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Effect of various substituents on intramolecular 1,1-vinylboration, synthesis of 1-silacyclobutene derivatives

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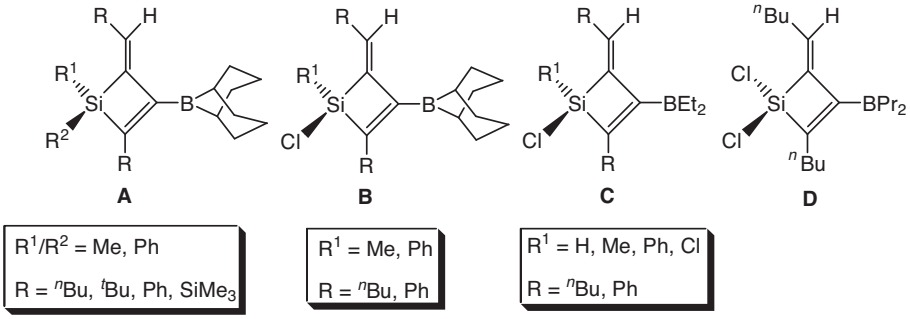
The reaction of 1-boryl-1-alkenyl chlorosilane derivatives with alkynyllithium reagents [Li-C≡C-R^3 (R^3 = Ph, $SiMe_3$)] at low temperature (–78 °C) affords alkenyl(alkyn-1-yl)silanes. These compounds are precursors of 1-silacyclobutene derivatives, which are formed via intramolecular 1,1-vinylboration. This reaction works for various groups at silicon (R^1/R^2: R^1 = H, Me, Ph; R^2 = Me, Ph) and at the C=C and C≡C units (R/R^3: R = ^{n}Bu, Ph; R^3 = ^{n}Bu, Ph, $SiMe_3$). The conversion into 1-silacyclobutene derivatives is incomplete only in the case of R^3 = $SiMe_3$. The reactions were monitored by NMR spectroscopy in order to elucidate the reaction mechanism, and the proposed structures of all new compounds follow from consistent sets of NMR parameters (^{1}H-, ^{13}C-, ^{11}B-, ^{29}Si-NMR).

Key Words: Alkynylsilanes, triorganoboranes, hydroboration, organoboration, silacyclobutenes, NMR

Introduction

Reactions involving 1,2-hydroboration and 1,1-organoboration have been widely used in organic[1–4] as well as in organometallic synthesis.[5–7] Among organometallic compounds the alkynyl metal compounds of group 14 elements such as alkyn-1-ylsilanes have been used in hydroboration and organoboration reactions. Both of these intermolecular reactions require totally different reaction conditions. For instance, 1,2-hydroboration of alkyn-1-ylsilanes takes place under mild reaction conditions,[8–16] in contrast to 1,1-organoboration, which requires more harsh reaction conditions.[5] Numerous novel organometallic compounds have been prepared taking advantage of 1,1-organoboration or 1,2-hydroboration.[17–29] In this context, the combination of 1,2-hydroboration and 1,1-

organoboration has led to a diverse field of heterocyclic chemistry comprising simple silicon heterocycles[30–33] as well as spirosilanes.[34,35] This combination is primarily based on the fact that 1,2-hydroboration allows one to introduce the boryl group into the molecule under mild reaction conditions. Then the activation energy for the 1,1-organoboration becomes lower, since this is now an intramolecular process. Therefore, these reactions take place more readily at comparatively low temperature and in a short time. We have reported 1-silacyclobutene derivatives **A-D**[36–38] (Scheme 1). These derivatives have been studied in solution by NMR and the molecular structure for one example has been determined by X-ray diffraction.[36]



Scheme 1. Examples of various substituted 1-silacyclobutene derivatives.

In continuation of our previous work, here we report the effect of $\equiv$C-R^3 substituents on intramolecular 1,1-vinylboration for syntheses of 1-silacyclobutene derivatives. Various groups R^3 = ^{n}Bu,Ph,SiMe$_3$ were considered for this study and their effect on the course of intramolecular reaction was explored. The intramolecular 1,1-vinylboration to afford 1-silacyclobutenes was hindered by R^3= SiMe$_3$. Alkenyl(alkyn-1-yl)silane derivatives instead of 1-silacyclobutenes were achieved in quantitative yield. In the case of R3= ^{n}Bu,Ph the reaction led to quantitative formation of 1-silacyclobutene derivatives.

