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Hydroboration of alkyn-1-yl(methyl)silanes bearing functional substituents at silicon

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Abstract

Alkyn-1-yl(methyl)silanes $Me_2(H)Si-C{\equiv}C-R$ (**1**), $Me(H)(Cl)Si-C{\equiv}C-R$ (**2**) and $Me_2(Cl)Si-C{\equiv}C-R$ (**3**) [R = Bu (**a**), ^{t}Bu (**b**), Ph (**c**), $SiMe_3$ (**d**)] react with 9-borabicyclo[3.3.1]nonane (9-BBN) by 1,2-*cis*-hydroboration to give selectively (except of **3d**) the alkenylsilanes **4** (from **1**), **5** (from **2**), and **6** (from **3**), in which the boryl group has become attached to the carbon atom adjacent to the silyl group bearing functional substituents. In the case of **3d**, a mixture consisting of the alkenes **6d** and the isomers **7d**, **8d** and **9d** is obtained. All products were characterised by NMR spectra (^{1}H-, ^{11}B-, ^{13}C- and ^{29}Si-NMR) in solution, and in the cases of **5c** and **6c**, the molecular structures in the solid state were determined by X-ray analysis.

Keywords: Alkenes; Silanes; Hydroboration; Isomerisation; NMR; X-ray

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1. Introduction

Successful hydroboration of alkyn-1-ylsilanes has been reported repeatedly [1,2]. However, in most cases, the alkenylsilanes thus obtained have been poorly characterised prior to further transformations. It has been shown that the range of products varies considerably with reaction conditions and the nature of the hydroboration reagent [3,4]. Molecular structures of solid alkenylsilanes, prepared by hydroboration of alkyn-1-ylsilanes, are unknown, and with few exceptions [5–7], the NMR spectroscopic data set for solution-state has remained far from complete. Moreover, hardly any attempt has been made to study the hydroboration of alkyn-1-ylsilanes bearing one or more functional substituents at silicon [6,7] or in which two different silyl groups are linked to the C≡C bond. In the present work we report on the hydroboration of the alkyn-1-ylsilanes **1**, **2** and **3** using 9-borabicyclo[3.3.1]nonane (9-BBN) [8,9] as the hydroborating reagent.

2. Results and discussion

2.1. Reactions of the alkyn-1-ylsilanes (1–3) with 9-BBN

The reaction of equimolar amounts of **1** with 9-BBN in pentane is complete after 2 h at room temperature, whereas the analogous hydroboration of **2** or **3** requires stirring for 4 days in pentane or several hours at 65 °C in hexane, respectively. Apparently, the presence of the Si-Cl bond reduces the reactivity of the C≡C bond towards hydroboration. As shown in Scheme 1, the regioselectivity of the hydroboration is the same as observed previously [1,2].

In the cases of **1d**, **2d** and **3d**, the Me_3Si group might compete with the other silyl group for directing the course of hydroboration. Therefore, it is remarkable that the boron atom in **4d** and **5d** is linked to the carbon

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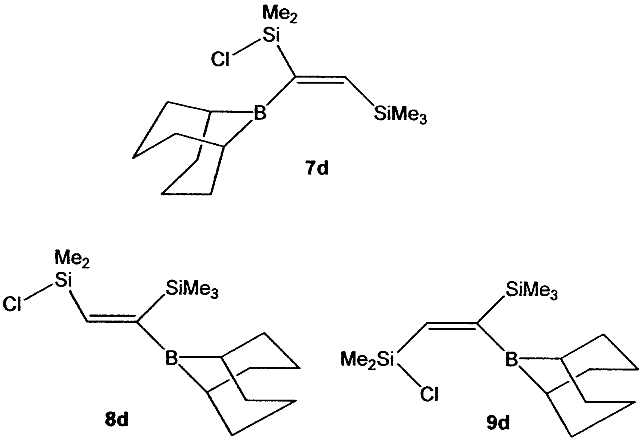
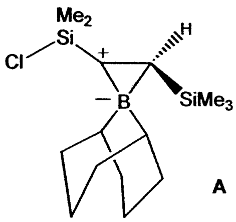
atom next to the silicon atom bearing the functional substituent(s) with high selectivity (> 96%). However, the reaction of **3d** with 9-BBN affords a mixture containing **6d**, the (*E*)-isomer **7d**, and the (*Z*,*E*)-isomers **8d** and **9d**, in which the boron atom has become attached to the carbon atom adjacent to the Me_3Si group.



