1,2-Hydroboration of Alkyn-1-yl(chloro)silanes: Alkenes Bearing Chlorosilyl and Dialkylboryl Groups in Geminal Positions

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The 1,2-hydroboration of various alkyn-1-yl(chloro)silanes (**3** – **7**), derived from 1-hexyne (**a**) and ethynylbenzene (**b**), using 9-borabicyclo[3.3.1]nonane, 9-BBN, affords selectively alkene derivatives in which the dialkylboryl and chlorosilyl groups are in geminal positions at the C=C bond. The molecular structure of (*Z*)-α-(9-borabicyclo[3.3.1]non-9-yl)-α-dichloro(phenyl)silyl-styrene (**11b**) was determined by X-ray diffraction. All alkenes were characterised by a consistent set of NMR spectroscopic data (^{1}H, ^{11}B, ^{13}C, ^{29}Si NMR).

Key words: Alkynes, Alkenes, Boranes, Silanes, Hydroboration, NMR

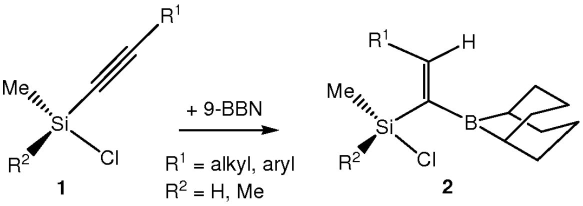
Introduction

There is considerable interest in the synthesis of alkenes bearing both boryl and silyl groups [1 – 9]. Among these, alkenes with silyl and boryl groups in geminal positions with functional group(s) at silicon would be highly welcome synthons for various transformations [7 – 9]. 1,2-Hydroboration of alkyn-1-ylsilanes appears to be an attractive route to such alkenes, if the 1,2-hydroboration proceeds in a regiospecific way. This has been shown for alkyn-1-yl(chloro)silanes of type **1** which react with 9-BBN to give **2** [8] (Scheme 1).

In the present work, analogous results were expected for a greater variety of substituents at silicon in the alkyn-1-yl(chloro)silanes **3** – **7**, including up to three Si–Cl functions as in **7**. One further goal was to obtain direct structural evidence for such alkenes related to **2**. Therefore, phenyl groups at both silicon and the C≡C bond have been introduced in order to obtain suitable crystalline products.

Results and Discussion

The alkyn-1-yl(chloro)silanes **3** – **7** were prepared in the usual way [10,11] from the respective chlorosilanes and alkynyllithium reagents. In general, this route leads to mixtures containing the desired products along with alkyn-1-ylsilanes, in which more than one Si–Cl function is substituted by an alkyn-1-yl group. Apparently, such side reactions cannot be suppressed, even by using a large excess of the starting chlorosilane. These mixtures can be separated by distillation to give the pure alkyn-1-yl(chloro)silanes **3** – **7** (see for example the ^{13}C NMR spectrum of **4a** in Fig. 1).



Scheme 1. Previous results [8] for 1,2-hydroboration of alkyn-1-yl(chloro)silanes using 9-BBN.

The 1,2-hydroboration of the alkyn-1-yl(chloro)silanes **3** – **7** (Scheme 2) is straightforward in most cases, as shown, and the alkenes **10** have already been used for further reactions [9].

The regioselectivity of the 1,2-hydroboration follows from a consistent set of NMR parameters (Table 1 and Experimental Section; *vide infra*). In the solid state, this stereochemistry is confirmed by an X-ray structure determination of the crystalline derivative **11b** (*vide infra*). Except for **9b** and **11b**, the alkenes **8** – **12** are colourless, air- and moisture-sensitive oils or waxy solids.

Solely in the case of the reaction of **3a** with 9-BBN, a mixture of isomers **8a** and **8a′** (see Fig. 2 for the ^{29}Si NMR spectrum) was obtained, independent of various reaction conditions. This result can be explained considering a fast second hydroboration of the

Table 1. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the alkenes **8 – 16**.

