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Boryl-substituted 1-silacyclobutenes. Formation and molecular structure

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The 1,2-hydroboration of the chloro(hexyn-1-yl)- (1a) and chloro(phenylethyn-1-yl)diphenylsilanes (1b) with 9-borabicyclo[3.3.1]nonane afforded selectively the alkenylsilanes 2a, b, in which the boryl and the silyl groups are linked to the same olefinic carbon atom. In case of 2a, treatment with phenylethynyl lithium gave a mixture of the alkyn-1-ylborate 3a and the alkenyl(phenylethynyl)diphenylsilanes 4a. In the case of 2b, only the alkyn-1-ylsilane 4b was identified as an intermediate. Both 4a, b slowly rearranged by intramolecular 1,1-vinylboration into the silacyclobutenes 5a, b. The intermediates were characterized by ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR spectroscopy in solution, and the molecular structure of the 1-silacyclobutene 5a was determined by X-ray analysis. The gas phase geometries of model molecules corresponding to 5a were optimized by MO calculations using DFT methods [B3LYP/6-311+G(d,p) level of theory], found to be in reasonable agreement with the results of the crystal structure determination, and NMR parameters were calculated at the same level of theory. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: silanes; heterocycles; hydroboration; organoboration; NMR; X-ray analysis; DFT calculations

INTRODUCTION

Regiospecific 1,2-hydroboration of alkyn-1-ylsilanes[1–9] affords useful starting materials for the synthesis of heterocycles, in particular if there is another functional group present at the silicon atom, as was shown previously for some alkyn-1-yl(chloro)methylsilanes (Scheme 1).[10] The alkenylsilanes of type A, similar to other alkenylsilanes bearing boryl groups at the C=C bond,[11–21] offer numerous possibilities for further transformations, in particular if the Si–Cl function and the boryl group become involved.[22–24]

The combination of intermolecular 1,2-hydroboration[1–9,25] with intramolecular 1,1-organoboration[26] is attractive, since it opens versatile routes to cyclic silanes.[24,27,28] In this context we have reported on the synthesis of silacyclobutenes of type B.[24] However, direct structural evidence was missing, and intermediates could not be identified unambiguously. Therefore, we have examined this sequence of reactions again, starting from the corresponding diphenylsilanes. It was hoped that the course of the 1,2-hydroboartion would not be changed by the Si-phenyl groups, and that the stepwise conversion of the type A into type B silanes would proceed more slowly, allowing for the detection of intermediates, which can be either alkyn-1-ylsilanes or both alkyn-1-ylborates and alkyn-1-ylsilanes. Moreover, it seemed conceivable that phenyl groups at the silicon atom would increase the chances of obtaining suitable crystalline materials for X-ray analysis, as has been shown previously.[27,28]

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RESULTS AND DISCUSSION

Hydroboration of alkyn-1-yl(chloro)diphenylsilanes 1 with 9-BBN

The 1 : 1 reaction of **1a** or **1b** with 9-BBN (Scheme 2) affords selectively the alkenylsilanes as a colorless air-sensitive oil (**2a**) or a waxy solid (**2b**) that can be used without further purification. Thus, the phenyl groups at silicon do not affect the regiospecific character of the 1,2-hydroboration.

Reaction of the alkenyl(chloro)diphenylsilanes 2 with PhC≡CLi

There are two electrophilic centres present in **2**, one at silicon and the other at boron. Hence, the reaction of **2** with PhC≡CLi

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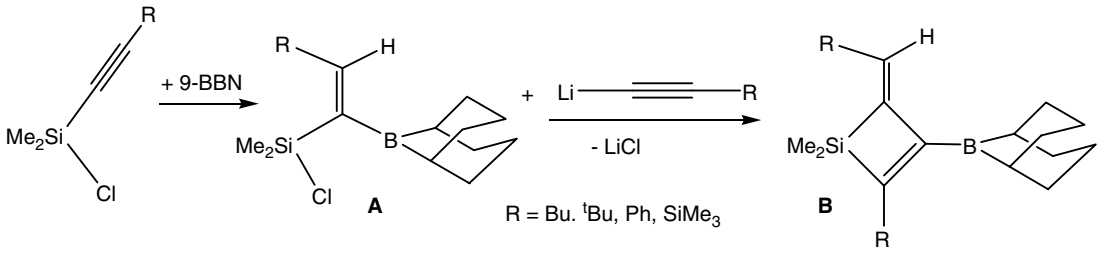
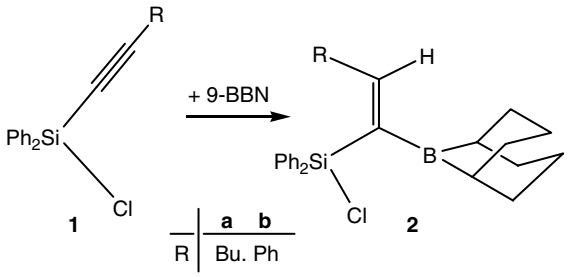


