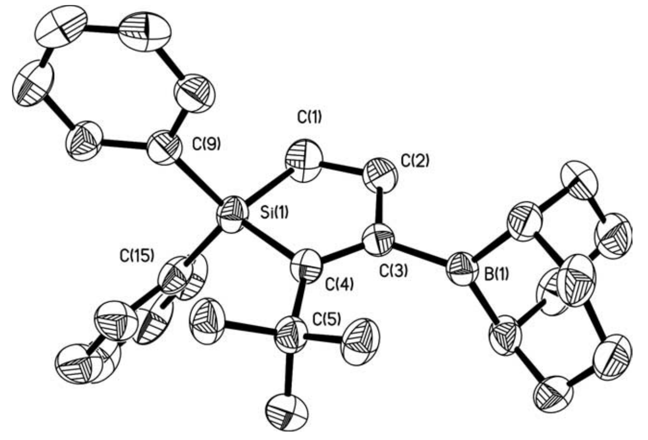


Fig. 4. ORTEP plot (50%) of the molecular structure of the 1-silacyclopent-2-ene **5a** (hydrogen atoms have been omitted for clarity). Selected bond lengths [pm] and angles [°]: Si1–C1, 186.8(2); Si1–C4, 1.87.8(2); Si1–C9, 188.0(2); Si1–C15, 188.7(2); C1–C2, 152.9(2); C2–C3, 153.1(2); C3–C4, 135.0(2); C3–B1, 157.0(2); C4–C5, 152.7(2) and C1–Si1–C4, 93.66(8); C1–Si1–C9, 111.29(10); C4–Si1–C9, 113.25(7); C1–Si1–C15, 113.61(9); C4–Si1–C15, 116.00(8); C9–Si1–C15, 108.49(8); C2–C1–Si1, 106.23(12); C1–C2–C3, 112.15(14); C4–C3–C2, 116.89(13); C4–C3–B1, 128.89(14); C2–C3–B1, 114.22(13); C3–C4–C5, 123.40(13); C3–C4–Si1, 110.35(11); C5–C4–Si1, 126.23(11).

surroundings of the boron atom are trigonal planar within the experimental error and the BC_2 plane of the 9-BBN unit is oriented almost orthogonal to the SiC_4 plane (96°). Most of the C–C bond lengths are in the expected range except of C2–C3 (153.1(2) pm) and C3–C4 (135.0(2) pm), both being slightly elongated. This is in agreement with hyperconjugation [20] involving the C–C σ bonds and the empty p_z orbital at the boron atom [21].

3. Experimental

3.1. General

All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. Solvents were distilled from Na metal in an atmosphere of argon. The starting materials were prepared as described above or were commercially available [*n*-butyllithium (1.6 M in hexane), terminal alkynes, chlorosilanes, 9-BBN] and used without further purification. NMR measurements: Bruker ARX 250 and DRX 500: ^{1}H, ^{13}C ^{11}B, ^{29}Si NMR (refocused INEPT [20] based on $^{2,3}J(^{29}Si,^{1}H) = 7$ Hz). Chemical shifts are given with respect to Me_4Si [$\delta^{1}H$ $(C_6D_5H) = 7.15$; $\delta^{13}C$ $(C_6D_6) = 128.0$; $\delta^{29}Si = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz; $\delta^{11}B = 0$ for external $BF_3–OEt_2$ with $\Xi(^{11}B) = 32.083971$ MHz]. EI-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet; the *m/z* data refer to the isotopes ^{1}H, ^{12}C, ^{11}B and ^{28}Si. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

*3.2. Preparation of alkyn-1-ylsilanes **1a–c**, **2a,c** and **3a,c***

The solution of the respective freshly prepared lithium alkynide in THF was cooled to 0 °C, and the equimolar amount of the dimethyl(vinyl)-, diphenyl(vinyl)-chlorosilane or allyl(dimethyl)chlorosilane was added at 0 °C. After the mixture was kept stirring for 1 h at room temperature, THF was removed in vacuo and the residual oil was dissolved in pentane. Insoluble materials were filtered off, pentane was removed in vacuo, and fractional distillation at reduced pressure gave the silanes **1a–c**, **2a,c** and **3a,c** as colourless liquids.