	δ^{13}C Si(B)C=	δ^{13}C R1C=	δ^{13}C Ph(Si)/R2	δ^{13}C R1	δ^{13}C BBN	δ^{11}B	δ^{29}Si
8a[b]	143.0 (br) [65.1]	161.7	135.3 (*i*) [74.1], 131.2 (*o*), 127.6 (*m*), 128.2 (*p*)	35.3, 31.2, 21.9, 13.5	33.4, 33.3, 30.5 (br), 23.2	81.4	−54.2
8a′	139.2 (br) [57.2]	166.8	134.0 (*i*) [66.1], 130.3 (*o*), 128.1 (*m*), 133.9 (*p*)	35.1, 31.1, 22.4, 13.9	33.9, 33.8, 30.3 (br), 23.1	81.4	−38.5
8b	142.3 (br)	159.9	134.2 (*i*) [76.9], 134.3 (*o*), 128.1 (*m*), 129.3 (*p*)	138.5 (*i*), 130.4 (*o*), 129.4 (*m*), 128.2 (*p*)	34.5, 34.2, 31.3 (br), 23.4	82.2	−12.0
9a	144.0 (br)	161.5	137.5 (*i*) [74.6], 133.5 (*o*), 127.9 (*m*), 129.9 (*p*), 4.2 [58.9] (SiMe)	35.3, 23.1, 22.4, 13.5	33.9, 33.8, 31.2 (br), 31.1	81.6	7.6
9b[b]	148.3 (br)	156.1	133.8 (*i*) [70.9], 134.0 (*o*), 129.2 (*m*), 130.4 (*p*), 3.7 [59.8] (SiMe)	138.0 (*i*), 130.2 (*o*), 129.0 (*m*), 128.2 (*p*)	34.7, 34.4, 31.9 (br), 23.5	82.2	7.9
10a	142.9 (br)	163.3	136.0 (*i*) [77.8], 134.9 (*o*), 128.3 (*m*), 130.4 (*p*)	35.9, 31.2, 22.6, 13.9	34.2, 31.6 (br), 23.4	81.7	−5.7
10b	144.3 (br)	157.9	135.4 (*i*) [78.9], 134.5 (*o*), 127.8 (*m*), 128.7 (*p*)	138.3 (*i*), 130.0 (*o*), 129.4 (*m*), 127.5 (*p*)	34.2, 31.6 (br), 23.1	83.1	−2.1
11a	141.6 (br)	164.8	135.3 (*i*) [90.7], 133.3 (*o*), 128.2 (*m*), 131.2 (*p*)	35.3, 30.9, 22.4, 13.9	34.0, 31.2 (br), 23.0	82.7	3.4
11b	143.9 (br) [79.2]	158.6	138.2 (*i*) [92.7], 133.3 (*o*), 128.0 (*m*), 128.2 (*p*)	132.7 (*i*), 129.4 (*o*), 127.9 (*m*), 125.4 (*p*),	34.3, 31.6 (br), 23.1	83.6	2.2
12a[b]	141.8 (br)	167.0	–	35.4, 31.1, 22.8, 14.1	34.5, 31.6 (br), 23.4	81.5	−3.9
12b[b]	143.0 (br) [95.7]	160.8	–	138.0 (*i*), 130.4 (*o*), 129.8 (*m*), 128.4 (*p*)	34.7, 31.9 (br), 23.4	81.3	−4.8

[a] Measured in $CDCl_3$at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling [15]; some coupling constants $^1J(^{29}Si,^{13}C)$ are given in brackets; [b] measured in C_6D_6.

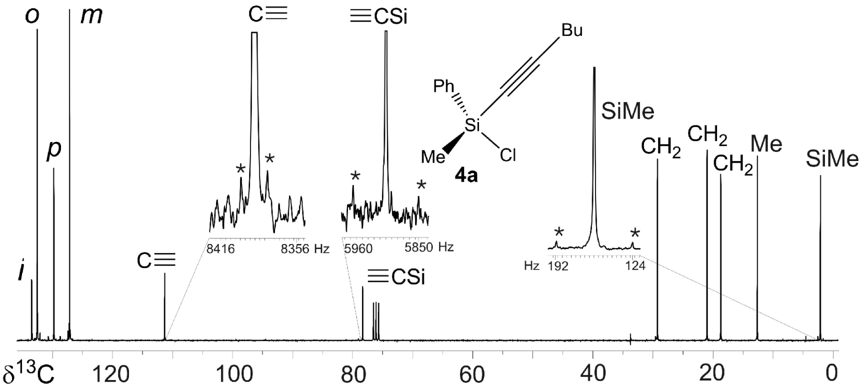


Fig. 1. 75.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the alkyn-1-yl(chloro)silane **4a** in $CDCl_3$ at 23 °C. Expansions are given for the signals showing ^{29}Si satellites, marked by asterisks, corresponding to $^1J(^{29}Si,^{13}C)$ and $^2J(^{29}Si,^{13}C)$.

alkene **8a** leading to 1,1,1-diboryl(silyl)hexane or 1,2-diboryl-1-silylhexane (both were not detected) as intermediates (Scheme 3), which upon dehydroboration afford mainly the mixture of the isomers **8a** and **8a′**. There are two additional signal of appreciable intensity in the ^{29}Si NMR spectrum at $\delta = -43.7$ and -54.0 which can be tentatively assigned to the isomers **8a″** and **8a‴** (Fig. 2). The presence of **8a′** in the mixture is readily shown by the set of NMR parameters (Fig. 2, Table 1 and Experimental Section).

