

Synthesis and Molecular Structure of Silole Derivatives Bearing Functional Groups on Silicon: 1,1-Organoboration of Dialkynylsilanes

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Keywords: Main group elements / Silicon / Boron / Alkynes / Heterocyclic compounds

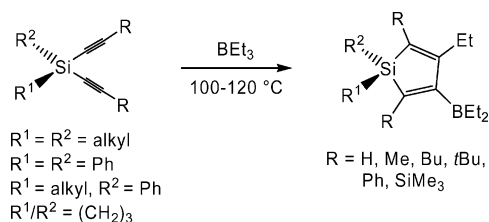
Various dialkynylsilanes bearing Si–H or SiCl functions in addition to the alkynyl groups react with an excess of triethylborane after heating at 100–110 °C for several days via slow intermolecular 1,1-ethylboration followed by fast intramolecular 1,1-vinylboration to give Si-functional substituted siloles. Similarly, the reactions with 9-ethyl-9-borabicyclo[3.3.1]nonane afford polycyclic compounds containing the silole ring. Protodeborylation with an excess of acetic acid

leads to simultaneous substitution of BEt₂ and Si–H functions to give 1-acetoxysiloles. All new siloles were characterized by NMR spectroscopy in solution (¹H, ¹¹B, ¹³C, ²⁹Si NMR), and for one example of a polycyclic silole derivative the molecular structure was determined by X-ray analysis.

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Introduction

Siloles attract increasingly attention owing to their photo-physical properties.^[1–4] Various synthetic procedures have become available,^[5] most of which are multistep procedures, not generally applicable to introduce a wide range of different substituents at the silicon or the ring carbon atoms. In this context 1,1-organoboration^[6] has paved a convenient way to siloles bearing numerous different substituents in the 2–5 positions.^[7] Recently, it was shown that siloles bearing various organyl groups at silicon can be easily prepared via 1,1-organoboration (Scheme 1),^[8,9] and the mechanism of this reaction is fairly well understood. The reaction proceeds in the first step via intermolecular 1,1-ethylboration, followed in the second step by intramolecular 1,1-vinylboration.^[6–9]



Scheme 1. 1,1-Organoboration of dialkynylsilanes leading in high yield to siloles.

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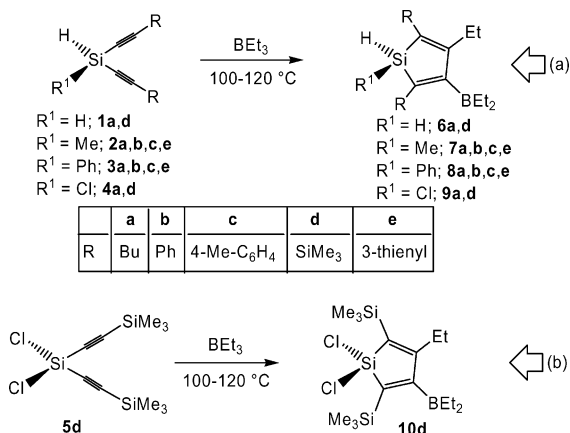
In the present work, we report on attempts to use appropriate dialkynylsilanes in 1,1-organoboration reactions to synthesize siloles bearing one or two functional groups, in particular hydrogen and chlorine, at the silicon atom. Clearly, such siloles invite for further transformation taking advantage of the reactive Si–H and/or Si–Cl bonds. The reaction conditions (Scheme 1) require thermally fairly robust triorganoboranes, and for this purpose we have selected triethylborane (BEt₃) and 9-ethyl-9-borabicyclo[3.3.1]nonane (Et-9BBN).

Results and Discussion

The dialkynylsilanes **1–5** (Scheme 2) were prepared by the reaction of trichlorosilane or tetrachlorosilane with the respective alkynyllithium reagent. In general, these reactions afforded mixtures of alkynylsilanes, in which less or more than two Si–Cl were replaced by the Si–C≡C–R functions.^[9a] These mixtures were separated by distillation in order to use the pure dialkynylsilanes for the 1,1-organoboration reactions (Scheme 2).

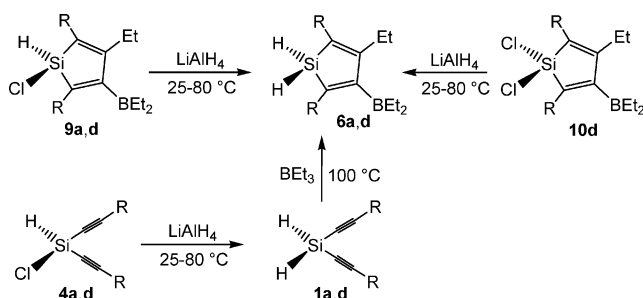
The siloles **6–10** were obtained in > 90% yield and high purity in most cases as colorless or yellowish air- and moisture sensitive oils. In the case of siloles containing the SiCl₂ unit, the successful 1,1-organoboration reaction was found to be restricted to **5d** leading to **10d** (Scheme 2, b). With substituents (R = alkyl or aryl) other than R = SiMe₃, the products were silacyclobutene derivatives^[9a,10] or complex mixtures of these heterocycles with siloles and other unidentified products.^[9a]

The alkynylsilanes **1a** and **1d**, precursors of the siloles **6a,d**, were most conveniently prepared by the reaction of the respective chlorosilanes Cl(H)Si(C≡C–R)₂ with Li-



Scheme 2. Synthesis of Si-functionally substituted silole derivatives via 1,1-organoboration reactions.

AlH₄. Alternatively, the siloles **9a,d** containing the Si(H)Cl or the silole **10d** were converted into **6a** or **6d**, respectively, by treatment with LiAlH₄ (Scheme 3).



Scheme 3. Three routes to siloles containing the SiH₂ moiety.

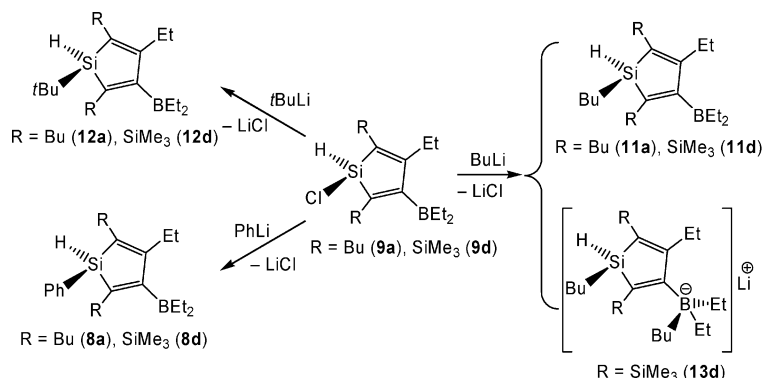
The availability of the Si–Cl bond in siloles is an important starting point to explore the chemistry of siloles.^[5] Here, we report some preliminary first results for our new siloles with respect to the introduction of various organyl substituents at silicon, starting from the siloles **9a,d**

(Scheme 4). The reactions with *t*BuLi and PhLi afforded the siloles **12a,d** and **8a**, respectively, along with minor amounts of side products. The major side reaction, in the cases of *n*BuLi and PhLi, concerned the formation of tetraorganoborates, e.g. **13d** (ca. 10–20% in repeated experiments), which could not be completely suppressed. Expectedly, this was not a problem with the more bulky *tert*-butyl group (**12a,d**), although the reaction of **9d** with *t*BuLi proceeded rather slowly, and the conditions have not been optimized as yet.

All siloles **6–12** were characterised in solution by their typical NMR spectroscopic data (Table 1). Most noteworthy in this respect were the ²⁹Si NMR spectra which were recorded in many cases with a signal-to-noise ratio to show the ¹³C satellites owing to ²⁹Si–¹³C spin spin coupling (e.g. Figure 1). Similarly, the ¹³C NMR spectra (e.g. Figure 2), are valuable in particular for the olefinic range, showing the typical pattern of one broad [¹³C(B–C³=)] and three sharp [¹³C(C^{2,4,5})] NMR signals with the ²⁹Si satellites for the determination of ⁿJ(²⁹Si, ¹³C) (*n* = 1,2). The latter coupling constants serve for assignments as conclusive information complementary to the ²⁹Si NMR spectra.