Experimental section

All preparative work and handling of air sensitive chemicals were carried out by observing precautions to exclude oxygen and moisture. Dry solvents and oven-dried glassware were used throughout. Dialkyn-1-ylsilanes **1**,**2**[39–41] and alkenyl(chloro)silanes **3**-**5**[42,43] were prepared following the literature procedure. Trimethylsilylethyne, *n*-butyllithium in hexane (1.6 M), and 9-borabicyclo[3.3.1]nonane (9-BBN) were commercial products and were used without further purification. NMR spectra: Varian Inova 300 MHz and 400 MHz spectrometers (23 $\pm$ 1 °C), both equipped with multinuclear units, using C_6D_6 solutions, if not mentioned (ca. 10%-15% v/v) in 5 mm tubes. Chemical shifts are given with respect to $SiMe_4$ [δ^1H (C_6D_5H) = 7.15, δ^{13}C (C_6D_6) = 128.0, δ^{29}Si = 0 for $SiMe_4$ with $\Xi(^{29}Si)$ = 19.867187 MHz], and δ^{11}B = 0 for BF_3-OEt_2 with $\Xi(^{11}B)$ = 32.083971 MHz. ^{29}Si-NMR spectra were recorded using the refocused INEPT pulse sequence with ^{1}H decoupling,[44–47] based on $^3J(^{29}Si\text{-}C{=}C\text{-}^1H)$ = 25-30 Hz or $^1J(^{29}Si\text{-}^1H)$ = 180-200 Hz (after optimization of the respective refocusing delays).

Reaction of Li-C≡C-R^3 with alkenylchlorosilanes 3-5 to afford alkenyl(alkyn-1-yl)silanes 8-12.

A solution of the alkenylsilane, **3b** (1.8g, 5.22 mmol) in hexane (5 mL) was prepared and slowly added to an equimolar freshly prepared suspension of Li-C≡C-$SiMe_3$ at –78 °C in hexane (10 mL). The reaction mixture was allowed to warm to room temperature, and was kept stirring for 3 h. Then solid materials, mainly LiCl, were separated, and the solvent was removed in a vacuum. A colorless oily liquid was left, identified as a mixture of **6b** (borate) (≈ 20%, NMR data) and **9b**. Other alkyn-1-ylsilanes (**8c**, **9c**, **10** - **12**) were obtained following the same procedure. All the alkenyl(alkyn-1-yl)silanes were obtained in reasonably pure form except that the compound **4c** afforded a mixture of **7c** (borate-like intermediate) and **11c**.

6b: ^{13}C-NMR (75.4 MHz): δ [$J(^{29}Si,^{13}C)$] = 1.0 ($SiMe_3$), 153.7 (=CH), 153.0^{br} (BC=), 79.3 [95.6] (Me_3Si-C≡), 106.8^{br} (≡C-B), 135.8, 135.2, 130.0, 128.2 (Si-Ph), Bu and 9-BBN carbons were not assigned; ^{29}Si-NMR (59.6 MHz): δ = –19.9, –38.2; ^{11}B-NMR (96.2 MHz): δ = –16.3.

7c: ^{1}H-NMR (400 MHz): δ = 0.03 (s, 9H, $SiMe_3$), 0.27 (s, 3H, SiMe), 1.07-1.98 (m, 14H, BBN), 6.93-7.63 (m, 10H, SiPh, Ph), 8.04 (s, 1H, =CH, $^3J(^{29}Si,^1H)$ = 17.6 Hz); ^{13}C-NMR (100.5 MHz): δ [$J(^{29}Si,^{13}C)$] = 0.8 [57.3] (SiMe), –1.2 [54.9] ($SiMe_3$), 155.8 (=CH), 151.2^{br} (BC=), 34.7, 34.6, 31.9^{br}, 23.7 (9-BBN), 107.9 [91.5] (Me_3Si-C≡), 106.2^{br} (≡C-B), 138.2 [73.7, *i*] (SiPh), 140.5 [4.5, *i*] (Ph) other carbons were not assigned; ^{29}Si-NMR (59.6 MHz): δ = –17.6, –11.6; ^{11}B-NMR (96.2 MHz): δ = –16.8.

9b: ^{1}H-NMR (300 MHz): δ = 0.3 (s, 9H, $SiMe_3$), 0.8, 1.3-1.4, 2.2 (t, m, m, t, 9H, Bu), 1.3-2.2 (m, 14H, 9-BBN), 5.6 (s, 1H, $^1J(^{29}Si,^1H)$ = 189.1 Hz, Si-H), 6.5 (t, 1H, $^3J(^1H,^1H)$ = 7.5 Hz, =CH), 7.2-7.9 (m, 5H, Si-Ph).

9c:^{1}H-NMR (300 MHz): δ = –0.1 (s, 9H, $SiMe_3$), 1.2-2.0 (m, 14H, 9-BBN), 5.3 (s, 1H, $^1J(^{29}Si,^1H)$ = 211.3 Hz, Si-H), 8.1 (s, 1H, $^3J(^{29}Si,^1H)$ = 17.7 Hz, =CH), 6.8-7.6 (m, 10H, Si-Ph, Ph).

10b:^{1}H-NMR (300 MHz): δ = 0.6 (s, 3H, Si-Me), 0.8, 1.2-2.4 (t, m, m, 9-BBN, Bu), 7.0 (t, 1H, $^3J(^1H,^1H)$ = 7.3 Hz, =CH), 7.2-7.7 (m, 10H, Ph, Si-Ph).

10c: ^{1}H-NMR (300 MHz): δ = 0.12 (s, 3H, Si-Me), 1.0-1.5 (m, 14H, 9-BBN), 6.5-7.4 (m, 15H, Ph, Si-Ph), 7.8 (s, 1H, $^3J(^{29}Si,^1H)$ = 17.9 Hz, =CH).