1a: b.p. = 49–54 °C (15 Torr). ^{1}H NMR: $\delta = 0.16$ (s, 6 H, Me$_2$Si); 1.19 (s, 9 H, ^{t}Bu), 5.80 (dd, 1 H, =CH$_2$, 19.8 Hz, 4.2 Hz; $^{3}J(^{29}\mathrm{Si},^{1}\mathrm{H}) = 9.4$ Hz), 5.94 (dd, 1H, =CH$_2$, 14.5 Hz, 4.2 Hz, $^{3}J(^{29}\mathrm{Si},^{1}\mathrm{H}) = 16.7$ Hz), 6.09 (dd, 1H, =CH, 19.8 Hz, 14.5 Hz, $^{2}J(^{29}\mathrm{Si},^{1}\mathrm{H}) = 14.7$ Hz). ^{13}C NMR: δ [$J(^{29}\mathrm{Si},^{13}\mathrm{C})$] = −1.1 [57.7] (Me$_2$Si), 28.2 (^{t}Bu); 31.0 (^{t}Bu), 79.6 [90.7] (≡C–Si), 117.2 [16.6] (≡C–^{t}Bu), 132.4 {<2] (=CH$_2$); 137.5 [71.3] (=CH). ^{29}Si NMR: $\delta = -25.5$. **1b**: b.p. = 63–68 °C (15 Torr). ^{1}H NMR: $\delta = 0.47$ (s, 6H, Me$_2$Si), 6.09 (dd, 1H, =CH$_2$, 20.0 Hz, 3.9 Hz, ^{3}J (^{29}Si,^{1}H) = 9.6 Hz), 6.21 (dd, 1H, =CH$_2$, 14.4 Hz, 3.9 Hz, $^{3}J(^{29}\mathrm{Si},^{1}\mathrm{H}) = 17.4$ Hz), 6.35 (dd, 1H, =CH, 20.0 Hz, 14.4 Hz, $^{2}J(^{29}\mathrm{Si},^{1}\mathrm{H}) = 7.6$ Hz), 7.4 (m, 3H, Ph), 7.6 (m, 2H, Ph). ^{13}C NMR: δ [J (^{20}Si,^{13}C)] = −1.5 [58.0] (Me$_2$Si), 91.8 [87.3] (≡C–Si), 106.2 [16.4] (C–Ph), 123.0, 128.1, 128.5, 131.9 (Ph), 133.1 [<2] (=CH$_2$), 136.4 [71.9] (=CH). ^{29}Si NMR: $\delta = -24.4$. **1c**: b.p. = 52–57 °C (15 Torr). ^{1}H NMR: $\delta = 0.19$ (s, 9H, Me$_3$Si), 0.23 (s, 6H, Me$_2$Si), 5.86 (dd, 1H, =CH$_2$, 20.0 Hz, 3.9 Hz), 6.01 (dd, 1H, =CH$_2$, 14.7 Hz, 3.9 Hz), 6.12 (dd, 1H, =CH, 20.0 Hz, 14.7 Hz). ^{13}C NMR: δ [J (^{29}Si,^{13}C)] = −1.5 [57.6] (Me$_2$Si), −0.1 [56.3] (Me$_3$Si), 111.4 [80.6, 12.4] (≡C–Si). 115.1 [76.4, 12.7] (C–Si), 133.1 [<2] (=CH$_2$), 136.4 [71.6] (=CH). ^{29}Si NMR: δ ($J(^{29}\mathrm{Si},^{29}\mathrm{Si})$) = −25.8 (1.7) (Me$_2$Si), −18.7 (1.7) (Me$_3$Si).