Formulae 7d, 8d, 9d

Although this loss of regioselectivity might be traced to the more severe reaction conditions, the presence of *cis*/*trans* isomers is less easy to explain. Recently we have studied the reaction of bis(trimethylsilyl)ethyne, $Me_3Si{-}C{\equiv}C{-}SiMe_3$, with 9-BBN: hydroboration leads first to the expected (*Z*)-isomer, and then, after several days at room temperature, complete rearrangement into the (*E*)-isomer takes place [10]. It has been suggested [10] that reactive structures (see **A**), based on π-σ delocalisation involving the boryl group and the stabilising effect exerted by silyl groups on positively charged centres in β-position [11], play an important role.

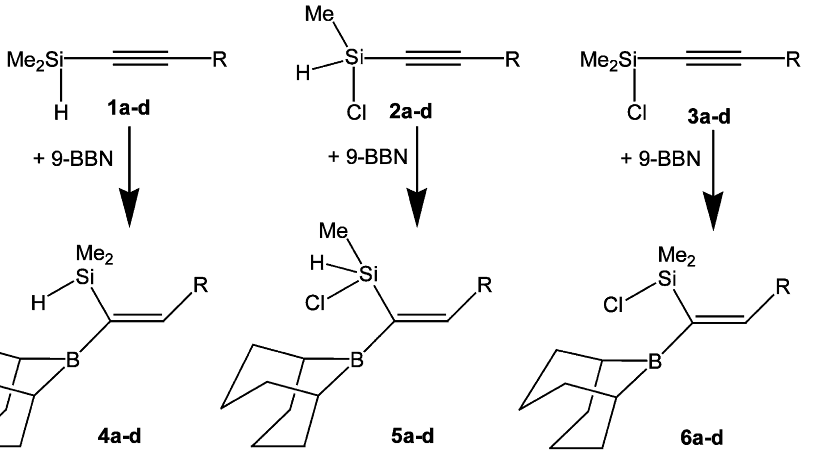


Formula A

All alkenylsilanes **4**–**6** and the mixture containing **6d**–**9d** are sensitive to air and moisture. The compounds are colourless, oily liquids or solids (**5c** and **6c**), and can be stored for prolonged time without decomposition. The compound **5d** and similar derivatives have already been shown to be versatile synthons for heterocyclic synthesis [6,7].

2.2. NMR spectroscopic results

Structural assignments of the alkenylsilanes **4**–**6** and of the mixture containing **6d**–**9d** in solution are based on a consistent set of ^1H (see Section 4), ^{11}B-, ^{13}C- and ^{29}Si-NMR data (Table 1). The region for olefinic carbon atoms in the ^{13}C-NMR spectra is particularly instructive since there is a sharp and a weak, broad ^{13}C-NMR signal in each case. The broadening is due to partially relaxed scalar $^{13}C{-}^{11}B$ spin–spin coupling [12,13]. In the cases of **4**–**6**, the sharp signals are not accompanied by ^{29}Si satellites (except for **4d**, **5d** and **6d** with R = $SiMe_3$) which indicates that both the boryl and the functionally substituted silyl group must be linked to the same olefinic carbon atom. In the cases of **8d** and **9d**, the sharp signals show ^{29}Si satellites corresponding to $^1J(^{29}Si,^{13}C)$, and the magnitude of these coupling



R	Bu	*t*Bu	Ph	$SiMe_3$
	a	**b**	**c**	**d**

Scheme 1.