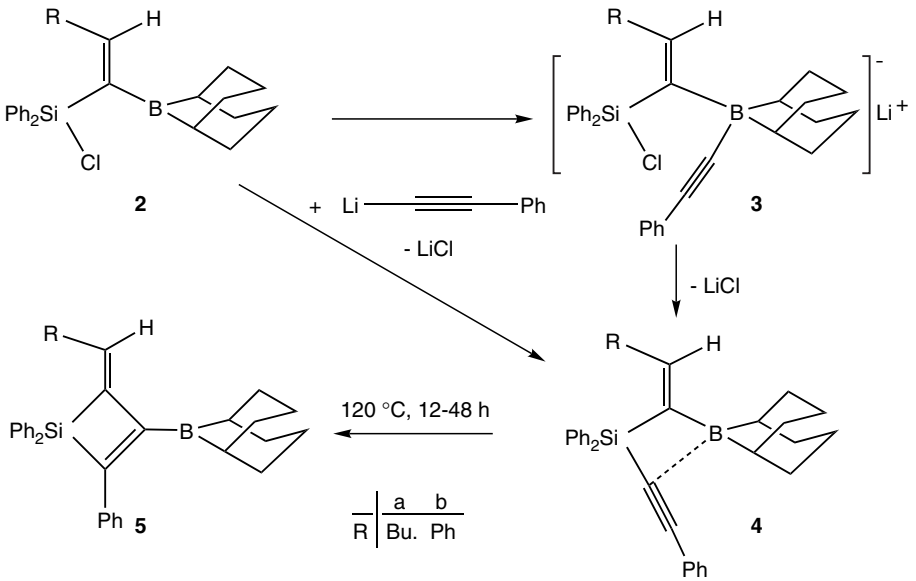
Scheme 1. Formation of 1-silacyclobutene derivatives by the combination of 1,2-hydroboration and intramolecular 1,1-organoboration.



Scheme 2. Regioselective 1,2-hydroboration of alkyn-1-yl(chloro)diphenylsilanes.

could lead either to an alkyn-1-ylborate or directly to an alkyn-1-ylsilane by elimination of LiCl. As shown in Scheme 3, a borate intermediates **3a** is present (cf. ^{11}B NMR), which eliminates LiCl, accompanied by migration of the alkynyl group from boron to silicon to give the alkyn-1-ylsilanes **4a** (cf. ^{29}Si NMR). In the case of **2b**, the same route cannot be excluded, although the borate **3b** was not detected. Finally, prolonged heating in boiling toluene or benzene is required to induce the intramolecular 1,1-vinylboration in both **4a** and **4b**, by which the 1-silacyclobutenes **5a** and **5b** are formed selectively.

The intermediates **3a, 4a** and **4b** can be readily identified by their typical NMR signals (see Fig. 1 for ^{13}C NMR). The borate **3a** shows the ^{11}B NMR signal at low frequency in the range characteristic for tetraorganoborates.[29] This signal decreases in intensity, and the signal at high frequency, typical of three-coordinate boron,[29] increases again. At the same time, the ^{29}Si NMR signal[30–34] of **3a** loses intensity, giving rise to a signal at lower frequency typical of the alkyn-1-ylsilane **4a**. After prolonged periods of heating, these low-frequency signals for **4a** and **4b** are being replaced by new signals at higher frequency for the silacyclobutenes **5a** and **5b** (see Fig. 2 for ^{13}C NMR with the typical signals for the ring carbon atoms C-2, C-3 and C-4). Relevant ^{11}B, ^{13}C and ^{29}Si NMR data for **2, 3** and **4** are collected in Table 1, and Table 2 lists such data



Scheme 3. Reactions of alkenyl(chloro)diphenylsilanes with phenylethynyl lithium to a borate or directly to the alkyn-1-yl-diphenmylsilanes, followed by intramolecular 1,1-vinylboration.

