

1-1-2010

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KHAN, EZZAT and WRACKMEYER, BERND (2010) "Effect of various substituents on intramolecular 1,1-vinylboration, synthesis of 1-silacyclobutene derivatives," *Turkish Journal of Chemistry*. Vol. 34: No. 5, Article 10. <https://doi.org/10.3906/kim-0910-20>
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Effect of various substituents on intramolecular 1,1-vinylboration, synthesis of 1-silacyclobutene derivatives

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Received 08.10.2009

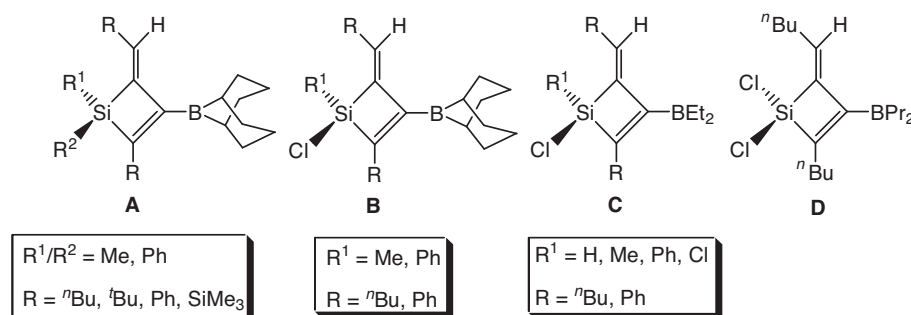
The reaction of 1-boryl-1-alkenyl chlorosilane derivatives with alkynyllithium reagents [$\text{Li-C}\equiv\text{C-R}^3$ ($\text{R}^3 = \text{Ph, SiMe}_3$)] at low temperature (-78°C) affords alkenyl(alkyn-1-yl)silanes. These compounds are precursors of 1-silacyclobutene derivatives, which are formed via intramolecular 1,1-vinylboration. This reaction works for various groups at silicon (R^1/R^2 : $\text{R}^1 = \text{H, Me, Ph}$; $\text{R}^2 = \text{Me, Ph}$) and at the $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ units (R/R^3 : $\text{R} = n\text{Bu, Ph}$; $\text{R}^3 = n\text{Bu, Ph, SiMe}_3$). The conversion into 1-silacyclobutene derivatives is incomplete only in the case of $\text{R}^3 = \text{SiMe}_3$. 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 ($^1\text{H-}$, $^{13}\text{C-}$, $^{11}\text{B-}$, $^{29}\text{Si-NMR}$).

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

Introduction

Reactions involving 1,2-hydroboration and 1,1-organoboration have been widely used in organic¹⁻⁴ 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 spiro-silanes.^{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 $\equiv\text{C-R}^3$ substituents on intramolecular 1,1-vinylboration for syntheses of 1-silacyclobutene derivatives. Various groups $\text{R}^3 = {}^n\text{Bu, Ph, SiMe}_3$ 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 $\text{R}^3 = \text{SiMe}_3$. Alkenyl(alkyn-1-yl)silane derivatives instead of 1-silacyclobutenes were achieved in quantitative yield. In the case of $\text{R}^3 = {}^n\text{Bu, Ph}$ 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. Trimethylsilylthyne, *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 ± 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 [$\delta^1\text{H}$ ($\text{C}_6\text{D}_5\text{H}$) = 7.15, $\delta^{13}\text{C}$ (C_6D_6) = 128.0, $\delta^{29}\text{Si} = 0$ for SiMe_4 with $\Xi(^{29}\text{Si}) = 19.867187$ MHz], and $\delta^{11}\text{B} = 0$ for $\text{BF}_3\text{-OEt}_2$ with $\Xi(^{11}\text{B}) = 32.083971$ MHz. ^{29}Si -NMR spectra were recorded using the refocused INEPT pulse sequence with ^1H decoupling,^{44–47} based on $^3J(^{29}\text{Si}-\text{C}=\text{C}-^1\text{H}) = 25\text{-}30$ Hz or $^1J(^{29}\text{Si}-^1\text{H}) = 180\text{-}200$ Hz (after optimization of the respective refocusing delays).

Reaction of Li-C≡C-R³ 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-SiMe₃ 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: ¹³C-NMR (75.4 MHz): δ [*J*(²⁹Si, ¹³C)] = 1.0 (SiMe₃), 153.7 (=CH), 153.0^{br} (BC=), 79.3 [95.6] (Me₃Si-C≡), 106.8^{br} (≡C-B), 135.8, 135.2, 130.0, 128.2 (Si-Ph), Bu and 9-BBN carbons were not assigned; ²⁹Si-NMR (59.6 MHz): δ = -19.9, -38.2; ¹¹B-NMR (96.2 MHz): δ = -16.3.

7c: ¹H-NMR (400 MHz): δ = 0.03 (s, 9H, SiMe₃), 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, ³*J*(²⁹Si, ¹H) = 17.6 Hz); ¹³C-NMR (100.5 MHz): δ [*J*(²⁹Si, ¹³C)] = 0.8 [57.3] (SiMe), -1.2 [54.9] (SiMe₃), 155.8 (=CH), 151.2^{br} (BC=), 34.7, 34.6, 31.9^{br}, 23.7 (9-BBN), 107.9 [91.5] (Me₃Si-C≡), 106.2^{br} (≡C-B), 138.2 [73.7, *i*] (SiPh), 140.5 [4.5, *i*] (Ph) other carbons were not assigned; ²⁹Si-NMR (59.6 MHz): δ = -17.6, -11.6; ¹¹B-NMR (96.2 MHz): δ = -16.8.

9b: ¹H-NMR (300 MHz): δ = 0.3 (s, 9H, SiMe₃), 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, ¹*J*(²⁹Si, ¹H) = 189.1 Hz, Si-H), 6.5 (t, 1H, ³*J*(¹H, ¹H) = 7.5 Hz, =CH), 7.2-7.9 (m, 5H, Si-Ph).

9c: ¹H-NMR (300 MHz): δ = -0.1 (s, 9H, SiMe₃), 1.2-2.0 (m, 14H, 9-BBN), 5.3 (s, 1H, ¹*J*(²⁹Si, ¹H) = 211.3 Hz, Si-H), 8.1 (s, 1H, ³*J*(²⁹Si, ¹H) = 17.7 Hz, =CH), 6.8-7.6 (m, 10H, Si-Ph, Ph).

10b: ¹H-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, ³*J*(¹H, ¹H) = 7.3 Hz, =CH), 7.2-7.7 (m, 10H, Ph, Si-Ph).

10c: ¹H-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, ³*J*(²⁹Si, ¹H) = 17.9 Hz, =CH).

11b: ¹H-NMR (300 MHz): δ = -0.1 (s, 9H, SiMe₃), 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, ³*J*(¹H, ¹H) = 7.3 Hz, =CH), 7.0, 7.5 (m, m, 5H, SiPh).

11c: ¹H-NMR (300 MHz): δ = 0.03 (s, 9H, SiMe₃), 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, ³*J*(²⁹Si, ¹H) = 15.8 Hz, =CH).

12b: ¹H-NMR (300 MHz) = 0.2 (s, 9H, SiMe₃), 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, ³*J*(¹H, ¹H) = 7.6 Hz, =CH), 7.3-7.6 (m, 10H, SiPh₂).

12c: ¹H-NMR (C₆D₆) = 0.03 (s, 9H, SiMe₃), 1.3-2.6 (m, 14H, 9-BBN), 6.9-7.8 (m, 15H, SiPh₂, Ph), 8.3 (s, 1H, ³*J*(²⁹Si, ¹H) = 22.3 Hz, =CH).

