Siloles Bearing Si-Vinyl and Si-Allyl Functions. 1,1-Organoboration and Protodeborylation

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1,1-Organoboration of dialkyn-1-yl(divinyl)silanes, dialkyn-1-yl(organo)(vinyl)silanes and dialkyn-1-yl(allyl)(methyl)silane using triethylborane, BEt_3, or 9-ethyl-9-borabicyclo[3.3.1]nonane, Et-9-BBN, afforded selectively silole derivatives with Si-vinyl and Si-allyl functions, respectively, bearing the dialkylboryl group in 3-position. The siloles are formed *via* intermolecular 1,1-alkylboration, followed by intramolecular 1,1-vinylboration. In the cases of several 3-diethylboryl-substituted siloles, smooth and essentially quantitative protodeborylation could be achieved by the reaction of the siloles with an excess of acetic acid at ambient temperature. All new siloles were characterized in solution by multinuclear magnetic resonance spectroscopy (^{1}H, ^{13}C, ^{11}B and ^{29}Si NMR).

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

Introduction

Siloles [1] attract increasing interest owing to their photophysical properties [2, 3] which depend on the substituents at the silicon and the ring carbon atoms. A versatile synthesis of siloles aiming for the introduction of different substituents at all ring positions has been developed, taking advantage of 1,1-organoboration [4, 5] of dialkyn-1-ylsilanes. For this purpose, thermally robust triorganoboranes such as triethylborane, BEt_3, or 9-ethyl-9-borabicyclo[3.3.1]nonane, Et-9-BBN, have to be used [5 – 7]. Alternatively, triarylboranes [8] or the extremely Lewis-acidic tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, have also proved useful [9]. So far we have accomplished the straightforward synthesis of numerous siloles of type **A** and **B**, some of which could readily be protodeborylated to give the siloles **C** (Scheme 1).

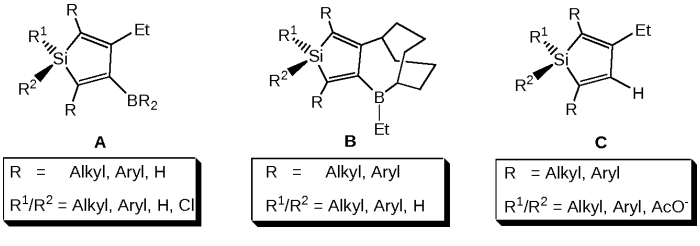
In the present work, we report on the first examples of siloles, obtained *via* 1,1-organoboration starting from dialkyn-1-ylsilanes, with vinyl group(s) or an allyl group at silicon. This can be useful for further transformation of the siloles and also for incorporating the siloles into polymers.

Results and Discussion

1,1-Organoboration

The reactions of the respective alkynyllithium reagents with diorganosilicon dichlorides [10, 11] led to the dialkyn-1-ylsilanes **1** – **5** (Schemes 2 – 5), of which **5** was obtained by consecutive reactions of dichloro(divinyl)silane in the first step with hexyn-1-yllithium ^{n}Bu-C≡C–Li, and in the second step with 4-^{t}Bu-C_6H_4-C≡C–Li. The dialkyn-1-ylsilanes were purified by distillation and characterized by NMR spectroscopy (*e. g.* Fig. 1). The NMR data of these starting alkynes will be described elsewhere [12].

Treatment of the dialkyn-1-yl(organo)vinylsilanes **1** and **2** with an excess of BEt_3 at 100 – 120 °C



Scheme 1. Some silole derivatives bearing various substituents at different positions, prepared by 1,1-organoboration (**A**, **B**), followed by protodeborylation (**C**), reported so far.

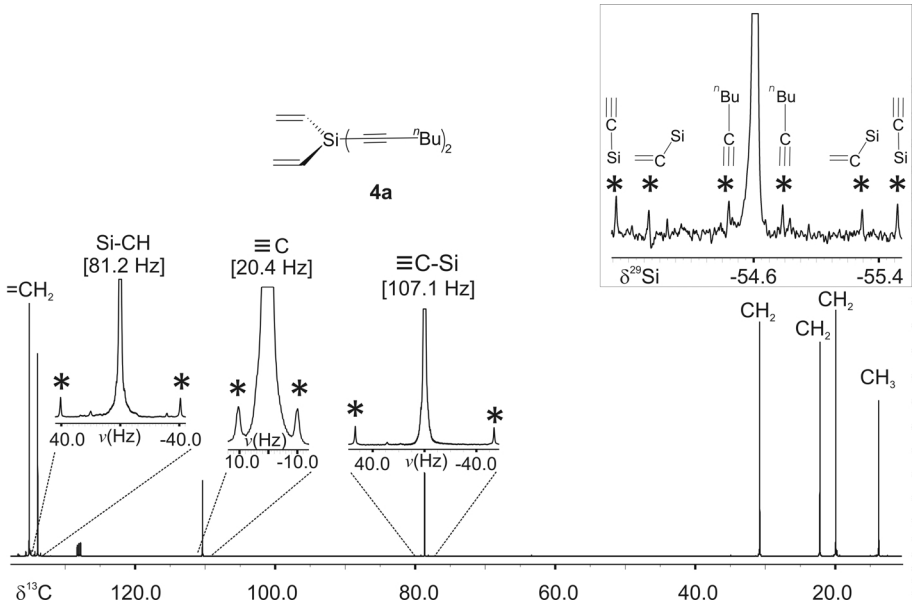
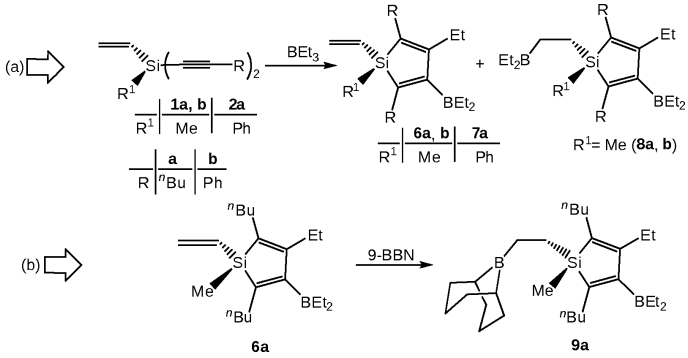


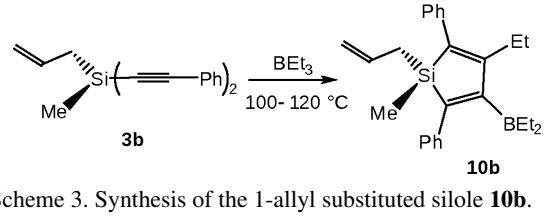
Fig. 1. 100.5 MHz $^{13}C\{^1H\}$ and 59.6 MHz $^{29}Si\{^1H\}$ (upper insert) NMR spectra of dihexyn-1-yldivinylsilane (**4a**) (in C_6D_6, 23 °C). Satellite signals marked by asterisks correspond to $J(^{29}Si, ^{13}C)$.