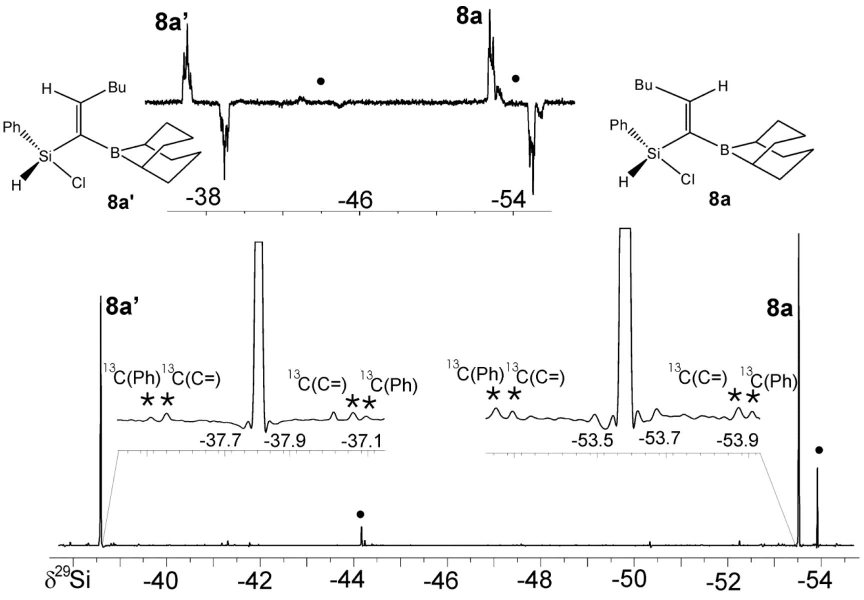
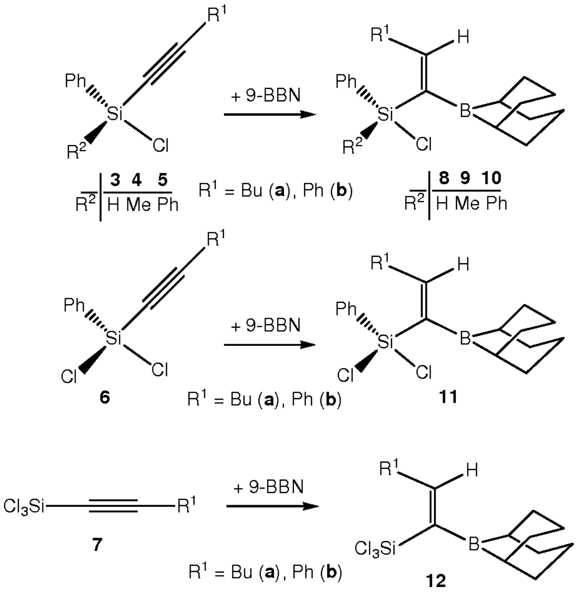


Fig. 2. 79.47 MHz ^{29}Si NMR spectra (INEPT) of the mixture of isomers **8a** and **8a′**. The upper trace shows the ^{1}H coupled spectrum, the middle traces show expansions of the ^{1}H decoupled ^{29}Si NMR signals with ^{13}C satellites, and the lower trace shows the full spectrum. Additional signals, marked with filled circles, are tentatively assigned to the isomers **8a″** and **8a‴** (δ^{29}Si = −43.7, $^{1}J(^{29}\text{Si},^{1}\text{H})$ = 197.0 Hz; δ^{29}Si = −54.0, $^{1}J(^{29}\text{Si},^{1}\text{H})$ = 208.3 Hz); see Scheme 3.