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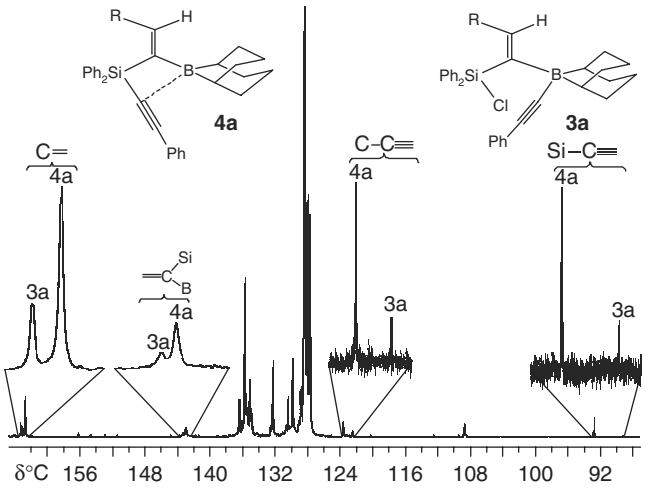

Figure 1. $^{13}C\{^1H\}$ NMR spectrum (100.5 MHz) of the reaction mixture containing the hexyn-1-ylborate **3a** and hexyn-1-ylsilane **4a** (solution in C_6D_6) showing the region for alkynyl, olefinic and phenyl carbon atoms. The $^{13}C(B–C\equiv)$ signal of **3a** could not be assigned unambiguously since it is very broad and of weak intensity.[48] It should be in the region of $\delta^{13}C = 102 \pm 2$.

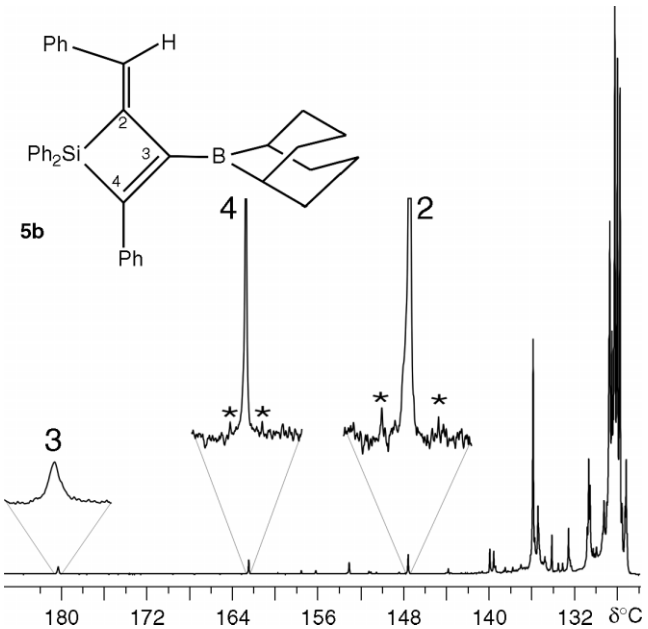

Figure 2. $^{13}C\{^1H\}$ NMR spectrum (100.5 MHz) of the crude reaction mixture containing mainly the silacyclobutene **5b** (in C_6D_6) showing the range for phenyl and olefinic carbon atoms. The ^{29}Si satellites in the expanded regions are marked by asterisks. Note the typically broad signal[45–48] of the carbon atom C-3 linked to boron.

for the silacyclobutenes **5** together with one example of type B (Scheme 1) for comparison.