Another thermally fairly stable (with respect to 1,2-dehydroboration) trialkylborane is 9-ethyl-9-borabicyclo[3.3.1]nonane (Et-9-BBN).^[11] The dialkynylsilanes **2** and **3** were shown to react with Et-9-BBN selectively by twofold expansion of the bicyclic ring system (Scheme 5) to give the polycyclic silole derivatives **14** and **15**, again in high yield and purity as oils or crystalline solids (vide infra). The proposed solution-state structures of the siloles **14** and **15** follow from a consistent NMR spectroscopic data set (Table 2).

The molecular structure of the silole **15b** (Figure 3) was determined by X-ray analysis. Intermolecular interactions appear to be negligible. The structural parameters of the silole ring are typical.^[5,12] Expectedly, the endocyclic bond angle C1–Si1–C13 is small [92.3(2)°]. All atoms of the silole ring are almost in the same plane (mean deviation 2.6 pm). The surroundings of the boron atom are trigonal planar, and the plane C7B1C20 forms an angle of 122.0° relative to the silole ring. The phenyl groups C1–Ph and C13–Ph are twisted by 119.5° and 25.7°, respectively, against the sil-



Scheme 4. Replacement of Si–Cl function in the siloles **9a,d** by Si-alkyl or Si-Ph groups.

Table 1. ^{11}B , ^{13}C and ^{29}Si NMR spectroscopic data^[a] for the siloles **6–12**.

Si-R ¹		$\delta^{13}\text{C}$ C ²	C ³	C ⁴	C ⁵	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$
6a ^[b]	H	136.2 [65.2]	170.7 ^{br}	157.7 [10.3]	132.6 [70.1]	−41.1	86.0
6d ^[c]	H	141.3 [45.3] [63.8]	190.1 ^{br}	174.1 [11.1]	133.7 [48.2] [62.9]	−19.9 {10.3}; −10.0, −10.4(SiMe ₃)	88.1
7a ^[d]	Me	139.4 [64.4]	168.2 ^{br}	155.7 [11.6]	135.2 [69.0]	−15.9	87.0
7b ^[e]	Me	143.9 [63.8]	170.6 ^{br}	158.1 [10.1]	138.1 [67.2]	−12.2	87.2
7c ^[f]	Me	143.6 [63.9]	169.8 ^{br}	157.8 [10.5]	137.6 [67.5]	−12.6	87.1
7e ^[g]	Me	135.4 [64.6]	169.9 ^{br}	157.4 [10.4]	130.3 [68.4]	−11.8	86.9
8a ^[h]	Ph	138.7 [54.7]	169.8 ^{br}	157.4 [10.9]	134.9 [68.9]	−14.9	86.4
8b ^[i]	Ph	142.3 [65.1]	172.0 ^{br}	159.6 [10.5]	137.1 [68.4]	−12.9	86.8
8c ^[j]	Ph	142.0 [65.1]	171.3 ^{br}	159.3 [10.5]	136.7 [68.8]	−13.2	86.8
8e ^[k]	Ph	133.9 [65.4]	171.3 ^{br}	158.9 [10.5]	129.2 [68.5]	−11.9	86.8
9a ^[l]	Cl	135.3 [73.1]	169.1 ^{br}	157.2 [15.7]	131.7 [78.8]	−7.0	89.7
9d ^[l]	Cl	139.9 [48.3] [63.3]	186.9 ^{br}	173.3 [10.2] [12.7]	132.3 [55.6] [61.9]	9.8; −10.2, −9.8 (SiMe ₃)	87.1
10d ^[m]	Cl ₂	145.2	186.4 ^{br}	171.4	132.4	36.0; −9.2, −9.5 (SiMe ₃)	88.1
11a ^[n]	Bu	138.7	168.9 ^{br}	156.3	134.3	−12.8	86.7
11d ^[o]	Bu	143.5 [42.8] [62.9]	187.7 ^{br}	173.2 [10.7]	135.4 [48.1] [62.0]	10.0 {10.2}; −10.7, −11.1(SiMe ₃)	88.9
12a ^[p]	<i>t</i> Bu	133.7 [63.4]	168.9 ^{br}	156.7 [10.2]	137.7 [62.0]	−4.3	85.4
12d ^[q]	<i>t</i> Bu	143.2	188.6 ^{br}	175.3	135.7	21.3; −10.6, −10.9(SiMe ₃)	85.8

[a] Data measured at $23 \pm 1^\circ\text{C}$ as C_6D_6 solution (10–15% in 5 mm o.d. NMR tubes). Values in brackets are $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ and those in braces belong to $^2J(^{29}\text{Si}, ^{29}\text{Si})$. Superscript “br” means broad: ^{13}C nuclei directly linked to ^{11}B give broad signals as a result of partially relaxed ^{13}C – ^{11}B spin-spin coupling.^[17] [b] Other ^{13}C NMR spectroscopic data: $\delta = 22.6^{\text{br}}$, 9.2 (BEt₂), 32.8, 13.9 (Et), 14.28, 14.30, 23.3, 23.4, 24.9, 28.9, 34.9, 35.4 (Bu) ppm. [c] Other ^{13}C data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 22.4^{\text{br}}$, 9.4 (BEt₂), 30.2, 15.2 (Et), 1.4 [52.0, SiMe₃], 1.5 [51.6, SiMe₃] ppm. [d] Data taken from ref. ^[9b]. [e] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -6.8$ [49.8, Si-Me], 22.3^{br}, 9.7 (BEt₂), 24.7, 14.3 (Et), 141.7 [6.6, C-*i*], 140.6 [6.0, C-*i*], 128.8, 128.8, 128.6, 128.0, 126.5 (C-*p*), 126.0 (C-*p*) (Ph) ppm. [f] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -6.6$ [49.6, SiMe], 22.3^{br}, 9.8 (BEt₂), 24.8, 14.4 (Et), 138.9 [6.6, C-*i*], 137.7 [6.1, C-*i*], 129.6 (C-*o*), 129.5 (C-*o*), 128.6 (C-*m*), 128.0 (C-*m*), 135.9 (C-*p*), 135.2 (C-*p*), 21.2 (Me), 21.1 (Me) (4-Me-C₆H₄) ppm. [g] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = -6.1$ [49.4, Si-Me], 22.3^{br}, 9.6 (BEt₂), 25.7, 13.8 (Et), 142.3 [7.2], 139.9 [6.4], 128.9, 127.8, 126.2, 125.5, 121.0, 120.2 (3-thienyl) ppm. [h] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 34.9$, 34.3, 32.6, 28.8, 23.3, 23.3, 14.2, 14.2 (Bu), 22.9^{br}, 9.4 (BEt₂), 24.9, 14.1 (Et), 134.0 [63.5, C-*i*], 135.6 (C-*o*), 129.8 (C-*p*), 128.5 (C-*m*) (SiPh) ppm. [i] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 22.3^{\text{br}}$, 9.9 (BEt₂), 24.9, 14.3 (Et) 141.4 [6.7, C-*i*], 140.2 [5.9, C-*i*], 128.72, 128.65, 128.64, 128.63, 126.6 (C-*p*), 126.1 (C-*p*) (Ph), 131.9 [67.4, C-*i*], 135.7 (C-*o*), 128.3 (C-*m*), 128.7 (C-*p*) (SiPh) ppm. [j] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 22.3^{\text{br}}$, 9.9 (BEt₂); 24.9, 14.4 (Et), 138.6 [6.7, C-*i*], 137.3 (C-*i*), 129.6, 129.5, 128.7, 128.6, 136.1 (C-*p*), 135.4 (C-*p*), 21.0 (Me), 21.1 (Me) (4-Me-C₆H₄), 132.2 [67.4, C-*i*], 135.8 (C-*o*) 128.2 (C-*m*), 130.3 (C-*p*) (SiPh). [k] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 22.4^{\text{br}}$, 9.6 (BEt₂), 25.9, 13.8 (Et), 132.3 [67.2, C-*i*], 135.7 (C-*o*), 128.7 (C-*m*), 130.4 (C-*p*) (SiPh), 142.0 [7.3], 139.6 [6.5], 129.2, 127.9, 126.2, 125.4, 121.4, 120.7 (3-thienyl) ppm. [l] Data taken from ref. ^[9a]. [m] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 0.76$ [53.4, SiMe₃], 0.84 [54.2, SiMe₃], 23.0^{br}, 9.3 (BEt₂), 30.7, 13.9 (Et). [n] Other ^{13}C NMR spectroscopic data: $\delta = 11.2$, 14.0, 24.7, 33.0 (SiBu), 14.31, 14.34, 23.3, 23.4, 26.5, 29.1, 34.5, 35.1 (Bu), 22.8^{br}, 9.3 (BEt₂), 27.2, 14.1 (Et). [o] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 1.57$ [51.6, SiMe₃], 1.62 [51.8, SiMe₃], 12.3 [48.1], 26.6 [6.5], 26.3, 15.4 (SiBu), 22.8^{br}, 9.6, 9.5 (BEt₂), 30.3, 14.0 (Et) ppm. [p] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 27.7$, 17.6 [53.6] (*t*Bu), 14.3, 14.4, 23.3, 23.4, 24.9, 29.5, 34.9, 35.5 (Bu), 22.7^{br}, 22.8^{br}, 9.2, 9.3 (BEt₂), 33.6, 14.3 (Et) ppm. [q] Other ^{13}C NMR spectroscopic data: $\delta [J(^{29}\text{Si}, ^{13}\text{C})] = 2.2$, 2.3 [54.7, 53.2, SiMe₃], 11.6 [49.9], 29.4 (*t*Bu), 22.3^{br}, 9.5 (BEt₂), 32.0, 14.4 (Et) ppm.

