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Combination of 1,2-hydroboration and 1,1-organoboration: synthesis of novel organo-substituted 1-silacyclobutenes†

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The reaction of di(alkyn-1-yl)silanes Me(R)Si(C≡C^{t}Bu)$_2$ [1; R = Me (a), H (b)] with diethylborane or 9-borabicyclo[3.3.1]nonane in a 1 : 1 ratio affords the 1-silacyclobutene derivatives 6a, 7a,b as a result of intermolecular 1,1-hydroboration followed by intramolecular 1,1-organoboration. Intermediates, in which both an alkenyl and an alkynyl group are linked to silicon (2a, 3a), were identified and prepared independently by the reaction of the corresponding chlorosilane 5a with the lithium alkynide LiC≡C^{t}Bu. This procedure also opened the way to a stepwise synthesis of 1-silacyclobutenes with a choice of substituents in the 2,4-positions (6b and 9a). 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). Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: boron; heterocycles; hydroboration; organoboration; multinuclear magnetic resonance; silanes

INTRODUCTION

1,2-Hydroboration of alkyn-1-ylsilanes can be fairly regiospecific[1–9] if the alkynyl group bears a substituent other than hydrogen. Then, the boron atom becomes linked preferably to the alkyne carbon atom bearing the silyl group. A bulky alkyl group at the C≡C bond, most conveniently a ^{t}Bu group, induces close to 100% regiospecificity if diethylborane[10] or 9-borabicyclo[3.3.1]nonane (9-BBN)[11] are used as hydroborating reagents. Recently, it has been shown that 1,2-hydroboration using 9-BBN can be regiospecific even in the presence of two different silyl groups at the C≡C bond.[12] This has led to useful synthons for heterocyclic chemistry, such as **A** or **B**. Treatment of **A** or **B** with lithium alkynides should give either borates **C** or new alkyn-1-ylsilanes such as **D**, both of which could undergo intramolecular rearrangements corresponding either to the reactions of alkyn-1-ylborates with electrophiles[13–15] or to 1,1-organoboration reactions.[16] On the other hand, the controlled 1 : 1 reaction of Me$_2$Si(C≡C^{t}Bu)$_2$ (**1a**) or Me(H)Si(C≡C^{t}Bu)$_2$ (**1b**) with dialkylborane, R$_2$BH, should also give **D** or **E** by 1,2-hydroboration. In **D** and **E**, the second ^{t}BuC≡C group is already present and ready for intramolecular 1,1-organoboration. In this work, we report that compounds of type **1** are attractive starting materials for the combination of 1,2-hydroboration and 1,1-organoboration, and that compounds of type **A** or **B** with R$_2$B = Et$_2$B or 9-BBN are again[10,11] useful starting materials for heterocyclic synthesis.

RESULTS AND DISCUSSION

Hydroboration of bis(alkyn-1-yl) dimethylsilanes 1 with 'Et$_2$BH' or 9-BBBN

The 1 : 1 reaction of **1a** with tetraethyldiborane(6)[17] (Et$_2$BH is used for simplicity: tetraethyldiborane(6) is usually obtained and used as a mixture with triethylborane and small amounts

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†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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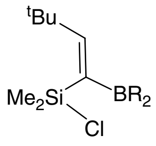
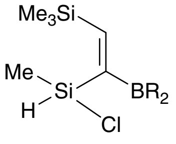

A

R = alkyl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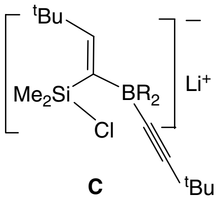
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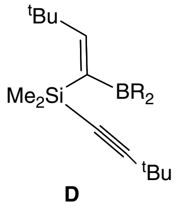
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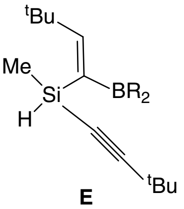
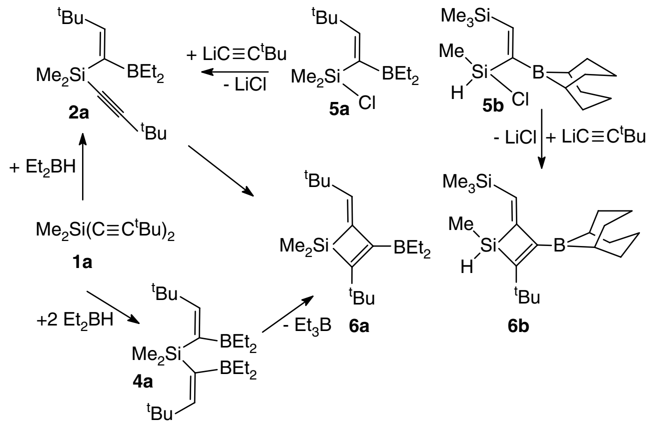

E

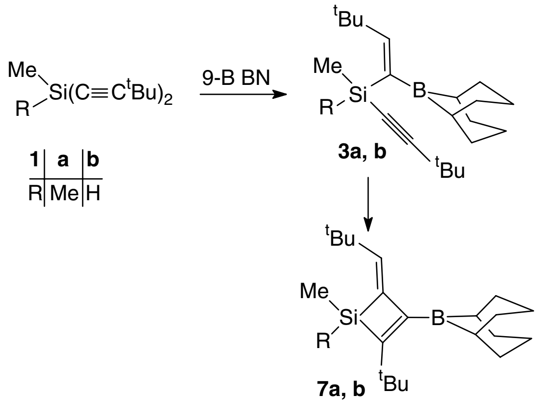
of other ethyldiboranes(6)), shown in Scheme 1, or of **1a** or **1b** with 9-BBN (Scheme 2) affords selectively the alkenes **2a** and **3a,b**. The compound **2a** is also formed by treatment of the chlorosilane **5a** (type **A**) with one equivalent of ^{t}BuC≡CLi. The compounds **2a** and **3a,b** in benzene or toluene solution rearrange slowly at room temperature or within 2–3 h at 80 °C into the cyclic silanes **6a** and **7a,b** respectively. This rearrangement is highly selective. In contrast, when the chlorosilane **5b** (type **B**) is treated with ^{t}BuC≡CLi, intermediates are not detected, and the final product is the cyclic silane **6b** (Scheme 1). If two equivalents of Et_2BH are offered in the reaction with **1a**, the bis(alkenyl)silane **4a** is formed. Heating of solutions of **4a** at reflux in benzene also leads to **6a**. However, numerous other unidentified products are formed at the same time. If $Me_2Si(C{\equiv}CMe)_2$ is used instead of **1a**, then the initial formation of products analogous to **D** and **4a** can be deduced from the ^{29}Si NMR spectra (signals at $\delta^{29}Si = -33.8$ corresponding to type **D**, and at $\delta^{29}Si = -31.2$ corresponding to **4a**). However, there were many additional small ^{29}Si NMR signals that became dominant after several hours, indicating the progress of complex reactions. It has been shown that these reactions, depending on reaction conditions, lead to organo-substituted 1-carba-*arachno*-pentaboranes(10)[18,19] or to a tricyclic tetraboradisiladodecane.[20] Monitoring of the reactions by using IR spectroscopy was not conclusive, since the bands for ν(C≡C) or ν(C=C) respectively, in the starting materials, intermediates and products overlap. Similarly, mass spectra of the products were not useful for structural assignments owing to the low intensity of the peaks of the respective molecular ions (in the electron impact (EI) mass spectra) and the extreme sensitivity of the products towards traces of oxygen. Thus, the proposed structures are based on NMR spectroscopy (*vide infra*), using a multinuclear approach, of the reaction solutions and of solutions after isolating the products.

Reaction of the chlorosilane 5a with $Me_3SiC{\equiv}CLi$

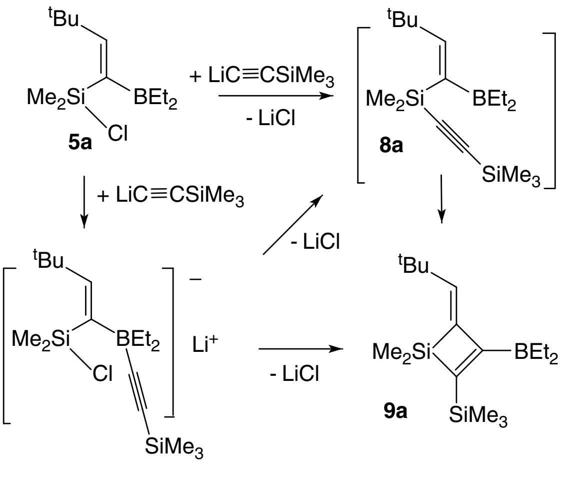
Chlorosilanes of type **A** or **B** contain two electrophilic centres, one at the silicon and the other one at the boron atom. In the reactions of **5a** or **5b** with ^{t}BuC≡CLi (Scheme 1) we could not detect (^{11}B and ^{29}Si NMR) the intermediate formation of a 1-alkynylborate of type **C** (a possible product if the nucleophilic attack takes place preferably at the site of the boron atom) on the way to **2a**. Thus, the reaction of **5a** with $Me_3SiC{\equiv}CLi$ served two purposes: (i) looking again for a borate intermediate of type **C** prior to elimination of LiCl, and (ii) establishing a stepwise route to the novel 1-sila-cyclobutenes. As shown in Scheme 3, neither a borate intermediate nor the silane **8a**, analogous to **2a**, were detected. Therefore, the 1-silacyclobutene **9a** is formed either by fast intramolecular reaction of a short-lived borate or by fast rearrangement of the unstable silane **8a**.



Scheme 1.



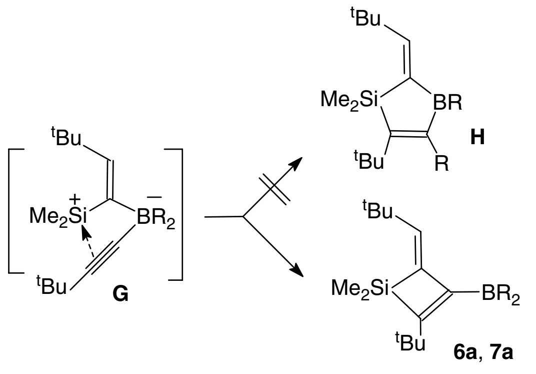
Scheme 2.



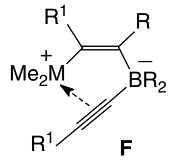
Scheme 3.

Proposed mechanism of the intramolecular rearrangement of 2a and 3a,b

It has been shown previously that intramolecular 1,1-organoboration reactions lead to siloles, germoles, stannoles 1,4-stannabora-2,5-cyclohexadienes, and plumboles and 1,4-plumbabora-2,5-cyclohexadienes.[16] In the cases of the tin and lead heterocycles, zwitterionic intermediates have been isolated and their molecular structures characterized by X-ray analysis.[21–23] Therefore, reactive species of type **E** are firmly established as intermediates in intramolecular 1,1-organoboration reactions. In analogy, we propose (Scheme 4) that the alkyn-1-ylsilanes of type **C** rearrange at first into the short-lived zwitterionic intermediate **F**, which is reminiscent of **E**. Then, starting from **F** there are two alternatives for 1,1-organoboration: either a group R (alkylboration) or the olefinic carbon atom from the =C–B bond (vinylboration) is transferred to the adjacent alkynyl carbon atom. The former reaction would give a five-membered ring **G**, which was not observed, whereas the latter reaction leads to **H**, in agreement with the experimental results for **6a**, and **7a,b**.



Scheme 4.



F

M = Sn, Pb

The present results indicate that the combination of 1,2-hydroboration and intramolecular 1,1-organoboration provides a new route to 1-silacyclobutene derivatives. Previously, such compounds have been obtained by various methods, some of which are transition-metal mediated[24–26] or are based on inter- and intra-molecular [2 + 2]cycloadditions.[27–30]

NMR spectroscopic results

The ^{11}B, ^{13}C and ^{29}Si NMR data of the compounds **2, 3** and **4** are collected in Table 1, and those of the 1-silacyclobutene derivatives are given in Table 2. ^{1}H NMR data are given in the Experimental section. The consistent data set is in complete agreement with the proposed structures. The chemical shifts δ^{11}B cover a small range, typical of three-coordinate boron atoms in triorganoboranes, with little or negligible BC(pp)π interactions.[31] The ^{29}Si NMR spectra,[32–35] measured by using ^{1}H$\rightarrow$^{29}Si polarization transfer, e.g. via the insensitive nucleus enhanced by polarization transfer (INEPT) pulse sequence,[36–39] are particularly useful for monitoring the progress of the reaction and to identify intermediates and products by observing the respective ^{13}C satellite signals (see Figs 1 and 2). All ^{29}Si NMR signals of intermediates or products are slightly broadened owing to unresolved scalar ^{29}Si–^{11}B spin–spin coupling across two or three bonds.[40] The ^{29}Si resonances of the alkenylsilanes **2a, 3a** and **4** are at rather low frequency (compare δ^{29}Si [$Me_2Si(CH{=}CH_2)_2$] − 13.7[32–35]). This is ascribed to the boryl groups in geminal position with respect to silicon at the C=C bond. The preferred orientation of the CCB plane of the boryl group relative to the π system of the C=C bond also seems to have an influence. The Et_2B group prefers an orthogonal arrangement of the CBC and the B–C=C planes, whereas the 9-BBN group can adopt a parallel arrangement of these planes. This is particularly evident from the δ^{13}C data of the olefinic carbon atom in β-position relative to the boron atom.[41,42] Comparison of the data, e.g. for **2a** and **3a** shows significant deshielding of the respective ^{13}C nucleus in the latter compound. This marked deshielding influence of the 9-BBN group in comparison with the Et_2B group is no longer evident in the case of the 3-dialkylboryl-1-silacyclobutene derivatives, e.g. δ^{13}C(4) of **6a** and **7a** (Table 2), since the steric repulsion exerted by the ^{t}Bu group in 4-position enforces both boryl groups to adopt the orthogonal arrangement. The combined information from ^{1}H, ^{29}Si and ^{13}C NMR data allows for conclusive structural assignment of the final products. In the ^{13}C NMR spectra, the observation

Table 1. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the alkenyl(alkynyl)silanes **2a**, **3a** and of the bis(alkenyl)silane **4a**

Compound BR$_2$	**2a** BEt$_2$	**3a** 9-BBN	**4a** BEt$_2$
$\delta^{13}\mathrm{C}(^t\mathrm{Bu}\mathbf{CH}{=})$	150.9	165.2	149.4
$\delta^{13}\mathrm{C}(\mathrm{B}\mathbf{C}(\mathrm{Si}){=})$	145.5 (br) [60.9][b]	144.5 (br)	149.9 (br) [56.9][c]
$\delta^{13}\mathrm{C}(\mathrm{Si}\mathbf{Me})$	3.2 [56.7][b]	3.5 [57.0]	5.2 [52.9]
$\delta^{13}\mathrm{C}(\mathrm{B}\mathbf{R}_2)$	21.7 (br), 9.5	31.6 (br), 34.7, 23.5	21.4 (br), 9.0
$\delta^{13}\mathrm{C}(^t\mathbf{Bu}\mathrm{C}{=})$	36.7, 30.8	36.7, 30.7	37.3, 30.9
$\delta^{13}\mathrm{C}(\mathbf{C}{\equiv}\mathbf{C}^t\mathrm{Bu})$	83.4 [86.5][b], 116.5 [15.8][b]	84.8 [87.0], 116.4 [15.8]	—
$\delta^{13}\mathrm{C}(^t\mathbf{Bu}\mathrm{C}{\equiv})$	28.1, 30.9	28.3, 30.9	—
$\delta^{29}\mathrm{Si}$	−36.1	−31.5	−30.2
$\delta^{11}\mathrm{B}$	+81.4	+81.7	+82.5

[a] Measured in C_6D_6 at 20 °C; coupling constants $J(^{29}\mathrm{Si},^{13}\mathrm{C})$ [±0.1 Hz] are given in brackets; (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar $^{13}\mathrm{C}-^{11}\mathrm{B}$ spin–spin coupling.

[b] Measured from the ^{29}Si NMR spectrum (see Fig. 1); isotope-induced shifts $^1\Delta^{12/13}\mathrm{C}_{\mathrm{Me}}(^{29}\mathrm{Si}) = +1.0$ ppb; $^1\Delta^{12/13}\mathrm{C}_{\mathrm{C}=}(^{29}\mathrm{Si}) = -5.0$ ppb; $^1\Delta^{12/13}\mathrm{C}_{\mathrm{C}\equiv}(^{29}\mathrm{Si}) = -13.1$ ppb; compare with **1**: $^1\Delta^{12/13}\mathrm{C}_{\mathrm{Me}}(^{29}\mathrm{Si}) = \pm 0$ ppb; $^1\Delta^{12/13}\mathrm{C}_{\mathrm{C}\equiv}(^{29}\mathrm{Si}) = -19.4$ ppb.

[c] Measured from the ^{29}Si NMR spectrum; isotope-induced shifts $^1\Delta^{12/13}\mathrm{C}_{\mathrm{Me}}(^{29}\mathrm{Si}) = -3.5$ ppb; $^1\Delta^{12/13}\mathrm{C}_{\mathrm{C}=}(^{29}\mathrm{Si}) = -6.5$ ppb.

Table 2. ^{11}B, ^{13}C, ^{29}Si NMR data[a] of the heterocycles **6a**,**b**, **7a**,**b** and **9a**

Compound BR$_2$	**6a**[b] BEt$_2$	**6b** 9-BBN	**7a**[c] 9-BBN	**7b** 9-BBN	**9a** BEt$_2$
$\delta^{13}\mathrm{C}(^t\mathrm{Bu}\mathbf{CH}{=})$	138.0	129.2 [70.4]	140.0	141.0	140.7
$\delta^{13}\mathrm{C}(\mathbf{C}(2))$	141.8 [50.8][b]	161.0 [54.4]	142.8 [52.6]	138.8	146.7 [49.9][c] [15.8][c,d]
$\delta^{13}\mathrm{C}(\mathbf{C}(3))$	172.5 (br)	178.7 (br)	173.4 (br)	175.6 (br)	193.8 (br)
$\delta^{13}\mathrm{C}(\mathbf{C}(4))$	166.8 [54.1][b]	171.6 [53.5]	169.0 [54.1]	167.0 [54.0]	157.1 [40.5][c] [64.9][c,e]
$\delta^{13}\mathrm{C}(\mathrm{Si}\mathbf{Me})$	1.4 [45.9][b]	−1.2 [44.4], −0.1 [51.6] (Me$_3$Si)	1.5 [44.6]	−0.6 [45.0]	2.1 [51.3][c]
$\delta^{13}\mathrm{C}(\mathrm{B}\mathbf{R}_2)$	21.2 (br), 8.9	32.6 (br), 33.9, 34.0, 23.1	32.6 (br), 33.7, 23.6	32.5 (br), 34.2, 34.3, 23.7	22.0 (br), 9.0
$\delta^{13}\mathrm{C}(^t\mathbf{Bu}\mathrm{C}{=})$	34.0 [3.6], 29.8 [8.0]	—	not assigned[g]	34.9, 30.4	34.7, 30.2
$\delta^{13}\mathrm{C}(^t\mathbf{Bu}\mathrm{C}(4))$	34.8 [5.3], 30.5 [<2]	35.1, 31.7	not assigned[g]	35.4, 32.0	—
$\delta^{13}\mathrm{C}(\mathbf{Me}_3\mathrm{Si}\text{-}4)$		—	—	—	0.3 [51.4][c]
$\delta^{29}\mathrm{Si}$	+8.9	−8.7 [6.9], −6.6 (SiMe$_3$)	+8.9	−10.5	+17.2, −12.0 (4-SiMe$_3$)[f]
$\delta^{11}\mathrm{B}$	87.0	86.9	86.4	87.5	+86.7

[a] Measured in C_6D_6 at 20 °C; coupling constants $J(^{29}\mathrm{Si},^{13}\mathrm{C})$ are given in brackets [±0.2 Hz]; (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar $^{13}\mathrm{C}-^{11}\mathrm{B}$ coupling.

[b] Measured from the ^{29}Si NMR spectrum.

[c] Coupling constants $^nJ(^{29}\mathrm{Si},^{13}\mathrm{C})$ measured from the ^{29}Si NMR spectrum (see Fig. 2) in agreement with data from the ^{13}C NMR spectrum (see Fig. 4); isotope-induced shifts $^1\Delta^{12/13}\mathrm{C}_{\mathrm{Me}}(^{29}\mathrm{SiMe}_3) = -4.3$ ppb; $^1\Delta^{12/13}\mathrm{C}(4)(^{29}\mathrm{SiMe}_3) = -4.5$ ppb; isotope-induced shifts $^1\Delta^{12/13}\mathrm{C}(^{29}\mathrm{SiMe}_2)$ were not sufficiently accurate owing to the effect of temperature gradients in the sample.

[d] $^3J(^{29}\mathrm{Si},^{13}\mathrm{C})$.

[e] Coupling with ^{29}Si of the Me$_3$Si group.

[f] $^2J(^{29}\mathrm{Si},^{29}\mathrm{Si}) = 8.6$ Hz.

[g] Overlapping signals with region of 9-BBN signals.

of broad ^{13}C NMR signals, as a result of partially relaxed $^{13}\mathrm{C}-^{11}\mathrm{B}$ spin–spin coupling,[43] is helpful for the assignment as well as the detection of ^{29}Si satellite signals owing to the coupling constants $^nJ(^{29}\mathrm{Si}, ^{13}\mathrm{C})$ ($n = 1$, 3) (see Figs 3 and 4). These data can then be compared with the coupling constants $^nJ(^{29}\mathrm{Si}, ^{13}\mathrm{C})$ measured from the ^{29}Si NMR spectra (see Figs 1 and 2). Observation of ^{13}C satellites in ^{13}C NMR spectra, e.g. of **7a**, indicates that the olefinic ^{13}C (=CH) nucleus is linked to a ^{t}Bu group, which excludes any other cyclic structure.

CONCLUSIONS

Although the combination of 1,2-hydroboration and 1,1-organoboration has been applied unintentionally in previous work,[44] the present results demonstrate that it can be developed into a versatile synthetic method. The 1-silacyclobutene derivatives reported here for the first time open numerous possibilities for further transformations considering the reactive B–C bonds, the diene system, the Si–C bonds, and, in the cases of **6b** and **7b**, also the Si–H bond.

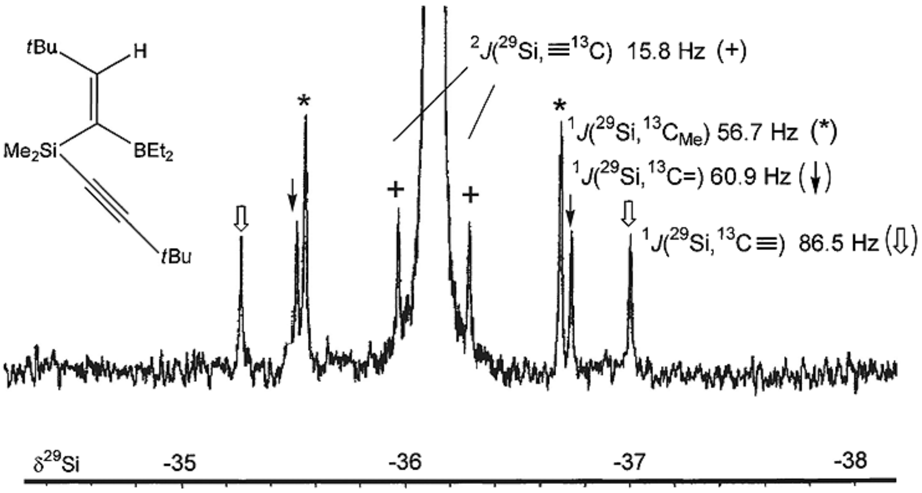


Figure 1. 99.8 MHz ^{29}Si{^{1}H} NMR spectrum of **2a** (15% in C_6D_6), measured by using the INEPT pulse sequence,[36–39] based on $^2J(^{29}Si, ^1H) = 7$ Hz (acquisition time 6 s, repetition time 8 s, result of 256 transients). Four different sets of ^{13}C satellites are resolved as indicated (see Table 1 for isotope-induced chemical shifts $^1\Delta^{12/13}C(^{29}Si)$).

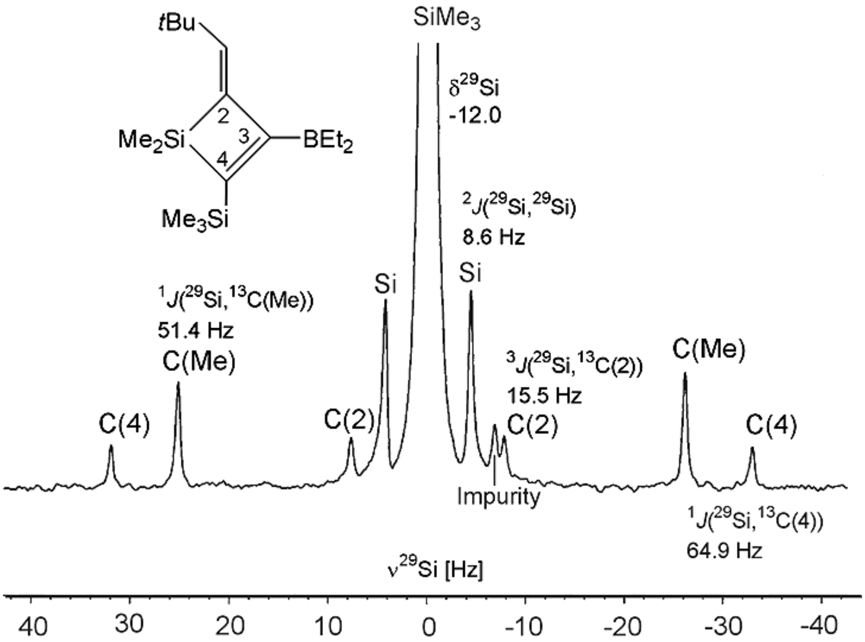


Figure 2. 99.8 MHz ^{29}Si{^{1}H} NMR spectrum of **9a** (10% in C_6D_6), showing the ^{29}Si(SiMe$_3$) signal, measured by using the INEPT pulse sequence,[36–39] based on $^2J(^{29}Si, ^1H) = 7$ Hz (acquisition time 4.5 s, repetition time 6 s; result of 384 transients. In addition to the ^{29}Si satellites corresponding to $^2J(^{29}Si,^{29}Si)$, all pairs of ^{13}C satellites for $^1J(^{29}Si,^{13}C)$ and one pair for $^3J(^{29}Si,^{13}C)$ are resolved as indicated.

EXPERIMENTAL

Starting materials and measurements

All preparations and handling of samples was carried out under an inert atmosphere (argon or nitrogen), and carefully oven-dried glassware and dry solvents were used. BuLi in hexane (1.6 M), 9-BBN and triethylborane were commercial products. The di(alkyn-1-yl)silanes **1a** and **1b**[45,46] and the alkyn-1-yl(chloro)silanes **5a**[10] and **5b**[11] were prepared following literature procedures. The reagent 'Et$_2$BH'[17] was prepared as described and the hydride concentration (1.17%) was determined by ^{11}B NMR spectroscopy.[47]

Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet; the *m*/*z* data refer to the isotopes ^{1}H, ^{11}B, ^{12}C, ^{28}Si. NMR measurements in C_6D_6 (concentration *ca* 5–10%)

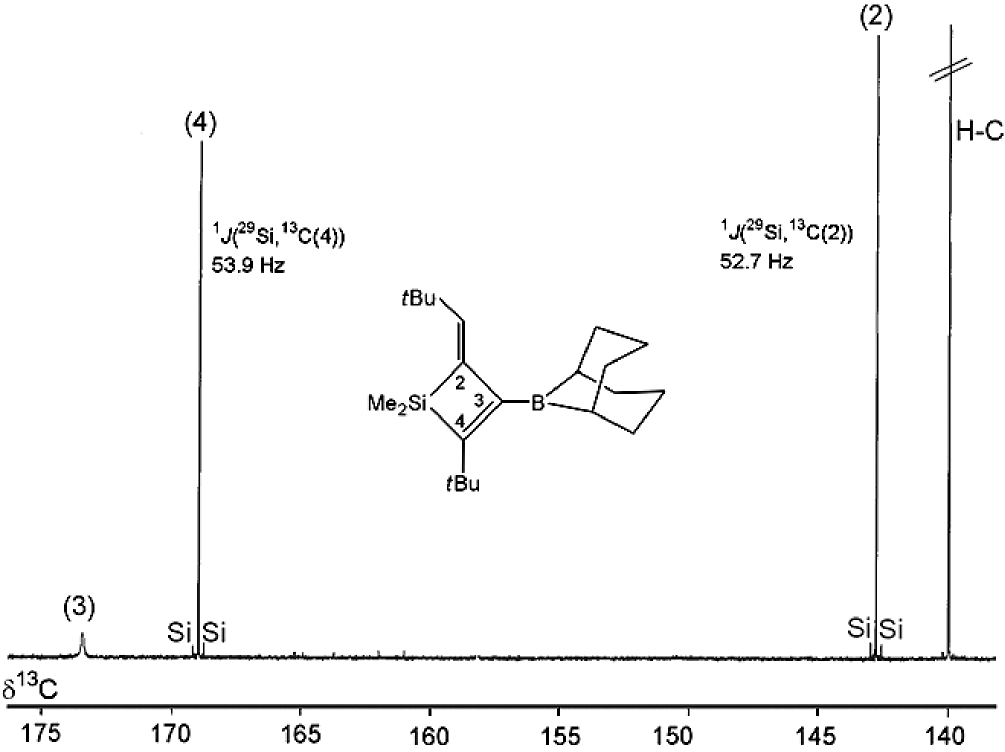


Figure 3. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the 1-silacyclobutene **7a** in C_6D_6 (10%) (acquisition time 1.8 s; 30° pulse, result of 6000 transients; 3.5 h of spectrometer time).

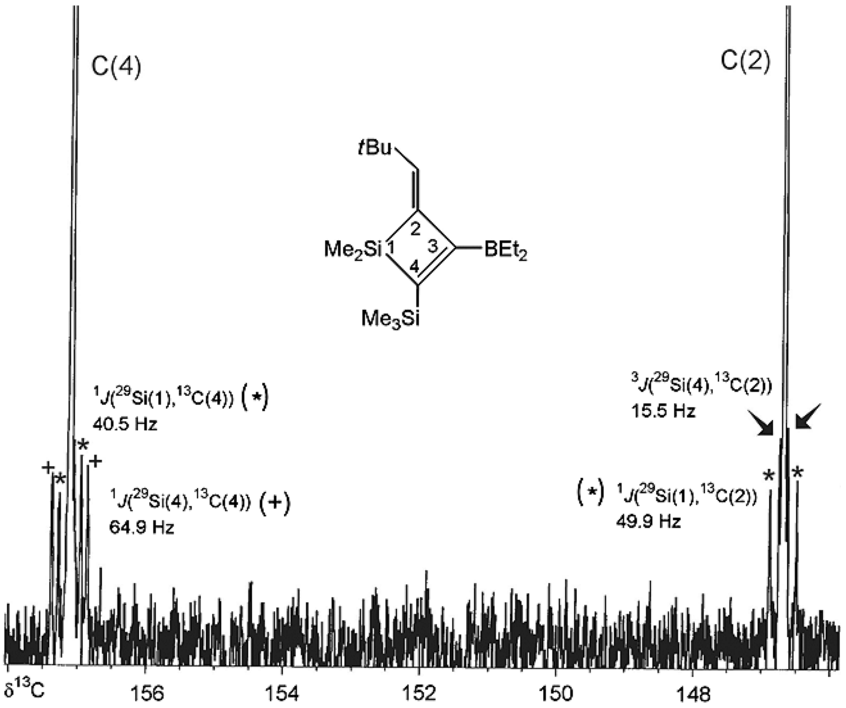


Figure 4. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the 1-silacyclobutene **9a** in C_6D_6 (10%), measured by the refocused INEPT pulse sequence,[36–39] based on $^3J(^{13}C,Si,C,^1H) = 3$ Hz (acquisition time 5 s, repetition time 5 s; result of 32 transients). Even after 5 min of spectrometer time the ^{29}Si satellites are clearly visible for the ^{13}C NMR signals of the quaternary $^{13}C(2,4)$ nuclei.

with samples in 5 mm tubes at 23 ± 1 °C: Bruker ARX 250 and Bruker DRX 500 spectrometers for ^{1}H, ^{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 are given to ±0.1-ppm, although the experimental data set would allow for greater accuracy. However, using different spectrometers, the reproducibility of the δ values is not as accurate as the coupling constants J. ^{29}Si NMR spectra were measured by using the refocused INEPT pulse sequence,[36–38] based on $^2J(^{29}Si, ^1H_{Me})$ (*ca* 7 Hz) and $^3J(^{29}SiC{=}C\,^1H)$ (*ca* 23 Hz). Isotope-induced chemical shifts $^1\Delta\ ^{12/13}C(^{29}Si)$ (ppb) are given with a negative sign if the signal of the heavy isotopomer is shifted to low frequency with respect to that of the lighter isotopomer. The digital resolution was set to 0.03 Hz in order to measure isotope effects precisely, which also allows one to measure coupling constants $J(^{29}Si, ^{13}C)$ much more accurately than from routine ^{13}C NMR spectra. ^{13}C NMR signals of the quaternary carbon atoms are readily observed by using the INEPT technique based on long-range coupling constants $^nJ(^{13}C, ^1H)$ ($n = 2, 3$; mainly for $n = 3$ arising from SiMe groups) in order to observe ^{29}Si satellites within a short time (see Fig. 4).

*Hydroboration of **1a** with one equivalent of 'Et$_2$BH' to give pure **2a***

A solution of the silane **1a** (0.3 g, 1.36 mmol) in C_6D_6 (0.7 ml) was placed in an NMR tube and the corresponding amount of 'Et_2BH'[17] was injected in several portions through a syringe into this solution. The progress of the reaction was monitored by ^{1}H and ^{29}Si NMR. Addition of one equivalent of hydride afforded pure **2a**. After several hours at room temperature, partial rearrangement of **2a** into **6a** became apparent, and after 6 h at 80 °C the conversion was complete. **2a**: ^{1}H NMR (C_6D_6; 250.1 MHz): $\delta = 0.20$ (s, 6H, $SiMe_2$), 1.00, 0.98 (s, s, 9H, 9H, $\equiv C{-}^tBu$, $=C{-}^tBu$), 1.3–0.8 (m, 10H, BEt_2), 5.57 (s, 1H, =CH; $^3J(^{29}Si, ^1H) = 18.6$ Hz). **6a**: ^{1}H NMR (C_6D_6; 250.1 MHz): $\delta = 0.38$ (s, 6H, $SiMe_2$), 0.97, 0.98 (s, s, 9H, 9H, $=C{-}^tBu$, $=C{-}^tBu$), 0.84–1.31 (m, 10H, BEt_2), 5.23 (s, 1H, =CH; $^3J(^{29}Si, ^1H) = 18.3$ Hz).

*Hydroboration of **1a** with two equivalents of 'Et$_2$BH' to give **4a***

The silane **1a** (1.7 g, 7.7 mmol) was added in one portion to a cold (−78 °C), stirred solution of 'Et_2BH'[17] in hexane (20 ml), containing 15 mmol of hydride. After warming to room temperature, all volatile materials were removed *in vacuo* and an oily liquid (2.72 g, >98%) was left, identified as the pure (>95%; containing a small amount of the 1-silacyclobutene **6a**) dialkenylsilane **4a**. Heating of **4a** at 60–70 °C in benzene induces decomposition and formation of the 1-silacyclobutene **6a** (70%; 30% are other unidentified silanes: $\delta^{29}Si$ −15.3, −9.5, −3.4, 1.0). **4a**: ^{1}H NMR (C_6D_6; 250.1 MHz): $\delta = 0.25$ (s, 6H, $SiMe_2$), 1.08 (s, 18H, $=C{-}^tBu$), 0.96–1.28 (m, 20H, BEt_2), 5.56 (s, 2H, =CH; $^3J(^{29}Si, ^1H) = 20.2$ Hz). MS: 360 (8%, M^+), 209 (100%).

*Hydroboration of **1a** with 9-BBN*

After addition of 9-BBN (0.24 g, 2 mmol) in one portion to a solution of **1a** (0.44 g, 2 mmol) in toluene (3 ml), the mixture was stirred for 3 h at room temperature. ^{1}H and ^{29}Si NMR spectra showed that 85% of **1a** was converted selectively into **3a**. On keeping this solution at room temperature for a further 12 h, **1a** was found to consumed completely but, at the same time, **3a** had rearranged to *ca* 50% into the silacyclobutene **7a**. Heating of this mixture for 3 h at 80 °C led to complete conversion into **7a**. **3a**: ^{1}H NMR (toluene-d_8; 250.1 MHz): $\delta = 0.41$ (s, 6H, $SiMe_2$), 1.13, 1.35 (s, s, 9H, 9H, $\equiv C{-}^tBu$, $=C{-}^tBu$), 1.95–1.35 (m, 14H, 9-BBN), 5.87 (s, 1H, =CH; $^3J(^{29}Si, ^1H) = 19.4$ Hz). **7a**: ^{1}H NMR (C_6D_6; 250.1 MHz): $\delta = 0.49$ (s, 6H, $SiMe_2$), 1.08, 1.06 (s, s, 9H, 9H, $=C{-}^tBu$, $=C{-}^tBu$), 2.3–1.5 (m, 14H, 9-BBN), 5.77 (s, 1H, =CH; $^3J(^{29}Si, ^1H) = 18.4$ Hz).

*Hydroboration of **1b** with 9-BBN to give **7b***

A suspension/solution of 9-BBN (0.58 g, 4.8 mmol) in toluene was prepared, and **1b** (0.989 g, 4.8 mmol) was added in one portion at room temperature. The mixture was heated at 100 °C for 24 h. Then, the toluene was removed *in vacuo* and a colourless oil was left (1.34 g, 85%), which was identified as pure **7b**. **7b**: ^{1}H NMR (C_6D_6; 250.1 MHz): $\delta = 0.46$ (d, 3H, SiMe; $^3J(^1H,Si,C, ^1H) = 3.6$ Hz), 1.04, 1.02 (s, s, 9H, 9H, $=C{-}^tBu$, $=C{-}^tBu$), 2.0–1.3 (m, 14H, 9-BBN), 5.39 (q, 1H, SiH; $^3J(^1H,Si,C, ^1H) = 3.6$ Hz; $^1J(^{29}Si, ^1H) = 188.5$ Hz), 5.80 (s, 1H, =CH; $^3J(^{29}Si, ^1H) = 18.0$ Hz).

*Reaction of the chlorosilane **5a** with LiC≡C^{t}Bu to give first **2a** and then **6a***

The chlorosilane **5a** (1.189 g, 4.86 mmol) was added in one portion to a vigorously stirred, freshly prepared, cooled (−78 °C) suspension of $LiC{\equiv}C^tBu$ in hexane (15 ml). After 4 h at −78 °C and 2 h at room temperature, insoluble material was filtered off, and the solvent was removed *in vacuo*. The oily residue contained mainly the products **2a** and **6a** in a ratio of 2 : 1 (*vide supra* for ^{1}H NMR data), and heating of the mixture in benzene for 6 h at reflux converted **2a** into **6a**.

*Reaction of the chlorosilane **5a** with LiC≡CSiMe$_3$ to give the 1-silacyclobutene **9a***

A freshly prepared suspension of $LiC{\equiv}CSiMe_3$ (4.87 mmol) in hexane (15 ml) was cooled to −78 °C, and the chlorosilane **5a** was added under vigorous stirring in one portion. After keeping this mixture stirring for 4 h at −78 °C and for 2 h at room temperature, insoluble material was filtered off, and volatile material was removed *in vacuo*. A colourless oil (1.10 g, 74%) was left, and identified as pure **9a**. **9a**: ^{1}H NMR (C_6D_6; 250.1 MHz): $\delta = 0.00$ (s, 9H, $SiMe_3$), 0.37 (s, 6H, $SiMe_2$), 0.97 (s, 9H, $=C{-}^tBu$), 1.02–1.27 (m, 10H, BEt_2), 5.35 (s, 1H, =CH; $^3J(^{29}Si, ^1H) = 18.5$ Hz).

Reaction of the chlorosilane **5b** *with LiC≡C^{t}Bu to give the 1-silacyclobutene* **6b**

The same procedure was used as described for **9a**, except that the reaction mixture was heated at reflux for 24 h. A colourless, oily product was isolated (0.50 g, 83%), and identified as pure **6b**. **6b**: ^{1}H NMR (C_6D_6; 250.1 MHz): $\delta = 0.22$ (s, 9H, $SiMe_3$), 0.55 (d, 3H, SiMe; $^3J(^1H,Si,C,^1H) = 3.65$ Hz), 1.14 (s, 9H, =C–^{t}Bu), 2.0–1.3 (m, 14H, 9-BBN), 5.49 (q, 1H, SiH; $^3J(^1H,Si,C,^1H) = 3.5$ Hz; $^1J(^{29}Si,^1H) = 188.4$ Hz), 6.16 (s, 1H, =CH; $^3J(^{29}Si,^1H) = 22.8$ Hz; $^2J(^{29}Si,^1H) = 5.9$ Hz).

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