Table 1
^{11}B-, ^{13}C- and ^{29}Is-NMR data [a] of the alkenes **4**–**9**

	δ^{13}C Si(B)C=	δ^{13}C RC=	δ^{13}C SiMe	δ^{13}C R	δ^{13}C BBN	δ^{11}B	δ^{29}Is
4a	145.2 (br) (57.9)	161.1	−1.9 (50.3)	34.9, 31.9, 22.9, 14.3	30.7 (br), 34.3, 23.8	80.8.6	−27.8
4b	143.6(br) (57.6)	168.8	−1.0 (51.0)	37.0, 31.0	31.2 (br), 34.5, 23.6	81.9	−27.5
4c [b]	149.2 (br) (55.8)	153.8	−1.7 (51.1)	140.3 (*i*), 128.9 (*o*), 128.0 (*m*), 127.8 (*p*)	30.8 (br), 34.1, 23.3	82.3	−26.3
4d	173.5 (br) (55.4)	159.0 (64.0)	−1.8 (49.9)	1.0 (51.5)	31.3 (br), 34.2, 23.6	82.0	−21.7, −9.9 (SiMe$_3$), ⟨8.1⟩
5a	141.8 (br) (64.1)	165.2	2.3 (56.1)	34.9, 31.5, 22.8, 14.2	30.7 (br), 34.2, 34.3, 23.7	80.8	−4.5
5b	140.5 (br) (65.6)	170.6	3.1 (56.9)	37.4, 30.7	31.6 (br), 34.2, 34.9, 23.6	82.1	−4.3
5c	145.5 (br) (64.7)	157.9	2.3 (57.3)	139.5 (*i*), 129.4 (*o*), 129.3 (*m*), 128.5 (*p*)	31.3 (br), 34.5, 34.6, 23.7	84.7	−3.1
5d	168.0 (br) (64.2)	164.2 (61.0)	2.3 (56.0)	0.8 (52.0)	31.3 (br), 34.1, 34.4, 23.5	82.2	−1.5 −8.8 (SiMe$_3$), ⟨9.1⟩
6a	146.5 (br) (64.5)	159.6	5.4 (56.9)	35.3, 31.8, 22.9, 14.3	31.4 (br), 34.4, 23.6	81.8	17.5
6b [c]	145.1 (br) (66.0)	163.6	7.1 (57.9)	36.6, 30.5	32.2 (br), 33.6, 23.6	82.1	17.8
6c	151.1(br) (63.5)	153.3	5.2 (57.2)	140.8 (*i*), 128.8 (*o*), 128.7 (*m*), 128.4 (*p*)	31.8 (br), 34.6, 23.6	83.5	18.6
6d	173.1 (br) (64.5)	157.5 (62.7)	5.3 (56.5)	0.8 (52.1)	– [d]	82.0– [d]	17.0, −9.2 (SiMe$_3$), ⟨7.4⟩
7d	183.0 (br)	150.8 (62.8)	4.3 (58.5)	1.8 (51.5)	– [d]	82.0– [d]	13.8, −9.4 (SiMe$_3$), ⟨15.3⟩
8d	173.5 (br)	143.1 [e] (76.3)	3.8 (58.0)	0.7 (51.1)	– [d]	82.0– [d]	19.3 −9.8 (SiMe$_3$), ⟨8.0⟩
9d	183.4 (br)	140.0 [e] (75.0)	3.4 (56.4)	1.7 (52.3)	– [d]	82.0– [d]	19.8 0.0 (SiMe$_3$), ⟨15.0⟩

[a] In C_6D_6, if not noted otherwise; coupling constants $^1J(^{29}\mathrm{Si},^{13}\mathrm{C})$ are given in parentheses, and $J(^{29}\mathrm{Si},^{29}\mathrm{Si})$ in ⟨ ⟩ (all accurate to at least ±0.3 Hz); (br) denotes the broadened ^{13}C-NMR signal of a carbon atom linked to boron.

[b] In $CDCl_3$.

[c] Data from Ref. [7].

[d] Overlapping resonance signals of all four isomers without assignment.

[e] ^{13}C(=C(H)SiMe$_2$Cl) signal.

constants is typical [14] for silicon bearing an Si–Cl function.