Scheme 2. Synthesis of 1,1-organo(vinyl)siloles and hydroboration of the Si–CH=CH_2 function.

(Scheme 2a) afforded the siloles **6** and **7** in essentially quantitative yield. The progress of the reaction was monitored by NMR spectroscopy. In the case of **1**, the reaction proceeded further, if heating was unnecessarily continued for prolonged periods of time. Then, BEt_3 turned out to act as a hydroborating reagent [13, 14], and in repeated experiments variable amounts of the siloles **6** were converted into siloles **8** *via* hydroboration of the Si–CH=CH_2 group (see Fig. 2 for relevant ^{13}C NMR spectra). This was confirmed (Scheme 2b) by the quantitative hydroboration of **6a** using 9-BBN [15] as a common hydroborating reagent. The comparison of the NMR data sets of **8** and **9a** was conclusive.

The successful syntheses of siloles bearing one Si-vinyl function prompted us to study the case of allyl(methyl)bis(phenylethynyl)silane **3b** (Scheme 3),



Scheme 3. Synthesis of the 1-allyl substituted silole **10b**.

and silole **10b** was obtained without appreciable side reactions.

Dialkyn-1-yl(divinyl)silanes **4** were treated with BEt_3 in excess (Scheme 4) in the same way as described above. Three straightforward examples of 1,1-divinylsiloles **11** were obtained in essentially quantitative yield (Scheme 4a). The dialkyn-1-yl(divinyl)silane **5** contains two different alkyn-1-yl groups. Apparently, attack of the Si–C≡C-^{n}Bu was preferred over that

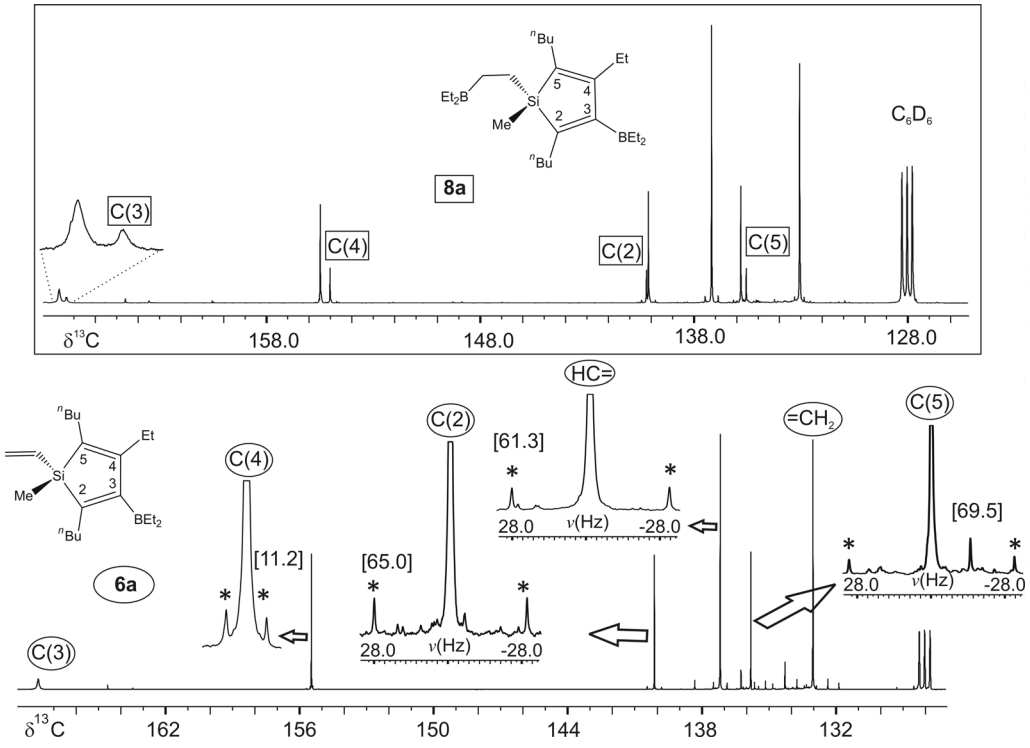
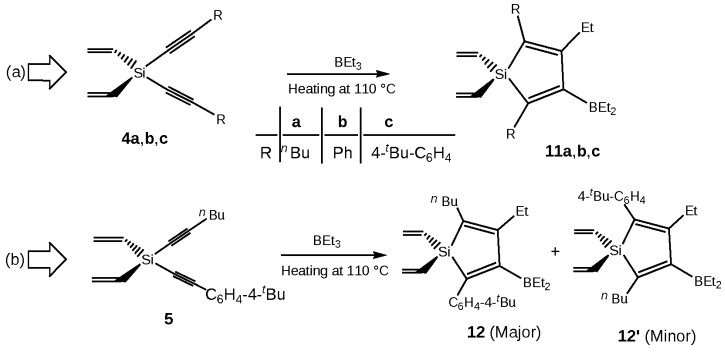


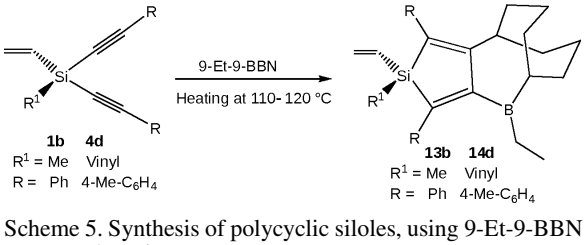
Fig. 2. Part of the 100.5 MHz $^{13}C\{^1H\}$ NMR spectra of silole **6a**, (bottom, after heating the mixture of **1a** in BEt_3 for 3 d at 100 – 120 °C). The upper trace illustrates the result of the same reaction after 13 d at 100 – 120 °C: **6a** and **8a**. ^{29}Si satellite signals marked by asterisks correspond to $^nJ(^{29}Si, ^{13}C)$ (n = 1,2), and J values are given in brackets. The typically broad $^{13}C(3)$ NMR signal indicates the linkage C–B by partially relaxed ^{13}C-^{11}B spin-spin coupling [16].



Scheme 4. 1,1-Divinyl silole derivatives bearing identical (**11**) or different substituents (**12**) at 2- and 5-positions.

at the Si–C≡C-C_6H_4-4-^{t}Bu unit, leading to **12**, and only about 25 % of the other isomer **12′** was formed (Scheme 4b; see also Fig. 3 for relevant NMR spectra).

Similar to BEt_3, 9-ethyl-9-borabicyclo[3.3.1]nonane [17], Et-9-BBN, is sufficiently stable to survive the harsh reaction conditions required for the 1,1-organoboration of many alkyn-1-ylsilanes. The reaction (Scheme 5) proceeds as described previously for $Me_2Si(C{\equiv}C\text{-}Ph)_2$ [7a] by twofold expansion of the bi-



Scheme 5. Synthesis of polycyclic siloles, using 9-Et-9-BBN as organoborating reagent.

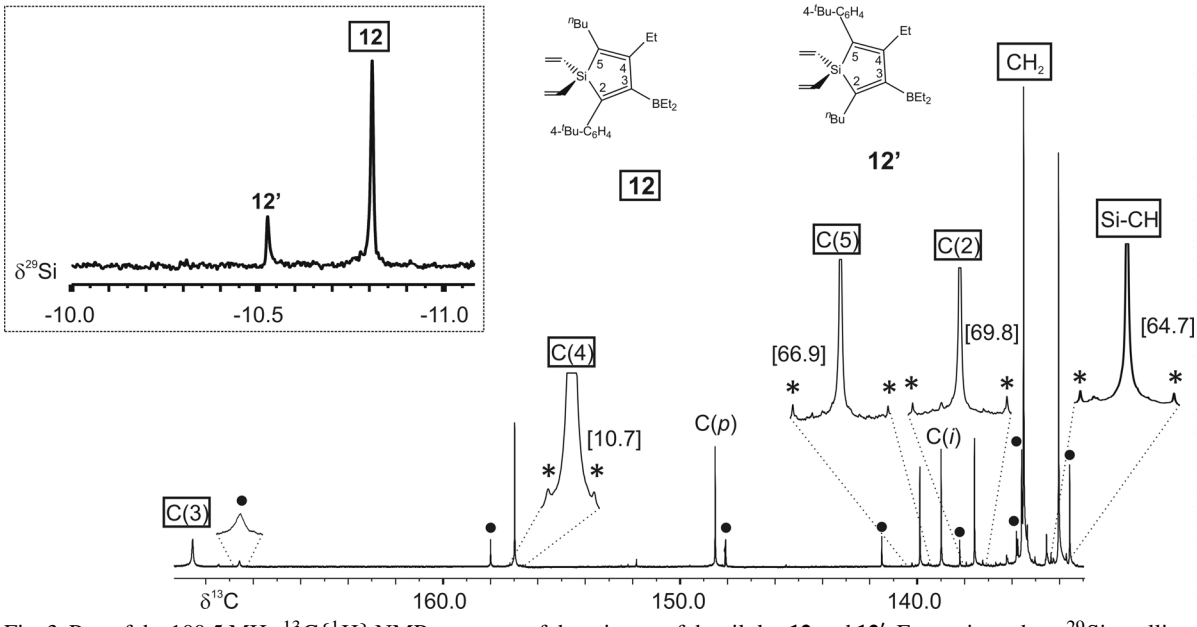
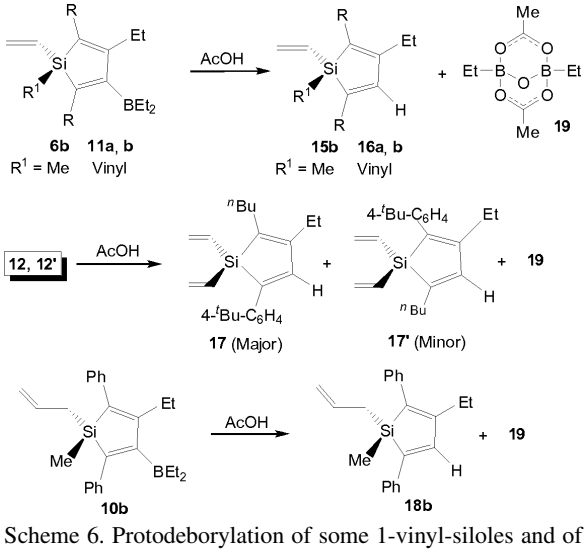


Fig. 3. Part of the 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum of the mixture of the siloles **12** and **12′**. Expansions show ^{29}Si satellites (asterisks) corresponding to $^1J(^{29}Si, ^{13}C)$ and $^2J(^{29}Si, ^{13}C)$. Signals belonging to the isomer **12′** are marked by filled circles (see also Table 1 for details). Note the broad B-C(3) NMR signals [16]. The insert shows the 79.4 MHz $^{29}Si\{^1H\}$ NMR spectrum with signals for both isomers **12** and **12′**.

cyclic structure to give the polycyclic siloles **13** and **14** without any side products. The analogous silole with R = Ph containing the Si(Ph)H unit has already been characterized by X-ray diffration [7b].