11b:^{1}H-NMR (300 MHz): δ = –0.1 (s, 9H, $SiMe_3$), 0.5 (s, 3H, SiMe), 0.6, 1.0, 1.2, 2.3 (t, m, m, m, 9H, Bu), 1.2-1.8 (m, 14H, 9-BBN), 6.9 (t, 1H, $^3J(^1H,^1H)$ = 7.3 Hz, =CH), 7.0, 7.5 (m, m, 5H, SiPh).

11c: ^{1}H-NMR (300 MHz): δ = 0.03 (s, 9H, $SiMe_3$), 0.3 (s, 3H, SiMe), 1.07-1.98 (m, 14H, 9-BBN), 6.9-7.6 (m, 10H, SiPh, Ph), 8.00 (s, 1H, $^3J(^{29}Si,^1H)$ = 15.8 Hz, =CH).

12b: ^{1}H-NMR (300 MHz) = 0.2 (s, 9H, $SiMe_3$), 0.8, 0.9-1.3, 2.3 (t, m, m, 9H, Bu), 1.3-1.8 (m, 14H, 9–BBN), 7.2 (t, 1H, $^3J(^1H,^1H)$ = 7.6 Hz, =CH), 7.3-7.6 (m, 10H, $SiPh_2$).

12c: ^{1}H-NMR (C_6D_6) = 0.03 (s, 9H, $SiMe_3$), 1.3-2.6 (m, 14H, 9-BBN), 6.9-7.8 (m, 15H, $SiPh_2$, Ph), 8.3 (s, 1H, ^3J (^{29}Si, ^1H) = 22.3 Hz, =CH).

Conversion of alkenyl(alkyn-1-yl)silanes 8-11 into 1-silacyclobutene derivatives

Compound **8c** was sealed as C_6D_6 solution in an NMR tube and was kept at 80-120 °C. The reaction was continuously monitored by NMR spectroscopy (mainly ^{29}Si- and ^{1}H-NMR). The intramolecular rearrangement

was complete in 21 h and 1-silacyclobutene **15c** was achieved in almost quantitative amount (ca. 90%). All other 1-silacyclobutene derivatives were obtained in the same way, except that the time taken by each reaction was slightly different (**16b**: 21 h, **16c** 48 h, **17c**: 12 h at 25 °C).

15c: ^{1}H-NMR (300 MHz): δ = 1.1-1.9 (m, 14H, 9-BBN), 4.8 (s, 1H, $^{1}J(^{29}\mathrm{Si},^{1}\mathrm{H})$ = 196.9 Hz, Si-H), 6.0 (s, 1H, ^{3}J (^{29}Si, ^{1}H) = 18.6 Hz, =CH), 6.7-7.6 (m, 15H, Si-Ph, Ph, Ph).

16b: ^{1}H-NMR data (300 MHz): δ = 0.4 (s, 3H, SiMe), 0.9, 0.8-1.0, 1.7 (t, m, m, 9H, Bu), 1.0-1.7 (m, 14H, BBN), 5.8 (t, 1H, =CH, $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 7.2 Hz), 6.6-7.4 (m, 10H, Si-Ph, Ph).

16c: ^{1}H-NMR data (300 MHz): δ = 0.2 (s, 3H, Si-Me), 0.9-1.7 (m, 14H, 9-BBN), 6.7-7.4 (m, 15H, Si-Ph, 2 × Ph), 7.9 (s, 1H, $^{3}J(^{29}\mathrm{Si}, ^{1}\mathrm{H})$ = 15.7 Hz, =CH).

17c: ^{1}H-NMR (400 MHz): δ = 0.05 (s, 9H, $SiMe_3$), 0.44 (s, 3H, Si-Me), 1.07-1.98 (m, 14H, BBN), other signals were not assigned.

Reaction of dialkyn-1-ylsilanes, 1a, c, and 2b with 9-BBN to afford alkenyl(alkyn-1-yl)silanes, 13a,c, 14c, and their conversion into 1-silacyclobutenes 18c and 19c

A solution of silane **1a** (0.50 g, 3.67 mmol) in C_6D_6 (1.5 mL) was mixed with one equivalent of 9-BBN dimer (0.448 g, 3.67 mmol). The mixture was heated to 80 °C for 5 min to give **13a**. During this time 9-BBN was completely consumed (monitored by ^{11}B-NMR). The 1,2-hydroboration of **1c** and **2b** was carried out in the same way leading to alkenyl(alkyn-1-yl)silanes **13c** (after 5 min at 80 °C) and **14c** (after 10 min at 80 °C). The samples were further heated at the same temperature. In the case of **13a,** heating caused extensive decomposition and identification of products was not possible. Heating of the silanes **13c** and **14c** led to 1-silacyclobutene derivatives, **18c** (1-2 h at 80 °C) and **19c** (8 h at 120 °C), respectively.

13a: ^{1}H-NMR (400 MHz): δ = 0.3 (s, 6H, $SiMe_2$), 1.5, 1.6 (s, s, 3H, 3H, 2Me), 1.4-1.9 (m, 14H, 9-BBN), 6.9 (q, 1H, =CH).