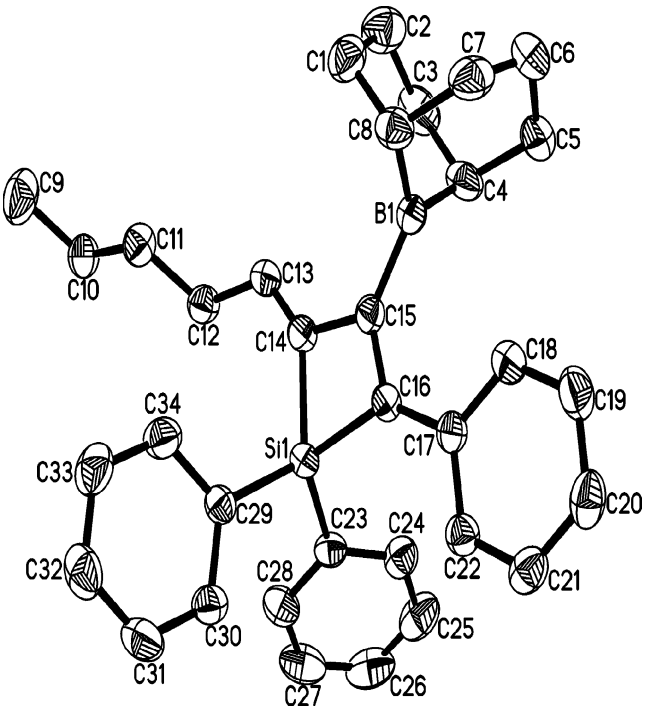

Figure 3. Molecular structure of the 1-silacyclobutene **5a**; ORTEP plot (50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and bond angles (deg): C4–B1 156.1(3), C8–B1 155.9(2), C13–C14 132.6(2), C14–C15 149.6(2), C14–Si1 187.40(16), C15–C16 137.4(2), C15–B1 156.1(2), C16–C17 145.5(2), C16–Si1 185.91(15), C23–Si1 187.18(16), C29–Si1 186.58(16); C13–C14–C15 130.23(15), C15–C14–Si1 88.32(10), C14–C15–C16 104.22 (13), C14–C15–B1 125.10(14), C16–C15–B1 130.68(14), C15–C16–C17 129.78(14), C15–C16–Si1 92.70(10), C17–C16–Si1 137.51(12), C8–B1–C15 123.81(15), C4–B1–C15 124.19(15), C16–Si1–C29 119.50(7), C16–Si1–C23 114.35(7), C23–Si1–C29 109.84(7), C14–Si1–C16 74.76(7), C14–Si1–C23 119.02(7), C14–Si1–C29 115.89(7), C4–B1–C8 111.44(14).

X-Ray analysis of the 1-silacyclobutene 5a

The molecular structure of the 1-silacyclobutene **5a** is shown in Fig. 2 together with selected structural parameters. Intermolecular contacts are negligible. There is an expectedly acute endocyclic bond angle C–Si–C = 74.76(7)°. The C═C bonds are almost exactly in one plane, and therefore, the four-member ring is planar within the experimental error. The CBC plane of the boryl group is oriented almost perpendicular (85.3°) to the silacyclobutene plane. This is an ideal situation for hyperconjugation involving C–C σ bonds and the empty p_z orbital at the boron atom.[35–38] Indeed, the elongated bond lengths of C15═C16 [137.4(2) pm], when compared with the other double bond C13═C14 [132.6(2) pm] may be interpreted in this way. The plane of the phenyl group at C16 is only slightly twisted by 4.6° against the plane of the four-member

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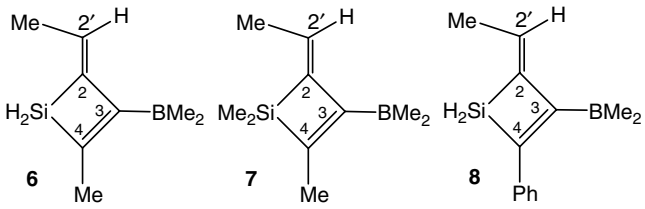
Table 1. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the alkenyl(chloro)diphenylsilanes **2a,b**, alkyn-1-ylborate **3a** and of alkenyl(alkyn-1-yl)diphenylsilanes **4a,b**