Protodeborylation of siloles bearing the diethylboryl group in 3-position

We have previously shown that protodeborylation of siloles [7, 18] works efficiently with acetic acid in excess at r. t. In the course of these reactions (Scheme 6), in each case, the diethylboryl group is converted into the bicyclic boron-oxygen compound **19** [18], and the siloles **15** – **18** were obtained and readily characterized by their consistent NMR data sets (Table 2) The vinyl group(s) (see *e. g*. Fig. 4 for ^{13}C NMR spectra of **11a**) or the allyl group (see Fig. 5 for the ^{29}Si NMR spectrum of **18b**) are left untouched, ready for further transformations. The siloles **13** and **14** did not react with acetic acid under these conditions.



Scheme 6. Protodeborylation of some 1-vinyl-siloles and of a 1-allyl-silole.

Chemical shifts $\delta^{11}B$, $\delta^{13}C$, $\delta^{29}Si$ and coupling constants $^1J(^{29}Si,^{13}C)$

The nature of the π system of the siloles is influenced by the various substituents in positions 1 – 5, and this should be reflected to some extent by the chemical shifts of ^{13}C and ^{29}Si nuclei. For the siloles bearing the dialkylboryl group in 3-position, the $\delta^{11}B$ data are typical of triorganoboranes without BC(*pp*) π interactions [16a, 19]. This is in agreement with a preferred conformation in which the ring plane and the C_2B plane of the dialkylboryl group are close to perpendicular. Thus, the

Table 1. ^{11}B, ^{13}C and ^{29}Si NMR data[a] for siloles **6** – **14**.

	δ ^{13}C(2)	δ ^{13}C(3)	δ ^{13}C(4)	δ ^{13}C(5)	δ ^{29}Si	δ ^{11}B
6a[b]	140.1 [65.0]	167.7 (br)	155.5 [11.2]	135.8 [69.5]	−3.5	86.8
6b[c]	144.6 [64.3]	169.9 (br)	157.6 [10.1]	139.2 [68.0]	−1.1	85.1
7a[d]	139.7 [65.9]	169.2 (br)	157.0 [11.1]	135.7 [62.6]	−8.4	86.5
8a[e]	140.2 [62.4]	167.4 (br)	155.0 [8.8]	135.6 [67.1]	9.7	85.6
8b[f]	145.3 [64.4]	169.7 (br)	157.3 [9.2]	139.5 [65.1]	12.3	85.1
9a[g]	140.3 [62.7]	167.4 (br)	155.1 [10.1]	135.6 [67.1]	9.6	87.9
10b[h]	144.7 [63.2]	169.7 (br)	157.5 [9.7]	139.0 [66.5]	6.9	86.5
11a[i]	139.1 [66.3]	168.8 (br)	156.7 [11.0]	135.1 [70.6]	−11.7	87.1
11b[j]	143.1 [65.7]	170.9 (br)	158.6 [10.2]	138.1 [69.2]	−10.0	86.2
11c[k]	142.4 [66.4]	170.3 (br)	158.4 [10.3]	137.5 [69.6]	−10.2	86.9
12[l]	139.9 [66.9]	170.5 (br)	157.0 [10.7]	137.6 [69.8]	−10.8	86.3
12′ [m]	141.5 [65.7]	168.6 (br)	158.0 [10.5]	135.8 [n. o.]	−10.5	86.3
13b[n]	148.0 [64.3]	171.1 (br)	166.8 [9.0]	136.0 [66.5]	−1.6	88.1
14d[o]	146.4 [65.9]	171.2 (br)	167.7 [9.2]	134.4 [69.7]	−10.8	87.9