13c: ^{1}H-NMR (400 MHz): δ = 1.0-1.7 (m, 14H, 9-BBN), –0.05 (s, 6H, $SiMe_2$), 6.5-7.0 (m, 10H, Ph, Ph), 7.6 (s, 1H, =CH, $^{3}J(^{29}\mathrm{Si}, ^{1}\mathrm{H})$ = 17.5 Hz).

14b: ^{1}H-NMR (400 MHz): δ = 2.2, 1.2-1.1, 1.0, 0.59 (m, m, m, t, 9H, =C-Bu), 1.9, 1.2-1.1, 0.58 (m, m, t, 9H, ≡C-Bu), 1.5-1.8 (m, 14H, 9-BBN), 7.1 (t, 1H, =CH, $^{3}J(^{1}\mathrm{H}, ^{1}\mathrm{H})$ = 7.2 Hz), 7.0-7.1, 7.74, 7.72 (m, d, d, 10H, $SiPh_2$).

1-Silacyclobutene derivatives

18c: ^{1}H-NMR (400 MHz): δ = 0.7 (s, 6H, $SiMe_2$), 1.3-2.0 (m, 14H, 9-BBN), 6.8-7.3 (m, 1H, 10H, =CH, Ph, Ph).

19b: ^{1}H-NMR (400 MHz): δ = 0.5, 1.3-1.0, 2.0, 2.4 (t, m, m, m, 18H, Bu, Bu), 1.7-1.8 (m, 14H, 9-BBN), 5.9 (t, 1H, =CH), 6.9-7.7 (m, 10H, $SiPh_2$).

Results and discussion

The alkenylsilanes **3-5** bearing Si-Cl function are useful synthons for further transformations.[36,48] They were prepared by the reaction of the respective alkyn-1-yl(chloro)silanes with 9-borabicyclo[3.3.1]nonane, adopting the literature procedure.[42,43] Alkenylsilanes analogous to **3-5** have been studied in solution and solid state by

Table 1. ^{11}B-, ^{13}C-, and ^{29}Si-NMR data[a] of alkyn-1-ylsilanes **9-14**.

	δ^{13}C (BC=)	δ^{13}C (=C)	δ^{13}C (Si-C≡)	δ^{13}C (≡C)	δ^{29}Si	δ^{11}B
9b[b]	143.8[br]	162.1	93.9	111.8	–17.5, –53.2	82.6
9c[c]	141.6[br]	159.4	109.4 [83.8] [12.4]	118.7 [76.3] [12.7]	–18.7, –51.8	82.4
10b[d]	141.2[br]	161.3	94.0 [87.8]	107.8 [16.9]	–32.6	81.6
10c[e]	147.8[br]	155.7	93.7 [88.8]	108.4 [16.5]	–31.8	82.4
11b[f]	143.9[br]	161.5	113.5 [81.1] [12.4]	116.1 [77.5] [12.0]	–19.4, –34.1	80.9
11c[g]	147.7[br]	154.1	113.2 [81.9] [12.3]	116.9 [77.1] [12.4]	–19.2, –33.1	82.9
12b[h]	142.8[br]	162.8	112.3 [84.3] [11.4]	118.0 [76.7] [12.3]	–18.6, –37.3	81.2
12c[i]	144.8[br]	158.0	111.2 [86.1] [12.6]	118.1 [76.8] [12.8]	–18.9, –36.6	82.2
13a[j]	148.3[br] [62.7]	152.3	84.8 [88.4]	103.6 [17.3]	–30.4	81.0
13c[k]	150.6[br] [62.3]	153.3	95.6 [85.0]	106.9 [15.9]	–28.2	82.9
14b[l]	143.9[br]	161.8	82.8 [95.7]	111.2 [17.2]	–36.8	83.5

[a] Measured in C_6D_6 at 23 °C, coupling constants $J(^{29}Si,^{13}C)$ [± 0.4 Hz] are given in square brackets, [br] denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{11}B-^{13}C spin-spin coupling.[52]

[b] other ^{13}C-NMR data: δ = 0.5 ($SiMe_3$), 137.8, 135.1, 129.2, 129.3 (Si-Ph), Bu carbons could not be assigned.

[c] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = –0.3 [55.9, $SiMe_3$], 34.5, 34.3, 31.2[br], 23.7 (9-BBN), 139.5, 134.2 [74.9], 135.3, 130.0, 128.4, 129.9, 129.2, 128.2 (Si-Ph, Ph).

[d] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = 0.8 [58.6, Si-Me], 34.7, 34.6, 31.8[br], 23.7 (9-BBN), 35.1, 27.2, 23.0, 14.4 (Bu), 140.5, 138.5 [74.0], 134.8, 132.2, 128.4, 128.1, 129.6, 123.7 (Si-Ph, Ph).

[e] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = 0.1 [58.3, Si-Me], 34.4, 34.4, 31.4[br], 23.6 (9-BBN), 138.2 [71.9], 134.6, 134.6, 132.3, 132.2, 129.6, 129.8, 123.2 (Si-Ph, Ph).