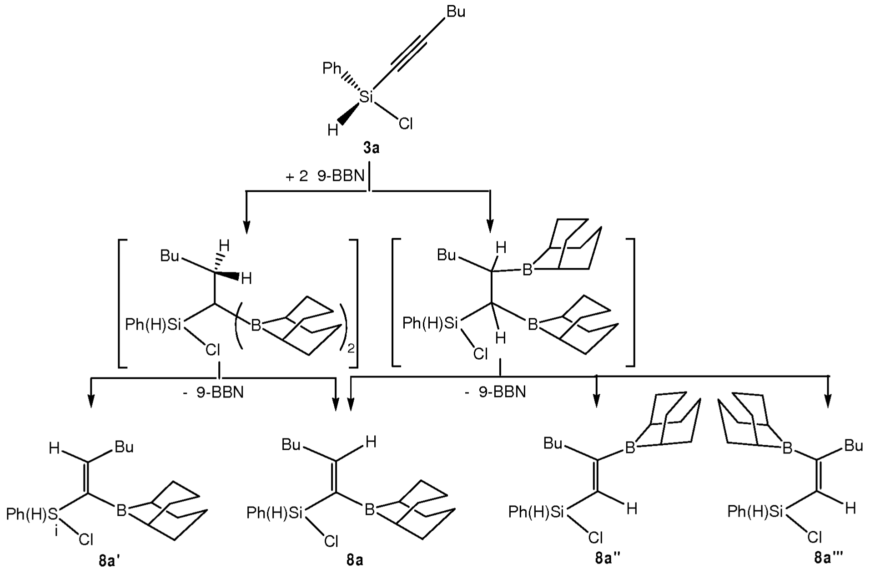
Scheme 2. Present results for 1,2-hydroboration of alkyn-1-yl(chloro)silanes with various substituents on silicon, using 9-BBN.

The stereochemistry proposed for the solution-state structure of the alkenes **8**–**12** is in agreement with the results of ^{1}H NMR spectroscopy using ^{1}H/^{1}H-NOE difference spectra [14]. The pattern of substituents at the C=C bond can also be assigned unambiguously on the basis of the ^{13}C NMR data. An inspection of Table 1 clearly indicates that the alkenes possess analogous structures. In the olefinic range, the presence of a broad weak signal is typical for the B–C bond [15]. The sharp signal for the other olefinic carbon atom does not show ^{29}Si satellites ($^{2}J(^{29}\text{Si},^{13}\text{C}) < 3$ Hz) which means that the silyl group is attached to the same olefinic carbon atom as the boryl group. In principle, this can be shown in ^{13}C NMR spectra by ^{29}Si satellites corresponding to $^{1}J(^{29}\text{Si},^{13}\text{C})$. However, these signals are weak and broad and therefore, it is difficult to obtain the signal-to-noise ratio required for this purpose. The most convenient access to these data $^{1}J(^{29}\text{Si},^{13}\text{C})$ is provided by observing the ^{13}C satellites in the ^{29}Si NMR spectra. This is shown in Fig. 2 and also in Fig. 3. The presence of the boryl group at the same olefinc carbon typically [16] reduces the magnitude of $^{1}J(^{29}\text{Si},^{13}\text{C})$ in the order of 10 to 15 Hz in comparison with other alkenylsilanes.

The ^{11}B chemical shifts [17] are characteristic for alkenyl(dialkyl)boranes, in which a conformation is preferred where the boryl group is significantly twisted against the B–C=C plane. The ^{29}Si chemical shifts are in the expected range considering the various substituent effects [16]. The fairly large difference between the δ^{29}Si values for **8a** and **8a′** corresponds to the trend known for δ^{13}C of alkyl substituents in (*Z,E*)-alkenes [18].

*Structure determination of the alkene **11b***

The molecular structure of the alkene **11b** is shown in Fig. 3, together with selected structural parame-



Scheme 3. Potential reason for the loss of stereo- and regioselectivity of the 1,2-hydroboration of chloro(hexyn-1-yl)(phenyl)silane **3a**.