[a] Measured as C_6D_6 solution at 23 °C, coupling constants J(^{29}Si, ^{13}C) are given in brackets, br denotes broad ^{13}C resonance signals owing to partially relaxed scalar ^{13}C-^{11}B coupling [16], n. o. means not observed; [b] other ^{13}C NMR data: δ = −5.7 [49.3] (SiMe), 22.8 (br), 9.2 (BEt_2), 24.7, 14.2 (Et), 34.2, 33.6, 32.8, 28.8, 23.5, 23.49, 14.4, 14.3 (^{n}Bu), 133.1 (=CH_2), 137.2 [61.3] (Si–CH=); [c] other ^{13}C NMR data: δ = −6.5 [51.3] (SiMe), 22.3 (br), 9.8 (BEt_2), 24.7, 14.5 (Et), 142.0 [6.5], 141.0 [6.0], 128.7, 128.7, 128.3, 127.7, 126.4, 125.9 (Ph), 135.3 (=CH_2), 135.1 [63.7] (Si−CH=); [d] other ^{13}C NMR data: δ = 22.8 (br), 9.4 (BEt_2), 24.9, 14.1 (Et), 34.1, 33.5, 33.0, 29.0, 23.3, 14.1 (^{n}Bu), 135.2, 135.15, 128.3, 129.7, (SiPh), 135.0 (=CH_2), 133.9 [63.8] (Si−CH=); [e] other ^{13}C NMR data: δ = −3.9 [46.3] (SiMe), 34.2, 33.2, 29.1, 23.61, 23.6, 14.4 (^{n}Bu), 22.8 (br), 9.4 (BEt_2), 23.7, 13.4 (Et), 19.5 (br), 8.5 (BEt_2), 19.5 (br) (BCH_2), 6.6 [49.1] ($SiCH_2$); [f] other ^{13}C NMR data: δ = −4.8 [48.5] (SiMe), 22.4 (br), 10.0 (BEt_2), 24.7, 14.7 (Et), 19.5 (br), 8.5 (BEt_2), 6.1 [51.1] ($SiCH_2$), 19.4 (br) (BCH_2), 142.6 [6.4], 141.7 [5.8], 128.7, 128.8, 128.1, 127.5, 126.3, 125.8 (Ph); [g] other ^{13}C NMR data: δ = −4.0 [46.1] (SiMe), 22.8 (br), 8.5 (BEt_2), 24.7, 14.4 (Et), 6.5 [49.0] ($SiCH_2$], 20.6 (br) (BCH_2), 34.2, 33.7, 33.2, 29.2, 23.7, 23.6, 14.4, 14.4 (^{n}Bu), 33.7, 31.5 (br), 23.8 (9-BBN); [h] other ^{13}C NMR data: δ = −5.4 [49.5] (SiMe), 22.3 (br), 9.8 (BEt_2), 24.6, 14.5 (Et), 133.8 (=CH), 114.0 (H_2C=), 21.2 [46.2] ($SiCH_2$], 142.3 [6.7], 141.4 [5.9], 128.8, 128.7, 128.3, 127.6, 126.4, 125.9 (Ph); [i] other ^{13}C NMR data: δ = 24.8, 14.1 (Et), 22.8 (br), 9.3 (BEt_2), 34.3, 33.7, 32.9, 29.0, 23.5, 23.4, 14.3, 14.2 (^{n}Bu), 134.5 [63.8] (Si−CH=), 134.4 (=CH_2); [j] other ^{13}C NMR data: δ = 24.8, 14.4 (Et), 22.2 (br), 9.8 (BEt_2), 132.6 [66.4] (Si–CH=), 136.7 (=CH_2), 141.9 [6.4], 140.9 [5.8], 128.7, 128.7, 128.5, 128.0, 126.5, 125.0 (Ph); [k] other ^{13}C NMR data: δ = 24.9, 14.5 (Et), 22.2 (br), 9.9 (BEt_2), 133.1 [66.1] (Si–CH=), 136.5 (=CH_2), 149.0, 148.4, 138.9 [6.7], 138.0 [5.3], 128.4, 128.0, 125.6, 125.6, 34.5 (C), 34.5 (C), 31.6 (Me), 31.5 (Me) (4-^{t}Bu-C_6H_4); [l] other ^{13}C NMR data: δ = 24.6, 14.3 (Et), 22.1 (br), 9.8 (BEt_2), 34.5, 29.2, 23.5, 14.3 (^{n}Bu), 134.0 [64.7] (Si–CH=), 135.5 (=CH_2), 139.0, 128.0, 125.6, 148.5, 33.6 (C), 31.5 (Me) (4-^{t}Bu-C_6H_4); [m] other ^{13}C NMR data: δ = 25.3, 14.3 (Et), 22.8 (br), 9.4 (BEt_2), 34.2, 31.2, 23.4, 14.3 (^{n}Bu), 133.6 [64.9] (Si–CH=), 135.6 (=CH), 138.2, 128.4, 125.5, 148.1, 33.0 (C), 31.6 (Me) (4-^{t}Bu-C_6H_4); [n] other ^{13}C NMR data:δ = −6.6 (SiMe), 11.2, 21.6, 23.2, 22.4, 30.5, 30.7, 33.3, 34.9, 35.0 (Et-BC_8H_{14}), 143.1 [6.6], 141.2 [5.9], 128.6, 128.2, 127.9, 126.7, 125.8 (Ph), 135.2 (H_2C=), 134.9 (Si–CH=); [o] other ^{13}C NMR data: δ = 11.3, 21.5 (br), 21.2, 30.7, 31.2 (br), 34.9, 35.2 (Et-BC_8H_{14}), 136.3 (H_2C=), 132.9 (Si–CH=), 140.3 [5.6], 138.1, 137.0, 134.9, 129.34, 129.29, 128.4, 128.2, 21.2 (4-Me-C_6H_4).

Table 2. ^{13}C and ^{29}Si NMR data[a] for protodeborylated siloles **15** – **18**.

	δ ^{13}C(2)	δ ^{13}C(3)	δ ^{13}C(4)	δ ^{13}C(5)	δ ^{29}Si
15b[b]	143.3 [63.1]	142.9 [8.3]	155.1 [7.8]	137.3 [67.5]	−1.9
16a[c]	143.5 [65.3]	154.6 [8.9]	144.9 [9.4]	133.4 [69.6]	−12.7
16b[d]	142.1 [65.7]	156.0 [7.8]	143.7 [8.1]	135.9 [69.1]	−10.4
17[e]	139.9 [66.7]	155.0 [8.4]	143.2 [8.9]	135.7 [69.7]	−11.1
17′[f]	137.9	155.5	145.0	135.8	−11.7
18b[g]	143.4 [63.0]	142.6 [≈7]	155.0 [7.5]	137.4 [66.5]	6.1

[a] In C_6D_6 at 23 ± 1 °C; coupling constants J(^{29}Si, ^{13} C) are given in brackets [±0.3 Hz]; [b] other ^{13}C NMR data: δ = −6.4 [51.9] (SiMe), 24.8, 13.7 (Et), 134.6 [64.3], (Si–CH=), 135.6 (=CH_2), 140.5 [6.0], 139.1 [6.2], 129.0, 128.7, 128.4, 126.9, 127.3, 126.1 (Ph); [c] other ^{13}C data: δ = 23.9, 13.5 (Et), 33.6, 33.0, 32.6, 28.9, 23.3, 23.0, 14.2, 14.2 (^{n}Bu), 133.5 [64.9] (Si–CH=), 135.0 (H_2C=); [d] other ^{13}C NMR data: δ = 13.4, 24.8 (Et), 140.4 [5.4], 138.9 [5.3], 129.0, 128.7, 128.6, 127.1, 127.4, 126.1 (Ph), 132.1 [66.5] (Si–CH=), 137.1 (H_2C=); [e] other ^{13}C NMR data: δ = 24.0, 13.6 (Et), 34.5, 29.1, 23.3, 14.2 (^{n}Bu), 136.5 [5.4], 126.8, 125.7, 149.7, 33.5 (C), 31.4 (Me) (4-^{t}Bu-C_6H_4), 133.3 [65.5] (Si–CH=), 135.9 (H_2C=); [f] other ^{13}C NMR data: δ = 24.8, 13.6 (Et), 34.5, 31.1, 23.0, 14.1 (^{n}Bu), 136.7, 128.4, 125.5, 148.3, 33.1 (C), 31.5 (Me) (4-^{t}Bu-C_6H_4), 132.7 (Si–CH=), 136.1 (H_2C=); [g] other ^{13}C NMR data: δ = −5.4 [49.5] (SiMe), 24.6, 14.5 (Et), 133.8 (HC=), 114.0 (=CH_2), 21.2 [46.2] ($SiCH_2$), 142.3 [6.7], 141.4 [5.9], 128.8, 128.7, 128.3, 127.6, 126.4, 125.9, (Ph).

