

Triethylborane: An “Old” Reagent with New Functions.

1,2-Hydroboration

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In contrast with previous findings, triethylborane, BEt₃, can act as a hydroborating reagent. Thus, the reactions of BEt₃ with alkyn-1-yl(trichloro)silanes, di(alkyn-1-yl)dichlorosilanes, alkyn-1-yl(dichloro)vinylsilanes, trichloro(vinyl)silane, and dichloro(methyl)vinylsilane for several days in excess BEt₃ as the solvent at 100–120 °C were found to give exclusively products of 1,2-hydroboration. This unexpected behaviour was compared with that of tri-*n*-propylborane, B^{*n*}Pr₃, and 9-borabicyclo[3.3.1]nonane, 9-BBN in analogous reactions, 9-BBN being a well established hydroborating reagent. All products were characterised by a consistent set of NMR data (¹H, ¹¹B, ¹³C and ²⁹Si NMR).

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

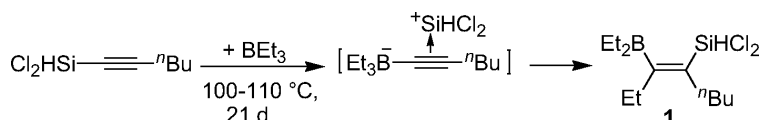
Introduction

The behaviour of trialkylboranes upon thermolysis has been studied repeatedly, starting with an early investigation of trimethyl- and triethylborane by Stock [1]. In the 1950ies and 1960ies, numerous publications appeared (see [2] for some of the most relevant references). For various non-cyclic and cyclic trialkylboranes, the results have been summarised in a review [3] and in an elaborate research paper [4]. Remarkably, the question of potential dehydroboration of BEt₃ into “Et₂BH”, or its dimer, and ethene has not been addressed in great detail. In a comprehensive review it has been stated [5] that B-Et groups in triorganoboranes in general do not undergo cleavage of the B–C(Et) bond. The examination of the dissociation of BEt₃ in the gas phase has shown that ethene elimination is extremely slow when compared with olefin elimination from other trialkylboranes [6].

We have frequently used BEt₃ for 1,1-ethylboration reactions [7] with alkyn-1-ylsilanes for prolonged periods of heating at about 100 °C, and we did observe cleavage of the B–C bonds, however, without any evidence for dehydroboration and formation of ethene

[8–12]. A typical example [12] related to the present study is shown in Scheme 1, where the cleavage of the Si–C≡ bond leads to a short-lived zwitterionic alkyn-1-ylborate-like intermediate. This intermediate rearranges into the alkene **1** bearing the boryl and silyl groups in *cis* positions at the C=C bond, and the Et₂B- and Et- groups are linked to the same carbon atom (1,1-ethylboration). Clearly, the product **1** [12] and the established mechanism for this type of reaction [7] bears no resemblance to the B–C bond cleavage *via* dehydroboration.

The formation of **1** [12] and of numerous other boryl-substituted alkenylsilanes by 1,1-ethylboration [8–12] prompted us to study the reaction of triethylborane with alkyn-1-yl(trichloro)- (**2**) and di(alkyn-1-yl)dichlorosilanes (**3**), Cl₃Si–C≡C–R¹ and Cl₂Si(C≡C–R¹)₂ with R¹ = *n*Bu (**a**) and Ph (**b**). Surprisingly, these reactions took a completely different course, when compared with Scheme 1, and BEt₃ turned out to behave like a hydroborating reagent. This was corroborated by analogous reactions using alkyn-1-yl(dichloro)vinylsilanes (**4**) and chloro(vinyl)silanes (**5**, **6**), and also by using tri-*n*-propylborane, B^{*n*}Pr₃, instead of BEt₃. Finally these results invited for a com-



Scheme 1. 1,1-Ethylboration of dichloro (hexyn-1-yl)silane *via* cleavage of the Si–C≡ bond [12].

Table 1. ^{13}C and ^{29}Si NMR data^a of the silanes **2–6**.

	$\delta^{13}\text{C}(\text{Si}-\text{C}\equiv); (\equiv\text{C})$	$\delta^{13}\text{C}(\text{Si}-\text{CH}\equiv); (= \text{CH}_2)$	$\delta^{13}\text{C}(\text{R}^1)$	$\delta^{29}\text{Si}$
2a	77.7 [177.6]; 114.1 [35.5]	–	29.6, 22.1, 19.4, 13.6	–32.0
3a	78.7 [157.8]; 112.6 [31.7]	–	29.7, 22.1, 19.5, 13.5	–48.8
4a	77.7 [139.8]; 113.9 [28.0]	132.3 [104.1]; 137.8 [13.2]	29.8, 22.0, 19.5, 13.5	–22.0
4b	85.8 [137.4]; 109.7 [27.6]	131.6 [104.5] 138.5; [< 3]	120.6(<i>i</i>), 132.6(<i>o</i>), 128.6(<i>m</i>), 130.4(<i>p</i>)	–20.9
5	–	131.2 [113.2]; 139.2 [< 3]	–	–3.2
6	–	133.3; 136.8	–; 4.8 (SiMe)	16.3

^a In C_6D_6 (10 %, v/v); coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ in Hz are given in brackets (± 0.4 Hz).