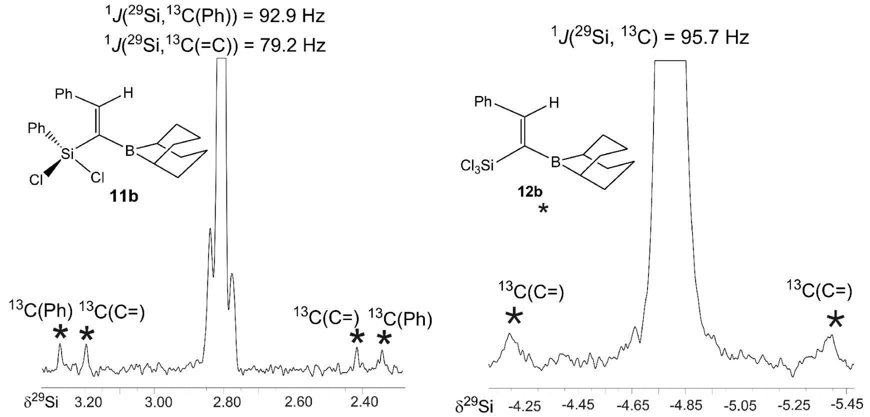


Fig. 3. 99.4 MHz (left) and 79.47 MHz (right) $^{29}Si\{^1H\}$ NMR spectra of the alkenyl(chloro)silanes **11b** and **12b**, respectively. The line widths of the ^{29}Si NMR signals increase with the number of chlorine atoms linked to silicon owing to unresolved scalar one-bond $^{35/37}Cl$–^{29}Si spin-spin coupling, and there is also a contribution from unresolved scalar two-bond coupling $^2J(^{29}Si,^{11}B)$. In the case of **11b**, further ^{13}C satellites are visible, close to the parent signal, which arise from $^nJ(^{29}Si,^{13}C)$ ($n \geq 2$).

ters. Intermolecular contacts are negligible. Silicon, boron and the C=C unit are in the same plane, The CBC plane of the 9-BBN unit is twisted against this plane by 18.3°, the planes of the C–Ph and Si–Ph rings by 33.1° and 64.6°, respectively. The distances between Cl1 and Cl2 and the boron atom are long (459.1 pm and 409.1 pm). All other bond lengths and angles are well comparable with structural data already published for alkenes of type **2** [6]. In the latter, it appears that the Si–Cl group prefers an orientation towards the boryl group, and one was tempted to propose a weak donor-acceptor interaction, a Si–Cl–B bridge, at least in the solid state. In solution, however, the NMR data for compounds of type **2** indicate the absence of such interactions. In the present work this is confirmed by the molecular structure of **11b**, where the phenyl group is close to the boron atom, and Si–Cl–B bridges can be clearly discarded.

Conclusions

1,2-Hydroboration of alkyn-1-ylsilanes bearing hydrogen, alkyl, phenyl and up to three chloro functions on silicon proceeds regio- and stereoselectively in such

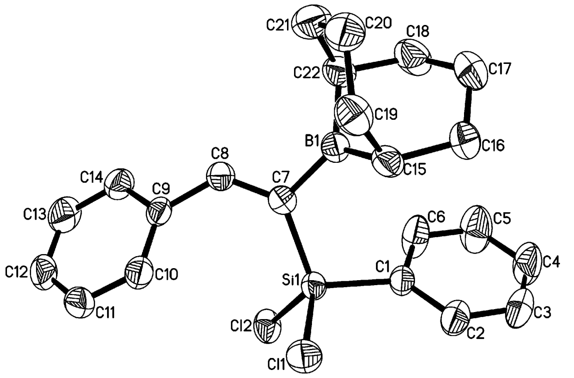


Fig. 4. Molecular structure of **11b** (ORTEP, at the 50 % probability level; hydrogen atoms omitted for clarity). Selected bond lengths (pm) and bond angles (deg): C1–Si1 185.2(2), C7–C8 135.0(3), C7–B1 156.1(3), C7–Si1 184.2(2), C15–C16 154.0(4), C15–C19 155.1(4), C15–B1 156.5(4), C16–C17 151.2(4), C19–C20 151.8(4), C22–B1 155.9(4), Si1–Cl1 204.86(9), Si1–Cl2 205.60(8); C8–C7–B1 116.5(2), C8–C7–Si1 127.5(2), B1–C7–Si1 115.9(2), C7–C8–C9 130.7(2), C22–B1–C15 111.4(2), C7–B1–C15 122.9(2), C7–Si1–C1 108.7(1), C7–Si1–Cl1 114.39(8), C1–Si1–Cl1 108.66(9), C7–Si1–Cl2 111.92(8), C1–Si1–Cl2 106.49(8), Cl1–Si1–Cl2 106.38(4).

a way that alkenylsilanes are formed, in which the boryl group becomes attached to the olefinic carbon atoms which already bear the silyl group. If the reaction cannot be controlled to proceed solely to the first step, stereoselectivity and to some extent regioselectivity are lost.