boryl group should not affect the silole π system. This is mirrored by the virtually unchanged chemical shifts δ^{29}Si [20] in 3-diethylboryl-substituted siloles (Table 1) and the corresponding protodeborylated siloles

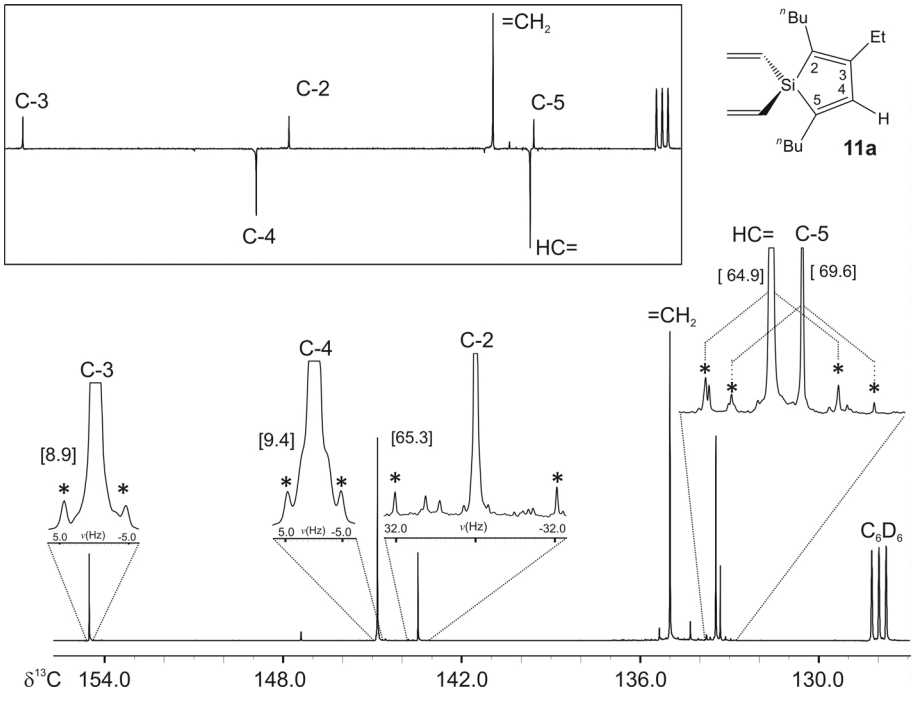


Fig. 4. Parts of the $^{13}C\{^1H\}$ NMR (100.5 MHz) spectrum of 2,5-dibutyl-3-ethyl-1,1-divinylsilole **11a**. ^{29}Si satellites (marked by asterisks in expansions) correspond to $J(^{29}Si, ^{13}C)$. The upper insert shows the *J*-modulated spectrum for assignment of C, CH and CH_2 carbons.

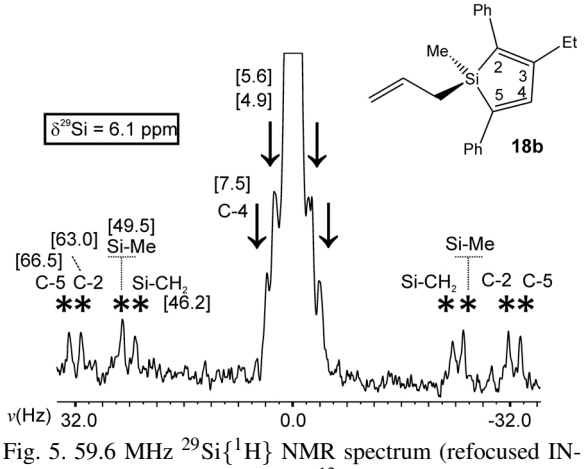


Fig. 5. 59.6 MHz $^{29}Si\{^1H\}$ NMR spectrum (refocused INEPT) of 1-allylsilole **18b**. The ^{13}C satellites belonging to $^1J(^{29}Si, ^{13}C)$ are marked by asterisks, and those marked by arrows (close to the parent signal) may be assigned to $^nJ(^{29}Si, ^{13}C)$ ($n \geq 2$).

(Table 2). This comparison is more straightforward than that of the $\delta^{13}C(2,3,4,5)$ data because of the intrinsic substituent effect exerted by the Et_2B group as compared to hydrogen. Another diagnostic criterion for potential changes of the π system is available in the coupling constants $^1J(^{29}Si,^{13}C(2,5))$ [20]. An inspection of these data in the Tables 1 and 2 shows that protodeborylation does not induce significant changes. This is also true for $^1J(^{29}Si,^{13}C)$ of all organyl groups exocyclicly attached to silicon.

Conclusions

Siloles bearing various substituents at the ring positions are readily available in high yield *via* 1,1-organoboration reactions. It is shown that this route to siloles also tolerates vinyl or allyl groups at the silicon atom. Furthermore, if triethylborane is used for the organoboration, the diethylboryl group can be removed by protodeborylation, and the diene system as well as the substituents at silicon (vinyl or allyl) are not affected. On the other hand, the hydroboration of the exocyclic vinyl group of **6a** indicates that much more chemistry can be done without disturbing the π system of the silole.

Experimental Section

Starting materials and measurements

The preparations and handling of all air- and moisture-sensitive samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware and dry solvents were used throughout. BuLi in hexane (1.6 M), all chlorosilanes, 1-hexyne, phenylethyne, 1-ethynyl-4-*tert*-butylbenzene, triethylborane BEt_3, and glacial acetic acid

were commercial products and were used as received. 9-Ethyl-9-borabicyclo[3.3.1]nonane [17], Et-9-BBN, dialkyn-1-yldivinylsilanes **4** and **5** [21] were prepared as described. Dialkyn-1-ylvinylsilanes were prepared according to analogous literature procedures [22]. Data related to their structures will be published elsewhere [12]. NMR spectra (^{1}H, ^{11}B, ^{13}C, ^{29}Si) were recorded in C_6D_6 (concentration *ca.* 10 – 15 %, v/v) with samples in 5 mm o. d. tubes at 23 ± 1 °C using Varian Inova 300 MHz and 400 MHz spectrometers; chemical shifts are given relative to Me_4Si [δ^1H (C_6D_5H) = 7.15; δ^{13}C (C_6D_6) = 128.0; δ^{29}Si = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz] and external BF_3-OEt_2 [δ^{11}B = 0 for $\Xi(^{11}B)$ = 32.083971 MHz]. Chemical shifts δ^1H are given to ±0.04 ppm, δ^{13}C and δ^{29}Si to ±0.1 ppm, and δ^{11}B to ±0.5 ppm. ^{29}Si NMR spectra were measured by using the refocused INEPT pulse sequence [23], based on $^{2/3}J(^{29}Si–C^1H{=}CH_2)$ and $^3J(^{29}Si,^1HC^4)$ 20 – 25 Hz (after optimization of the respective refocusing delays).