[f] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = –0.2 [56.3, $SiMe_3$], 1.0 [56.5, Si-Me], 34.4, 31.3[br], 23.7 (9-BBN), 35.6, 31.7, 22.9, 14.3 (Bu), 138.0 [72.8], 134.6, 129.6, 128.3 (*i, o, m, p,* Si-Ph).

[g] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = –0.003 [55.6, $SiMe_3$], –0.2 [56.4, Si-Me], 34.5, 34.6, 31.7[br], 23.7 (9-BBN), 140.7 [64.9], 141.4 [4.2] other carbons are without assignment.

[h] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = –0.2 [56.4, $SiMe_3$], 34.3, 31.4[br], 23.6 (9-BBN), 36.0, 27.2, 22.8, 14.1 (Bu), 136.2 [72.6], 135.6, 129.8, 129.3 (*i, o, m, p,* $SiPh_2$).

[i] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = –0.2 [56.4, $SiMe_3$], 34.5, 31.9[br], 23.6 (9-BBN), 136.3 [75.6], 135.6, 130.4, 128.2 (i, o, m, p, $SiPh_2$), 125.7, 135.4, 129.7, 139.5, (*i, o, m, p,* Ph).

[j] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = 1.8 [55.6, $SiMe_2$], 4.8 [8.6, C2–CH3), 4.7 (CH3). kother ^{13}C-NMR data: [$J(^{29}Si,^{13}C)$] = 1.9 [56.5, $SiMe_2$], 141.2, 132.1, 129.7, 129.2, 129.0, 128.6, 128.5, 123.9 (Ph carbons without assignment).

[l] other ^{13}C-NMR data: δ [$J(^{29}Si,^{13}C)$] = 35.9, 33.8, 31.5, 22.9, 22.2, 20.1, 14.1, 13.7 (Bu), 137.1 [74.5, i], 135.6 (o), 129.6 (p), 128.2 (m) ($SiPh_2$).

NMR spectroscopy and X-ray diffraction, respectively.[42,43] These silanes bear 2 electrophilic centres, one at silicon and the other at boron, and treatment with alkynyllithium reagents at low temperature (–78 °C) should afford either the borate-like intermediates, **6**, **7** and/or the alkenyl(alkyn-1-yl)silanes, **8-12** (Figure 1). Borate-like intermediates were detected in 2 cases, **6** and **7**, and their relevant NMR data were collected (Experimental section). It turned out that the borate-like intermediates are slowly converted into alkenyl(alkyn-1-yl)silanes by elimination of LiCl. The progress of the reaction becomes evident by ^{11}B-NMR spectroscopy. The ^{11}B-NMR signal at –16 ± 1 ppm (typical region for tetraorganoborates[49]) decreases in intensity, whereas the signal at +82 ± 1 ppm is increasing. The intermediates, **8-12**, were stable at room temperature and the relevant NMR data were collected (Table 1).