2a: b.p. = 142–148 °C (0.5 Torr). ^{1}H NMR: $\delta = 1.58$ (s, 9H, ^{t}Bu); 6.24 (dd, 1H, =CH$_2$, 20.0 Hz, 3.8 Hz); 6.48 (dd, 1H, =CH$_2$, 14.4 Hz, 3.8 Hz); 6.69 (dd, 1H, =CH, 20.0 Hz, 14.5 Hz); 7.6 (m, 6H, Ph); 7.9 (m, 4H, Ph). ^{13}C NMR: δ {$J(^{20}\mathrm{Si},^{13}\mathrm{C})$] = 28.4, 30.8 (^{t}Bu), 76.2 [99.2] (≡C–Si), 120.7 [17.6] (≡C–^{t}Bu), 127.8, 129.6, 134.2 [75.0], 135.0 (Ph), 133.6 [74.6] (=CH), 136.2 [<2] (=CH$_2$). ^{29}Si NMR: $\delta = -32.2$. **2c**: b.p. = 151–155 °C (0.5 Torr). ^{1}H NMR: $\delta = 0.40$ (s, 9H, Me$_3$Si), 6.14 (dd, 1H, =CH$_2$, 19.7 Hz, 4.1 Hz), 6.40 (dd, 1H, =CH$_2$, 14.3 Hz, 4.1 Hz), 6.59 (dd, 1H, =CH, 19.7 Hz, 14.3 Hz), 7.5 (m, 6H, Ph), 7.8 (m, 4H, Ph). ^{13}C NMR: δ [$J(^{20}\mathrm{Si},^{13}\mathrm{C})$] = −0.1 [56.6] (Me$_3$Si); 107.3 [88.3, 11.9] (≡C–SiPh$_2$), 119.3 [75.1, 13.3] (≡C–SiMe$_3$), 127.9, 129.8, 133-3 [76.9], 135.1(Ph), 132.8 [75.3] (CH=), 136.8 [<2] (=CH$_2$). ^{29}Si NMR: δ ($J(^{29}\mathrm{Si},^{29}\mathrm{Si})$) = −31.9 (1.7) (Ph$_2$Si), −16.7 (1.7) (Me$_3$Si).

3a: b.p. = 52–56 °C (15 Torr). ^{1}H NMR: $\delta = 0.24$ (s, 6H, Me$_2$Si), 1.26 (s, 9H, ^{t}Bu), 1.70 (dt, 2H, CH$_2$, 8.1 Hz, 3.4 Hz, $^{2}J(^{29}\mathrm{Si},^{1}\mathrm{H}) = 8.5$ Hz), 5.05 (m, 2H, =CH$_2$), 5.97 (ddt, 1H, =CH-, 17.5 Hz, 9.4 Hz, 8.1 Hz). ^{13}C NMR: δ [$J(^{20}\mathrm{Si},^{13}\mathrm{C})$] = −1.3 [56.8] (Me$_2$Si), 25.1 [52.4] (CH$_2$), 28.8 [3.4], 31.6 (^{t}Bu), 81.2 [88.3] (≡C–Si); 117.4 [16.0] (≡C–^{t}Bu), 114.3 (=CH$_2$), 134.9 (=CH–). ^{29}Si NMR: $\delta = -18.2$. **3c**: b.p. = 59–62 °C (15 Torr). ^{1}H NMR: $\delta = 0.12$ (s, 6H, Me$_2$Si), 0.13 (s, 9H, Me$_3$Si), 1.59 (dt, 2H, CH$_2$, 8.0 Hz, 1.0 Hz, $^{2}J(^{29}\mathrm{Si},^{1}\mathrm{H}) = 8.1$ Hz), 4.8–4.9 (m, 2H, =CH$_2$), 5.76 (ddt, 1H, –CH=, 16.8 Hz, 10.2 Hz, 8.0 Hz). ^{13}C NMR: [$J(^{29}\mathrm{Si},^{13}\mathrm{C})$] = −2.3 [56.8] (Me$_2$Si), −0.1 [56.1] (Me$_3$Si), 23.9 [52.4] (CH$_2$), 112.0 [77.9, 12.2] (≡C–SiMe$_2$), 114.9 [76.1, 12.1] (≡C–SiMe$_3$), 113.8 (=CH$_2$), 133.8 (=CH). ^{29}Si NMR: δ ($J(^{29}\mathrm{Si},^{29}\mathrm{Si})$) = −19.1 (1.6) (Me$_2$Si), −18.8 (1.6) (Me$_3$Si).