*1,1-Ethylboration of alkyn-1-ylsilanes **1** – **3***

An NMR tube was filled with **1a** (0.23 g: 0.99 mmol) and BEt_3 in excess. The NMR tube was sealed and kept at 100 – 120 °C (oil bath). After three days the NMR tube was cooled in liquid nitrogen, opened under argon, and all readily volatile materials were removed in a vacuum. The brown oily liquid left was identified as silole **6a**. A portion of silole **6a** was mixed with BEt_3 and kept under identical conditions in a sealed NMR tube. After 13 d the NMR tube was opened, all volatile materials were evaporated, and the oily liquid was identified as mixture of silole **6a** and **8a**. The reaction conditions for the synthesis of siloles **6b** and **8b** were similar, except that heating lasted for 5 d and 23 d, respectively. Reactions in the case of silole derivatives **7a** and **10b** continued for 8 d and 6 d, respectively.

6a: ^{1}H NMR (300 MHz): δ = 0.3 (s, 3H, SiMe), 0.7, 0.7, 1.3, 2.1 (t, t, m, m, 18H, ^{n}Bu), 1.1, 1.3 (t, m, 10H, BEt_2), 0.9, 2.3 (t, m, 5H, Et), 6.0 (dd, 1H, $J(^1H,^1H)$ = 4.0, 20.1 Hz, $=CH_2$), 6.1 (dd, 1H, $J(^1H,^1H)$ = 4.0, 14.6 Hz, $=CH_2$), 6.5 (dd, 1H, $J(^1H,^1H)$ = 14.6, 20.1 Hz, Si–CH=).

6b: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, SiMe), 1.1, 1.5 (t, m, 10H, BEt_2), 0.9, 2.3, 2.4 (t, m, m, 5H, Et), 5.9 (dd, 1H, $J(^1H,^1H)$ = 3.6, 20.2 Hz, $=CH_2$), 6.1 (dd, 1H, $J(^1H,^1H)$ = 3.6, 14.4 Hz, $=CH_2$), 6.4 (dd, 1H, $J(^1H,^1H)$ = 14.4, 20.2 Hz, Si–CH=), 7.2, 7.3 (m, m, 10H, Ph).

7a: ^{1}H NMR (300 MHz): δ = 0.7, 0.8, 1.2, 1.4, 2.1 (t, t, m, m, m, 18H, ^{n}Bu), 1.1, 1.4 (t, m, 10H, BEt_2), 0.9, 2.3 (t, m, 5H, Et), 6.0 (dd, 1H, $J(^1H,^1H)$ = 3.8, 20.3 Hz, $=CH_2$), 6.1 (dd, 1H, $J(^1H,^1H)$ = 3.8, 14.8 Hz, $=CH_2$), 6.5 (dd, 1H, $J(^1H,^1H)$ = 14.8, 20.3 Hz, Si–CH=), 7.2, 7.7 (m, m, 5H, SiPh).

10b: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, SiMe), 1.0, 1.3 (t, m, 10H, BEt_2), 0.8, 2.1, 2.2 (t, m, m, 5H, Et), 1.7, 4.8, 5.7 (d, m, m, 5H, All), 7.0 – 7.2 (m, 10H, Ph).

*Hydroborylation of the Si-vinyl group in silole **6a** using 9-BBN, synthesis of silole **9a***

A Schlenk tube was charged with the solution of silole **6a** (0.13 g, 0.39 mmol) in THF (5 mL), and one equivalent of solid 9-BBN (0.05 g; 0.39 mmol) was added in one portion. The reaction mixture was stirred at r. t. for 2 h. Then, the solvent and all other volatiles were removed, leaving silole **9a** as an oily liquid.

9a: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, SiMe), 0.9, 2.1, 2.3 (t, m, m, 5H, Et), 0.9 – 1.0, 1.2 – 1.8 (m, m, Bu, $Si(CH_2)_2$, BEt_2, 9-BBN).

*Synthesis of silole derivatives **11** and **12***

Reactions for the preparation of silole derivatives **11** and **12** were carried out under harsh reaction conditions as described above. All these compounds were obtained as viscous oils. The reaction times were different for these siloles: **11a** (2 d), **11b** (4 d), **11c** (10 d) and **12a**, **12a′** (5 d).

11a: ^{1}H NMR (400 MHz): δ = 1.0, 1.4 (t, m, 10H, BEt_2), 0.8, 2.1 (t, q, 5H, Et), 0.9, 0.9, 1.4, 2.1, 2.3 (t, t, m, t, t, 18H, ^{n}Bu), 5.9 (dd, 2H, $J(^1H,^1H)$ = 4.0, 20.1, $=CH_2$), 6.0 (dd, 2H, $J(^1H,^1H)$ = 4.0, 14.6, $=CH_2$), 6.3 (dd, 2H, $J(^1H,^1H)$ = 14.6, 20.1, Si–CH=).

11b: ^{1}H NMR (400 MHz): δ = 1.1, 1.5 (t, br, 10H, BEt_2), 0.9, 2.3 (t, q, 5H, Et), 6.0 (dd, 2H, $J(^1H,^1H)$ = 3.7, 20.0 Hz, $=CH_2$), 6.0 (dd, 2H, $J(^1H,^1H)$ = 3.7, 14.8 Hz, $=CH_2$), 6.3 (dd, 2H, $J(^1H,^1H)$ = 14.8, 20.0 Hz, HC=), 7.1 – 7.2, 7.3, 7.3 (m, m, m, 10H, Ph).