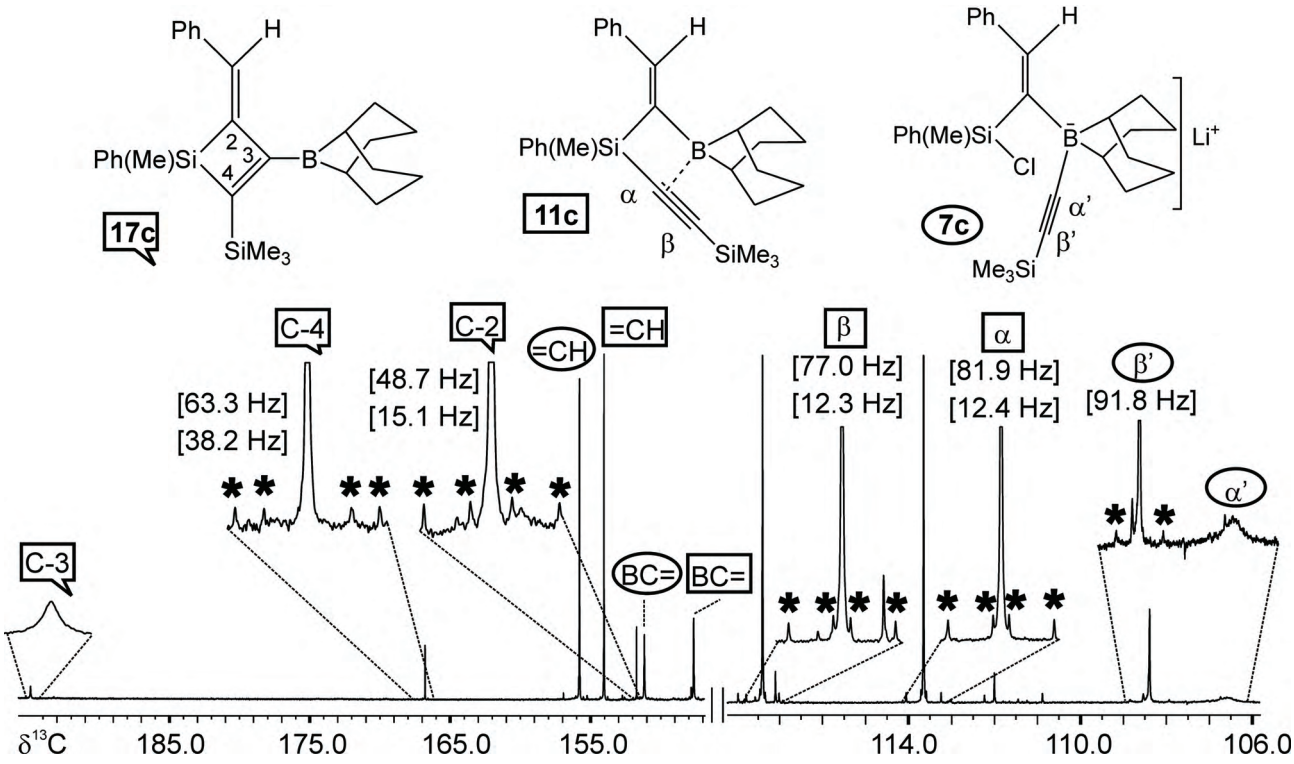
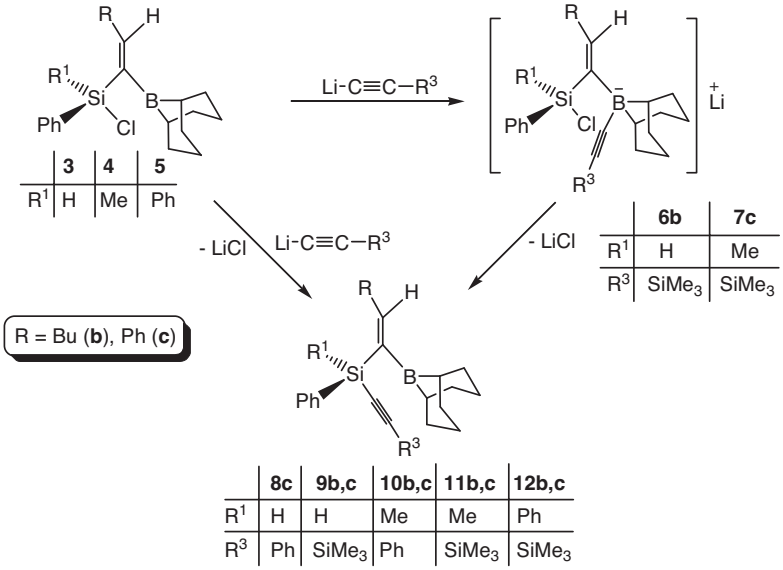


Figure 1

The alkenyl(alkyn-1-yl)silanes, **8-12**, obtained in Scheme 2 could be converted into useful products. They were heated at 80-100 °C for some time (0.5-48 h) and 1-silacyclobutene derivatives were achieved in reasonably pure form (> 90%) via intramolecular 1,1-vinylboration. The effect of C≡C-R^3 group (R^3 = ^{n}Bu, Ph, SiMe$_3$) was studied on the course of intramolecular 1,1-vinylboration. In the case of C≡C-^{n}Bu and C≡C-Ph functionalities the reactions led to quantitative formation of 1-silacyclobutene derivatives (Figure 2). On the other hand, the C≡C-SiMe$_3$ group did not allow the reaction to afford reasonable amounts (Figure 1, ca. 5%) of the desired 1-silacyclobutenes. It is known that alkenes bearing 2 silyl groups and 1 boryl group undergo 1,1-deorganoboration upon heating.[50] This would account for the observation of only a small amount of **17c** (Scheme 3). Further attempts to drive the equilibrium towards **17c** finally lead to decomposition.

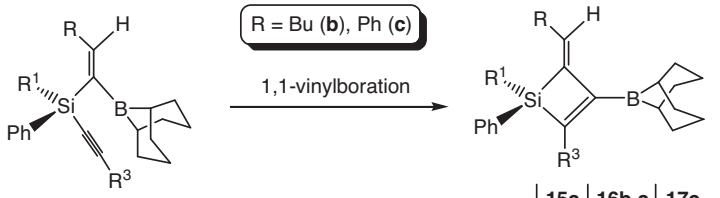


	3	4	5
R^1	H	Me	Ph

	6b	7c
R^1	H	Me
R^3	$SiMe_3$	$SiMe_3$

	8c	9b,c	10b,c	11b,c	12b,c
R^1	H	H	Me	Me	Ph
R^3	Ph	$SiMe_3$	Ph	$SiMe_3$	$SiMe_3$

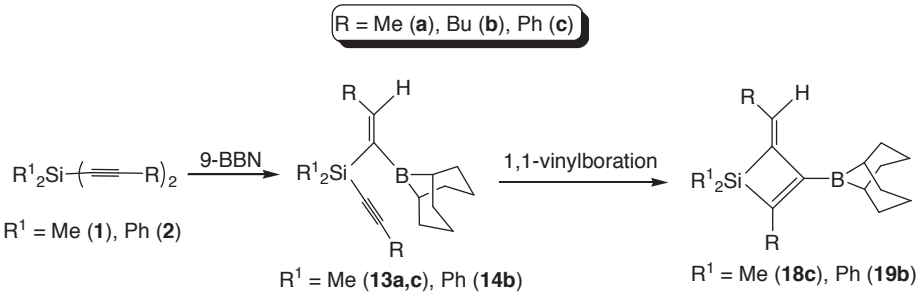
Scheme 2. Reactions of alkyn-1-yllithium reagents with alkenyl(chloro)silanes.