*3.3. Reaction of silanes **1a–c**, **2a,c** and **3a,c**, with 9-borabicyclo[3.3.1]nonane (9-BBN)*

3.3.1. General procedure

3.3.1.1. Reaction in toluene. To the mixture of 9-BBN (4–5 mmol) in 3 mL of toluene, the equimolar amount of the respective silane was added and the mixture was heated at reflux for 10 min. Then, the solvent was removed in vacuo and the oily residue was distilled under reduced pressure to give colourless oils (**4a–c**, **7a,c**) or crystallised from hexane to give white solids (**5a,c**).

3.3.1.2. Reaction in THF. To the solution of 9-BBN (4–5 mmol) in 5 mL of THF, the equimolar amount of the respective silane (in 5 mL of THF) was added at 0 °C. The immediate exothermic reaction gave the 1-silacyclopent-2-enes **4a–c** and **5a,c** and 1-silacyclohex-2-enes **7a,c**. The work-up procedure is the same as described above.

4a: 91%; b.p. = 132–135 °C (0.5 Torr). ^{1}H NMR: $\delta = 0.43$ (s, 6H, Me$_2$Si), 0.92 (m, 2H, CH$_2$Si), 1.26 (s, 9H, ^{t}Bu), 1.65 (m, 2H, BBN), 1.81 (m, 2H, BBN), 2.15 (m, 10H, BBN), 2.70 (m, 2H, CH$_2$).

4b: 88%; b.p. = 139–142 °C (0.5 Torr). ^{1}H NMR: $\delta = 0.31$ (s, 6H, Me$_2$Si), 1.02 (m, 2H, CH$_2$Si); 1.42 (m, 2H, BBN), 1.67 (m, 2H, BBN), 1.81 (m, 4H, BBN), 1.92 (m, 6H, BBN), 2.93 (m, 2H, CH$_2$), 7.09 (m, 3H, Ph), 7.21 (m, 2H, Ph).

4c: 86%; b.p. = 136–141 °C (0.5 Torr). ^{1}H NMR: $\delta = 0.32$ (s, 9H, Me$_3$Si), 0.38 (s, 6H, Me$_2$Si), 0.82 (m, 2H, CH$_2$Si), 1.58 (m, 2H, BBN), 1.86 (m, 2H, BBN), 2.10 (m, 10H, BBN), 2.88 (m, 2H, CH$_2$).

5a: 84%; m.p. = 122–126 °C. ^{1}H NMR: $\delta = 1.20$ (s, 9H, ^{t}Bu), 1.36 (m, 2H, CH$_2$Si), 1.8–2.1 (m, 14H, BBN), 2.78 (m, 2H, CH$_2$), 7.4 (m, 6H, Ph), 7.9 (m, 4H, Ph).

5c: ^{1}H NMR: $\delta = 0.22$ (s, 9H, Me_3Si), 1.26 (m, 2H, CH_2Si), 1.6–2.1 (m, 14H, BBN), 2.95 (m, 2H, CH_2), 7.3 (m, 6H, Ph), 7.8 (m, 4H, Ph).

7a: ^{1}H NMR: $\delta = 0.45$ (s, 6H, Me_2Si), 0.87 (m, 2H, CH_2Si), 1.25 (s, 9H, ^{t}Bu), 1.7–2.2 (m, 16H, BBN, CH_2B), 2.26 (m, 2H, CH_2).

7c: ^{1}H NMR: $\delta = 0.22$ (s, 9H, Me_3Si), 0.27 (s, 6H, Me_2Si), 0.73 (m, 2H, CH_2Si), 1.56 (m, 2H, BBN), 1.71 (m, 2H, CH_2), 1.82 (m, 2H, BBN), 2.08 (m, 10H, BBN), 2.23 (m, 2H, CH_2).