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

Compound **8c** was sealed as C₆D₆ solution in an NMR tube and was kept at 80-120 °C. The reaction was continuously monitored by NMR spectroscopy (mainly ²⁹Si- and ¹H-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: ¹H-NMR (300 MHz): δ = 1.1-1.9 (m, 14H, 9-BBN), 4.8 (s, 1H, $^1J(^{29}\text{Si}, ^1\text{H}) = 196.9$ Hz, Si-H), 6.0 (s, 1H, $^3J(^{29}\text{Si}, ^1\text{H}) = 18.6$ Hz, =CH), 6.7-7.6 (m, 15H, Si-Ph, Ph, Ph).

16b: ¹H-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, $^3J(^1\text{H}, ^1\text{H}) = 7.2$ Hz), 6.6-7.4 (m, 10H, Si-Ph, Ph).

16c: ¹H-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, $^3J(^{29}\text{Si}, ^1\text{H}) = 15.7$ Hz, =CH).

17c: ¹H-NMR (400 MHz): δ = 0.05 (s, 9H, SiMe₃), 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 C₆D₆ (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 ¹¹B-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: ¹H-NMR (400 MHz): δ = 0.3 (s, 6H, SiMe₂), 1.5, 1.6 (s, s, 3H, 3H, 2Me), 1.4-1.9 (m, 14H, 9-BBN), 6.9 (q, 1H, =CH).

13c: ¹H-NMR (400 MHz): δ = 1.0-1.7 (m, 14H, 9-BBN), -0.05 (s, 6H, SiMe₂), 6.5-7.0 (m, 10H, Ph, Ph), 7.6 (s, 1H, =CH, $^3J(^{29}\text{Si}, ^1\text{H}) = 17.5$ Hz).

14b: ¹H-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, $^3J(^1\text{H}, ^1\text{H}) = 7.2$ Hz), 7.0-7.1, 7.74, 7.72 (m, d, d, 10H, SiPh₂).

1-Silacyclobutene derivatives

18c: ¹H-NMR (400 MHz): δ = 0.7 (s, 6H, SiMe₂), 1.3-2.0 (m, 14H, 9-BBN), 6.8-7.3 (m, 1H, 10H, =CH, Ph, Ph).

19b: ¹H-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, SiPh₂).

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 alkyne-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. ¹¹B-, ¹³C-, and ²⁹Si-NMR data^a of alkyne-1-ylsilanes **9-14**.

	$\delta^{13}\text{C}$ (BC=)	$\delta^{13}\text{C}$ (=C)	$\delta^{13}\text{C}$ (Si-C \equiv)	$\delta^{13}\text{C}$ ($\equiv\text{C}$)	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$
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
12cⁱ	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 C₆D₆ at 23 °C, coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ [\pm 0.4 Hz] are given in square brackets, ^{br} denotes a broad ¹³C resonance signal as the result of partially relaxed scalar ¹¹B-¹³C spin-spin coupling.⁵²

^b other ¹³C-NMR data: δ = 0.5 (SiMe₃), 137.8, 135.1, 129.2, 129.3 (Si-Ph), Bu carbons could not be assigned.

^c other ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = -0.3 [55.9, SiMe₃], 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 ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 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 ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 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 ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = -0.2 [56.3, SiMe₃], 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 ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = -0.003 [55.6, SiMe₃], -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 ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = -0.2 [56.4, SiMe₃], 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*, SiPh₂).

ⁱ other ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = -0.2 [56.4, SiMe₃], 34.5, 31.9^{br}, 23.6 (9-BBN), 136.3 [75.6], 135.6, 130.4, 128.2 (*i, o, m, p*, SiPh₂), 125.7, 135.4, 129.7, 139.5, (*i, o, m, p*, Ph).

^j other ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 1.8 [55.6, SiMe₂], 4.8 [8.6, C2-CH₃], 4.7 (CH₃). kother ¹³C-NMR data: [$J(^{29}\text{Si}, ^{13}\text{C})$] = 1.9 [56.5, SiMe₂], 141.2, 132.1, 129.7, 129.2, 129.0, 128.6, 128.5, 123.9 (Ph carbons without assignment).

^l other ¹³C-NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 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*) (SiPh₂).