Experimental Section

All preparative work was carried out by observing necessary precautions to exclude traces of oxygen and moisture. The starting chlorosilanes, 1-hexyne, ethynylbenzene, butyllithium in hexane (1.6 M) and 9-BBN were used as commercial products without further purification. NMR spectra were recorded at 23 °C on Bruker DRX 500 or Varian Inova 300 and 400 spectrometers, all equipped with multinuclear units, using C_6D_6 or $CDCl_3$ solutions (*ca.* 10 – 15 % v/v) in 5 mm tubes. Chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_5H) = 7.15, δ^1H ($CDCl_3/CHCl_3$) = 7.25; δ^{13}C (C_6D_6) = 128.0, δ^{13}C ($CDCl_3$) = 77.0], δ^{29}Si = 0 for Me_4Si with $\Xi(^{29}Si)$ = 19.867187 MHz], and δ^{11}B = 0 for $BF_3 \cdot OEt_2$ with $\Xi(^{11}B)$ = 32.083971 MHz. ^{29}Si NMR spectra were recorded using the refocused INEPT pulse sequence with ^{1}H decoupling [19] based on $^1J(^{29}Si,^1H)$ (*ca.* 200 Hz), $^2J(^{29}Si,^1H_{Me})$, $^3J(^{29}Si,^1H_{Ph})$ (*ca.* 7 Hz) or $^3J(^{29}SiC{=}C^1H)$ (*ca.* 20 Hz). Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for ^{12}C, ^{1}H, ^{11}B, ^{35}Cl, ^{28}Si). The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

Synthesis of alkyn-1-yl(chloro)silanes

A freshly prepared suspension of the respective lithium alkynide (19.5 mmol) was cooled to −78 °C, and the respective chlorosilane was slowly added in 2 – 6 fold excess with constant stirring. The reaction mixture was warmed to r. t. and kept stirring for 3 – 4 h. The solution was filtered and volatiles were removed *in vacuo*. The colourless oily residue, a mixture of silanes, was subjected to fractional distillation.

3a: B. p. 105 – 115 °C/0.375 Torr. – ^{1}H NMR (300 MHz; $CDCl_3$): δ = 2.2, 1.5, 1.4, 0.9 (m, m, m, t, 9H, Bu), 4.8 (s, ^1J (^{29}Si, ^{1}H) = 224.9 Hz, 1H, SiH), 7.3 – 7.7 (m, 5H, SiPh). – ^{13}C NMR (75.8 MHz; $CDCl_3$): δ = 111.4 ($J(^{29}Si,^{13}C)$ = 20.1 Hz, C≡), 76.8 ($J(^{29}Si,^{13}C)$ = 105.5 Hz, ≡CSi), 134.5 (*o*-C), 131.8 ($J(^{29}Si,^{13}C)$ = 81.6 Hz, *i*-C), 130.0 (*p*-C), 128.0 (*m*-C, SiPh), 30.3, 21.9, 19.8, 13.6 (Bu). – ^{29}Si NMR (59.6 MHz; $CDCl_3$): δ = −65.8.

3b: B. p. 115 – 126 °C/0.375 Torr. – ^{1}H NMR (300 MHz; $CDCl_3$): δ = 5.4 (s, $^1J(^{29}Si,^1H)$ = 257.6 Hz, 1H, SiH), 7.1 – 7.7 (m, 10H, SiPh, Ph). – ^{13}C NMR (75.8 MHz; $CDCl_3$): δ = 121.2 ($J(^{29}Si,^{13}C)$ = 21.9 Hz, C≡), 85.7 ($J(^{29}Si,^{13}C)$ = 110.1 Hz, ≡CSi), 134.1(*o*-C), 133.2 ($J(^{29}Si,^{13}C)$ = 88.7 Hz, *i*-C), 129.4 (*p*-C), 128.3 (*m*-C, SiPh), 132.3 (*o*-C), 131.4 (*p*-C), 128.3 (*m*-C), 121.3 (*i*-C, Ph). – ^{29}Si NMR (59.6 MHz; $CDCl_3$): δ = −29.9.

