

Syntheses of 1,1-Organo-substituted Silole Derivatives. 1,1-Ethylboration, 1,1-Vinylboration and Protodeborylation

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Z. Naturforsch. **2009**, 64b, 995 – 1002; received June 9, 2009

1,1-Organoboration of dialkyn-1-ylsilanes using triethylborane, BEt₃, and 9-ethyl-9-borabicyclo[3.3.1]nonane, Et-9-BBN, was carried out at elevated temperatures, 100–120 °C. These reactions afforded selectively silole derivatives bearing the dialkylboryl group in 3-position. The siloles are formed *via* intermolecular 1,1-alkylboration, followed by intramolecular 1,1-vinylboration. Two examples of boryl-substituted siloles were treated with an excess of acetic acid at ambient temperature to afford the respective protodeborylated compounds. All new compounds were characterized in solution by multinuclear magnetic resonance spectroscopy (¹H, ¹³C, ¹¹B and ²⁹Si NMR).

Key words: Alkynylsilanes, Siloles, Organoboration, Triethylborane, NMR

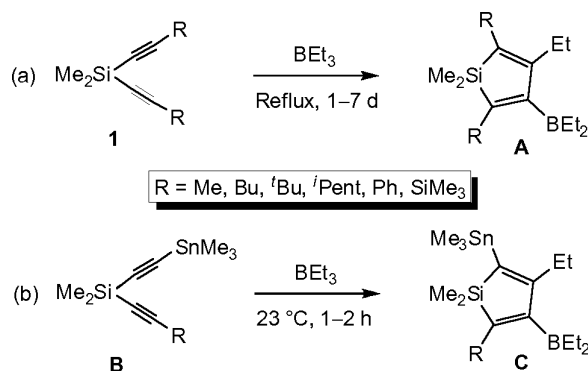
Introduction

Dialkyn-1-ylsilanes [1–3] and triorganoboranes [4–6] have numerous applications in chemistry. By combining these useful classes of compounds, it proved possible to develop a versatile synthesis of siloles [7–9] *via* organoboration reactions [10, 11]. Recently, it has been shown that siloles can also be obtained by using tris(pentafluorophenyl)borane, B(C₆F₅)₃, as the organoborating reagent [12]. Since siloles have become increasingly important owing to their peculiar photophysical properties [13–15], further efforts were made to use organoboration aiming for a greater variety of substituents in all five ring positions. So far, siloles of type **A** were obtained in high yield from dialkyn-1-yldimethylsilanes **1** (Scheme 1a) [10a], and similarly siloles **C** were prepared from **B**, however under less harsh conditions (Scheme 1b) [10b].

In the present report, we describe the synthesis of siloles analogous to **A** by varying the organyl groups linked to silicon and also by using 9-ethyl-9-borabicyclo[3.3.1]nonane (Et-9-BBN) instead of triethylborane, BEt₃, as an organoborating reagent.

Results and Discussion

The dialkyn-1-ylsilanes **2–5** were prepared in the usual way by the reactions of the respective alkynyl-lithium reagents with diorganosilicon dichlorides [16]. NMR spectroscopic data of the new alkyn-1-ylsilanes



Scheme 1. 1,1-Dimethylsilole derivatives obtained *via* 1,1-organoboration as described in ref. [10].

(**4a–d**) are listed in Table 1, and for the other precursor alkynes, such data will be described elsewhere [17].

The reaction of various dialkyn-1-yldiorganosilanes **2–5** with an excess of BEt₃ is shown in Scheme 2. The yields are essentially quantitative after prolonged periods of heating. The products are the siloles **6–8** which were obtained as air-sensitive oily liquids or waxy solids. Their purity and structure in solution follow from consistent sets of characteristic NMR data (Table 2). This is illustrated by the ¹³C NMR spectra in Fig. 1 which also shows the clean formation of the corresponding protodeborylated silole (*vide infra*).

In the case of **5**, the reaction afforded mainly (≈ 80 %) the silole **9** along with a small amount

Table 1. ^{13}C and ^{29}Si NMR data^a for the silane derivatives **4a–d**.

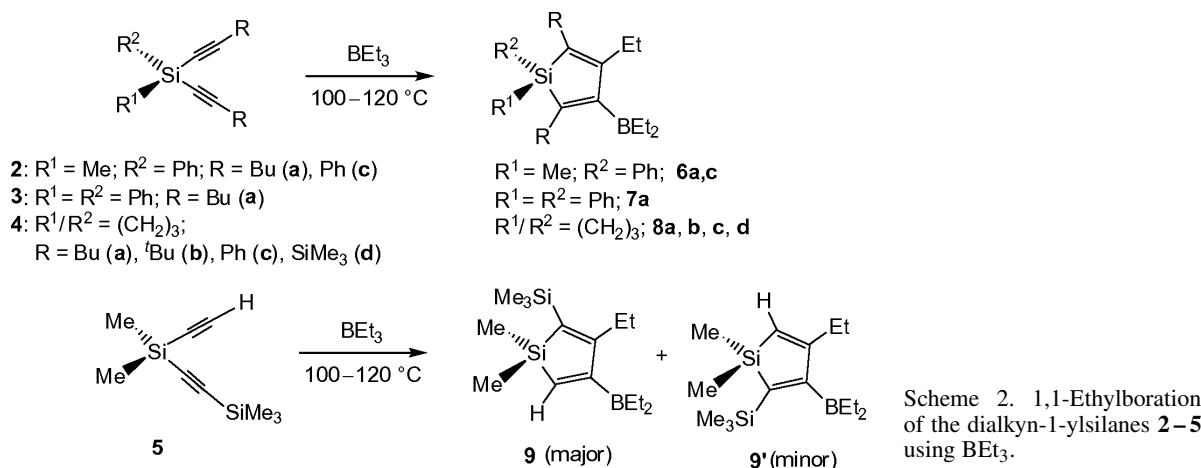
	$\delta^{13}\text{C}(\text{Si}-\text{C}\equiv)$	$\delta^{13}\text{C}(\text{C}\equiv\text{C})$	$\delta^{13}\text{C}(\text{Si}(\text{CH}_2)_3)$	$\delta^{13}\text{C}(\text{R})$	$\delta^{29}\text{Si}$
4a	80.7 [96.1]	110.5 [18.8]	17.1 [50.4], 18.7 [18.8]	13.6, 19.8, 22.1, 30.6 (R = ⁿ Bu)	−37.7
4b	78.8 [95.7]	118.3 [18.0]	17.3 [51.3], 18.1 [18.8]	28.4, 30.7 (R = ^t Bu)	−37.1
4c^b	89.7 [93.4]	108.6 [18.3]	17.2 [50.6], 19.2 [18.5]	122.9, 128.7, 132.6, 129.5 (<i>i, o, m, p</i>) (R = Ph)	−35.8
4d	108.1 [86.2]	117.7 [13.9] [75.1]	16.6 [49.9], 18.9 [18.7]	−0.4 [56.2] R = SiMe ₃)	−39.2, −17.9

^a Measured in C₆D₆ at 23 ± 1 °C, coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ [Hz] are given in brackets; ^b measured in CDCl₃.

Table 2. ^{11}B , ^{13}C and ^{29}Si NMR data^a for the siloles **6–11** and **A** [10a] for comparison.

	C-2	C-3	C-4	C-5	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$
A (R = Bu)	140.8 [64.1]	165.8 (br)	153.6 [10.7]	136.2 [68.2]	5.2	86.7
6a^b (Bu)	140.9 [64.5]	168.1 (br)	155.9 [11.2]	136.5 [69.9]	−0.4	88.1
6c^c (Ph)	140.9 [58.2]	170.4 (br)	157.9 [10.1]	134.7 [65.6]	1.9	87.0
7a^d (Bu)	140.0 [65.9]	169.6 (br)	157.6 [11.3]	134.8 [67.5]	−4.6	86.5
8a^e (Bu)	137.1 [59.0]	167.4 (br)	155.5 [10.4]	132.8 [63.1]	18.4	88.3
8b^f (^t Bu)	147.7 [59.7]	164.4 (br)	154.5 [11.6]	141.1 [n. d.]	22.7	89.0
8c^g (Ph)	142.2	169.3 (br)	157.7 [9.5]	141.0	19.9	89.2
8d^h (SiMe ₃)	142.1 [38.6, 63.6]	185.1 (br)	171.7 [8.1, 11.1]	134.0 [43.0, 62.2]	40.2	88.5
9ⁱ	133.9 [62.9, 51.5]	176.1 (br)	171.8 [5.1]	135.8 [60.5]	17.5, −11.4	87.6
11c^j (Ph)	149.7 [62.8]	169.7 (br)	165.4 [8.8]	137.6 [66.3]	6.9	87.8

^a Measured in C₆D₆ at 296 ± 1 K; coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ [Hz] are given in brackets; br denotes broad ^{13}C NMR signal owing to partially relaxed ^{13}C - ^{11}B spin-spin coupling [25]; ^b other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -5.5$ [49.4, Si-Me], 24.7, 14.2 (Et), 22.8 (br), 9.4 (BEt₂), 34.0, 33.4, 32.7, 28.8, 23.3, 23.3, 14.1, 14.2 (Bu), 136.3 [62.9], 134.5, 128.3, 129.5 (*i, o, m, p*, Si-Ph); ^c other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -6.4$ [51.4, Si-Me], 24.8, 14.5 (Et), 22.3 (br), 9.9 (BEt₂), 140.1 [65.5], 134.8, 128.7, 130.0 (*i, o, m, p*, Si-Ph), 145.0, 141.9, 128.7, 128.6, 128.2, 127.7, 125.9, 126.4 (*i, i, o, o, m, m, p, p*, Ph); ^d other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 34.0$, 33.4, 33.2, 29.1, 23.3, 14.2, 14.1 (Bu), 24.9, 14.0 (Et), 22.9 (br), 9.5 (BEt₂), 135.8 [62.1], 135.9, 128.4, 129.8 (*i, o, m, p*, SiPh₂); ^e other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 14.0$, 32.6 (Et), 22.8 (br), 9.2 (BEt₂), 14.8, 23.6, 28.4, 33.7, 34.0 (Bu), 14.3, 19.1 ((CH₂)₃); ^f other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 14.9$, 31.7 (Et), 22.5 (br), 10.2 (BEt₂), 32.9, 30.8 (^tBu), 16.0 [39.2], 18.6 [15.5] ((CH₂)₃); ^g other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 13.9$, 31.2 (Et), 22.0 (br), 9.4 (BEt₂), 128.4, 128.8, 126.9, 129.3 (*i, o, m, p*, Ph), 13.9 [40.3], 19.3 [16.4] (CH₂)₃; ^h other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 15.3$, 30.0 (Et), 23.0 (br), 9.4 (BEt₂), 1.6 [51.3, SiMe₃], 1.7 [51.6, SiMe₃], 14.3 [38.8], 19.0 [15.5] (CH₂)₃; ⁱ the silole **9** is numbered in this way for consistency of the data; other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -3.3$ [48.8, SiMe₃], 1.5 [51.3, SiMe₂], 9.2, 21.0 (br) (BEt₂), 14.4, 30.4 (Et); ^j other ^{13}C NMR data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -3.7$ [49.3, SiMe₂], 11.2, 22.7 (br), 21.7, 30.6, 34.8, 35.0 (br) (BEt, BC₈H₁₄), 134.3 [6.9, *i*], 141.6 [5.8, *i*], 128.7, 128.6, 128.0, 127.8, 126.6, 126.7 (2,5-Ph₂).



(< 5 %) of the silole **9'**, which results from intermolecular 1,1-ethylboration of the Si–C≡CH unit in the first

step. In contrast, **9** is formed by intermolecular 1,1-ethylboration of the more reactive Si–C≡C–SiMe₃ unit

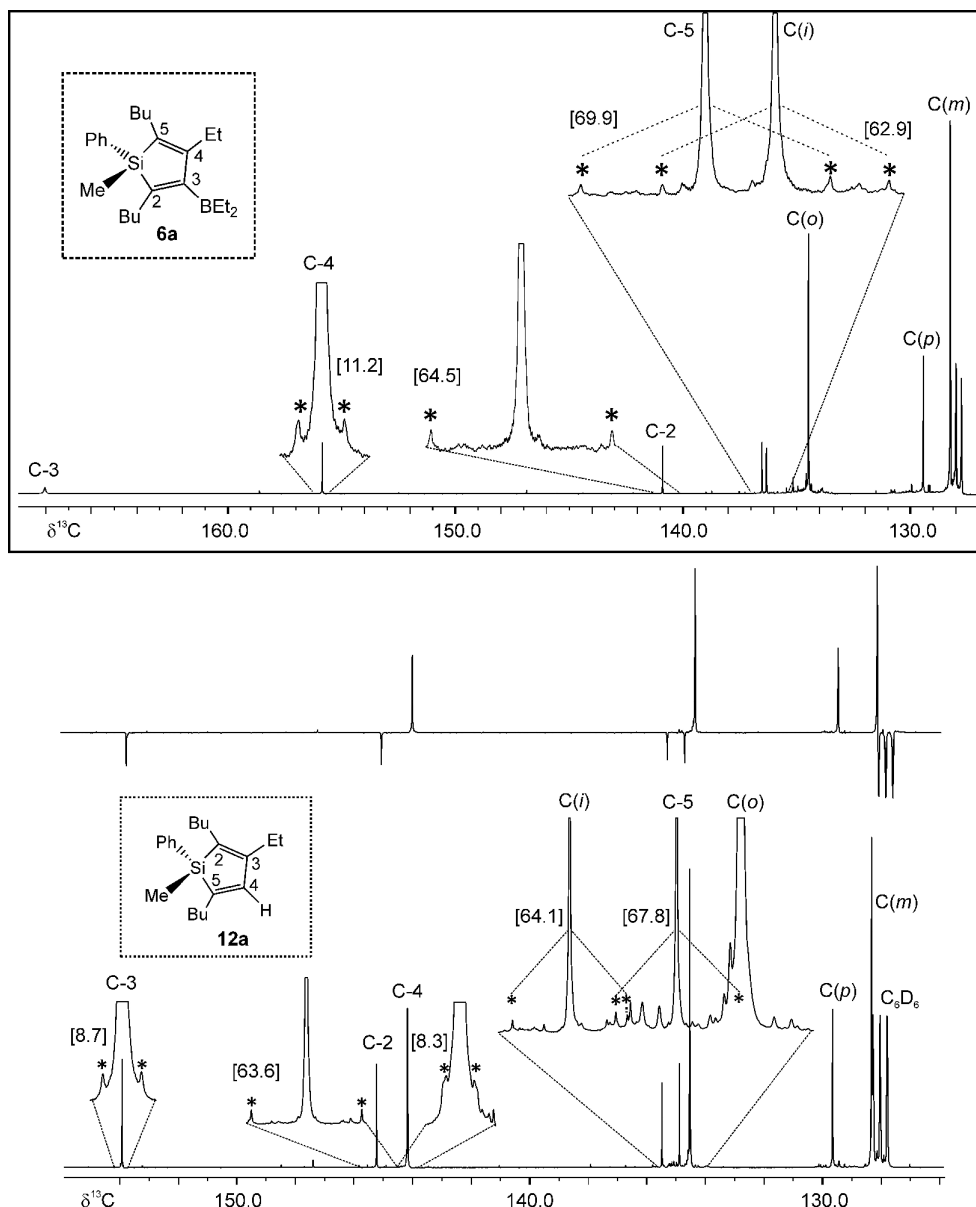
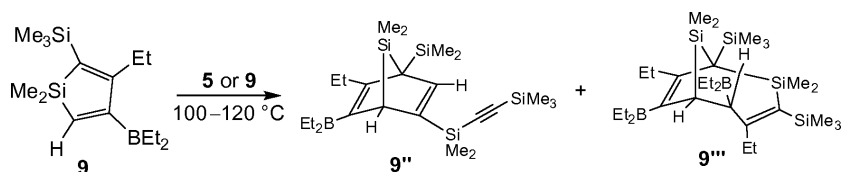


Fig. 1. Part of the 100.5 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the 3-diethylborylsilole derivative **6a** (upper inset). The same spectral region is shown for the protodeborylated silole **12a** (middle trace: J-modulated experiment in the middle and normal $^{13}\text{C}\{^1\text{H}\}$ NMR in the lower trace). ^{29}Si satellites (marked by asterisks in expansions) indicate coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ (values are given in brackets; see also Tables 2 and 3).



Scheme 3. [4+2]Cycloaddition reactions of the silole **9**.

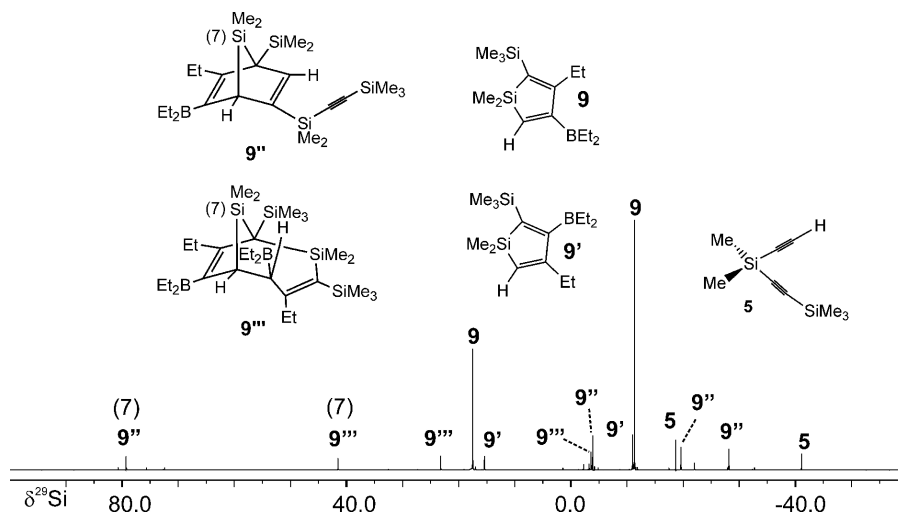
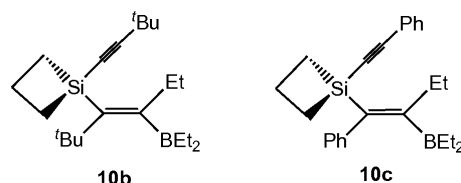


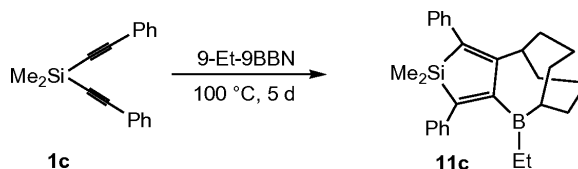
Fig. 2. 59.6 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (INEPT, refocused [23]) of the reaction mixture after 2 d of heating **5** in BEt_3 as a solvent at 110 °C. The mixture contains **5**, **9**, **9'**, **9''**, and **9'''**.

in the first step, followed by fast intramolecular 1,1-vinylboration of the $\text{Si}-\text{C}\equiv\text{C}-\text{H}$ unit. Under the reaction conditions, the silole derivative **9** reacts further (Scheme 3) *via* [4+2]cycloadditions, either with the starting silane **5** or with one of its kind to afford the 7-silanorbornadiene **9''** ($\approx 5\%$) and a tricyclic 7-silanorbornene derivative **9'''**, respectively. The NMR spectroscopic data, in particular those obtained from ^{29}Si NMR spectra, are very helpful (Fig. 2) in the identification of such products. For compound **9''**, all the ^{29}Si chemical shifts [$\delta^{29}\text{Si} = 79.0$ (7- SiMe_2), -3.9 (SiMe_3), -19.7 ($\text{C}\equiv\text{C}-\text{SiMe}_3$), -28.3 ppm (SiMe_2)] and relevant ^1H NMR signals [*e. g.* $\delta^1\text{H}(\text{=CH}) = 6.92$ ppm (d, $J(^1\text{H}, ^1\text{H}) = 1.5$ Hz)] can be found in the expected regions [18]. Numerous additional ^{29}Si NMR signals of low intensities grow with time, and from these it appears that **9** undergoes [4+2]cycloadditions with one of its kind to give **9'''**, for which at least the ^{29}Si NMR signal of the 7-silanorbornene unit ($\delta^{29}\text{Si} = 41.5$) [18]) as well as the ^{29}Si NMR signal of the SiMe_2 group as part of the silacyclopent-2-ene ring ($\delta^{29}\text{Si} = 23.2$) are typical. Other spurious signals may arise by 1,1-ethylboration of the $\text{Si}-\text{C}\equiv\text{C}-\text{H}$ unit in **9''** or by the – likely – formation of other isomers in the [4+2] cycloaddition reactions. Owing to the low concentration of the compounds **9''**, **9'''** and others, we did not attempt to assign ^1H and ^{13}C NMR signals to these compounds *i. e.*, **9''** and **9'''**.

In the cases of the 1,1-dialkyn-1-ylsilacyclobutane derivatives **4b** and **4c**, the reactions with BEt_3 lead to the siloles **8b, c** along with side products **10b, c** (Scheme 4), for which the stereochemistry does not



Scheme 4. Side products from the 1,1-organoboration of **4b, c**, unsuitable for further rearrangements to afford the corresponding silole derivatives.



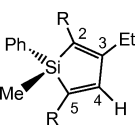
Scheme 5. 9-Ethyl-9-borabicyclo[3.3.1]nonane, 9-Et-9BBN, is used as an organoborating reagent to afford the polycyclic silole **11c**.

allow for a rearrangement towards ring closure. The corresponding *Z*-isomers were not detected.

The rate-determining step of the silole formation *via* 1,1-organoboration is the intermolecular 1,1-ethylboration in all cases, followed by the fast intramolecular 1,1-vinylboration, if the stereochemistry of the alkenyl-alkyn-1-ylsilane is favorable. In our previous work it was found that BEt_3 can react with certain alkyn-1-ylsilanes as a 1,2-hydroborating reagent [19, 20]. This was not observed in the present work.

The harsh reaction condition required for the 1,1-organoboration of dialkyn-1-ylsilanes restrict these reactions to thermally stable triorganoboranes. This

Table 3. ^{13}C and ^{29}Si NMR data^a for the siloles **12a**, **c**.

	12a	12c
		
$\delta^{13}\text{C}(\text{C-2})$	145.2 [63.6]	143.8 [64.2]
$\delta^{13}\text{C}(\text{C-3})$	144.2 [8.3]	143.3 [7.2]
$\delta^{13}\text{C}(\text{C-4})$	153.9 [8.7]	155.3 [7.9]
$\delta^{13}\text{C}(\text{C-5})$	134.9 [67.8]	138.1 [67.4]
$\delta^{13}\text{C}(\text{Et})$	13.7, 23.8	13.8, 24.8
$\delta^{13}\text{C}(\text{Si-Me})$	-6.2 [49.7]	-6.2 [51.9]
R = Bu (a) $\delta^{13}\text{C}(\text{Si-Ph})$	135.5 [64.1], 134.5, 128.3, 129.6 (<i>i, o, m, p</i>)	140.4 [5.8], 138.9 [5.9], 134.2 [66.5], 134.8, 130.1,
R = Ph (c) $\delta^{13}\text{C}(\text{R})$	14.1, 14.1, 22.9, 23.2, 28.7, 32.3, 32.8, 33.3	129.0, 128.7, 128.6, 128.3, 127.3, 126.9, 126.1 ^b
$\delta^{29}\text{Si}$	-1.6	1.0

^a Measured in C_6D_6 at 23 ± 1 °C, coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ [Hz] are given in brackets; ^b Ph carbons without assignment.

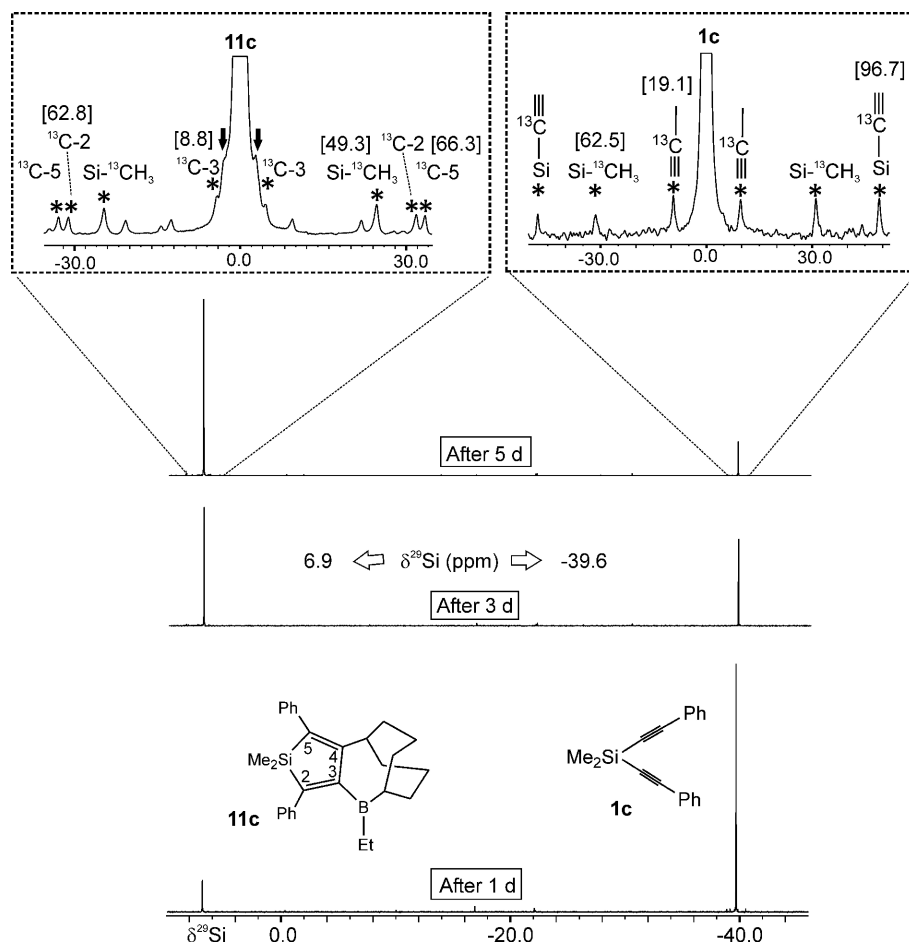
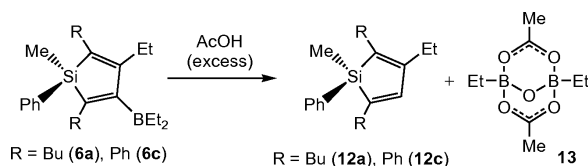


Fig. 3. Monitoring of the reaction of di(phenylethynyl) dimethylsilane **1c** with Et-9-BBN by ^{29}Si NMR spectroscopy (INEPT, refocused [23]). The ^{29}Si NMR signal for **1c** disappeared after 7 d. Expansions are shown for the two signals corresponding to **1c** and the silole **11c**, and ^{13}C satellite signals corresponding to coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ are marked by asterisks and arrows, respectively. All values (Table 2) are also evident from the respective ^{13}C NMR spectra.

condition is fulfilled by 9-ethyl-9-borabicyclo[3.3.1]nonane, Et-9-BBN, as shown in Scheme 5. The reaction proceeds by twofold ring expansion of the bicyclic system to give selectively the polycyclic silole **11c**. During the course of the reaction no intermediates or other products were observed (Fig. 3).

As an example for the protodeborylation of the siloles reported here, the siloles **6a,c** were treated with an excess of acetic acid (Scheme 6). These reactions afforded smoothly in essentially quantitative yield the siloles **12a, c** (see NMR data in Table 3, and also Fig. 1 for the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **12a**), along with



Scheme 6. Protodeborylation of two siloles using acetic acid.

the known bicyclic boron-oxygen compound **13** [21]. Interestingly, the silole **11c** does not react under the same conditions.

Conclusions

The synthesis of siloles *via* 1,1-organoboration of dialkyn-1-ylsilanes allows not only for variations of substituents in the positions 2–5 but also for introducing various organyl groups to silicon, including the access to chiral siloles. Particularly noteworthy in this context are also the new spirosilanes containing silacyclobutane units.

Experimental Section

All preparative work and handling of air-sensitive chemicals were carried out by observing precautions to exclude oxygen and moisture. Dichloromethylphenylsilane, dichlorodiphenylsilane, 1,1-dichloro-silacyclobutane, 1-hexyne, 3,3-dimethyl-but-1-yne, ethynylbenzene, trimethylsilyl-ethyne, *n*-butyllithium in hexane (1.6 M), and triethylborane (BEt₃) were commercial products and were used without further purification. 9-Etyl-9-borabicyclo[3.3.1]nonane, Et-9-BBN, was prepared according to the literature procedure [22]. The dialkyn-1-ylsilanes **2–5** were prepared in the usual way [16], and details including NMR spectroscopic data will be reported elsewhere [17]. NMR spectra: Bruker ARX 250 MHz or Varian Inova 300 MHz and 400 MHz spectrometers, all equipped with multinuclear units; measurements at 23 ± 1 °C in 5 mm (o. d.) tubes, using C₆D₆ solutions (*ca.* 10–15 % v/v), if not mentioned otherwise. Chemical shifts are given relative to SiMe₄ [$\delta^1\text{H}$ (C₆D₅H) = 7.15, $\delta^{13}\text{C}$ (C₆D₆) = 128.0, $\delta^{29}\text{Si}$ = 0 for SiMe₄ with $\mathcal{E}^{(29)\text{Si}}$ = 19.867187 MHz], and $\delta^{11}\text{B}$ = 0 for BF₃·OEt₂ with $\mathcal{E}^{(11)\text{B}}$ = 32.083971 MHz. ^{29}Si NMR spectra were recorded using the refocused INEPT pulse sequence with ^1H decoupling [23], based on $^{2/3}J(^{29}\text{Si}, ^1\text{H}) \approx 7\text{--}10\text{ Hz}$ (after optimization of the respective refocusing delays).

Reaction of dialkyn-1-ylsilanes **2–5** with triethylborane (typical procedure)

A Schlenk tube was charged with the dialkyn-1-ylsilane **2a** (0.5 g; 1.77 mmol) where an excess of BEt₃ (4 mL) served as reagent as well as solvent. The reaction mixture

was heated at 100–110 °C (oil bath temperature), and the progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 3 d, when the reaction was complete, all readily volatile materials were removed *in vacuo*, and the oily yellowish residue was identified as the pure (> 97 % according to ^1H NMR) silole **6a**. Except for the reaction time, the experimental procedure was identical for all other members of the series, **6c** (10 d), **7a** (23 d), **8a** (10 h), **8b** (7 d), **8c** (11 d), and **8d** (6 h). Siloles **8b** and **8c** were accompanied by alkenyl(alkyn-1-yl)silanes **10b** and **10c** for which the loss in stereoselectivity does not allow for further rearrangement.

6a: ^1H NMR (400 MHz): δ = 0.5 (s, 3H, $^2J(^{29}\text{Si}, ^1\text{H})$ = 6.5 Hz, Si-Me), 2.2, 1.0–0.9, 0.5, 0.5 (m, m, t, t, 18H, Bu), 1.8, 0.6 (m, t, 5H, Et), 1.8–1.9, 0.7 (m, t, 10H, BEt₂), 6.9–7.4 (m, 5H, Si-Ph).

6c: ^1H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 2.4, 0.9 (m, t, 5H, Et), 1.5, 1.1 (m, t, 10H, BEt₂), 7.3–7.7 (m, 15H, Si-Ph, Ph).

7a: ^1H NMR (400 MHz): δ = 2.1–1.9, 1.3, 0.9, 0.5, 0.4 (m, m, m, t, t, 18H, Bu), 2.2, 0.8 (m, t, 5H, Et), 1.1, 0.9 (m, t, 10H, BEt₂), 6.9–7.7 (m, 10H, SiPh₂).

8a: Yield = 98 %. – ^1H NMR (250 MHz): δ = 0.9, 2.0 (t, q, 5H, Et), 1.0, 1.4 (t-br, q-br, 10H, BEt₂), 0.9, 1.3–1.5, 2.2 (t, m, t, 18H, Bu), 1.6, 2.4 (t, quint, 6H, (CH₂)₃).

8b: ^1H NMR (250 MHz) data: δ = 0.9, 2.1 (t, q, 5H, Et), 1.1, 1.35–1.45 (t-br, m-br, 10H, BEt₂), 1.2, 1.3 (s, 18H, ^tBu), 1.7, 2.5 (dt, quint., 6H, $J(^1\text{H}, ^1\text{H})$ = 2.3, 8.5 Hz, (CH₂)₃).

8c: ^1H NMR (250 MHz): δ = 1.0, 1.5 (t-br, q-br, 10H, BEt₂), 1.2, 2.3 (t, q, 5H, Et), 1.5, 2.1 (t, quint., 6H, (CH₂)₃), 7.2–7.3, 7.3–7.5 (m, m, 10H, Ph).

8d: Yield = 98 %. – ^1H NMR (250 MHz): δ = 0.2, 0.3 (s, s, 18H, SiMe₃), 1.0, 2.2 (t, q, 5H, Et), 1.0, 1.4 (t-br, q-br, 10H, BEt₂), 1.6, 2.5 (t, quint., 6H, (CH₂)₃).

9: ^1H NMR (400 MHz): δ = 0.2 (s, 9H, SiMe₃), 0.2 (s, 6H, SiMe₂), 0.9, 2.4 (t, q, 5H, Et), 1.0, 1.3 (t, q, 10H, BEt₂), 5.9 (s, 1H, $^2J(^{29}\text{Si}, ^1\text{H})$ = 15.0 Hz, C⁵H).

9': ^1H NMR (400 MHz): δ = 5.8 (t, 1H, $^2J(^{29}\text{Si}, ^1\text{H})$ = 15.3 Hz, $^4J(^1\text{H}, ^1\text{H})$ = 1.9 Hz, C⁵H); ^{29}Si NMR (59.6 MHz): δ = –11.3, +15.4 ppm.

10b: ^1H NMR (250 MHz): δ = 1.1 (s, 9H, ^tBu), 1.4 (s, 9H, ^tBu). – ^{13}C NMR (62.8 MHz): δ = 82.8 ($\equiv\text{C}$), 116.3 (Si-C \equiv), 140.6 ($=\text{C}$), 168.4 (br, (B)C \equiv), 9.8, 22.4^{br} (BEt₂), 13.4, 14.2, 21.1 (Si(CH₂)₃), 31.0 (^tBu). – ^{29}Si NMR (49.7 MHz): δ = –12.9.

10c: ^1H NMR (250 MHz): δ = 1.0, 1.3 (t, q, 10H, BEt₂), 1.1, 2.0–2.5 (t, m, 5H, Et), 1.5, 2.0–2.5 (t, m, 6H, (CH₂)₃), 7.1–7.5 (m, 10H, Ph). – ^{13}C NMR (62.8 MHz): δ = 87.4 ($\equiv\text{C}$), 106.7 (Si-C \equiv), 136.4 ($=\text{C}$), 165.4^{br} ((B)C \equiv), 14.0, 26.4 (Et), 9.1, 22.0^{br} (BEt₂), 13.7, 14.4, 18.2 (Si(CH₂)₃). – ^{29}Si NMR (49.7 MHz): δ = –9.8.

Reaction of di(alkyn-1-yl)dimethylsilane 1c with 9-ethyl-9-borabicyclo[3.3.1]nonane, Et-9-BBN

A few crystals (0.20 g; 0.77 mmol) of the silane **1c** dissolved in C₆D₆ (*ca.* 0.5 mL) and Et-9-BBN (0.5 mL, in excess) were given into an NMR tube which was sealed under argon. The reaction mixture was heated to 102 ± 5 °C (oil bath temperature), and changes were monitored by ²⁹Si NMR spectroscopy (Fig. 3). After 7 d the NMR tube was cooled in liquid N₂ and opened carefully. The contents of the tube were dissolved in pentane (5 mL). After removing all volatiles including the excess of Et-9-BBN (*b. p.* = 40–42 °C/0.9 Torr) *in vacuo*, the pure silole (> 97 % according to ¹H NMR) **11c** was obtained as a waxy solid.

11c: ¹H NMR (400 MHz): δ = 0.2 (s, 6H, SiMe₂), 0.8, 1.1, 1.5, 1.7–1.8, 2.0, 2.1, 3.2 (t, b, m, m, m, m, m, 19H, B-Et, BC₈H₁₄), 6.8–7.1, 7.2, 7.3 (m, m, m, 10H, Ph).

Protodeborylation of siloles 6a and 6c (typical procedure)

The silole **6a** (1.0 g) was dissolved in pentane (10 mL), and glacial acetic acid (1.0 mL, in excess) was slowly added. The reaction mixture was stirred at r. t. After 40 min all readily volatile materials were removed under reduced pressure. The oily residue was identified as a mixture of the silole **12a**

and the bicyclic boron-oxygen compound **13** (¹H, ¹¹B, ¹³C and ²⁹Si NMR). The mixture was heated to 100 °C under vacuum (*ca.* 10^{–2} Torr) for 1 h, adopting the literature procedure [24] for separation of the boron-oxygen product **13**. The boron-oxygen compound was collected as a solid along the walls of the Schlenk tube. The oily residue contained mainly the desired protodeborylated silole **12a** (> 95 %; Fig. 1). The identical experimental procedure was adopted for protodeborylation of **12c**. The silole derivatives **12a** and **12c** are colorless oily liquids, stable in dry air, and they were fully characterized by multinuclear NMR spectroscopy (Table 3).

12a: ¹H NMR (400 MHz): δ = 0.5 (s, 3H, ²J(²⁹Si, ¹H) = 6.5 Hz, Si-Me), 1.1, 2.2 (t, q, 5H, Et), 0.7, 0.8, 1.1, 1.3, 2.3 (t, t, m, m, t, 18H, Bu), 6.5 (s, 1H, ³J(²⁹Si, ¹H) = 13.4 Hz, C⁴H), 7.5, 7.1 (m, m, 5H, Si-Ph).

12c: ¹H NMR (400 MHz): δ = 0.6 (s, 3H, ²J(²⁹Si, ¹H) = 6.6 Hz, Si-Me), 1.0, 2.4 (t, q, 5H, Et), 6.9–7.1, 7.4, 7.6, 7.9 (m, m, m, m, 15H, Si-Ph, Ph), 7.3 (s, 1H, ³J(²⁹Si, ¹H) = 13.1 Hz, C⁴H).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft. E. K. is grateful to DAAD and HEC (Pakistan) for a scholarship.

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