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 ($-78\text{ }^{\circ}\text{C}$) 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 $-16 \pm 1\text{ ppm}$ (typical region for tetraorganoborates⁴⁹) decreases in intensity, whereas the signal at $+82 \pm 1\text{ ppm}$ is increasing. The intermediates, **8-12**, were stable at room temperature and the relevant NMR data were collected (Table 1).

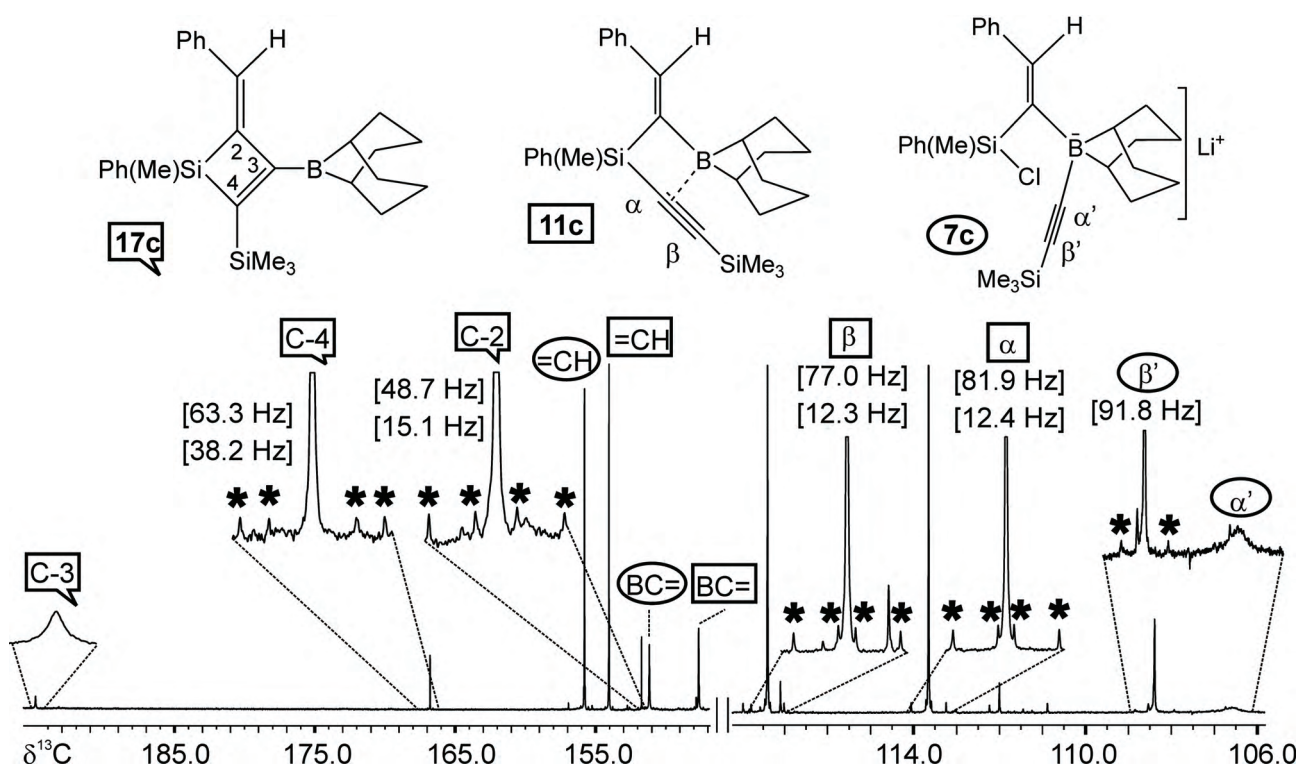
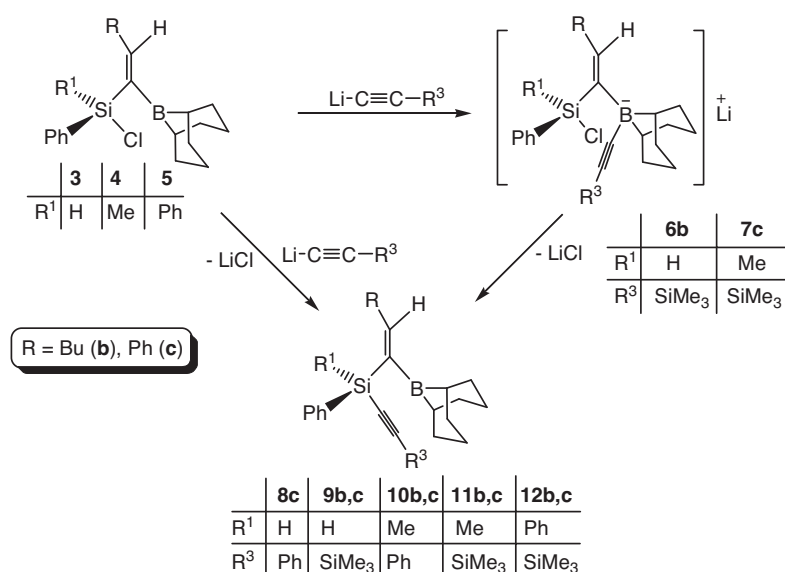
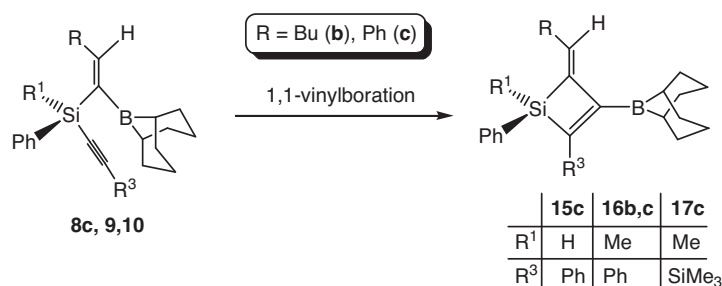


Figure 1

The alkenyl(alkyn-1-yl)silanes, **8-12**, obtained in Scheme 2 could be converted into useful products. They were heated at $80\text{-}100\text{ }^{\circ}\text{C}$ 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 $\text{C}\equiv\text{C}-\text{R}^3$ group ($\text{R}^3 = {}^n\text{Bu}$, Ph, SiMe_3) was studied on the course of intramolecular 1,1-vinylboration. In the case of $\text{C}\equiv\text{C}-{}^n\text{Bu}$ and $\text{C}\equiv\text{C}-\text{Ph}$ functionalities the reactions led to quantitative formation of 1-silacyclobutene derivatives (Figure 2). On the other hand, the $\text{C}\equiv\text{C}-\text{SiMe}_3$ 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.

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

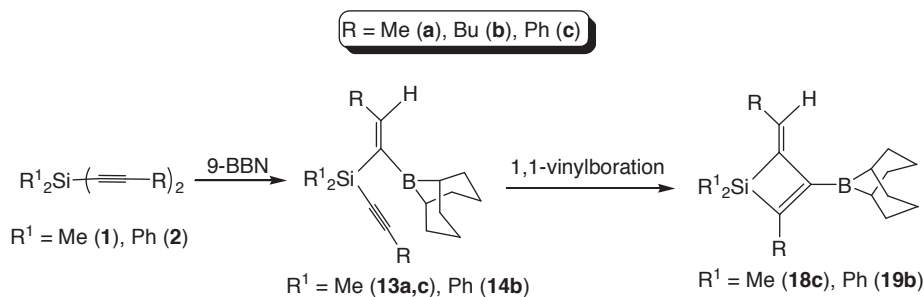
**Scheme 4.** Reaction of dialkyn-1-ylsilanes with one equivalent of 9-BBN. 1,2-Hydroboration is followed by 1,1-vinylboration.