3.4. Hydroboration of **3a** with 9-BBN

The mixture of the equimolar amounts of silane **3a** and 9-BBN (1–1.5 mmol) in 0.5 mL of C_6D_6 was sealed in the NMR tube and heated at 110 °C for 2–3 min. According to the NMR data (see, e.g., Fig. 3) the solution contained only the hydroboration product **8a**. Further heating at 110 °C for 10 min led to the quantitative formation of **7a**.

8a: ^{1}H NMR: $\delta = 0.34$ (s, 6H, Me_2Si), 0.86 (m, 2H, CH_2Si), 1.34 (s, 9H, ^{t}Bu), 1.39 (m, 2H, CH_2B), 1.69 (m, 2H, CH_2), 1.8–2.1 (m, 14H, BBN). ^{13}C NMR: $[J(^{29}Si,^{13}C)] = -0.4$ [55.3] (Me_2Si), 19.9 (CH_2), 21.0 [57.0] (CH_2Si), 28.9, 31.7 (^{t}Bu), 24.2. 31.8 (br), 34.0 (BBN), 33.1 (br, CH_2B), 82.0 [86.3] ($\equiv$C–Si), 116.8 [15.9] ($\equiv$C–^{t}Bu). ^{11}B NMR: $\delta = 80.6$. ^{29}Si NMR: $= -17.7$.

3.5. Protodeborylation of **5a**

To a solution of 0.507 g (1.23 mmol) of **5a** in 2 mL of toluene, 0.09 g (1.5 mmol) of AcOH was added. The mixture was heated at reflux for 6 h, and then all volatile materials were removed in vacuo, and the residue was chromatographed with pentane on silica to give 0.276 g (77%) of 2-*tert*-butyl-1,1-diphenyl-1-silacyclopent-2-ene **10a** as a colourless oil.

10a: ^{1}H NMR: $\delta = 1.20$ (s, 9H, ^{t}Bu), 1.31 (m, 2H, CH_2Si), 2.59 (m, 2H, CH_2), 6.76 (t, 1H, =CH, 2.8 Hz, $^{3}J(^{29}Si,^{1}H) = 14.9$ Hz), 7.3 (m, 6H, Ph), 7.8 (m, 4H, Ph).

3.6. X-Ray structural analysis of the 1-silacyclopent-2-ene **5a**

X-Ray crystal structure analysis of **5a** was performed using a STOE IPDS II equipped with a low temperature unit. Formula weight: 412.48. Temperature: 193(2) K. Wavelength: 71.069 pm. Crystal system: triclinic. Space group: $P\bar{1}$. Unit cell dimensions: $a = 751.90(6)$ pm, $\alpha = 82.704(6)°$, $b = 1042.94(8)$ pm, $\beta = 87.291(6)°$, $c = 1546.81(12)$ pm, $\gamma = 82.453(6)°$. Volume: 1.19217 (16) nm^{3}. $Z = 2$. Absorption coefficient = 0.111 mm^{-1}. $F(000) = 448$. Crystal size = $0.45 \times 0.20 \times 0.15$ mm^{3}. θ Range for data collection = 1.33–26.02°. Index ranges = $-8 \leqslant h \leqslant 9$, $-12 \leqslant k \leqslant 12$, $-19 \leqslant l \leqslant 19$. Reflections collected = 16938. Independent reflections = 4670 [$R_{(int)} = 0.0687$]. Completeness to $\theta = 26.02°$: 99.7%. Data/restraints/parameters = 4670/0/272. Goodness-of-fit on F^2: 1.032. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0430$; $wR_2 = 0.1136$. R indices (all data): $R_1 = 0.0589$; $wR_2 = 0.1193$. Largest difference peak and hole: 0.298 and −0.272 e Å^{-3}.

4. Supplementary information

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-260721 (**5a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44 1223/336033; e-mail: deposit@ccdc.cam.ac.uk].

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