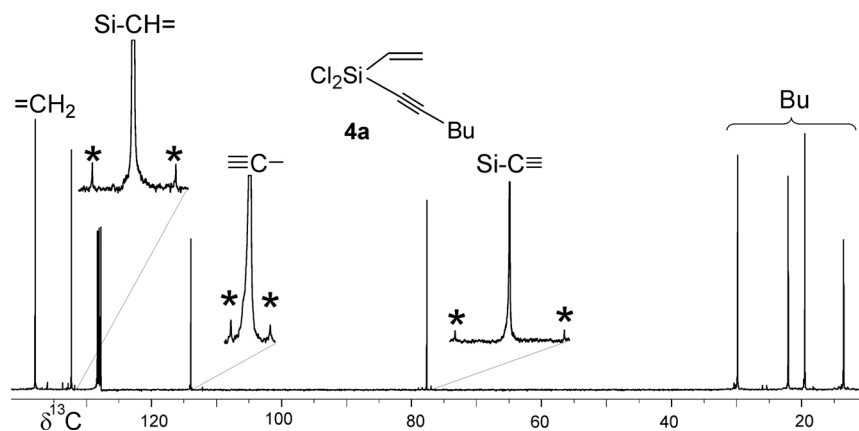
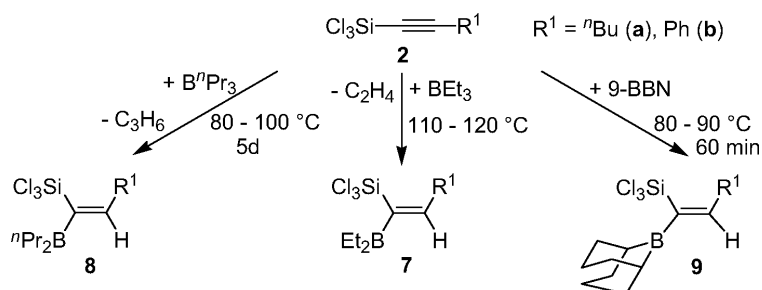


Fig. 1. 75.8 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of chloro(hexyn-1-yl)vinylsilane **4a** in C_6D_6 . ^{29}Si satellites corresponding to $^1J(^{29}\text{Si}, ^{13}\text{C})$ and $^2J(^{29}\text{Si}, ^{13}\text{C})$ in expanded parts are marked by asterisks.



Scheme 2. Triethylborane, BEt_3 , as a hydroborating agent towards alkyn-1-yl(trichloro)silanes, in comparison with B^nPr_3 and 9-BBN.

parison with those obtained by using a conventional hydroborating reagent such as 9-borabicyclo[3.3.1]nonane, 9-BBN.

Results and Discussion

The alkyn-1-yl(chloro)silanes **2–4** were prepared from the reactions of SiCl_4 or $\text{Cl}_3\text{Si}-\text{CH}=\text{CH}_2$ with the alkynyl lithium reagents $\text{Li}-\text{C}\equiv\text{C}-^n\text{Bu}$ or $\text{Li}-\text{C}\equiv\text{C}-\text{Ph}$ and purified by fractional distillation. ^{13}C and ^{29}Si NMR data are given in Table 1, and a representative ^{13}C NMR spectrum of **4a** is shown in Fig. 1.

The results for the treatment of **2** with BEt_3 , B^nPr_3 and 9-BBN are summarised in Scheme 2. The formation of the alkenylsilane **9**, the expected product of

regiospecific 1,2-hydroboration as reported previously [13], is complete after 30–60 min in boiling benzene. In contrast, the reaction of **2** with BEt_3 requires about 24–28 d in boiling BEt_3 (closed Schlenk tube, oil bath temperature 120°C) for $> 80\%$ conversion. The products **7** and **7'** have been identified by their characteristic NMR properties (Table 2, Experimental Section, and Fig. 2), which are completely different from those of **1**, but are corresponding closely to those of **9** [13]. The reaction solution contains ethene.

After removing all readily volatile materials the (*Z*)-alkenes **7** are left as oily liquids containing small amounts of the (*E*)-isomers **7'**. The latter can be formed by double hydroboration of the $\text{C}\equiv\text{C}$ bond, followed by dehydroboration, giving rise to loss of stereoselectivity (Scheme 3).

Table 2. ^{11}B , ^{13}C and ^{29}Si NMR data^a of the alkenes **7–9** (Scheme 2).

	$\delta^{13}\text{C}$ (Si(B)C=)	$\delta^{13}\text{C}$ (=C(H)R ