Hydroboration of Bis(trimethylsilylethynyl)silanes with 9-Borabicyclo[3.3.1]nonane. A New Route to 1-Sila-3-cyclopentenes and to a 1-Sila-2,4-cyclopentadiene

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The hydroboration of bis(trimethylsilylethynyl)silanes $Me(R)Si(C{\equiv}C{-}SiMe_3)_2$ **1a** (R = Me) and **1b** (R = H) with 9-borabicyclo[3.3.1]nonane (9-BBN) does not give products related to the usual *cis*-1,2-hydroboration of one or both C≡C bonds. Instead, the major products obtained from **1a** are the two isomers of 2,5-bis(trimethylsilyl)-2,5-bis[9-(9-borabicyclo[3.3.1]-nonyl)]-1-sila-3-cyclopentene **2a** and **2a′** (silolenes), and from the reaction of **1b** with 9-BBN solely the silolene **2b** can be isolated. The silolenes **2a** and **2b** were studied by X-ray structural analysis. The reaction of **1a** with 9-BBN in a 1:1 molar ratio gave a mixture of products, consisting of the silolenes **2a** and **2a′**, some unidentified material, and 2,5-bis(trimethylsilyl)-3-[9-(9-borabicyclo[3.3.1]nonyl)]-1-sila-2,4-cyclopentadiene **3a**. The silole **3a** was then prepared in pure state by the reaction of **1a** with 9-isobutyl-9-borabicyclo[3.3.1]nonane in boiling toluene, where the borane decomposes slowly into isobutene and 9-BBN which is trapped by **1a**. The proposed structures of the heterocycles **2** and **3** in solution follow from a consistent set of NMR data (^{1}H, ^{11}B, ^{13}C, ^{29}Si NMR).

Key words: Alkynes, Silole, Hydroboration, Isomerisation, NMR

Introduction

At a first glance, hydroboration of alkyn-1-yl-silanes appears to be a straightforward route towards organometallic-substituted alkenes as the result of *cis*-addition of the B–H moiety to the C≡C bond. In most cases it was reported that these reactions are regiospecific, and that the boryl group becomes attached to the carbon atom bearing the silyl group [1]. However, there are also reports which indicate that predictions concerning potential hydroboration products of alkyn-1-yl-silanes should be met with caution, since a wide range of different types of products has been obtained, depending on reaction conditions and on the substituents at the C≡C bond, including the nature of the silyl group [2–4]. Recently, we have found that bis(trimethylsilyl)ethyne, $Me_3Si{-}C{\equiv}C{-}SiMe_3$ (**A**), reacts initially with 9-bora-bicyclo[3.3.1]nonane (9-BBN), as expected, by 1,2-hydroboration to give **B**, followed by isomerisation to **C** and further transformations, possibly *via* the alkene **D**, to the allene **E** (Scheme 1) [5]. In the present work, we have studied the reactions of bis(trimethylsilylethynyl)dimethylsilane **1a** and -methylsilane **1b** with 9-BBN in order to look for further alternatives to common hydroboration reactions. To the best of our knowledge, hydroboration of the silanes **1** has not been reported so far.

Results and Discussion

*Reaction of bis(trimethylsilylethynyl)dimethylsilane, $Me_2Si(C{\equiv}C{-}SiMe_3)_2$ **1a**, with 9-BBN*

When **1a** was treated with an equimolar amount of 9-BBN (for simplicity, the formula of the monomer is used; in non-donor solvents, 9-BBN is present as a dimer [6]), a complex mixture was formed which could not be separated. Acoording to the ^{29}Si NMR spectra, a small amount of **1a** (δ^{29}Si −42.5 [7]) was left, and a signal at δ^{29}Si −18.5 indicates the presence of an alkyn-1-yl(tri-alkyl)silane [8]; in addition to numerous weak ^{29}Si NMR signals, four signals could subsequently be assigned to the silolenes **2a** and **2a′**, and the three strongest signals (δ^{29}Si 20.4, −7.3, −10.3) were shwon to belong to the silole **3a** (*vide infra*). The reaction of **1a** with two equivalents of 9-BBN confirmed the assignment, since the ^{29}Si NMR signals

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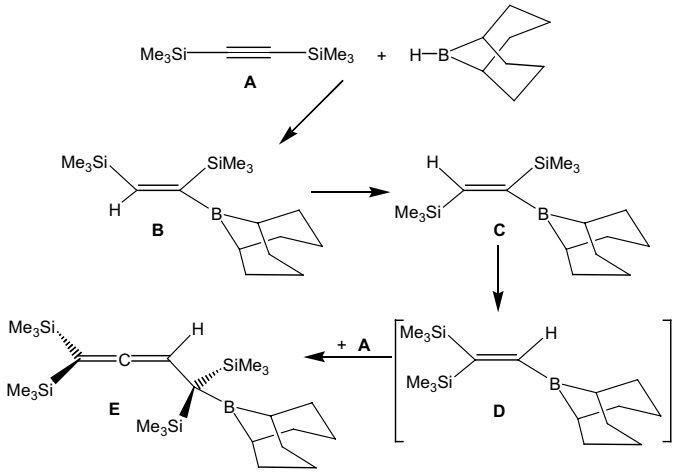
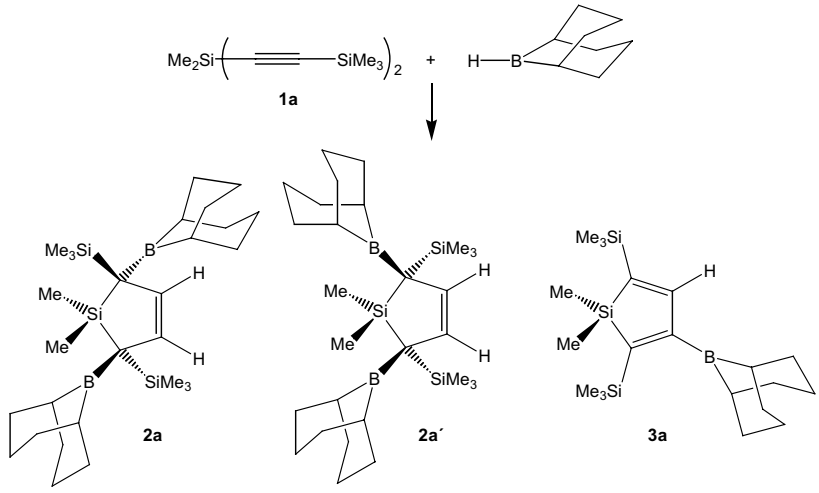


Scheme 1.

of **2a** and **2a′** became the dominant signals (Fig. 1). The isomer **2a** was crystallised selectively from hexane solutions at −85 °C which enabled to determine its molecular structure in the solid state (*vide infra*) and to assign the ^{29}Si (Fig. 2), ^{13}C and relevant ^{1}H NMR signals. In the case of **2a**, there is only one ^{1}H(SiMe$_2$) and one ^{13}C(SiMe$_2$) NMR signal, whereas there are two signals each in the case of **2a′**. Otherwise there are only slight differences between **2a** and **2a′** in the chemical shifts δ^{1}H, δ^{11}B and δ^{13}C. The ^{11}B NMR signals of **2a** and **2a′** are broad ($h_{1/2}$ > 400 Hz) and found in the range δ^{11}B 86 ± 1, typical [9] of boron atoms surrounded by three alkyl groups. The ^{13}C NMR signals of the ring carbon atoms in 2,5-position are broad as a result of partially relaxed ^{13}C-^{11}B spin-spin coupling [10].

Although there are some routes to silolenes described in the literature [11, 12], the present synthesis allows for the first time to prepare organometallic-substituted silolenes which may have further synthetic potential considering in particular the reactivity of the B–C bonds and the chiral centres in 1- (**2b**) and 2,5-positions (**2a**, **b**). In addition to being attractive synthons in organic synthesis, silolenes are of interest as polymer precursors.



Scheme 2.

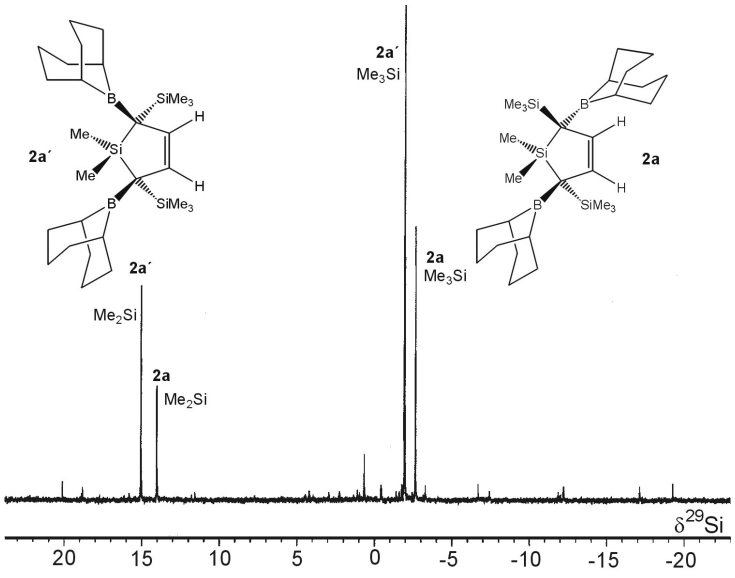


Fig. 1. 49.7 MHz $^{29}Si\{^1H\}$ NMR spectrum (refocused INEPT pulse sequence [26]) of the reaction mixture containing the silolenes **2a** and **2a′**, after treating **1a** with two equivalents of 9-BBN, passing the solution through a short column of silica, and washing with ether/pentane (1:1). The solvents were removed in vacuo, and the oily residue was dissolved in C_6D_6 (*ca.* 30/70 v/v). All weak ^{29}Si NMR signals belong to unidentified silanes.

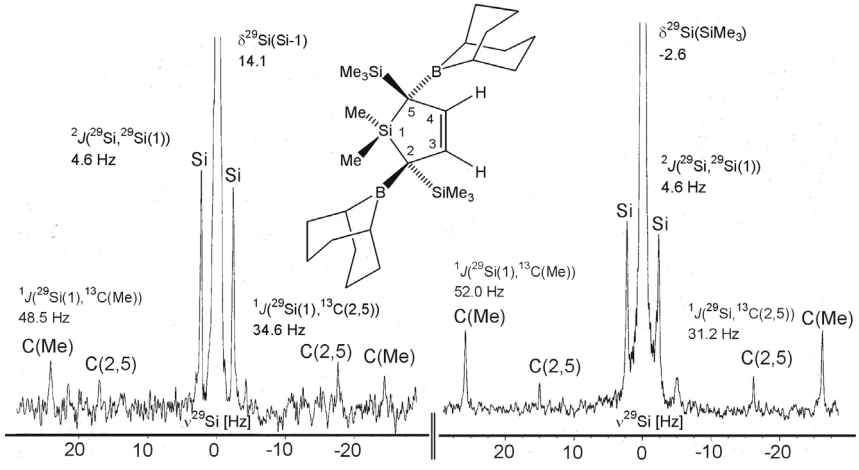
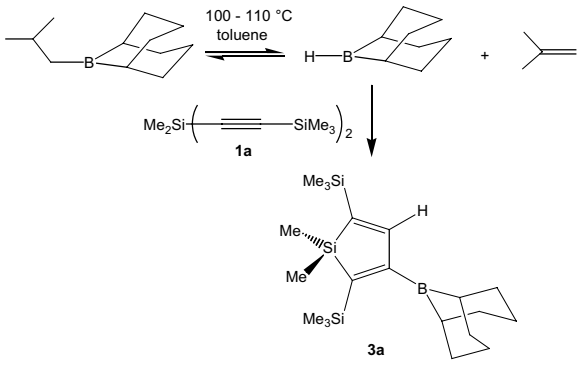


Fig. 2. Expanded regions of the 49.7 MHz $^{29}Si\{^1H\}$ NMR spectrum (refocused INEPT pulse sequence [26]) of the silolene **2a** (*ca.* 3% in C_6D_6) which crystallised from pentane at low temperature. The spectrum is the result of 3000 transients, recorded with an acquisition time of 5 s and a repetition delay of 6 s. The ^{29}Si and ^{13}C satellites are marked. Note the small magnitude of $^1J(^{29}Si,^{13}C(2,5))$; owing to the broad, low-intensity $^{13}C(2,5)$ NMR signal, this coupling constant cannot be measured from ^{13}C NMR spectra.

Reaction of bis(trimethylsilylethynyl)dimethylsilane, $Me_2Si(C{\equiv}C{-}SiMe_3)_2$ **1a**, *with 9-^{i}Bu–9-BBN*

Since the 1:1 reaction of **1a** with 9-BBN did not afford pure products, a different strategy was developed. It is well known that many trialkylboranes undergo dehydroboration at elevated temperatures [13]. Thus, 9-isobutyl-9-borabicyclo[3.3.1]nonane, ^{i}Bu–9-BBN [14], which itself does not react with **1a**, should slowly decompose into isobutene and 9-BBN at 100–110 °C. Under these conditions, 9-BBN should then be present *in situ* in low concenration as a reactive monomer. This monomer will be trapped immediately either by isobutene, which gives back ^{i}Bu–9-BBN, or by **1a**. Indeed, the NMR spectra of reaction solutions indicate that isobutene and a single silicon-containing species are the dominant products (Scheme 3).



Scheme 3.

The silane can be purified by crystallisation, and was identified as the 1-sila-2,4-cyclopentadiene **3a**. In agreement with ^{13}C NMR spectra of other 2,5-bis(trimethylsilyl)-substituted siloles [7,15], there are three sharp and one broad ^{13}C NMR signals for **3a**. Two of the sharp signals are accompanied each by two pairs of ^{29}Si satellites corrresponding to $^{1}J(^{29}\mathrm{Si},^{13}\mathrm{C})$. The third sharp ^{13}C NMR signal belongs to a =CH moiety ($^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 154.0 Hz) and is accompanied by three pairs of ^{29}Si satellites corresponding to $^{2}J(^{29}\mathrm{Si},^{13}\mathrm{C})$ and $^{3}J(^{29}\mathrm{Si},^{13}\mathrm{C})$ (8.9, 11.8 and 11.9 Hz). Most of these couplings are found again by observing the ^{13}C satellites in the ^{29}Si NMR spectrum of **3a** (Fig. 3). The same strategy does not work with **1b**, since **1b** reacts in boiling toluene with ^{t}Bu–9-BBN, and a complex mixture of compounds is formed.

By comparison with Fig. 1, it is evident from Fig. 3 that **3a** is not contaminated with more than 0.5% of the silolenes **2a** or **2a′**. Similarly, there are also no other species present, in which Me_3Si groups are attached to C=C bond, since the typical range between δ^{29}Si −5 to −14 is completely free of signals except for those of **3a**. This is the first time that a silole has been prepared by "hydroboration". Numerous siloles have become available by 1,1-organoboration reactions [7, 15–17].

Reaction of bis(trimethylsilylethynyl)methylsilane, $Me(H)Si(C{\equiv}C{-}SiMe_3)_2$ **1b**, *with 9-BBN*

In contrast to **1a**, treatment of the silane **1b** with 9-BBN in a 1:1 or 1:2 molar ratio affords only one defined product which could be isolated, the silolene **2b**, an analogue to **2a**. Repeated crystallisation of **2b** from pentane, hexane or toluene at low temperature gave crystalline material which was studied by X-ray structural analysis (*vide infra*). If solid samples of **2a** were left in contact with air, oxidation of the Si–H or any of the B–C bonds appeared to be very slow. Instead, it was found,

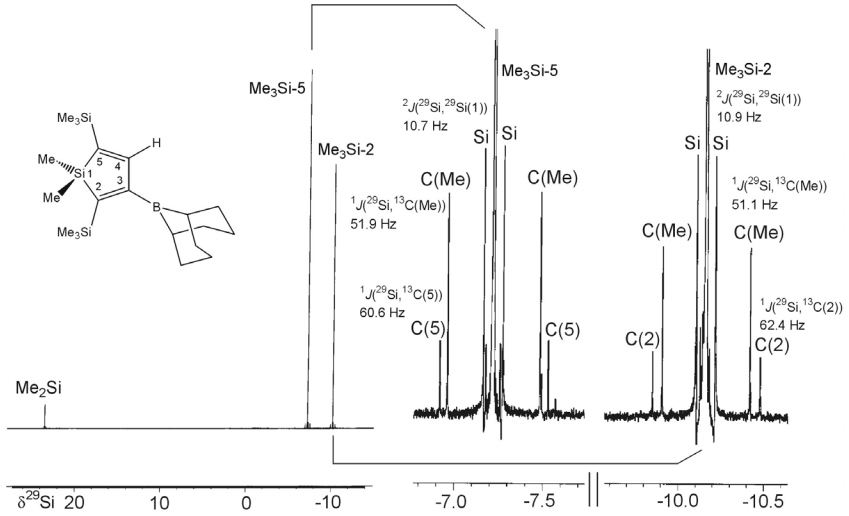
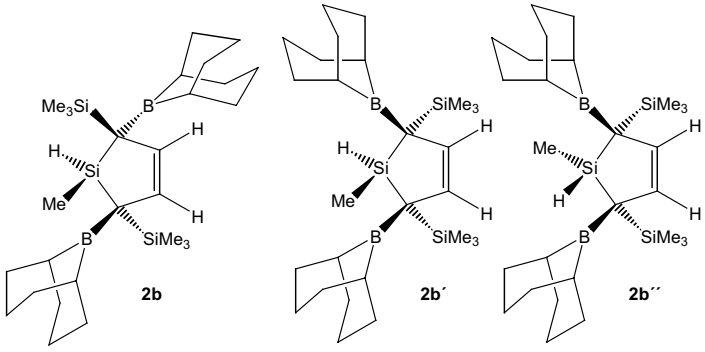


Fig. 3. 99.5 MHz ^{29}Si{^{1}H} NMR spectrum (refocused INEPT pulse sequence [26]) of the silole **3a** (crystalline material, *ca.* 20 mg, dissolved in 0.6 ml of C_6D_6). The spectrum is the result of 1200 transients (acquisition time 8 s; repetition time 8 s). The ^{29}Si and ^{13}C satellites are marked. Additional ^{13}C satellites for long-range couplings are resolved (see Table 1). The ^{29}Si satellites are out of phase, typical of homonuclear spin-spin coupling, for which the magnetisation is not refocused in the INEPT pulse sequence.



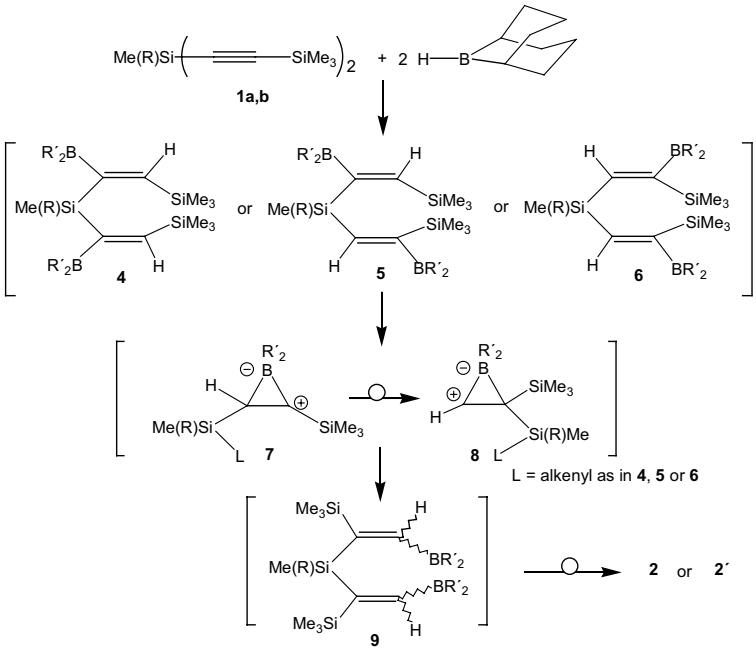
Formulae **2b**, **2b′**, **2b″**.

after the material had been redissolved, that mixtures of **2b** and one of its isomer **2b′** or **2b″** were formed. We have not made a great effort to distinguish between **2b′**and **2b″** by NMR. NOE difference spectra should give the answer; however, the results were not conclusive. Both isomers should give one ^{13}C NMR signal each for the ring carbon atoms in 2,5 and 3,4 positions, and one $^{29}Si(SiMe_3)$ NMR signal, in agreement with the experiment. In contrast, the structure of **2b** requires two signals each for the ring carbon atoms in 2,5 and 3,4 positions, two $^{1}H(=CH)$ signals and two $^{29}Si(SiMe_3)$ signals which are all observed.

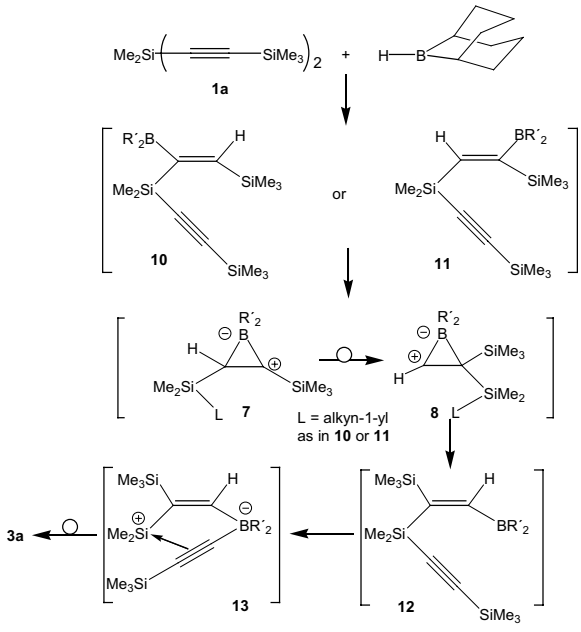
Proposed mechanism of the formation of the silolenes **2** *and the silole* **3a**

If one assumes that *cis*-1,2-hydroboration is the first step in the reaction of **1** with 9-BBN, the final products must be the result of isomerisation and rearrangement. The reaction of $Me_3Si-C\equiv C-SiMe_3$ (**A**) with 9-BBN has shown that isomerisation takes place readily (see Scheme 1) [5]. In the case of the reaction of **1a** with 9-BBN, we have to differentiate between a 1:2 (Scheme 4) and a 1:1 molar ratio (Scheme 5).

The first step (*cis*-1,2-hydroboration) in the 1:2 reaction (Scheme 4) can lead to a mixture of the



Scheme 4.



Scheme 5.

compounds **4–6**. These isomerise to give **9** (most likely also as a mixture of isomers) *via* the intermediates **7** and **8**. These intermediates should be considered because of $\pi-\sigma$ delocalisation [5, 18], since the boryl group is expected to prefer an orthogonal arrangement with respect to the C=C–B plane [19]. The driving force for the isomerisation of **4–6** to **9** is the more favourable stabilisation of the positive charge by two silyl groups in β-position [20], as in the case of **8**. Compounds of type **9** are known to rearrange into five-membered rings [21,22], as was found here in the cases of **2** and **2′**.

In the 1:1 reaction of **1a** with 9-BBN (Scheme 5), the hydroboration can be controlled (*vide supra*) in such a way that only one of the two C≡C bonds is involved which can lead to the isomers **10** and **11**. Apparently the second methyl group at silicon instead of hydrogen helps to reduce the reactivity of the C≡C bonds towards 9-BBN. Again, the intermediates of type **7** and **8** are proposed to be responsible for a fast isomerisation process which then leads to the next intermediate **12**. Under the reaction conditions, **12** is not stable and undergoes an intramolecular 1,1-vinylboration reaction to give finally **3a**. This type of reaction is well known in the synthesis of metalloles *via* 1,1-organoboration [16]. Zwitterionic intermediates of type **13** have been isolated under mild conditions, and have been structurally characterised when a Me_2Sn [23] or a Me_2Pb moiety [24] was in place of the Me_2Si unit.