4a: B. p. 82 – 88 °C/0.375 Torr. – ^{1}H NMR (300 MHz; $CDCl_3$): δ = 2.2, 1.4, 1.3, 0.7 (m, m, m, t, 9H, Bu), 0.6 (s, 3H, SiMe), 7.2 – 7.6 (m, 5H, SiPh). – ^{13}C NMR (75.8 MHz; $CDCl_3$): δ = 112.3 ($J(^{29}Si,^{13}C)$ = 21.3 Hz, C≡), 79.4 ($J(^{29}Si,^{13}C)$ = 110.7 Hz, ≡CSi), 134.4 ($J(^{29}Si,^{13}C)$ = 86.4, *i*-C), 133.5 (*o*-C), 130.8 (*p*-C), 128.2 (*m*-C, SiPh), 3.0 ($J(^{29}Si,^{13}C)$ = 67.7 Hz, SiMe), 30.2, 21.9, 19.6, 13.5 (Bu). – ^{29}Si NMR (59.6 MHz; $CDCl_3$): δ = −10.4.

7a: B. p. 72 – 74 °C/0.375 Torr. – ^{1}H NMR (300 MHz; C_6D_6): δ = 1.9, 1.2, 0.7 (m, m, t, 9H, Bu). – ^{13}C NMR (75.8 MHz; C_6D_6): δ = 114.1 ($J(^{29}Si,^{13}C)$ = 35.5 Hz, C≡), 77.7 ($J(^{29}Si,^{13}C)$ = 177.6; ≡CSi), 29.6, 22.1, 19.4, 13.6 (Bu). – ^{29}Si NMR (59.6 MHz; C_6D_6): δ = −32.0. – IR: ν(C≡C) = 2281.0 cm^{-1}. – EI-MS: m/z (%) = 215 (8) [M^+], 172 (62) [$M^+ - C_3H_7$], 135 (38), 81 (100), 43 (90), 41 (60), 39 (20).

Hydroboration of the alkyn-1-yl(chloro)silanes with 9-BBN. General Procedure

Pure **3a** (1.01 g, 4.51 mmol) was dissolved in toluene (10 ml) and 9-BBN (0.56 g, 4.51 mmol) was added as a solid in one portion. The reaction mixture was heated to reflux for 30 min, the solvent was removed *in vacuo*, and the remaining colourless oil was identified as a mixture of **8a** and **8a′**. This reaction was also carried out with the same result at r. t., when it was complete after 12 h in the same solvent. The procedure for the preparation of the other alkenylsilanes is the same, except for a heating period of 3 h for **10a**, 2 h for **9a**, 1 h for **10b**, **11b** and 0.5 h for **8b**, **9b**, **11a** and **12b**. In case of **12a**, the reaction was carried out at the same temperature in a sealed NMR tube using benzene as the solvent, and the reaction was complete after 1 h. The yield of the products was essentially quantitative.