Compound	2a	2b[b]	3a	4a	4b
δ^{13}C(R**C**H=)	163.3	157.9	163.2	162.6	158.0
δ^{13}C[**B**C(Si)=]	142.9 (br)	144.3 (br)	143.4 (br)	142.9 (br)	145.0 (br)
δ^{13}C(SiPh)	136.0(77.8)(*i*), 134.9(*o*), 130.4(*p*), 128.3(*m*)	138.3(*i*), 134.5(*o*), 128.7(*p*), 127.8(*m*)	136.2(*i*), 135.1(*o*), 130.5(*p*), 128.9(*m*)	136.4 (74.9)(*i*), 135.7(*o*), 129.8(*p*), 128.4(*m*)	136.5 (76)(*i*), 135.7(*o*), 129.7(*p*), 128.4(*m*)
δ^{13}C(9-BBN)	34.2, 31.6 (br), 23.4	34.2, 31.6 (br), 23.1	34.3, 31.6 (br), 23.4	34.3, 31.4 (br), 23.5	34.5, 32.1 (br), 23.6
δ^{13}C(**R**C=)	36.0, 31.2, 22.6, 13.9	135.4(*i*), 130.0(*o*), 129.4(*m*), 127.5(*p*)	35.9, 31.2, 22.6, 13.9	36.0, 31.4, 22.7, 14.0	139.6, 137.9, 132.6, 132.4, 128.5, 127.9, 125.7, 123.6[c]
δ^{13}C(**Ph**C≡)	—	—	135.4, 134.9, 132.6, 132.3, 130.7, 130.4, 123.7, 122.5[c]		
δ^{13}C(**C**≡CPh)	—	—	n. o.(br)	92.7 (91.5)	92.1
δ^{13}C(Ph**C**≡)	—	—	89.1	108.6	109.1
δ^{29}Si	−5.7	−2.1	−16.0	−35.7	−35.3
δ^{11}B	81.7	85.1	−16.5	83.1	83.6

[a] Measured in C_6D_6 at 23 °C; coupling constants $J(^{29}Si, ^{13}C)$ [±0.4 Hz] are given in parenthesis; n.o., not observed; (br), a broad ^{13}C resonance signal as the result of partially relaxed scalar $^{13}C-^{11}B$ spin–spin coupling.[45–48]
[b] Measured in $CDCl_3$.
[c] Phenyl carbons without assignment.



Scheme 4. Model 1-silacyclobutene molecules used for DFT calculations of gas phase geometries and NMR parameters.

ring. All other bond lengths and angles appear to be in the expected ranges.

DFT calculations

The geometry of the silacyclobutene ring established here by experimental data is reproduced by DFT calculations at the B3LYP/6–311 + G(d,p) level of theory.[39–43] using the Gaussian 03 program package.[44] Selected calculated structural data for the molecules **6**–**8** (Scheme 4) are given in Table 3 together with some NMR parameters, calculated at the same level of theory.

The calculated gas phase geometries compare well with that of **5a** in the solid state. The ^{11}B, ^{13}C and ^{29}Si chemical shifts also agree well with experimental data given for the effect of different substituents. The calculated coupling constants $^1J(^{29}Si, ^{13}C)$ are somewhat smaller in magnitude than the experimental data. However, the analogous effect is found for tetramethylsilane [$^1J(^{29}Si, ^{13}C) = 50.8$ Hz (exp.) and 44.3 Hz (calcd)[34]].

CONCLUSIONS

The previously proposed mechanism for the combination of 1,2-hydroboration/1,1-organoboration has been confirmed by the results presented here, together with the first direct structural evidence for a silacyclobutene ring. When compared with other methods[49–55] for the synthesis of silacyclobutenes, the route outlined in this work has distinct advantages.

EXPERIMENTAL

Starting materials, measurements and calculations

The preparations and all handling of samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware and dry solvents were used throughout. BuLi in hexane (1.6 M), 9-borabicyclo[3.3.1]nonane, phenylacetylene (Aldrich) and dichlorodiphenylsilane (ABCR) were commercial products. The alkyn-1-yl(chloro)diphenylsilanes **1a** and **1b** were prepared adapting literature procedure.[56,57] NMR measurements in C_6D_6 (concentration ca. 5–10%) were

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Table 2. ^{11}B, ^{13}C, ^{29}Si NMR data[a] of the silacyclobutenes

Compound	**5a**	**5b**	**B** (R = ^{t}Bu)
δ^{13}C(**R**CH═)	140.0	139.6	140.0
δ^{13}C[**C**(2)]	146.4	147.6 (53.0)	142.8 (52.6)
δ^{13}C[**C**(3)]	163.4 (br)	180.4 (br)	173.4 (br)
δ^{13}C[**C**(4)]	158.8 (n.m.)	162.5 (55.8)	169.0 (54.1)
δ^{13}C($SiPh_2$)	139.9(*i*), 135.8(*o*), 130.6(*p*), 128.6(*m*)	139.6(*i*), 136.0(*o*), 130.7(*p*), 128.8(*m*)	1.5 (44.6) [$SiMe_2$]
δ^{13}C(9-BBN)	34.3, 32.3 (br), 23.6	34.4, 32.4 (br), 23.6	32.6, 33.7 (br), 23.6
δ^{13}C(**R**C═)	35.4, 32.5, 22.7, 14.1	135.5, 134.2, 132.7, 130.6, 128.9, 128.6, 127.4, 127.2[b]	—
δ^{13}C[**Ph**C(4)]	135.1(*i*), 130.7(*o*), 128.7(m), 127.4(*p*)		—
δ^{29}Si	−2.0	−1.4	8.9
δ^{11}B	89.1	89.6	86.4

[a] Measured in C_6D_6 at 23 °C; coupling constants $J(^{29}Si, ^{13}C)$ are given in parenthesis [±0.4 Hz]; (br), a broad ^{13}C resonance signal as the result of partially relaxed scalar $^{13}C-^{11}B$ coupling.[45–48]
[b] Phenyl carbons without assignment.

Table 3. Selected calculated structural parameters and NMR parameters[a] of the silacyclobutenes 6–8

Compound	**6**	**7**	**8**	**5a** (exp.)
d(Si–C2)	188.7	189.3	188.7	187.40 (10)
		188.8 (Me)		
d(Si–C4)	188.2	188.8	188.8	185.91 (15)
d(C2–C2′)	133.7	133.8	134.0	132.6 (2)
d(C3–C4)	137.5	137.5	137.9	137.4 (2)
d(C2–C3)	150.1	150.2	149.4	149.6 (2)
d(C3–B)	157.0	156.9	156.9	156.1 (2)
C2–Si–C4	74.4	74.1	74.4	74.76 (7)
Me–Si–Me	—	109.2	—	109.84 (7) (Ph–Si–Ph)
Si–C2–C3	88.4	88.5	88.5	88.32 (10)
C2–C3–C4	104.7	104.7	104.8	104.22 (13)
C3–C4–Si	92.5	92.6	92.3	92.70 (10)
δ^{11}B	79.0	79.4	84.9[b]	89.1
δ^{13}C (C2, C2′, C3, C4)	146.3, 131.6, 189.5, 165.6	154.4, 129.0, 184.9, 175.0	147.0, 135.1. 192.8, 155.4	147.6, 140.0, 180.4, 168.0
δ^{29}Si	−36.3	14.7	−40.3	−2.0, 8.9 (B)
$\lvert^1J[^{29}Si, ^{13}C(2)]\rvert$[c]	46.6	45.2	48.8	53.0 (**5b**). 52.6 (B)
$\lvert^1J[^{29}Si, ^{13}C(4)]\rvert$[c]	48.4	47.2	49.9	55.8 (**5b**), 54.1 (B)
$\lvert^1J[^{29}Si, ^{13}C(Me)]\rvert$[c]	—	36.7, 37.8	—	44.6 (B)

[a] B3LYP/6–311 + G(d,p); calcd. $\sigma(^{13}C)$ data are converted to $\delta^{13}C$ data by $\delta^{13}C = \sigma(^{13}C)\ [SiMe_4] - \sigma(^{13}C)$, with $\sigma(^{13}C)\ [SiMe_4] = 184.0$, $\delta^{13}C\ [SiMe_4] = 0$; calcd $\sigma(^{11}B)$ data are converted to $\delta^{11}B$ data by $\delta^{11}B = \sigma(^{11}B)\ [B_2H_6] - \sigma(^{11}B) + 18$, with $\sigma(^{11}B)\ [B_2H_6] = 84.1$, $\delta^{11}B\ [B_2H_6] = 18.0$ and $\delta^{11}B\ [BF_3{-}OEt_2] = 0$; calcd $\sigma(^{29}Si)$ data are converted to $\delta^{29}Si$ data by $\delta^{29}Si = \sigma(^{29}Si)\ [SiMe_4] - \sigma(^{29}Si)$, with $\sigma(^{29}Si)\ [SiMe_4] = 340.1$, $\delta^{29}Si\ [SiMe_4] = 0$.
[b] Steric interactions between the phenyl and the BMe_2 groups lead to a twist of the BC_2 plana against the ring plane, similar to the real situation in the cases of **5**. Therefore, the calcd $\delta^{11}B$ value for **8** is more close to the experimental data.
[c] Adding of about 15% from the calcd. value gives data close to experimental results.

carried out with samples in 5 mm tubes at 23 ± 1 °C. A Varian Inova 300 spectrometer was used for ^1H, ^{11}B, ^{13}C and ^{29}Si NMR; chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_5H) = 7.15; $\delta^{13}C$ (C_6D_6) = 128.0; $\delta^{29}Si = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz]; external $BF_3{-}OEt_2$ [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz]. Chemical shifts δ^1H are given to ±0.03 ppm, $\delta^{13}C$ and $\delta^{29}Si$ to ±0.1 ppm, and $\delta^{11}B$ to ±0.3 ppm. ^{29}Si NMR spectra were measured using the refocused INEPT pulse sequence,[58–61] based on $^3J(^{29}Si, ^1H_{Ph})$ (ca. 7 Hz) and $^3J(^{29}SiC{=}C^1H)$ (ca. 20 Hz). The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

MO calculations were carried out using the Gaussian 03 (Revision B02)[44] program package by optimizing geometries at the B3LYP/6–311 + G(d,p) level of theory, and the calculations of NMR parameters such as chemical shifts and coupling constants were performed at the same level.

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Synthesis of the alkyn-1-yl(chloro)diphenylsilanes 1a,b

A suspension of RC≡C–Li (R = Bu, Ph; 19.5 mmol) was prepared in hexane (60 ml), and the solution was cooled to −78 °C. Then dichlorodiphenylsilane (8.5 ml, 39mmol, in 2-fold excess) was added dropwise with constant stirring. The reaction mixture was warmed to room temperature and kept stirring for 3–4 h. The solution was filtered and volatiles were removed *in vacuo*. The colorless oily residue was identified as a mixture of $Ph_2(Cl)Si–C≡C–R$ and $Ph_2Si–(C≡C–R)_2$. Pure samples of **1a,b** was obtained by fractional distillation with yields ranging from 35 to 50% in repeated experiments.

1a: b.p. = 110–120 °C (0.375 Torr). ^{1}H NMR ($CDCl_3$): δ = 2.5, 1.5, 1.7, 1.0 (m, m, m, t, 9H, Bu); 7.5–7.9 (m, 10H, $SiPh_2$); ^{13}C NMR: δ [$J(^{29}Si, ^{13}C)$ = 134.3 (*o*), 133.0 [80.2] (*i*), 130.8 (*p*), 128.0 (*m*) (Ph_2Si); 113.8 [22.2] (≡C); 78.1 [114.4] (SiC≡); 30.1, 21.9, 19.7, 13.5 (Bu); ^{29}Si NMR: δ = −20.0.

1b: b.p. = 170–175 °C (0.375 Torr). ^{1}H NMR ($CDCl_3$): δ = 7.4–7.9 (m, 15H, $SiPh_2$, Ph); ^{13}C NMR: δ [$J(^{29}Si, ^{13}C)$] = 134.7 (*o*), 132.8 [89.5] (*i*), 129.8 (*p*), 128.5 (*m*) (Ph_2Si); 132.6 (*p*), 131.1 (*o*), 128.6 (*m*), 121.8 (*i*) (Ph); 110.2 [28.0] (≡C); 87.3 [118.1] (SiC≡); ^{29}Si NMR: δ = −19.1.

Hydroboration of 1a,b with one equivalent of 9-BBN to give the alkenyl(diphenyl)silanes 2a,b

$Ph_2(Cl)Si–C≡C–Bu$ (1.12 g, 3.70 mmol) was dissolved in toluene (10 ml) and 9-BBN (0.46 g, 3.70 mmol) was added as a solid in one portion. The reaction mixture was heated to reflux at 130 °C for 3 h, solvent was removed in vacuum and the colorless oil remaining was identified as pure **2a**, formed in essentially quantitative yield. The alkenylsilane **2b** was obtained in the same way, except for a heating period of 1 h.

2a: ^{1}H NMR (C_6D_6): δ = 2.2, 1.2, 1.0, 0.7 (m, m, m, t, 9H, Bu), 1.3–1.9 (m, 14H, 9-BBN), 7.2 (t, 1H, =CH, ^3J (^{1}H, ^{1}H) = 7.4 Hz), 7.1–7.7 (m, 10H, $SiPh_2$).