X-ray structural analyses of the silolenes **2a** *and* **2b**

The molecular structure of **2a** is shown in Fig. 4. The five-membered ring is planar within experimental error. All Si–C bond lengths for ring carbon atoms are longer than those for methyl carbon atoms. The endocyclic bond angle at silicon (97.3(2)°) is only slightly smaller than the exocyclic one (100.3(2)°). The surroundings of the aliphatic ring carbon atoms deviate little from a regular tetrahedron, with the endocyclic bond angle C(13)C(9)Si(2) (100.5(3)°) being more acute than the tetrahedral angle.

The exact determination of the molecular structure of **2b** was not possible, although different crystals obtained from repeated attempts at crystallisation were studied. This can be due either to disorder or to twinned crystals (Fig. 5). Refinement of the structure assuming twinned crystals (inversion twin) did not reveal significant changes in the atomic parameters and *R* values. Therefore,

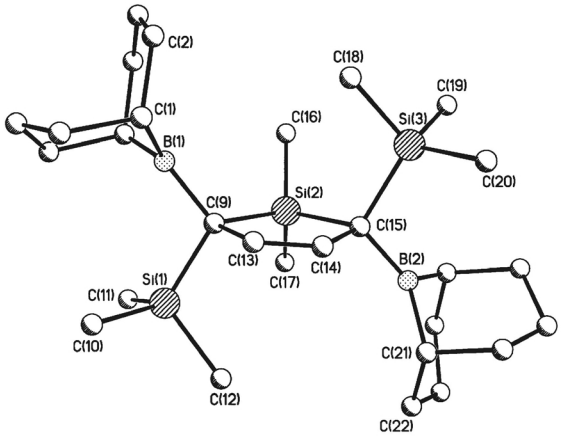


Fig. 4. Molecular structure of **2a** (hydrogen atoms are omitted for clarity); selected bond lengths [pm] and angles [°]: Si(2)–C(9) 191.8(4), Si(2)–C(15) 192.1(4), Si(2)–C(16) 187.0(4), Si(2)–C(17) 185.7(5), Si(1)–C(9) 191.8(4), Si(3)–C(15) 191.2(4), Si(1)–C(10) 188.8(5), Si(1)–C(11) 186.4(5), Si(1)–C(12) 186.4 (5), B(1)–C(9) 156.9(6), B(1)–C(1) 158.0(7), C(13)–C(14) 131.1(6), C(9)–C(13) 152.3(5)C(14)–C(15) 153.6(6); C(16)Si(2)C(17) 100.3(2), C(9)Si(2)C(15) 97.3(2), B(1)C(9)Si(1) 110.2(3), Si(1)C(9)Si(2) 112.1(2), Si(2)C(9)C(13)100.5(3).

a decision between disorder or twinned crystals cannot be reached. The quality of the data set does not encourage a detailed comparison of the structural features of **2a** and **2b**. However, the conclusions drawn from the NMR spectra in solution are confirmed. The surroundings of the boron atoms are trigonal planar within experimental error.

Conclusions

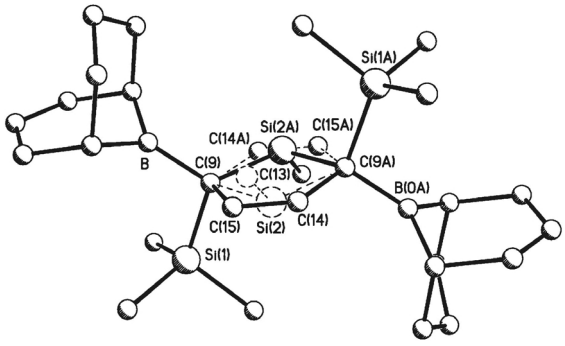


Fig. 5. Molecular structure of **2b** (hydrogen atoms are omitted for clarity); the disorder (or the effect of an inversion twin crystal) is indicated by the dashed circles for the atoms C(14), C(15), C(13) and Si(2).

Although hydroboration reaction of organometallic-substituted alkynes may proceed initially with the usual stereo- and regioselectivity, isomerisation processes may be initiated, and unexpected products be formed by irreversible rearrangements. This is shown by the formation of silolenes and a silole with substituent patterns not related in a straightforward way to the primary hydroboration products.