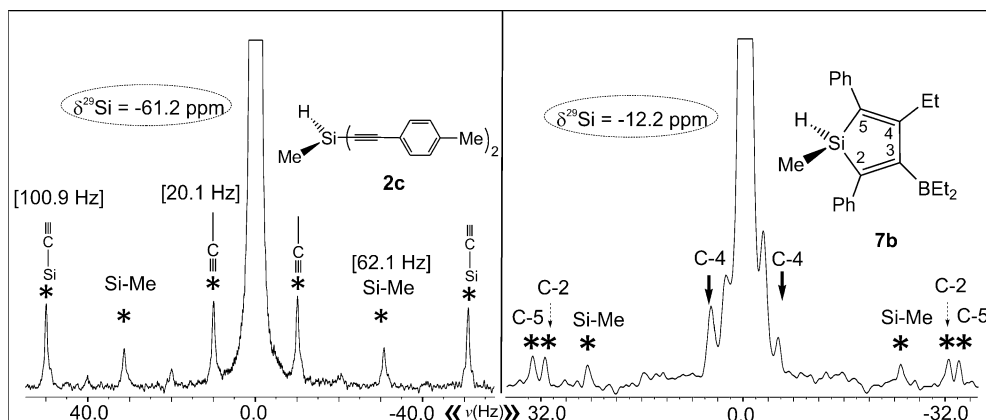


Figure 1. Examples of 59.6 MHz $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra refocused INEPT^[16] of a dialkynylsilane (**2c**) and a silole (**7b**), showing the ^{13}C satellites corresponding to $^nJ(^{29}\text{Si}, ^{13}\text{C})$ as indicated by asterisks and arrows.

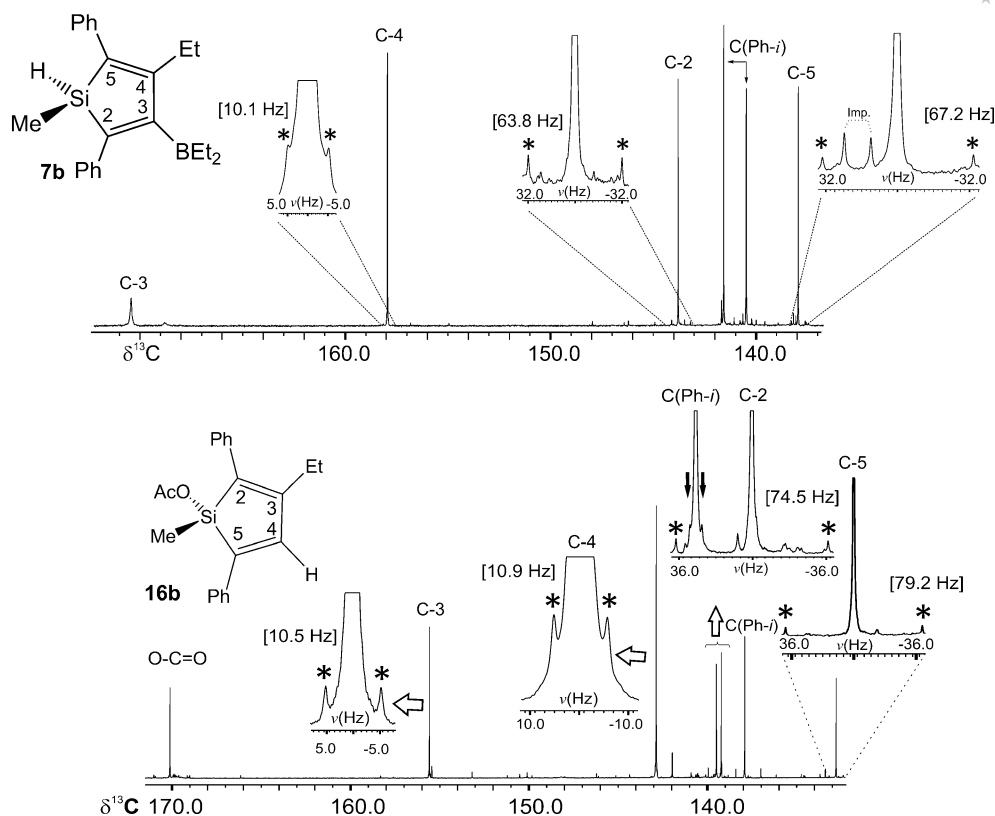
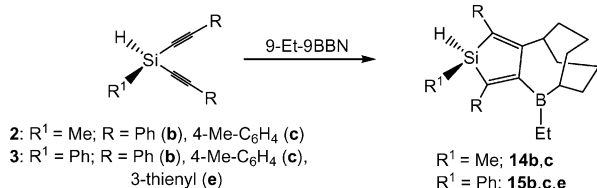


Figure 2. Parts of 100.5 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the silole **7b** (upper trace), and the 1-acetoxysilole **16b** (lower trace); ^{29}Si satellites are marked by asterisks corresponding to $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ belonging to the silole ring. Note the broad and fairly weak $^{13}\text{C}^3$ NMR signal for **7b**, owing to partially relaxed scalar ^{13}C – ^{11}B spin-spin coupling.^[17] In **16b** the satellite signals marked by black arrows correspond to $^2J(^{29}\text{Si}, ^{13}\text{C}(\text{Ph}-i))$.



Scheme 5. Reactions of dialkynylsilanes with Et-9-BBN.

ole ring. The bond lengths between the ring carbon atoms are slightly elongated when compared with other siloles^[5,12] which in the case of C2–C12 [151.6(6) pm] and C12–C13 [137.3(6) pm], might be explained by hyperconjugative effects.^[13] These can be stronger, if the diorganoboryl group is allowed to adopt a perpendicular orientation of the BC2 plane with respect to the silole ring. So far only two other examples of a 3-boryl-substituted silole have been structur-

Table 2. ^{11}B , ^{13}C and ^{29}Si NMR spectroscopic data^[a] for polycyclic siloles **14** and **15**.