	15c	16b,c	17c
R^1	H	Me	Me
R^3	Ph	Ph	$SiMe_3$

Scheme 3. Formation of 1-silacyclobutene derivatives.

The desired 1-silacyclobutene derivatives could also be obtained by the reaction of dialkyn-1-ylsilanes with one equivalent of 9-BBN (Scheme 4). Hydroboration of one alkyn-1-yl group affords selectively intermediates **13** and **14** (Figure 2, upper spectrum). On heating, these intermediates rearrange in the same way as observed for **8-12**, and some 1-silacyclobutene derivatives were formed in almost quantitative yield ($> 90\%$; see Figure 2). Surprisingly the C≡C-Me group did not favour the formation of 1-silacyclobutene and decomposition was observed at 80 °C immediately after formation of alkenyl(propyn-1-yl)silane **13a**.



Scheme 4. Reaction of dialkyn-1-ylsilanes with one equivalent of 9-BBN. 1,2-Hydroboration is followed by 1,1-vinylboration.

Table 2. ^{11}B-, ^{13}C-, and ^{29}Si-NMR dataa of 1-silacyclobutene derivatives **15-19.**

	δ^{13}C (HC=)	δ^{13}C (C-2)	δ^{13}C (C-3)	δ^{13}C (C-4)	δ^{29}Si	δ^{11}B
15c[b]	140.0	147.6 [54.3]	180.4^{br}	162.5 [55.4]	–10.5	85.0
16a[c]	140.1	147.0 [55.1]	177.9^{br}	159.8 [54.9]	3.2	87.2
16c[d]	140.8	148.8 [53.0]	178.7^{br}	163.3 [55.2]	7.9	86.0
17c[e]	139.8	151.7 [48.7] [15.1]	194.9^{br}	166.8 [38.2] [63.3]	–11.6, –12.9	88.2
18c[f]	132.4	150.2 [52.1]	175.9^{br}	164.6 [53.6]	11.5	87.4
19b[g]	135.6	146.0 [54.9]	178.6^{br}	166.9 [53.4]	–0.3	86.7

[a] Measured in C_6D_6 at 23 °C, coupling constants J(^{29}Si,^{13}C) are given in square brackets [± 0.4 Hz], n.m. means not measured, superscript ^{br} denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{11}B-^{13}C coupling.[52]

[b] other ^{13}C-NMR data: δ [J(^{29}Si,^{13}C)] = 34.4, 32.4^{br}, 23.5 (9-BBN), 134.2 [64.8], 135.9, 128.7, 130.6 (*i, o, m, p,* Si-Ph), 135.5, 132.6, 130.7, 128.8, 128.5, 128.4, 127.6, 127.2 (Ph).

[c] other ^{13}C-NMR data: δ [J(^{29}Si,^{13}C)] = –3.1 [64.8, Si-Me], 34.2, 31.1^{br}, 23.6 (9-BBN), 35.0, 32.6, 22.7, 14.2 (Bu), 136.5 [62.8], 134.6, 128.5, 130.5 (*i, o, m, p,* Si-Ph), 132.5, 128.6, 128.3, 127.1 (*i, o, m, p,* Ph).

[d] other ^{13}C-NMR data: δ [J(^{29}Si,^{13}C)] = –1.3 [52.3, Si-Me], 34.7, 32.4^{br}, 23.6 (9-BBN), 140.7 [65.1], 134.6, 128.3, 129.1 (*i, o, m, p,* Si-Ph), 132.5, 132.3, 128.8, 128.5, 128.2, 128.1, 127.1, 126.8 (Ph).

[e] other ^{13}C-NMR data: δ [J(^{29}Si,^{13}C)] = –2.1 (SiMe3), 0.3 (Si-Me), 33.8, 33.7, 32.4^{br}, 23.5 (9-BBN), Ph and Si-Ph carbons are without assignment.

[f] other ^{13}C-NMR data: δ [J(^{29}Si,^{13}C)] = –0.01 [46.3, SiMe2], 34.3, 32.1^{br}, 23.6 (9-BBN), 140.5 (i), 140.1 (i), 128.9, 128.6, 128.2, 127.4, 127.0, 126.6 (Ph).

[g] other ^{13}C-NMR data: δ [J(^{29}Si,^{13}C)] = 33.4, 31.9^{br}, 23.5 (9-BBN), 35.1, 34.4, 33.1, 32.6, 23.1, 22.7, 14.2, 14.0 (Bu), 135.5 [62.7], 135.7, 130.2, 128.4, (*i, o, m, p,* $SiPh_2$).