Experimental Section

All preparative work as well as handling of samples for NMR measurements was carried out by observing necessary precautions to exclude traces of oxygen and moisture. Solvents were dried by standard methods; 9-BBN was used as a commercial product without further purification, ^{i}Bu–9-BBN was available [14], and **1a**, **b** were prepared following related literature procedures [25]. NMR spectra were recorded at 25 °C on Bruker ARX 250 or DRX 500 spectrometers, all equipped with multinuclear units, using C_6D_6 or $CDCl_3$ solutions in 5 mm tubes. Chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_5H) = 7.15; ($CDCl_3$/$CHCl_3$) = 7.24; δ^{13}C (C_6D_6) = 128.0, ($CDCl_3$) = 77.0; δ^{29}Si = 0 for Me_4Si with Ξ(^{29}Si) = 19.867187 MHz]. ^{29}Si NMR spectra were measured using the

Table 1. ^{11}B, ^{13}C, and ^{29}Si NMR data[a] of the silolenes **2** and the silole **3a**.

	2a (R = Me)	**2a′** (R = Me)	**2b** (R = H)	**2b′** (R = H)	**3a**
δ^{13}C(2)	44.8 (br)	44.0 (br)	41.7 (br) (29.9; $SiMe_3$)	41.2 (br) (28.5; $SiMe_3$) (37.6; Si-1)	154.4 (62.4; $SiMe_3$) 45.9 (Si-1)
δ^{13}C(3)	132.9	132.2	130.6	130.2	178.1 (br)
δ^{13}C(4)	132.9	132.2	131.6	130.2	155.9 (8.1; 2-$SiMe_3$) (11.9; 5-$SiMe_3$) 12.0 (Si-1)
δ^{13}C(5)	44.8 (br)	44.0 (br)	42.2 (br) (27.2; $SiMe_3$)	41.2 (br)	148.3 (60.6;$SiMe_3$) (60.4; Si-1)
δ^{13}C(MeSi-1)	7.0 (48.5)	7.1 (48.5) 7.2 (48.6)	–0.3 (48.7)	–2.0 (49.3)	–2.8 (47.6)
δ^{13}C(2,5-$SiMe_3$)	2.7 (52.0)	3.1 (52.0)	0.5 (52.6) 1.2 (51.9)	0.8 (52.6)	2.2 (51.1) –0.2 (51.9)
δ^{13}C(9-BBN)	31.1 (br) 34.1, 33.9, 23.3	30.8 (br) 34.3, 23.5	30.4 (br) 33.5, 33.3, 22.8	29.9 (br) 33.3, 33.2, 23.0	33.3 (br) 34.4, 23.4
δ^{29}Si(Si-1)	14.1 (4.6)	15.0 (4.7)	–5.4 (5.1)	0	23.5 (10.9, 10.7)
δ^{29}Si(2,5-Si)	–2.6 (4.6)	–1.6 (4.7)	–2.5, –1.1 (5.1)	0.1 (5.0) 0.7 (5.0)	–10.1 (10.9) –7.2 (10.7)
δ^{11}B	86.5	86.5	85.0	85.7	85.7

[a] In C_6D_6 at 23 °C. Coupling constants to ^{29}Si (±0.2 Hz) are given in parentheses; (br) denotes broad signals due to partially relaxed ^{13}C-$^{10/11}$B coupling.

refocused INEPT pulse sequence with ^{1}H decoupling [26]. In the case of the reactions of **1b**, the pulse sequence was based on $^1J(^{29}Si,^1H)$ and, alternatively, on $^2J(^{29}Si,^1H_{Me})$. Optimised low power levels for ^{1}H decoupling were used together with fairly long acquisition times (5 to 10 s) and repetition delays (8–10 s) in order to record the sharp signals with their undistorted line shape (no effects due to truncation of the FID, and artificial broadening induced by temperature gradients within the sample). Melting points (uncorrected) were measured in sealed capillaries using a Büchi 510 melting point apparatus.

2,5-Bis(9-borabicyclo[3.3.1]non-9-yl)-2,5-bis(trimethylsilyl)-1,1-dimethyl-1-sila-3-cyclopentenes **2a**, **2a′**

A mixture of **1a** (0.64 g, 2.5 mmol) and 9-BBN (0.61 g; 5 mmol) in toluene (30 ml) was heated at 110 °C for 12 h. The solvent was removed *in vacuo*, and a light-yellow oil remained. This was redissolved in hexane, passed through a short column (6 × 2 cm) filled with silica, and eluated with hexane or ether/pentane (see Fig. 1). After removing most of the hexane, and keeping the concentrated solution for several days at −85 °C, the compound **2a** crystallised as a colourless solid (0.30 g, 24%; m.p. 117 °C). **2a**: ^{1}H NMR (250.13 MHz; C_6D_6): δ = 0.19 (s, 18H, 2,5-$SiMe_3$), 0.37 (s, 6H, $SiMe_2$), 2.0–1.5 (m, 28H, 9-BBN), 5.99 (s, 2H, =CH). **2a′**: ^{1}H NMR (250.13 MHz; C_6D_6): δ = 0.15 (s, 18H, 2,5-$SiMe_3$), 0.37, 0.55 (s, s, 3H, 3H, $SiMe_2$), 2.0–1.4 (m, 28H, 9-BBN), 5.98 (s, 2H, =CH).