8a: ^{1}H NMR (300 MHz; CDCl$_3$): δ = 2.4, 1.3 – 1.6, 1.0 (m, m, t, 9H, Bu), 1.4 – 1.8 (m, 14H, 9-BBN), 5.1 (s, $^1J(^{29}\mathrm{Si},^1\mathrm{H})$ = 205.3 Hz, 1H, SiH), 7.3 (t, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 7.1 Hz, 1H, =CH), 7.4 – 7.8 (m, 5H, SiPh). **8a′**: ^{1}H NMR (300 MHz; CDCl$_3$): δ = 2.5, 1.3 – 1.6, 0.9 (m, m, t, 9H, Bu), 1.4 – 1.8 (m, 14H, 9-BBN), 5.2 (s, $^1J(^{29}\mathrm{Si},\,^1\mathrm{H})$ = 189.6 Hz, 1H, SiH), 7.1 (t, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 7.1 Hz, 1H, =CH), 7.4 – 7.8 (m, 5H, SiPh). **8b**: ^{1}H NMR (300 MHz; CDCl$_3$): δ = 1.5 – 1.9 (m, 14H, 9-BBN), 5.5 (s, $^1J(^{29}\mathrm{Si},\,^1\mathrm{H})$ = 237.5 Hz, 1H, SiH) 7.2 – 7.6 (m, 10H, SiPh, Ph), 8.2 (s, $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 20.4 Hz, 1H, =CH). **9a**: ^{1}H NMR (300 MHz; CDCl$_3$): δ = 0.6 (s, 3H, SiMe), 2.2, 1.4, 1.3, 0.7 (m, m, m, t, 9H, Bu), 1.5 – 1.8 (m, 14H, 9-BBN), 6.9 (t, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 7.2 Hz, 1H, =CH) and 7.2 – 7.6 (m, 5H, SiPh). **9b**: Yield after recrystalisation from pentane at r. t. was 75 %; m. p. 58 – 60 °C. – ^{1}H NMR (300 MHz; C$_6$D$_6$) δ = 0.3 (s, 3H, SiMe), 1.5 – 1.9 (m, 14H, 9-BBN), 8.0 (s, $^3J(^{29}\mathrm{Si},\,^1\mathrm{H})$ = 20.3 Hz, =CH), 7.0 – 7.4 (m, 10H, SiPh, Ph). **10a**: ^{1}H NMR (300 MHz; C$_6$D$_6$): δ = 2.2, 1.2, 1.0, 0.7 (m, m, m, t, 9H, Bu), 1.3 – 1.9 (m, 14H, 9-BBN), 7.2 (t, $^3\mathrm{J}\ (^1\mathrm{H},^1\mathrm{H})$ = 7.4 Hz, 1H, =CH), 7.1 – 7.7 (m, 10H, SiPh$_2$). **10b**: ^{1}H NMR (300 MHz; CDCl$_3$): δ = 8.1 (s, $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 20.5 Hz, =CH), 1.1 – 1.7 (m, 14H, 9-BBN) and 6.8 – 7.5 (m, 15H, SiPh$_2$, Ph). **11a**: ^{1}H NMR (300 MHz; CDCl$_3$): δ = 2.1, 1.1, 1.0, 0.5 (m, m, m, t, 9H, Bu), 1.4 – 1.6 (m, 14H, 9-BBN), 6.9 (t, 1H, =CH $^3J(^1\mathrm{H},^1\mathrm{H})$ = 7.5 Hz) and 7.1 – 7.5 (m, 5H, SiPh). **11b**: Yield after recrystalisation from hexane/chloroform (4 : 1) at r. t. was 80 %; m. p. 74 – 75 °C. – ^{1}H NMR (300 MHz; CDCl$_3$): δ = 7.8 (s, $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 25.7 Hz, =CH), 1.0 – 2.0 (m, 14H, 9.BBN) and 6.8 – 7.4 (m, 10H, SiPh, Ph). **12a**: ^{1}H NMR (300 MHz; C$_6$D$_6$): δ = 2.5, 1.1 – 1.3, 0.8 (m, m, t, 9H, Bu), 7.0 (t, $^3J(^1\mathrm{H},^1\mathrm{H})$ = 7.8 Hz, 1H, =CH), 1.3 – 1.9 (m, 14H, 9-BBN). – EI-MS: *m/z* (%) = 336 (28) [M$^+$], 279 (7) [M$^+$ – C$_4$H$_9$], 266 (5), 135 (8), 110 (100), 82 (65). **12b**: ^{1}H NMR (300 MHz; C$_6$D$_6$): δ = 1.3 – 2.0 (m, 14H, 9-BBN), 7.8 (s, $^3J(^{29}\mathrm{Si},^1\mathrm{H})$ = 33.2 Hz, 1H, =CH), 6.9 – 7.2 (m, 5H, Ph). – EI-MS: *m/z* (%) = 256 (1) [M$^+$], 236 (23) [M$^+$ – C$_8$H$_{14}$B], 103 (100), 110 (32), 82 (48).

X-ray structure determination of the alkene ***11b***

The X-ray structure determination of **11b** was carried out at 191(2) K on a single crystal selected at r. t. in perfluorinated oil [20] using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit; λ = 0.71069 Å, M_r = 399.22, monoclinic, space group $P2_1/n$, a = 6.5500(4), b = 22.9790(16), c = 13.8360(10) Å, β = 95.305(5)°, V = 2073.6(2) Å^3, $Z = 4$, $\mu(\mathrm{Mo}\,K_\alpha)$ = 0.374 mm^{-1}, $F(000)$ = 840 e, crystal size: $0.87 \times 0.32 \times 0.28$ mm^3, θ range for data collection: 1.72 – 25.70°, *hkl* ranges: $-7 \le h \le 7$, $-27 \le k \le 27$, $-16 \le l \le 16$, reflections collected: 26069, independent reflections: 3096 (R_int = 0.0648), completeness to θ = 25.70°: 99.5 %, data/restraints/parameters: 3096/0/239. Goodness-of-fit on F^2: 1.001, final R indices ($I \ge 2\sigma(I)$): $R1$ = 0.0487, $wR2$ = 0.1277, R indices (all data): $R1$ = 0.0641, $wR2$ = 0.1350, largest difference peak and hole in final difference map: 0.858/−0.319 e Å^{-3}. Structure solution and refinement were accomplished using SIR97 [21], SHELXL-97 [22] and WinGX [23].

CCDC 617200 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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