The ^{11}B-NMR signals of the alkenylsilanes are not highly diagnostic for structural assignments. However, they are found in a narrow range, characteristic [13b,c,15] of alkenylboranes with small or negligible CB(pp)π interactions. Further valuable, complementary evidence for the proposed structures is provided by ^{29}Si-NMR spectra which can readily be measured to show ^{13}C satellites (Fig. 1) or ^{29}Si satellites (**4d**–**9d**). The ^{13}C satellites enable one to determine in particular those coupling constants $^1J(^{29}\mathrm{Si},^{13}\mathrm{C})$ which are not readily available from ^{13}C-NMR spectra, considering the broad and weak ^{13}C-NMR signals of quaternary carbon atoms linked to boron. Since $|^3J(^{29}\mathrm{Si},^{29}\mathrm{Si})_{trans}| > |^3J(^{29}\mathrm{Si},^{29}\mathrm{Si})_{cis}|$ (see Table 1 for **6d** and **7d** or **8d** and **9d**), a further tool for structural assignments is at hand.

The growing evidence for weak Si–H–B bridges in alkenes which bear a Me$_2$(H)Si and a boryl group in *cis*-positions [16] prompted us to look for this particular structural feature in the case of the alkenes **4** and **5**, where these groups are in geminal positions. However, the δ^{29}Si and δ^{11}B of **4** and **5** do not reflect any significant Si–H–B interarctions, and the most typical effect, the marked isotope-induced chemical shifts $^2\Delta^{10/11}$B(^{29}Si) mediated by Si–H–B bridges [16,17], was not observed. Similarly, any Si–Cl–B bridging [17] in **5** or **6** must be extremely weak in solution, in agreement with the rather large B···Cl separation in the solid-state molecular structures of both **5c** and **6c** (vide infra).

2.3. X-ray structural analysis of the alkenylsilanes **5c** and **6c**

The molecular structures of **5c** and **6c** are shown in the Figs. 2 and 3, respectively, and selected bond lengths and angles are given in Table 2. Intermolecular interactions appear to be weak and do not have any significant influence on the molecular structures. The structural parameters of both compounds are similar although they crystallise in different crystal systems [triclinic (**5c**), and monoclinic (**6c**)]. Repulsion between the substituents at the C = C bond leads to geometrical distortions. Thus, the substituents at the C=C bond are not in one plane: e.g. the silyl and the boryl groups are shifted out of the C=C–C(Ph) plane by about 10° to either side. The boryl group is twisted against the C=C–B plane by 38° in **5c** and 55° in **6c** which reflects the greater sterical demand of the Me$_2$(Cl)Si group when compared with the Me(H)(Cl)Si group. The plane of the phenyl group forms an angle with the C=C–C(Ph) plane of 32.6° in **5c** and 43° in **6c**; the difference is again most likely due to the greater bulkiness of the Me$_2$(Cl)Si group in **6c**. In both molecules the Cl···B separations are fairly long (351.7 pm in **5c** and 333.2 pm in **6c**), indicating