NMR spectroscopic studies

The ^{11}B-, ^{13}C-, and ^{29}Si-NMR data for alkenyl(alkyn-1-yl)silanes (**9-14**) and 1-silacyclobutene derivatives (**15-19**) are listed in Tables 1 and 2, respectively. The data for borate-like intermediates (**6** and **7**) and ^{1}H-NMR data for all the new compounds are collected in the Experimental section. The data sets compare well with the previously reported data[36–38] and are in full agreement with the proposed structures. All compounds, i.e. alkenyl(alkyn-1-yl)silanes, borate-like intermediates, and 1-silacyclobutene derivatives, could be identified from their characteristic NMR parameters (see Figures 1 and 2). The ^{11}B chemical shifts for alkenyl(alkyn-1-yl)silanes and 1-silacyclobutenes cover a narrow range (δ^{11}B = 82-89 ppm), typical of triorganoboranes without significant BC(pp) π interactions.[51] For all products the ^{13}C-NMR data are useful to corroborate the proposed structures. Many ^{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.[52] The ^{29}Si-NMR spectra are helpful in monitoring of the reactions, and δ^{29}Si data are markedly different for starting silanes (**1**, **2**), alkenylsilanes (**3-5**), borates (**6**, **7**), alkenyl(alkyn-1-yl)silanes (**8-14**), and

1-silacyclobutene derivatives (**15**-**19**). In the ^{1}H-NMR spectra a singlet for the olefinic proton of the C=CH(R) group is accompanied by ^{29}Si satellites [$^{3}J(^{29}\mathrm{Si},^{1}\mathrm{H}) \approx 25$ Hz], which shows that 1,2-hydroboration has taken place. The value of $^{3}J(^{29}\mathrm{Si},^{1}\mathrm{H})$ coupling constants is helpful in identification of products (1-silacyclobutenes) and their precursors, the alkenyl(alkyn-1-yl)silanes.

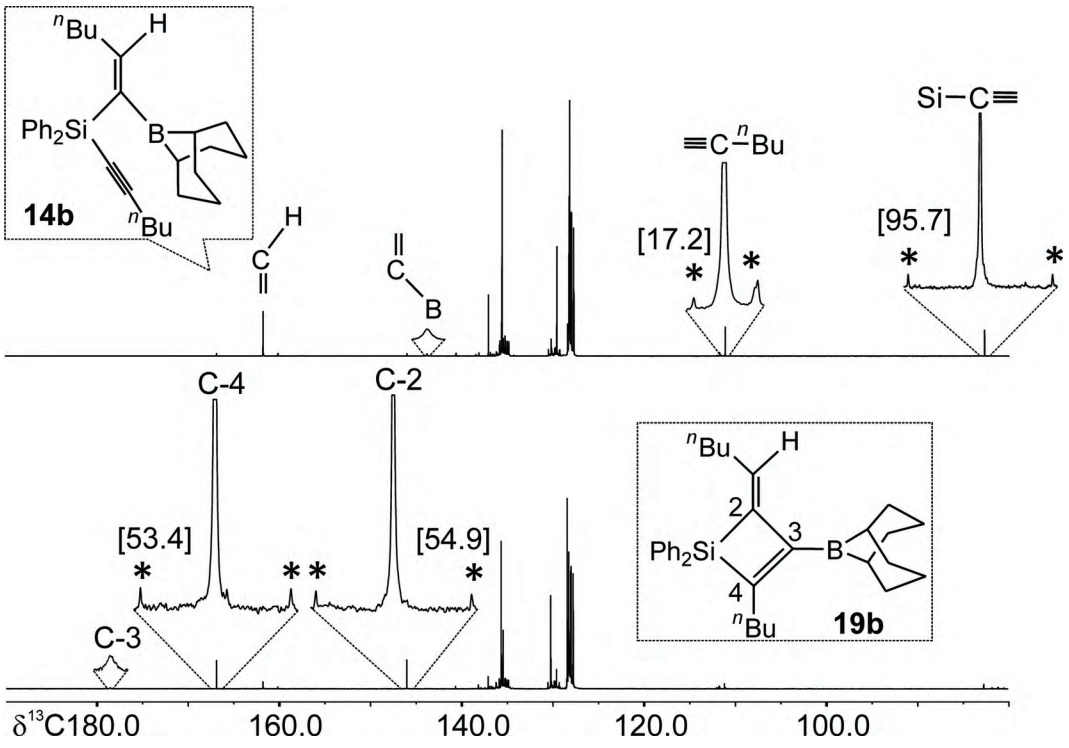


Figure 2

Conclusions

We have shown that various 1-silacyclobutene derivatives are accessible via 1,2-hydroboration followed by 1,1-vinylboration. The synthetic approach is efficient and a variety of functionalities such as Si-organyl as well as Si-H can be included. The synthetic route is limited to $\mathrm{R}^{3} = \mathrm{SiMe}_3$ which afforded alkenyl(alkyn-1-yl)silanes instead of 1-silacyclobutenes. The new compounds alkenyl(alkyn-1-yl)silanes bear numerous reactive sites such as C=C bond, C≡C bond, the boryl group, and the Si-H function, which are expected to possess further utility and can be used for development of suitable chemistry.

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