Si–R ¹		$\delta^{13}\text{C}$ C ²	C ³	C ⁴	C ⁵	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$
Me	14b ^[b]	147.5 ^[g]	171.6 ^{br}	167.4 [8.8]	134.9 [67.4]	–13.5 ^[g]	88.0
	14c ^[c]	147.3 [64.0] ^[g]	170.7 ^{br}	167.2 [9.4]	134.4 [68.2]	–13.2 ^[g]	87.8
Ph	15b ^[d]	145.9 [61.0]	173.3 ^{br}	169.1 [9.1]	133.7 [67.2]	–13.5 ^[g]	88.1
	15c ^[e]	142.6 ^[g]	172.4 ^{br}	168.9 [9.1]	133.3 [68.9]	–13.8 ^[g]	88.1
	15e ^[f]	143.9 ^[g]	172.5 ^{br}	169.0 [9.3]	133.7 ^[g]	–12.7 ^[g]	88.0

[a] Measured in C_6D_6 at 23 °C, coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ are listed in square brackets, ^{br} denotes broadened ^{13}C NMR signals owing to ^{13}C – ^{11}B scalar spin-spin coupling.^[17] [b] Other ^{13}C NMR spectroscopic data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = –6.8^[g] (SiMe), 11.2, 21.8, 22.3^{br}, 23.2^{br}, 30.5, 30.7, 34.8, 34.9^{br} (Et-BC₈H₁₄), 142.9^[g] (C-*i*), 140.9 [5.8, C-*i*], 128.8 (C-*o*), 128.7 (C-*o*), 128.5 (C-*m*), 128.0 (C-*m*), 126.8 (C-*p*), 125.9 (C-*p*) (Ph). [c] Other ^{13}C NMR spectroscopic data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = –6.7^[g] [49.4, SiMe], 30.7^{br}, 34.9, 34.8, 30.5^{br}, 21.7, 11.3 (Et-BC₈H₁₄), 140.1^[g] [6.4, C-*i*], 137.9 [6.1, C-*i*], 136.2, 135.1, 129.5, 129.4, 128.5, 128.3, 21.2, 21.2 (4-Me-C₆H₄). [d] Also measured at 40 °C and 60 °C (see e.g. Figure 4), other ^{13}C NMR spectroscopic data: δ = 11.3, 21.7, 22.0^[g], 22.3^[g], 30.6, 34.9, 35.0^{br} (Et-BC₈H₁₄), 140.5^[g] (C-*i*), 137.5 (C-*i*), 135.8, 132.1^[g] (C-*i*), 130.4, 128.7, 128.7, 128.6, 128.3, 126.9, 126.0 (Ph, SiPh). [e] Other ^{13}C NMR spectroscopic data: δ = 35.1^{br}, 30.7, 23.7^{br}, 23.6, 11.4 (Et-BC₈H₁₄), 145.8^[g] (C-*i*), 139.9^[g] (C-*i*), 129.5 (C-*o*), 129.4 (C-*o*), 128.6 (C-*m*), 128.6 (C-*m*), 136.5 (C-*p*), 135.2 (C-*p*), 21.0 (Me), 21.1 (Me) (4-Me-C₆H₄), 132.5^[g] (C-*i*), 135.9 (C-*o*), 128.3 (C-*m*), 130.3 (C-*p*) (SiPh). [f] Other ^{13}C NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 11.3, 2.15, 23.6^{br}, 30.5, 30.9, 33.9, 35.0^{br}, 35.3 (Et-BC₈H₁₄), 139.8 [6.6], 138.8, [g] 129.0, 128.0, 126.2, 125.3, 120.8, 120.5 (3-thienyl), 132.3^[g] (C-*i*) 135.9 (C-*o*), 128.7 (C-*m*), 130.5 (C-*p*) (SiPh) ppm. [g] ^{13}C and ^{29}Si NMR signals are exchange broadened.

ally characterized, which were obtained by 1,1-organoboration of dialkynyl-diorganosilanes with $\text{B}(\text{C}_6\text{F}_5)_3$.^[14] Apparently, the $\text{B}(\text{C}_6\text{F}_5)_2$ in 3- and the C_6F_5 groups in 4-position take no major influence on the distances and bond angles in the silole ring.

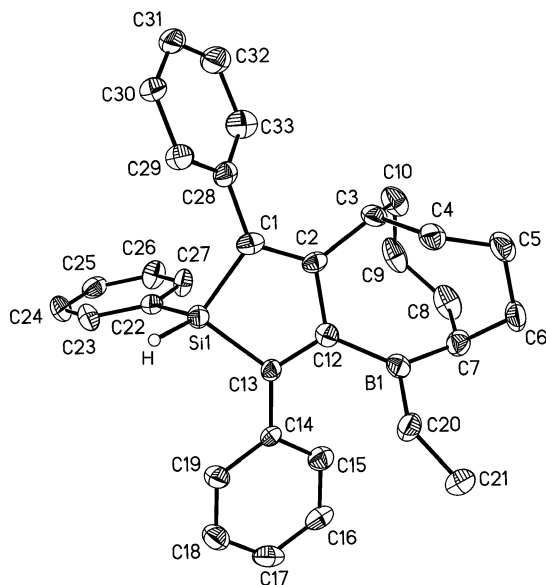


Figure 3. Molecular structure of the polycyclic silole **15b** (ORTEP plot, 40% probability, hydrogen atoms except Si–H are omitted for clarity) Selected bond lengths [pm] and angles [°]: C1–C2 135.1(6), C2–C12 151.6(6), C12–C13 137.3(6), C13–Si1 186.1(4), C1–Si1 185.4(4), C22–Si1 186.7(4), C1–C28 148.0(6), C2–C3 151.0(6), C13–C14 147.1(6), C7–B1 157.7(7), B1–C12 157.0(7), B1–C20 158.3(6), C2–C1–Si1 108.3(3), C1–C2–C12 116.4(4), C13–C12–C2 113.9(4), C12–C13–Si1 108.6(3), C1–Si1–C13 92.3(2), C1–Si1–C22 112.6(2), C28–C1–Si1 125.2(3), C12–B1–C7 127.0(4), C12–B1–C20 115.1(4), C7–B1–C20 117.8(4).

In the case of **15b**, the conformation of the two rings with the bridge head atoms C3 and C7 are different. This is noteworthy, since it explains the somewhat puzzling ^1H , ^{13}C and ^{29}Si NMR spectra in solution (Figure 4).

The ^1H , ^{13}C NMR spectra measured at room temperature of the siloles **14** and **15** reveal the expected signals, of which however, some are unexpectedly broad, and the ^{29}Si NMR signals are severely broadened, similar to the $^1\text{H}(\text{Si}-\text{H})$ resonances (see Figure 4). Since the silicon atom is a chiral center, there should be four signals for the $^{13}\text{C}(\text{CH}_2^b)$ and two for the $^{13}\text{C}(\text{CH}_2^c)$ nuclei, all of which should be sharp. These signals, however, are extremely broad, barely visible at room temperature, and they become sharper at 60 °C. Similarly, both the $^1\text{H}(\text{Si}-\text{H})$ and ^{29}Si NMR signals become much sharper with increasing temperature. This behavior can be understood considering the solid-state molecular structure, e.g. of **15b**. In solution at room temperature, the inversion of the two different rings containing carbon atoms a, b¹, c¹, d and a, b², c², d, is slow relative to the NMR time scale. At higher temperature, the rate of ring inversion increases, and the rings adopt on average the structure depicted schematically in Figure 4. As shown, these dynamic processes also affect the line widths of some of the $^{13}\text{C}(\text{phenyl})$ and of the $^{13}\text{C}(\text{C}^2)$ NMR signals.

Prior to certain further applications of the new siloles, it might be useful to remove the boryl group by protodeborylation reactions. In the case of the diethylboryl-substituted siloles, treatment with an excess of acetic acid serves for this purpose,^[15] as shown for the siloles **7** and **8** (Scheme 6). The protodeborylation is accompanied by substitution of the Si–H function. Apparently other carboxylic acids can also be used. In the cases shown in Scheme 6, the bicyclic boron–oxygen compounds **19** and **20** are formed.^[15] The siloles **16–18** are readily characterized by their NMR spectroscopic data (Table 3; see also Figure 2 and Figure 5).