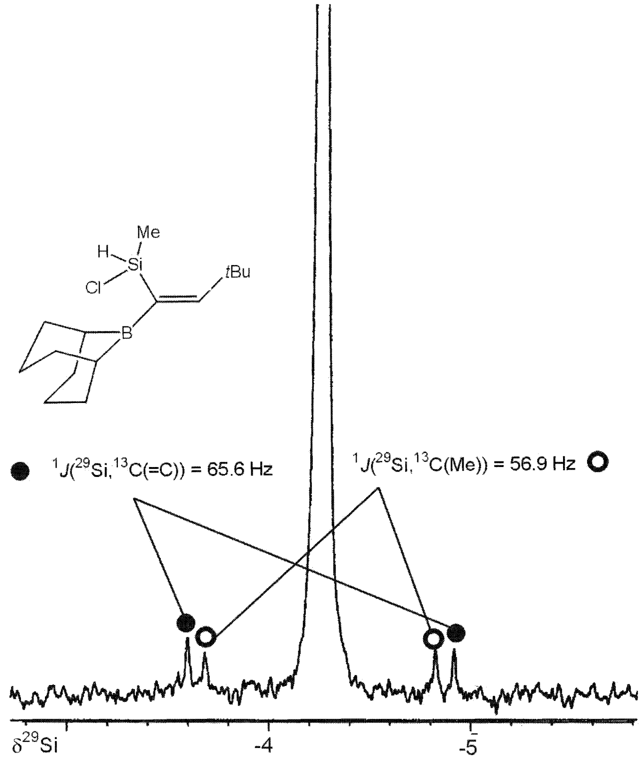


Fig. 1. 49.7 MHz ^{29}Si{^{1}H}-NMR spectrum of **5b** (ca. 15% v/v in C_6D_6, 23±1 °C; result of 128 transients; acquisition time 6 s; repetition time 10 s; INEPT, based on $^1J(^{29}$Si,^{1}H) = 227.4 Hz), showing the two pairs of ^{13}C satellite signals. One pair, for $^1J(^{29}$Si,^{13}C(Me)), marked by open circles, is known from the ^{13}C-NMR spectrum, whereas the coupling constant $^1J(^{29}$Si,^{13}C(= C)), satellites marked by filled circles, cannot be determined from ^{13}C-NMR owing to the weak broad ^{13}C-NMR signal.

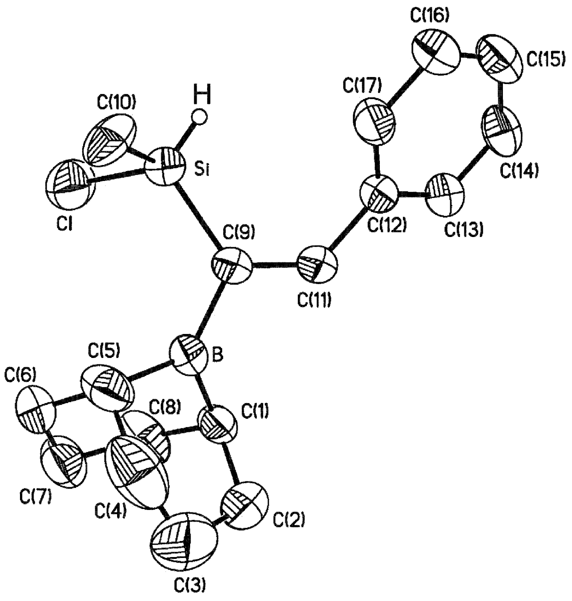


Fig. 2. ORTEP plot (50% probability level; hydrogen atoms, except of Si–H, are omitted for clarity) of the molecular structure of **5c** (see Table 2 for selected bond lengths and angles).

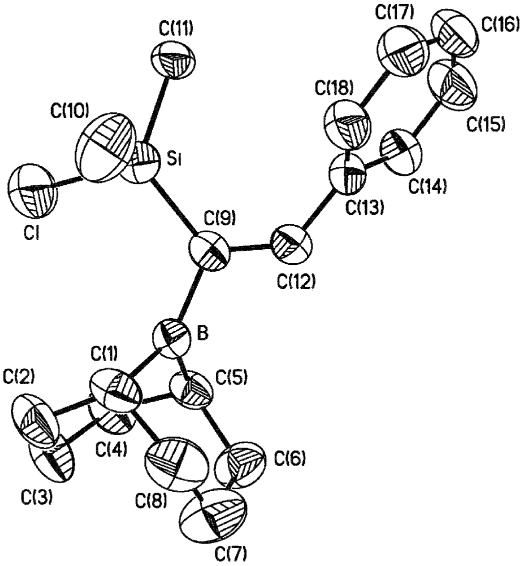


Fig. 3. ORTEP plot (50% probability level; hydrogen atoms are omitted for clarity) of the molecular structure of **6c** (see Table 2 for selected bond lengths and angles).