11c: ^{1}H NMR (400 MHz): δ = 0.9, 1.3 (t, m, 10H, BEt_2), 0.7, 2.2 (t, q, 5H, Et), 6.2 (dd, 2H, Si–CH=), 5.8 (m, 4H, $=CH_2$), 1.0, 1.1, 6.9, 7.1 (s, s, m, m, 26H, 4-^{t}Bu-C_6H_4).

12a: ^{1}H NMR (400 MHz): δ = 0.9, 1.2 – 1.4 (t, m, 10H, BEt_2), 0.8, 2.0 (t, m, 5H, Et), 0.8, 1.2 – 1.4, 2.3 (t, m, t, 9H, ^{n}Bu), 5.9 (dd, 2H, $J(^1H,^1H)$ = 3.8, 14.8 Hz, $=CH_2$), 5.9 (dd, 2H, $J(^1H,^1H)$ = 3.8, 19.8 Hz, $=CH_2$), 6.2 (dd, 2H, $J(^1H,^1H)$ = 14.8, 19.8 Hz, Si–CH=), 1.1, 6.9, 7.1 (s, m, m, 13H, 4-^{t}Bu-C_6H_4).

*1,1-Organoboration of silanes **1b** and **4d** using 9-ethyl-9-borabicyclo[3.3.1]nonane*

Silane **1b** (1 g, 3.7 mmol) was filled together with an excess (1 mL, 0.72 g, 5.6 mmol) of 9-ethyl-9-borabicyclo-[3.3.1]nonane into an NMR tube. The NMR tube was sealed and heated at 120 °C (oil bath). The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. After 15 h the reaction was found to be complete, and all readily volatile materials were removed *in vacuo* (*ca.* 10^{-1} Torr). Finally, excess of Et-9-BBN was removed by heating at 60 – 70 °C *in vacuo*. The remaining oily product was identified as pure **13b** in > 95 % yield and high purity (99 %). The silole **14d**

was obtained in the same way. Silole derivatives **13b** and **14d** were air- and moisture-sensitive oily liquids.

13b: ^{1}H NMR data (400 MHz): δ = 0.5 (s, 3H, SiMe), 0.8, 1.1, 1.5, 1.7, 2.0 – 2.1, 3.3 (t, m, m, m, m, m, 19H, Et-BC_8H_{14}), 5.9 – 6.2 (m, 3H, Si-Vinyl), 6.9, 7.0 – 7.2, 7.3 (m, m, m, 10H, Ph).

14d: ^{1}H NMR data (300 MHz): δ = 1.1, 1.4, 1.4 – 1.8, 3.4 (t, q, m, m, 19H, Et-BC_8H_{14}), 5.9 – 6.1, 6.3 (m, m, 6H, Si–CH=CH_2), 2.1, 6.9 – 7.1 (s, m, m, 13H, 4-^{t}Bu-C_6H_4).

*Protodeborylation of the silole derivatives **6**, **10**, **11**, and **12***

The protodeborylation of the silole derivatives was carried out following literature procedures [18, 21].

15b: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, SiMe), 0.8, 2.3 (t, m, 5H, Et), 5.8 (dd, 1H, $J(^1H,^1H)$ = 3.5, 20.3 Hz, =CH_2), 5.9 (dd, 1H, $J(^1H,^1H)$ = 3.5, 14.6 Hz, =CH_2), 6.2 (dd, 1H, $J(^1H,^1H)$ = 14.6, 20.3 Hz, Si–CH=), 7.0 – 7.2, 7.4 (m, m, 11H, C^4H, Ph).

16a: ^{1}H NMR (400 MHz): δ = 0.8, 0.8, 1.2, 1.4, 2.2, 2.3 (t, t, m, m, t, t, 18H, ^{n}Bu), 0.9, 2.1 (t, q, 5H, Et), 5.9 (dd, 2H, $J(^1H,^1H)$ = 4.1, 20.0 Hz, =CH_2), 5.9 (dd, 2H, $J(^1H,^1H)$ = 4.1, 14.8 Hz, =CH_2), 6.1 (dd, 2H, $J(^1H,^1H)$ = 14.8, 20.0 Hz, Si–CH=), 6.4 (m, 1H, $^3J(^{29}Si,^1H)$ = 13.8 Hz, C^4H).

16b: ^{1}H NMR (400 MHz): δ = 0.9, 2.3 (t, q, 5H, Et), 5.9 (dd, 2H, $J(^1H,^1H)$ = 3.5, 20.1 Hz, =CH_2), 5.9 (dd, 2H, $J(^1H,^1H)$ = 3.5, 14.9 Hz, =CH_2), 6.2 (dd, 2H, $J(^1H,^1H)$ = 14.8, 20.1 Hz, Si–CH=), 7.0 – 7.2, 7.3, 7.5 (m, m, m, 11H, Ph, C^4H).

17: ^{1}H NMR (400 MHz): δ = 0.9, 1.3, 2.4 (t, m, t, 9H, ^{n}Bu), 1.0, 2.3 (t, q, 5H, Et), 6.0 (dd, 2H, $J(^1H,^1H)$ = 3.9, 19.9 Hz, =CH_2), 6.1 (dd, 2H, $J(^1H,^1H)$ = 3.9, 15.0 Hz, =CH_2), 6.3 (dd, 2H, $J(^1H,^1H)$ = 15.0, 19.9 Hz, Si–CH=), 7.2 (s, 1H, $^3J(^{29}Si,^1H)$ = 13.3 Hz, C^4H), 1.2, 7.3, 7.5 (s, m, m, 13H, 4-^{t}Bu-C_6H_4).

17′: ^{1}H NMR (400 MHz): δ = 6.6 (m, 1H, C^4H), other protons were not assigned owing to overlap with signals belonging to silole **17a**.

18b: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, SiMe), 1.0, 2.3 (t, m, 5H, Et), 1.7 (d, 2H, $J(^1H,^1H)$ = 8.0 Hz, Si–CH_2), 4.7 (m, 1H, =CH), 5.6 (m, 2H, =CH_2), 7.1, 7.2, 7.4 (m, m, m, 11H, C^4H, Ph).

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