2,5-Bis(9-borabicyclo[3.3.1]non-9-yl)-2,5-bis(trimethylsilyl)-1-methyl-1-sila-3-cyclopentene **2b**

Solid 9-BBN (2.41 g, 20 mmol) was added in one portion to a cooled (0 °C) solution of **1b** (2.36 g, 9.9 mmol) in toluene (20 ml). The mixture was heated at 110 °C for 24 h. Then all volatile materials were removed *in vacuo*. A colourless, waxy solid remained which was dissolved in hexane (5 ml). After cooling to −30 °C, colourless crystals of **2b** were obtained (3.1 g, 65%; m.p. 66–69 °C). A sample of solid **2b** (0.5 g) was exposed to air for 24 h, after which it was redissolved in $CDCl_3$. Rearrangement into **2b′** had taken place. **2b**: ^{1}H NMR (250.13 MHz; $CDCl_3$): δ ($J(^{29}Si,^1H)$) = 0.14 (s, 18H, 2,5-$SiMe_3$), 0.54 (d, 3H, SiMe; $^3J(^1H,Si,C,^1H)$ = 4.2 Hz), 1.3–1.9 (m, 28H, 9-BBN), 4.6 (185.6) (q, 1H, SiH; $^3J(^1H,Si,C,^1H)$ = 4.2 Hz), 5.99 (s, 2H, =CH). **2b′**: ^{1}H NMR (250.13 MHz; $CDCl_3$): δ ($J(^{29}Si,^1H)$) = 0.14 (s, 18H, 2,5-$SiMe_3$), 0.60 (d, 3H, SiMe; $^3J(^1H,Si,C,^1H)$ = 4.3 Hz), 1.3–1.9 (m, 28H, 9-BBN), 4.55 (181.9) (q, 1H, SiH; $^3J(^1H,Si,C,^1H)$ = 4.3 Hz), 6.0 (s, 2H, =CH).

3-(Borabicyclo[3.3.1]non-9-yl)]-2,5-bis(trimethylsilyl)-1,1-dimethyl-1-sila-2,4-cyclopentadiene **3a**

Compound **1a** (1.43 g, 5.7 mmol) was dissolved in toluene (20 ml), and 9-^{i}Bu–9-BBN (1.11 ml,

Table 2. Data relevant to the X-ray analyses (298 K) of the silolenes **2a** and **2b**.

	2a	**2b**
Formula	$C_{28}H_{54}B_2Si_3$	$C_{27}H_{52}B_2Si_3$
Crystal	irregular block	colourless plate
Dimensions (mm)	0.22 × 0.16 × 0.12	0.18 × 0.12 × 0.07
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Lattice parameters [pm, °]	a = 1192.51(11)	a = 689.65(15)
	b = 1931.44(16)	b = 1152.3(4)
	c = 1355.08(12)	c = 1842.0(4)
	β = 99.915(7)	β = 96.487(7)
Z	4	2
Absorption coefficient μ (mm^{-1})	0.169	0.324
Diffractometer	Siemens P4, (Mo-K$_\alpha$, λ = 71.073 pm), graphite monochromator	
Measuring range (ϑ)	2–25	2–25
Reflections collected	6548	3556
Independent reflections ($I > 2\sigma(I)$)	2772	2119
Absorption correction	not applied	
Refined parameters	298	164
$R1/wR2$ ($I > 2\sigma(I)$)	0.070/0.166	0.121/0.278
Max./min. residual electron density (e pm^{-3} 10^{-6})	0.27/−0.19	0.41/−0.42

5.7 mmol) was added in one portion at room temperature. The mixture was heated at 110 °C for 50 h, and then, all volatile materials were removed *in vacuo*. The oily residue was dissolved in hexane (5 ml), and after repeated crystallisation at −85 °C the product **3a** was obtained as a colourless solid (0.96 g, 45%; m.p. 98 °C). **3a**: ^{1}H NMR (250.13 MHz; C_6D_6): δ = 0.22, 0.26 (s, s, 9H, 9H, 2,5-$SiMe_3$), 0.32 (s, 6H, $SiMe_2$), 1.96–1.4 (m, 14H, 9-BBN), 7.71 (s, 1H, =CH; $^3J(^{29}Si,^1H)_{cis}$ = 7.4 Hz; $^3J(^{29}Si,^1H)_{trans}$ = 17.2 Hz).

Crystal structure determinations of the silolenes **2a** *and* **2b** [27]

Single crystals of **2a** and **2b**, recrystallised from pentane at −85 °C and toluene at −20 °C, respectively, were sealed under argon in Lindemann capillaries. Information relevant to the crystal structure determinations is given in Table 2.

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[27] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-205243 (**2a**), and CCDC-205244 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44(0)1223/336033; e-mail: deposit@ccdc.cam.ac.uk].