Table 2
Selected bond lengths (pm) and angles (°) determined by X-ray structural analysis for the compounds **5c** and **6c**

	5c	**6c**
Bond lenghts		
Si–C(9)	186.3(3)	185.5(4)
Si–Cl	206.3(2)	208.0(2)
Si–C(Me)	187.2(4)	188.6(5)
		189.9(4)
B–C(9)	156.1(5)	156.6(5)
B–C(1)	155.8(5)	156.1(6)
B–C(5)	157.2(5)	157.2(6)
C=C	134.8(5)	134.7(5)
C(1)–C(2)	153.3(4)	153.5(6)
C(1)–C(8)	154.9(6)	153.5(7)
C(2)–C(3)	150.4(8)	152.0(7)
C(7)–C(8)	150.1(6)	150.9(8)
Bond angles		
=C–C(Ph)	147.6(5)	147.2(5)
B–C(9)–Si	120.1(2)	119.4(3)
Si–C(9)=C	123.8(3)	124.8(3)
B–C(9)=C	116.0(3)	115.7(3)
C(1)–B–C(5)	110.4(3)	111.0(3)
C(9)=C–C(Ph)	130.3(3)	128.4(3)

extremely weak or even negligible bonding interactions. This is in agreement with the exactly trigonal planar surroundings of the boron atoms. All bond lengths are in the expected ranges [18,19]. There is a slight elongation of all bonds in β-positions to the boron atom (C=C, =C–Si, C–C in the 9-BBN fragment) which can be explained by hyperconjugative effects, similar to observations for the bonding situation in triethylborane [20].

3. Conclusions

Hydroboration of alkyn(1-yl(methyl)silanes proceeds with high stereo- and regioselectivity in most cases. The geminal positions of the boryl and the functionally substituted silyl group at the C=C bond makes these alkenes useful synthons for further transformations. The directing influence of the functionally substituted silyl group (even in the presence of a Me_3Si group in **4d** and **5d**) is noteworthy. This regioselectivity is observed in spite of the rather crowded situation at the C=C bond as shown by the molecular structures in the solid state.

4. Experimental

4.1. General

Preparation and handling of all compounds were carried out in an atmosphere of dry argon, observing all necessary precautions to exclude air and moisture. Starting materials were commercially available (9-BBN) or were prepared (alkyn-1-ylsilanes) following literature procedures [21]. NMR measurements in C_6D_6, if not mentioned otherwise, with samples in 5 mm tubes at 23 ± 1 °C: Bruker ARX 250 and Bruker DRX 500: ^1H-, ^{11}B-, ^{13}C- and ^{29}Si-NMR (refocused INEPT [22] based on $^1J(^{29}Si,^1H)$ ca. 185 Hz, $^2J(^{29}Si,^1H_{Me})$ ca. 7 Hz); chemical shifts are given with respect to Me_4Si [δ^1H $(C_6D_5H) = 7.15$; $\delta^{13}C$ $(C_6D_6) = 128.0$; $\delta^{29}Si = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz]]; external $BF_3{-}OEt_2$ [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz]. IR spectra (**4** and **5**: narrow range of $\nu(Si{-}H) = 2115 \pm 10$ cm^{-1}) were recorded using a Perkin Elmer instrument Spectrum 2000 FT IR, and EIMS spectra were measured with a Finnigan MAT 8500 spectrometer (ionisation energy 70eV) with direct inlet (all compounds **4**–**6** showed the respective molecular ion peaks with low intensity).

4.2. Reaction of the alkyn-1-ylsilanes (1) with 9-BBN (general procedure)

The alkyn-1-ylsilanes **1** (2 mmol) were dissolved in pentane (10 ml), and the solution was cooled to −78 °C. Then an equimolar amount of 9-BBN was added as a solid in one portion. The mixtures were warmed to room temperature and kept stirring for 2 h. Then volatile materials were removed in vacuo, and colourless, oily liquids were left, identified as the pure (> 95% by ^1H-NMR) alkenes **4a**–**d**.