Conclusions

Siloles bearing functional substituents at silicon can be obtained in high yield by a straightforward one-step synthesis via 1,1-organoboration of appropriate dialkynylsilanes. These functionalities invite for numerous further transformations which may include novel silylium cations, silylenes and also silole anions and silole dianions.

Experimental Section

General: All manipulations and preparative work with air and moisture sensitive chemicals were carried out under dry argon atmosphere. Dialkynylsilanes were prepared and purified following reported procedures,^[9a,18] and were fully characterized by multinuclear NMR spectroscopy.^[21] Other chemicals such as, *n*-butyllithium (1.6 M in Hexane), *tert*-butyllithium (1.7 M in pentane), phenyllithium (1.8 M in cyclohexane/diethyl ether), glacial acetic acid and triethylborane (BET_3) were commercial products and were used as received. Ethyl-9-borabicyclo[3.3.1]nonane was prepared according to the literature procedure.^[11] NMR spectra: Bruker ARX 250 or Varian Inova 300 and 400 spectrometers (23 ± 1 °C), all equipped with multinuclear units, using C_6D_6 solutions, if not mentioned other wise (ca. 10–15% v/v) in 5 mm o. d. tubes. Chemical shifts are given relative 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^[16] based on $^nJ(^{29}\text{Si}, ^1\text{H}(\text{Me/Ph})) \approx 7$ Hz ($n = 2, 3$), $^3J(^{29}\text{Si}, ^1\text{H}(\text{C}^4)) \approx 20\text{--}25$ Hz, and $^1J(^{29}\text{Si}, ^1\text{H}) \approx 200$ Hz (after optimization of the respective refocusing delays). EI-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet, the m/z data refer to the isotopes ^1H , ^{12}C , ^{11}B , ^{28}Si , ^{35}Cl . Elemental analyses (C/H) were performed on a Vario Elementar EL III. Melting points (uncorrected) were determined by using Büchi 510 melting point apparatus.

Syntheses of 2,5-Bis(alkyl/aryl)-3-diethylboryl-4-ethylsiloles 6–10 via 1,1-Ethylboration of Dialkynylsilanes 1–5: Methylbis(phenylethynyl)silane **2b** (2.97 g; 12.1 mmol) was filled into a Schlenk tube and triethylborane (5 mL) was added in excess. The reaction mixture was heated to 100–110 °C for 2 d. All volatiles were removed in vacuo, the yellow to brown oily liquid left was identified as silole **7b**. This experimental procedure and the work up procedure were identical for all other silole derivatives, except of slight differences in temperature and reaction times. Thus, the reaction of dihexyn-1-ylsilane **1a** with triethylborane was carried out at 80 °C and was found to be complete after 18 h to afford silole **6a**. Other examples

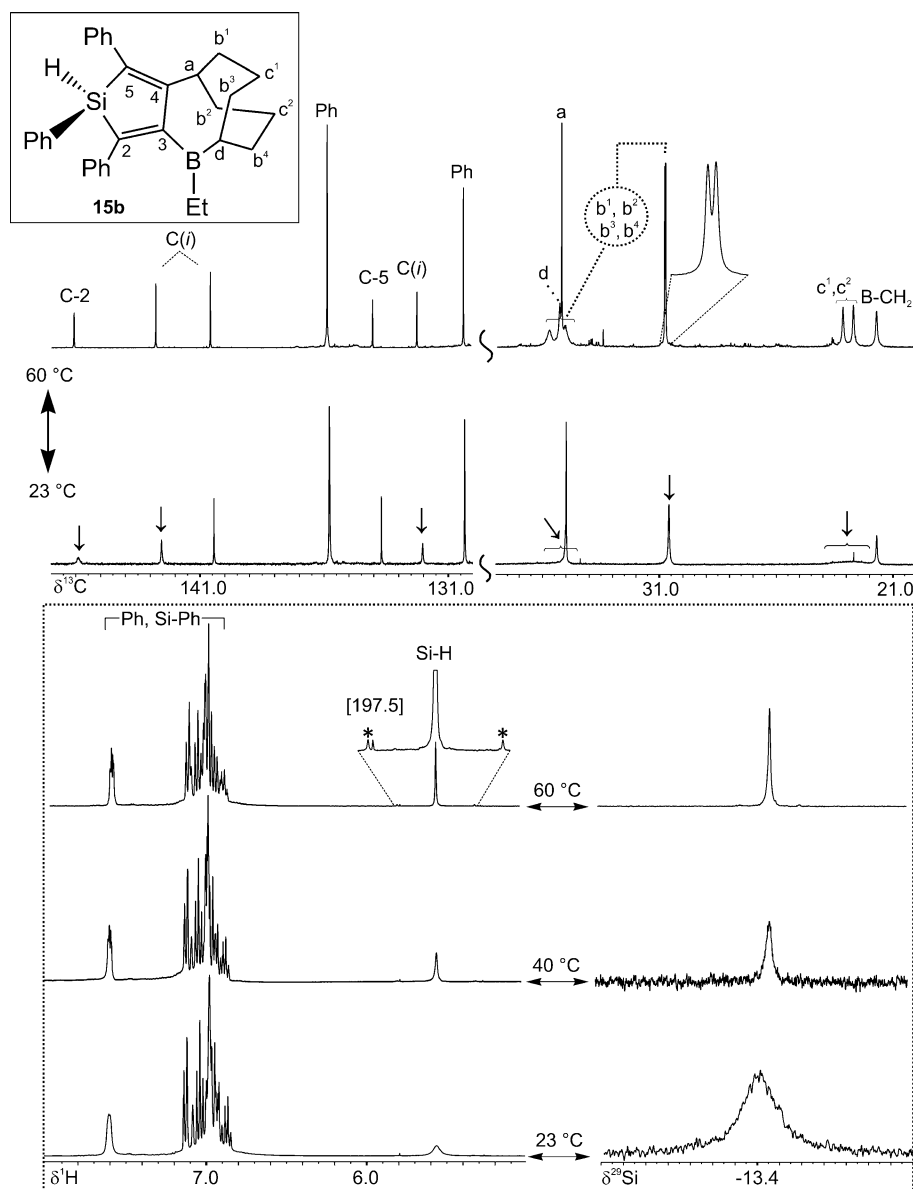
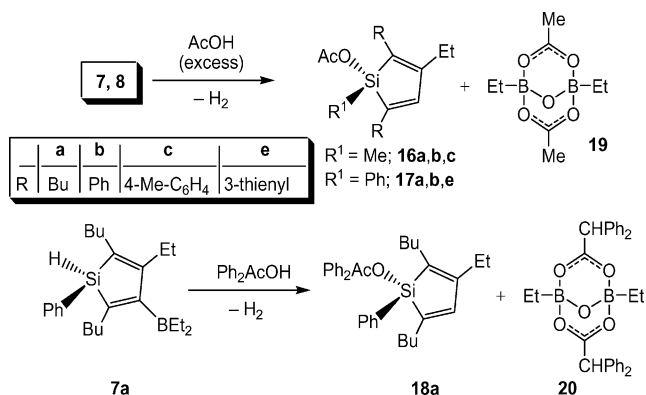


Figure 4. ^1H , ^{13}C (in part) and ^{29}Si NMR spectra of the silole **15b** measured at various temperatures. The ^{13}C NMR signals most notably broadened by dynamic processes are marked by arrows.



Scheme 6. Protodeborylation of the silole derivatives **7** and **8**.

are **6d** (18 h/80 °C), **7c** (2 d/105 °C), **7e** (ca. 70% after 2 d/110 °C), **8a,b,c,e** (≈ 95% after 7 d/105 °C), **10d** (40% after 5 d/105 °C).

6a: Yield 90%. ^1H NMR (250 MHz): δ = 0.75–0.95 (m, 12 H, CH₃, Bu, BEt₂, Et), 1.25–1.45 (m, 12 H, Bu, BCH₂), 2.05 [m, 2 H, (CH₂)-Et], 2.25 (m, 4 H, Bu), 4.36 [s, 2 H, $^1J(^{29}\text{Si}, ^1\text{H})$ = 189.1 Hz, SiH₂] ppm. Calcd. (found): C 74.45 (74.21), H 12.15 (12.07).

6d: Yield 70%. ^1H NMR (250 MHz): δ = 0.16, 0.25 (s, s, 18 H, SiMe₃), 0.93, 2.23 (t, q, 5 H, Et), 0.98, 1.35 [t (br), m, 10 H, BEt₂], 4.78 [s, $^1J(^{29}\text{Si}, ^1\text{H})$ = 189.8 Hz, 2 H, SiH₂] ppm. Calcd. (found): C 62.38 (61.95), H 10.18 (10.22).

7b: ^1H NMR (400 MHz): δ = 0.20 (d, 3J = 4.2 Hz, 3 H, SiMe), 0.95, 1.35 [t (br), br, 10 H, BEt₂], 0.77, 2.14, 2.34 (t, m, m, 5 H, Et), 5.03 [q, 3J = 4.2, $^1J(^{29}\text{Si}, ^1\text{H})$ = 190.9 Hz, 1 H, SiH], 6.93–7.05, 7.14–7.22 (m, m, 10 H, Ph) ppm. **7c**: ^1H NMR (400 MHz): δ = 0.25 (d, 3J = 4.2 Hz, 3 H, SiMe), 1.04, 1.39 [t (br), br, 10 H, BEt₂],

Table 3. ^{13}C and ^{29}Si NMR spectroscopic data^[a] for protodeborylated silole derivatives **21–23**.

Si–R ¹		$\delta^{13}\text{C}$					$\delta^{29}\text{Si}$
		MeCO ₂	C-2	C-3	C-4	C-5	
Me	16a ^[b]	171.3, 22.0	140.3 [79.2]	153.9 [11.3]	144.2 [11.9]	130.0 [79.8]	10.6
	16b ^[c]	170.1, 22.0	139.2 [74.4]	155.6 [10.4]	142.8 [10.9]	132.8 [79.0]	8.6
	16c ^[d]	170.0, 22.1	138.8 [74.4]	155.3 [10.5]	142.0 [10.3]	132.2 [79.3]	8.8
Ph	17a ^[e]	170.5, 22.1	140.3 [75.4]	155.4 [11.6]	145.3 [11.8]	132.5 [76.6]	−2.9
	17b ^[f]	169.6, 21.9	138.6 [76.2]	156.6 [10.6]	144.1 [10.8]	132.5 [80.5]	−5.9
	17e ^[g]	170.1, 22.1	132.5 [76.2]	157.2 [10.6]	145.0 [10.5]	124.6	−5.1
	18a ^[h]	171.9, 59.1 (Ph ₂ HCCO ₂)	139.9 [75.1]	155.6 [11.8]	145.5 [12.2]	132.1 [76.8]	−2.1

[a] Measured in C₆D₆ at 23 °C, coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ are given in brackets. [b] Other ^{13}C NMR spectroscopic data: $\delta[J(^{29}\text{Si}, ^{13}\text{C})] = -3.7$ [56.9, SiMe], 32.9, 32.5, 31.9, 28.2, 23.2, 23.0, 14.3, 14.2 (Bu), 23.7, 12.9 (Et) ppm. [c] Other ^{13}C NMR spectroscopic data: $\delta[J(^{29}\text{Si}, ^{13}\text{C})] = -3.6$ [59.8, SiMe], 24.8, 13.1 (Et), 139.5 [5.9, C-*i*], 137.9 [5.9, C-*i*], 129.1, 128.7, 128.5, 127.1, 127.7 (C-*p*), 126.4 (C-*p*) (Ph) ppm. [d] Other ^{13}C NMR spectroscopic data: $\delta[J(^{29}\text{Si}, ^{13}\text{C})] = -3.4$ [59.6, SiMe], 24.9, 13.2 (Et), 136.5 [5.9, C-*i*], 135.2 [5.9, C-*i*], 129.8 (C-*o*), 129.5 (C-*o*), 128.5 (C-*m*), 127.2 (C-*m*), 137.2 (C-*p*), 135.2 (C-*p*), 21.2 (Me), 21.3 (Me) (4-Me-C₆H₄) ppm. [e] Other ^{13}C NMR spectroscopic data: $\delta[J(^{29}\text{Si}, ^{13}\text{C})] = 24.1$, 13.0 (Et), 32.8, 32.4, 31.7, 28.3, 23.1, 22.9, 14.2, 14.1 (Bu), 135.1 (C-*i*), 134.3 (C-*o*), 128.4 (C-*m*), 130.5 (C-*p*) (SiPh) ppm. [f] Other ^{13}C NMR spectroscopic data: $\delta[J(^{29}\text{Si}, ^{13}\text{C})] = 25.0$, 13.2 (Et), 139.3 [5.9, C-*i*], 137.7 [5.6, C-*i*], 134.8, 131.1, 129.0, 128.7, 128.6, 128.6, 127.7, 127.2, 126.4 (SiPh, Ph) ppm. [g] Other ^{13}C NMR spectroscopic data: $\delta^{29}\text{Si}, ^{13}\text{C}] = 25.7$, 12.8 (Et), 130.9 [80.4, C-*i*], 135.7 (C-*o*), 128.7 (C-*m*), 131.2 (C-*p*) (Si-Ph), 139.3 [6.2], 138.8 [6.3], 128.5, 126.1, 125.7, 125.4, 123.2, 121.8 (3-thienyl) ppm. [h] Other ^{13}C NMR spectroscopic data: $\delta[J(^{29}\text{Si}, ^{13}\text{C})] = 24.1$, 13.0 (Et), 14.11, 14.14, 22.9, 23.1, 28.3, 31.7, 32.3, 32.7 (Bu), 139.3, 139.3, 129.2, 128.8, 128.8, 128.5, 127.4, 127.4 (Ph₂AcO), 132.2 [77.1, C-*i*], 134.3 (C-*o*), 129.2 (C-*m*), 130.6 (C-*p*) (SiPh) ppm.

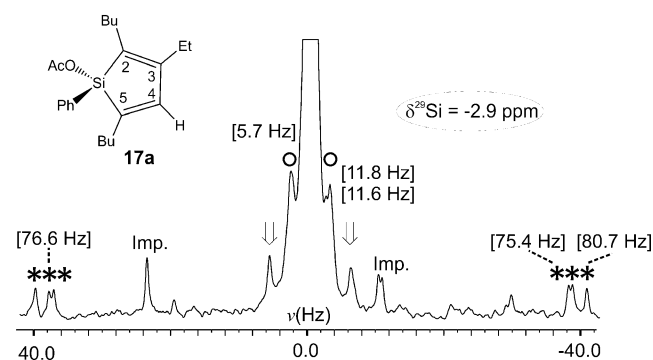


Figure 5. Expansion of 59.6 MHz, proton-decoupled ^{29}Si NMR spectra of **17b** (refocused INEPT^[16]). The ^{13}C satellites (asterisks) correspond to $^1J(^{29}\text{Si}, ^{13}\text{C})$, (arrows) to $^2J(^{29}\text{Si}, ^{13}\text{C}(\text{C}^3, \text{C}^4))$ (all values are in agreement with data taken from the ^{13}C NMR spectrum), and (open circles) to $^nJ(^{29}\text{Si}, ^{13}\text{C})$ ($n \geq 2$).

0.83, 2.19, 2.40 (t, m, m, 5 H, Et), 5.05 [q, $^3J = 4.2$, $^1J(^{29}\text{Si}, ^1\text{H}) = 190.0$ Hz, 1 H, SiH], 2.05, 2.12, 6.89, 7.01, 7.15, (s, s, m, m, m, 14 H, 4-Me-C₆H₄) ppm.

7e: ^1H NMR (400 MHz): $\delta = 0.28$ (d, $^2J = 4.1$ Hz, 3 H, SiMe), 1.08, 1.42 [t (br), br, 10 H, BEt₂], 0.91, 2.27 (t, m, 5 H, Et), 4.96 [q, $^2J = 4.1$, $^1J(^{29}\text{Si}, ^1\text{H}) = 190.5$ Hz, 1 H, SiH], 6.61–6.69, 6.88–6.93, 7.01 (m, m, m, 6 H, 3-thienyl) ppm.

8a: ^1H NMR (400 MHz): $\delta = 1.96$ –2.17, 1.10–1.38, 0.99 (m, m, t, 18 H, Bu), 1.28, 0.85 (m, t, 10 H, BEt₂), 1.27, 0.68 (m, t, 5 H, Et), 5.16 [s, $^1J(^{29}\text{Si}, ^1\text{H}) = 189.6$ Hz, 1 H, SiH], 7.15–7.56 (m, 5 H, SiPh) ppm.

8b: ^1H NMR (400 MHz): $\delta = 1.42$, 1.02 [t (br), br, 10 H, BEt₂], 0.86, 2.23, 2.36 (t, m, m, 5 H, Et), 5.52 [s, $^1J(^{29}\text{Si}, ^1\text{H}) = 197.4$ Hz, 1 H, SiH], 6.92–7.07, 7.18, 7.60 (m, m, m, 15 H, SiPh, Ph) ppm.

8c: ^1H NMR (300 MHz): $\delta = 1.11$, 1.50 [t (br), br, 10 H, BEt₂], 0.92, 2.33, 2.47 (t, m, m, 5 H, Et), 5.66 [s, $^1J(^{29}\text{Si}, ^1\text{H}) = 195.8$ Hz, 1 H, SiH], 1.98, 2.06, 6.79–7.21, 7.71 (s, s, m, m, 14 H, 4-Me-C₆H₄) ppm.

8e: ^1H NMR (400 MHz): $\delta = 1.05$, 1.49 (t, br, 10 H, BEt₂), 0.95, 2.32 (t, m, 5 H, Et), 5.49 [s, $^1J(^{29}\text{Si}, ^1\text{H}) = 197.1$ Hz, 1 H, SiH], 6.68, 6.73, 6.83, 6.94, 7.00 (m, m, m, m, m, 6 H, 3-thienyl), 7.08, 7.68 (m, m, 5 H, SiPh) ppm.

9a: Yield 86%; b. p. 120 °C/1.0 × 10^{−3} Torr. ^1H NMR (250 MHz): $\delta = 0.8$, 0.9, 1.3, 2.3 (t, t, m, t, 18 H, *n*Bu), 0.9, 2.0 (t, m, 5 H, Et), 0.9, 1.6 (t, br, 10 H, BEt₂), 5.5 [s, $^1J(^{29}\text{Si}, ^1\text{H}) = 237.4$ Hz, 1 H, Si-H] ppm. calcd. (found): C 66.36 (65.97), H 10.52 (10.43), Cl 10.88 (10.65).

9d: ^1H NMR (400 MHz): $\delta = 0.2$, 0.3 (s, s, 18 H, SiMe₃), 0.9, 2.2 (t, m, 5 H, Et), 0.9, 1.0, 1.3 (t, t, m, 10 H, BEt₂), 5.6 [s, $^1J(^{29}\text{Si}, ^1\text{H}) = 222.4$ Hz, 1 H, Si-H] ppm. EI-MS (70 eV): *m/z* (%) = 356 (62) [M⁺], 341 (46) [M⁺ − CH₃], 328 (100) [M⁺ − C₂H₅], 299 (19) [328 − C₂H₅], 283 (8) [M⁺ − SiMe₃], 263 (14) [no Cl], 219 (31) [no Cl], 201 (12) [no boron], 111 (50) [SiC₆H₁₁⁺], 97 (50) [Me₃Si-CC⁺], 73 (99) [SiMe₃⁺], 59 (26) [SiC₂H₇⁺].

10d: ^1H NMR (250 MHz): $\delta = 0.2$ [s (br), 18 H, SiMe₃], 0.7–2.2 (m, 15 H, BEt₂, Et) ppm. Calcd.(found): C 51.78 (51.12), H 8.47 (8.32), Cl 16.98 (16.76).

Synthesis of Siloles 8, 11 and 12: Silole **9a** (4.22 mg; 1.3 mmol) was dissolved in hexane (5 mL), the solution was cooled to −78 °C, and a slight excess of BuLi (0.9 mL; 1.4 mmol) was slowly added through a syringe. The reaction mixture was allowed to reach r. t. and was kept stirring for 12 h. Then the mixture was heated at 60 °C for 5 min. Solid materials were filtered off and all volatiles were removed under reduced pressure (20 Torr). The light yellow oily residue left was identified as 1,2,5-tributyl-3-diethylboryl-4-ethylsilole (**11a**) (> 95% by NMR). The same synthetic procedure was adopted for the preparation of silole **11b**. Substitution of the Si-Cl function in **9a** by the *t*Bu group using *t*BuLi was carried out in a similar way. The reaction afforded mainly the desired silole **12a** (> 70%) accompanied by starting material **9a** (ca. 10%). Low yield was achieved in the case of **12d** (ca. 40% by NMR), very low for silole **8a** (30%) and extremely low for **8d** (5%).

8d: ^1H NMR (250 MHz): $\delta = 0.03$, 0.14 (s, s, 18 H, SiMe₃), 4.88 [s, $^1J(^{29}\text{Si}, ^1\text{H}) = 185.2$ Hz, 1 H, SiH], 6.9–7.4 (m, 5 H, SiPh) ppm. ^{13}C NMR (62.9 MHz): $\delta = 0.5$, −0.6 (SiMe₃), 22.9 br, 9.4 (BEt₂) ppm. ^{29}Si NMR (49.7 MHz): $\delta = 4.6$, −10.2, −10.8 ppm.

11a: ^1H NMR (250 MHz): δ = 0.78, 0.88, 0.90, 1.35, 2.31 (t, t, t, m, m, 27 H, SiBu, Bu), 0.93, 2.03 (t, m, 5 H, Et), 1.06, 1.4–1.6 [t (br), br, 10 H, BEt_2], 4.78 [s, $^1J(^{29}\text{Si}, ^1\text{H})$ = 179.5 Hz, 1 H, SiH] ppm.

11d: Yield 92%. ^1H NMR (250 MHz): δ = 0.16, 0.26 (s, s, 18 H, SiMe_3), 0.84, 2.12 (t, m, 5 H, Et), 0.88, 0.93, 1.35–1.50 (t, t, m, 9 H, SiBu), 1.00, 1.35–1.50 [t (br), m, 10 H, BEt_2], 4.91 [s, $^1J(^{29}\text{Si}, ^1\text{H})$ = 183.7 Hz, 1 H, Si-H] ppm.

12a: ^1H NMR (250 MHz): δ = 0.87, 1.33, 2.2–2.4 (t, m, m, 18 H, Bu), 0.90, 2.03 (t, q, 5 H, Et), 1.05, 1.40–1.60 [t (br), m (br), 10 H, BEt_2], 1.11 (s, 9 H, *t*Bu), 4.53 [s, $^1J(^{29}\text{Si}, ^1\text{H})$ = 181.7 Hz, 1 H, SiH] ppm.

12d: ^1H NMR (250 MHz): δ = 0.19, 0.29 (s, s, 18 H, SiMe_3), 0.8–1.0, 2.25 [m (br), q, 5 H, Et], 1.13 (s, 9 H, *t*Bu), 0.8–1.0, 1.3–1.50 [m (br), m (br), 10 H, BEt_2], 4.84 [s, $^1J(^{29}\text{Si}, ^1\text{H})$ = 183.1 Hz, 1 H, SiH] ppm.

1,1-Organoboration of Dialkynylsilanes Using 9-Ethyl-9-borabicyclo[3.3.1]nonane: Silane **2b** (3 g) was filled into a Schlenk tube and mixed with an excess (5 mL) of 9-ethyl-9-borabicyclo[3.3.1]nonane. This mixture was heated at 120 °C (oil bath temperature). The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 12 h the reaction was found to be complete, and all readily volatile materials were removed in vacuo (ca. 10^{-1} Torr). Finally traces of Et-9-BBN had to be removed by heating at 60–70 °C in vacuo. The silole **14b** was obtained in > 90% yield and high purity (99%). The other siloles **14** and **15** were synthesized in the same way. Silole **15b** was dissolved in pentane, and after 4 d at ambient temperature rather small crystals were growing which could be isolated and used for X-ray structural analysis. Crystals, again very small, of the same silole could also be obtained in ethyl ether.

14b: Reaction time 10 h. ^1H NMR (400 MHz): δ = 0.23 (d, 3J = 3.8 Hz, 3 H, SiMe), 0.82, 1.11, 1.48–2.06, 3.33 (t, br, m, m, 19 H, Et-B C_8H_{14}), 5.06 [br., $^1J(^{29}\text{Si}, ^1\text{H})$ = 190.2 Hz, 1 H, SiH], 6.96–7.20 (m, 10 H, Ph) ppm. **14c:** Reaction time 12 h. ^1H NMR (400 MHz): δ = 0.27 (d, 3J = 3.8 Hz, 3 H, SiMe), 0.85, 1.16, 1.57–2.02, 3.46 (t, br, m, m, 19 H, Et- BC_8H_{14}), 2.11, 2.17, 6.96, 7.06, 7.16 (s, s, m, m, 14 H, 4-Me- C_6H_4), 5.15 [br., $^1J(^{29}\text{Si}, ^1\text{H})$ = 190.2 Hz, Si-H] ppm.

15b: Reaction time 3 d; Yield after recrystallization from pentane 87%; m.p. 111–115 °C. ^1H NMR (400 MHz): δ = 0.75, 1.05, 1.38, 1.57, 1.95, 3.27 [t, q (br), m, m, m, t, 19 H, Et- BC_8H_{14}], 5.32 [br., $^1J(^{29}\text{Si}, ^1\text{H})$ = 197.5 Hz, 1 H, SiH], 6.67–7.03, 7.48 (m, m, 15 H, SiPh, Ph) ppm.

15c: Reaction time 3 d. ^1H NMR (300 MHz): δ = 0.96, 1.34, 1.58–1.85, 3.53 [t, q (br), m, m, 19 H, Et- BC_8H_{14}], 5.67 [br., $^1J(^{29}\text{Si}, ^1\text{H})$ = 198.2 Hz, 1 H, SiH], 2.01, 2.07, 6.82–7.14, 7.70 (s, s, m, m, 14 H, 4-Me- C_6H_4) ppm. **15e:** Reaction time 4 d. ^1H NMR (400 MHz): δ = 1.21, 1.46, 1.86–2.14, 2.39, 3.86 (t, br, m, m, m, 19 H, Et- BC_8H_{14}), 5.67 (br., 1 H, Si-H), 6.86, 6.93, 7.06, 7.15 (m, m, m, m, 6 H, 3-thienyl), 7.41, 7.93 (m, m, 5 H, SiPh) ppm.

Protodeborylation of Siloles 7 and 8 with Acetic Acid or Diphenylacetic Acid: A solution of silole **7a** (1.2 g) in pentane (10 mL) was prepared in a Schlenk tube and glacial acetic acid (3 mL) was added in excess. The reaction mixture was stirred at room temperature for 40 min, and all readily volatile materials were removed under reduced pressure (10^{-2} Torr). The oily product left contained silole **16a** and the bicyclic boron–oxygen compound **19**. The experimental procedure for the synthesis of silole **16b,c** and **17a,b,e** was exactly the same. The compound **19** could be separated as described.^[15,19] The reaction of silole **7a** (1.04 g; 2.82 mmol) and di-

phenylacetic acid (1.22 g; 5.7 mmol; in slight excess) was carried out at 80–100 °C for 3–4 h. Silole **18a** was obtained along with a small amount of diphenylacetic acid which could not be completely separated.

16a: ^1H NMR (400 MHz): δ = 0.46 (s, 3 H, SiMe), 0.86–0.94, 1.26–1.56, 2.23–2.40 (m, m, m, 18 H, Bu), 1.19, 2.10 (t, m, 5 H, Et), 1.70 (s, 3 H, MeCO_2), 6.38 [s, $^3J(^{29}\text{Si}, ^1\text{H})$ = 17.1 Hz, 1 H, C^4H] ppm.

16b: ^1H NMR (400 MHz): δ = 0.54 (s, 3 H, SiMe), 0.91, 2.22 (t, m, 5 H, Et), 1.50 (s, 3 H, MeCO_2), 7.03 (t, 1 H, C^4H), 7.17, 7.24, 7.53 (m, m, m, 10 H, Ph) ppm.

16c: ^1H NMR (400 MHz): δ = 0.60 (s, 3 H, SiMe), 0.96, 2.28 (t, m, 5 H, Et), 1.55 (s, 3 H, MeCO_2), 7.10 [s, $^3J(^{29}\text{Si}, ^1\text{H})$ = 15.6 Hz, 1 H, C^4H], 2.09, 2.10, 7.01, 7.19, 7.48 (s, s, m, m, m, 14 H, 4-Me- C_6H_4) ppm. **17a:** ^1H NMR (400 MHz): δ = 0.70–0.97, 1.13, 2.15, 2.32 (overlapping multiplets, 23 H, Bu and Et), 1.46 (s, 3 H, MeCO_2), 6.48 (s, 1 H, C^4H), 7.14, 7.61 (m, m, 5 H, SiPh) ppm.

17b: ^1H NMR (400 MHz): δ = 0.91, 2.29 (t, m, 5 H, Et), 1.51 (s, 3 H, MeCO_2), 6.93, 7.05, 7.23, 7.49, 7.78 (m, m, m, m, m, 15 H, SiPh, Ph), 7.23 [t, $^3J(^{29}\text{Si}, ^1\text{H})$ = 16.0 Hz, 1 H, C^4H] ppm.

17e: ^1H NMR (400 MHz): δ = 1.03, 2.42 (t, m, 5 H, Et), 1.68 (s, 3 H, MeCO_2), 6.94–6.99, 7.06, 7.18, 7.23, 7.33, 7.78 (m, m, m, m, m, m, SiPh, C^4H , 3-thienyl) ppm.

18a: ^1H NMR (400 MHz): δ = 0.68, 0.68, 1.12, 1.29, 2.10–2.30 (t, t, m, m, m, 18 H, Bu), 0.89, 2.10–2.30 (t, m, 5 H, Et), 5.05 (s, 1 H, Ph_2CH), 6.50 [s, $^3J(^{29}\text{Si}, ^1\text{H})$ = 17.1 Hz, 1 H, C^4H], 6.92–7.07, 7.28, 7.54 (m, m, m, 15 H, SiPh, CPh_2) ppm.

X-ray Structural Analysis of 15b:^[20] The X-ray crystal structural analysis of **15b** was carried out for a single crystal (selected in perfluorinated oil^[21] at room temperature) at 133(2) K using a STOE IPDS II system (wavelength: λ = 0.71069 Å), equipped with an Oxford Cryostream low-temperature unit. Formula weight: 458.50. Crystal system: Monoclinic. Space group: $P2_1/c$. Unit cell dimensions: a = 9.6160 (10) Å, b = 15.248 (2) Å, c = 18.083 (2) Å, β = 102.2°. V = 2591.2 (5) Å³, Z = 4. Absorption coefficient μ = 0.11 mm⁻¹. $F(000)$: 984. Crystal size: 0.35 × 0.16 × 0.15 mm³. Theta range for data collection: 1.8–25.7°. Index ranges: $-11 \leq h \leq 11$, $-15 \leq k \leq 18$, $-21 \leq l \leq 22$. Reflections collected: 14705. Independent reflections [$I > 2\sigma(I)$]: 2825 [$R(\text{int})$ = 0.116]. Data/restraints/parameters: 2825/0/447. Goodness-of-fit on F^2 : 1.16. Final R indices [$F^2 > 2\sigma(F^2)$]: $R1$ = 0.089, $wR2$ = 0.157, R indices (all data): $R1$ = 0.155, $wR2$ = 0.139. Largest difference peak and hole: 0.23 and -0.25 e Å⁻³. Structure solutions and refinements were accomplished using SIR97,^[22] SHELXL-97,^[23] and WinGX.^[24]

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