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

	$\delta^{13}\text{C}$ (HC=)	$\delta^{13}\text{C}$ (C-2)	$\delta^{13}\text{C}$ (C-3)	$\delta^{13}\text{C}$ (C-4)	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$
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 $J(^{29}\text{Si}, ^{13}\text{C})$ 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: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 34.4, 32.4^{\text{br}}, 23.5$ (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: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -3.1$ [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: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -1.3$ [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: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -2.1$ (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: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -0.01$ [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: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 33.4, 31.9^{\text{br}}, 23.5$ (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*, SiPh₂).

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 ^1H -NMR data for all the new compounds are collected in the Experimental section. The data sets compare well with the previously reported data³⁶⁻³⁸ 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 ($\delta^{11}\text{B} = 82-89$ 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 [$^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$] 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 $\delta^{29}\text{Si}$ 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 $^1\text{H-NMR}$ spectra a singlet for the olefinic proton of the $\text{C}=\text{CH}(\text{R})$ group is accompanied by ^{29}Si satellites [$^3J(^{29}\text{Si}, ^1\text{H}) \approx 25 \text{ Hz}$], which shows that 1,2-hydroboration has taken place. The value of $^3J(^{29}\text{Si}, ^1\text{H})$ coupling constants is helpful in identification of products (1-silacyclobutenes) and their precursors, the alkenyl(alkyn-1-yl)silanes.

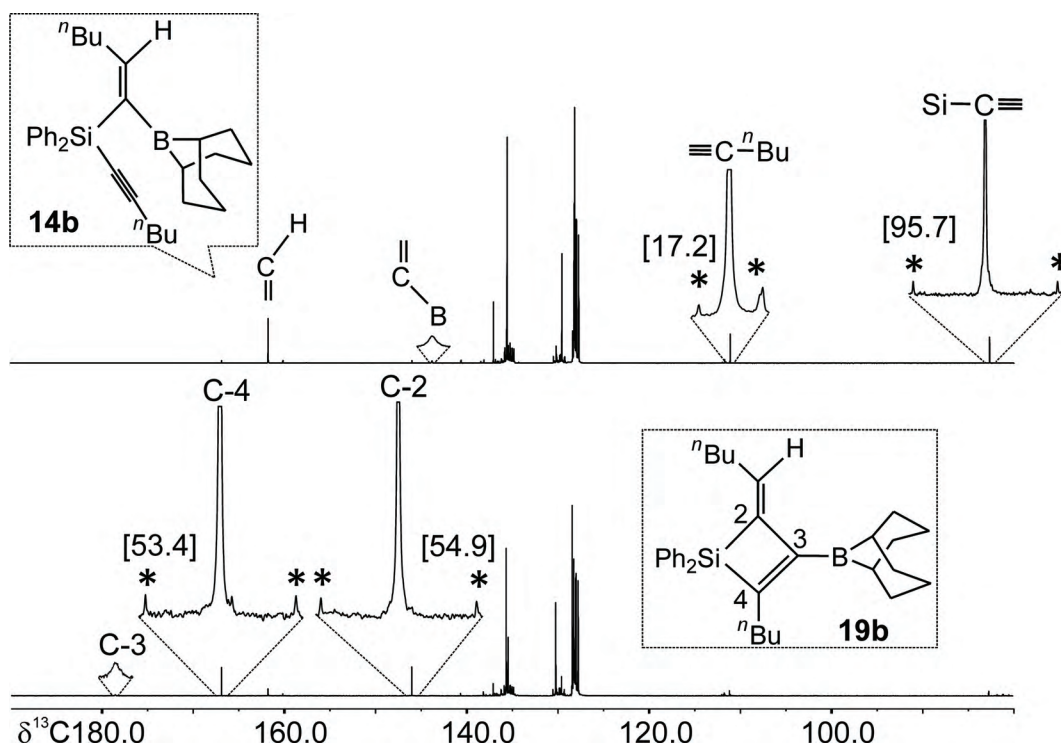


Figure 2

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 $\text{R}^3 = \text{SiMe}_3$ 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 $\text{C}=\text{C}$ bond, $\text{C}\equiv\text{C}$ 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.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft. E. K. is grateful to DAAD (Germany) and HEC (Pakistan) for a scholarship (code A/04/30788).

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