4a: ^1H-NMR (250 MHz): $\delta^1H = 0.24$ (d, $^3J(^1HSiC^1H) = 3.9$ Hz; 6H, $SiMe_2$), 0.84 (t, 3H, Me(Bu)), 2.31 (m, 2H, $=CCH_2$(Bu)), 4.57 (sp, $^3J(^1HSiC^1H) = 3.9$ Hz; 1H, SiH, $^1J(^{29}Si,^1H) = 183.5$ Hz), 7.05 (t, 1H, =CH), and overlapping multiplets for 9-BBN and $-CH_2CH_2$ (Bu). **4b**: ^1H-NMR (250 MHz): $\delta^1H = 0.30$ (d, $^3J(^1HSiC^1H) = 3.9$ Hz; 6H, $SiMe_2$), 1.20 (s, 9H, *t*Bu), 1.30–2.00 (m, 14H, 9-BBN), 4.80 (sp, $^3J(^1HSiC^1H) = 3.9$ Hz; 1H, SiH, $^1J(^{29}Si,^1H) = 185.3$ Hz), 7.13 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 18.0$ Hz). **4c**: ^1H-NMR ($CDCl_3$, 250 MHz): $\delta^1H = 0.22$ (s, $^3J(^1HSiC^1H) = 3.9$; 6H, $SiMe_2$), 1.20–2.00 (m, 14H, 9-BBN), 4.58 (sp, $^3J(^1HSiC^1H) = 3.9$; 1H, SiH, $^1J(^{29}Si,^1H) = 187.0$ Hz), 7.00–7.30 (m, 5H, =CPh), 8.00 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 15.7$ Hz). **4d**: ^1H-NMR (250 MHz): $\delta^1H = 0.26$ (d, $^3J(HSiC^1H) = 3.8$ Hz; 6H, $SiMe_2$), 0.27 (s, 9H, $SiMe_3$), 1.30–1.90 (m, 14H, 9-BBN), 4.64 (sp, $^3J(^1HSiC^1H) = 3.8$ Hz; 1H, SiH, $^1J(^{29}Si,^1H) = 185.0$ Hz), 7.45 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 24.0$ Hz; $^2J(^{29}Si,^1H) = 8.0$ Hz).

4.3. Reaction of the alkyn-1-ylsilanes (2) with 9-BBN (general procedure)

The procedure was the same as described for **1**, except that stirring at room temperature was continued for 4 d until the reaction was complete.

5a: ^1H-NMR (250 MHz): $\delta^1H = 0.52$ (d, $^3J(HSiC^1H) = 3.4$ Hz; 3H, SiMe), 0.81 (t, 3H, Me(Bu)), 2.33 (m, 2H, $=CCH_2$(Bu)), 5.47 (q, $^3J(HSiC^1H) = 3.4$ Hz; 1H, SiH, $^1J(^{29}Si,^1H) = 222.6$ Hz), 7.2 (t, 1H, =CH), and overlapping multiplets for 9-BBN and $-CH_2CH_2$ (Bu). **5b**: ^1H-NMR (250 MHz): $\delta^1H = 0.57$ (d, $^3J(HSiC^1H) = 3.3$ Hz; 3H, SiMe), 1.08 (s, 9H, *t*Bu), 1.40–2.00 (m, 14H, 9-BBN), 5.57 (q, $^3J(HSiC^1H) = 3.3$ Hz; 1H, SiH, $^1J(^{29}Si,^1H) = 227.4$ Hz), 7.02 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 22.7$ Hz). **5c**: yield after recrystallisation from pentane at −20 °C was 84%; m.p. 64–66 °C; ^1H-NMR (250 MHz): $\delta^1H = 0.53$ (d, $^3J(HSiC^1H) = 3.4$ Hz; 3H, SiMe), 1.40–2.10 (m, 14H, 9-BBN), 5.32 (q, $^3J(HSiC^1H) = 3.4$ Hz; 1H, SiH, $^1J(^{29}Si,^1H) = 229.3$ Hz), 7.20–7.40 (m, 5H, =CPh), 8.08 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 20.0$ Hz). **5d**: ^1H-NMR (250 MHz): $\delta^1H = 0.30$ (s, 9H, $SiMe_3$), 0.60 (d, $^3J(HSiC^1H) = 3.4$ Hz; 3H, SiMe), 1.30–2.0 (m, 14H, 9-BBN), 5.50 (q, $^3J(HSiC^1H) = 3.3$ Hz; 1H, SiH, $^1J(^{29}Si,^1H) = 222.9$ Hz), 7.60 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 28.5$ Hz, $^2J(^{29}Si,^1H) = 8.0$ Hz).

4.4. Reaction of the alkyn-1-ylsilanes (3) with 9-BBN (general procedure)

The procedure was the same as described for **1**, except that hexane served as the solvent, and that the mixture was heated at reflux for 20 h.

6a: ^1H-NMR (250 MHz): $\delta^1H = 0.56$ (s, 6H, $SiMe_2$), 0.83 (t, 3H, Me(Bu)), 2.26 (m, 2H, $=CCH_2$(Bu)), 6.80 (t, 1H, =CH), and overlapping multiplets for 9-BBN and CH_2CH_2 (Bu). **6b**: ^1H-NMR (250 MHz): $\delta^1H = 0.50$ (s, 6H, $SiMe_2$), 1.06 (s, 9H, *t*Bu)), 1.39–2.10 (m, 14H, 9-BBN), 6.70 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 22.0$ Hz). **6c**: yield after recrystallisation from pentane at −20 °C was

Table 3
Data relevant to the crystal structure determinations of **5c** and **6c** at 23 ± 1 °C

	5c	**6c**
Formula	$C_{18}H_{26}BClSi$	$C_{17}H_{24}BclSi$
Crystal	Colourless plate	Colourless plate
Dimensions (mm^3)	0.40 × 0.18 × 0.08	0.18 × 0.12 × 0.07
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	2095.4(2)	757.70(7)
b (Å)	651.45(11)	972.10(10)
c (Å)	1343.65(16)	1242.03(19)
α (°)	–	93.262(9)
β (°)	90.371(7)	98.005(7)
γ (°)	–	110.302(6)
V (10^6 pm^3)	1834.1(4)	844.17(17)
Z	4	2
Absorption coefficient μ (mm^{-1})	0.266	0.286
Diffractometer	Siemens P4, (Mo–K_α, $\lambda = 71.073$ pm); graphite monochromator	Siemens P4, (Mo–K_α, $\lambda = 71.073$ pm); graphite monochromator
Measuring range (ϑ)	3–25	3–25
Reflections collected	4306	3592
Independent reflections ($I > 2\sigma(I)$)	2193	2216
Absorption correction	Empirical (Ψ-scans)	No correction
Min./max. transmission	0.5455/0.5638	–
Refined parameters	191	182
wR_2/R_1 value ($I > 2\sigma(I)$)	0.072/0.198	0.082/0.153
Max./min. residual electron density (e pm^{-3} 10^{-6})	0.42/−0.46	0.43/−0.35

80%; m.p. 73–75 °C; ^{1}H-NMR (250 MHz): $\delta^1H = 0.43$ (s, 6H, $SiMe_2$), 1.40–2.10 (m, 14H, 9-BBN), 7.20–7.40 (m, 5H, =CPh), 7.87 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 19.6$ Hz). **6d**: ^{1}H-NMR (250 MHz): $\delta^1H = 0.18$ (s, 9H, $SiMe_3$), 0.51 (s, 6H, $SiMe_2$), 7.17 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 26.4$ Hz, $^2J(^{29}Si,^1H) = 4.6$ Hz), and overlapping resonances since **6d** is in mixture with **7d**–**9d**. **7d**: ^{1}H-NMR (250 MHz): $\delta^1H = 0.13$ (s, 9H, $SiMe_3$), 0.39 (s, 6H, $SiMe_2$), 6.80 (s, 1H, =CH, $^3J(^{29}Si,^1H) = 21.2$ Hz, $^2J(^{29}Si,^1H) = 5.9$ Hz), and overlapping resonances since **7d** is in mixture with **6d**, **8d** and **9d**.

*4.5. Crystal structure determinations of the alkenylsilanes **5c** and **6c***

Single crystals of **5c** and **6c**, respectively, recrystallised from pentane at −20 °C, were sealed under argon in a Lindemann capillary. The hydrogen atoms are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors. Further information is listed in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 192068 and 192067 for compounds **5c** and **6c**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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