2b: ^{1}H NMR ($CDCl_3$): δ = 1.1–1.7 (m, 14H, 9-BBN), 8.1 [s, 1H, =CH, $^3J(^{29}Si, ^1H)$ = 20.4 Hz], 6.8–7.5 (m, 15H, $SiPh_2$, Ph).

Reaction of the alkenyl(chloro)diphenylsilane 2a,b with LiC≡CPh to give borate 3a, alkyn-1-ylsilanes 4a,b and finally the silacyclobutenes 5a,b

To a freshly prepared suspension of PhC≡C–Li at −78 °C in 10 ml of hexane 1.62 g (3.84 mmol) of **2a** was added, the reaction mixture was warmed to room temperature, and was kept stirring for 3 h. Then solid materials were separated by filtration, and the solvent was removed *in vacuo*. A colorless oily liquid was left, which was identified as mixture of **3a** (borate) as a side product (~25% from proton NMR) and **4a**. The alkyn-1-ylsilane **4b** (without the borate **3b**) was obtained in the same way.

3a: ^{1}H NMR (C_6D_6) = 2.1, 0.7–0.9, 0.7 (m, m, t, 9H, Bu), 1.0–1.7 (m, 14H, 9–BBN). 7.2 (t, 1H, =CH, $^3J(^1H, ^1H)$ = 7.2 Hz), 6.8–7.7 (m, 15H, $SiPh_2$, Ph).

4a: ^{1}H NMR (C_6D_6): δ = 2.3, 0.7–0.9, 0.5 (m, m, t, 9H, Bu), 1.0–1.7 (m, 14H, 9-BBN), 7.1 (t, 1H, =CH, $^3J(^1H, ^1H)$ = 7.2 Hz), 6.8–7.7 (m, 15H, $SiPh_2$, Ph).

4b: δ ^{1}H (ppm) = 6.6–7.8 (m, 20H, $SiPh_2$, Ph, Ph), 8.1 [s, 1H, =CH, $^3J(^{29}Si, ^1H)$ = 17.8 Hz], 1.3–1.8 (m, 14H, 9-BBN).

The mixture of **3a** and **4a** was dissolved in toluene (3 ml), and heated at 120 °C overnight. Then the solvent was removed, leaving the crude product **5a**. The solid was taken up in pentane, and crystals of **5a** were obtained in ca. 30% yield after slow evaporation of the solvent at room temperature.

Compound **4b** was sealed as a C_6D_6-solution in an NMR tube and was kept at 120 °C. The intramolecular rearrangement into **5b** was complete in 48 h, as indicated by NMR spectra. The crude product **5b** can be obtained quantitatively.

5a: m.p. = 80 °C. ^{1}H NMR = 2.3, 1.2–1.3, 0.7 (m, m, t, 9H, Bu), 1.4–2.0 (m, 14H, 9BBN), 6.3 [t, 1H, =CH, $^3J(^1H, ^1H)$ = 7.2 Hz], 7.1–7.9 (m,15H, $SiPh_2$, Ph).

5b: ^{1}H NMR = 1.4–2.0 (m, 14H, 9–BBN), 7.4 [s, 1H, =CH, $^3J(^{29}Si, ^1H)$ = 19.6 Hz], 6.8–8.0 (m, 20H, $SiPh_2$, Ph, Ph).

X-Ray structural analysis of the silacyclobutene 5a

The X-ray crystal structural analysis of **5a** was carried out for a single crystal (0.20 × 0.46 × 0.70 mm^3; selected in perfluorinated oil[62] at room temperature) at 191(2) K using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit; wavelength: 0 71069 Å. $C_{34}H_{39}BSi$, M = 486.55. Triclinic space group: P-1 with unit cell dimensions: a = 9.9670(8), b = 11.6840(9), c = 13.5160(11) Å, α = 76.073(6)°, β = 88.097(7)°, γ = 68.209(6)°, V = 1415.8 (2) Å^3, Z = 2, D_x = 1.141 g cm^{-3}, μ = 0.103 mm^{-1}, range of θ = 2.2–25.1°. Reflections collected = 17682, independent reflections = 4990 [R_{int} = 0.043], parameters = 329. Final R indices [for 4297 reflections with $I > 2\sigma(I)$]: R = 0.043, wR^2 = 0.100; R (all data): R = 0.052, wR^2 = 0.104, GoF = 1.05. Structure solution and refinement were accomplished using SIR97,[63] SHELXL-97[64] and WinGX.[65] The data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 613924. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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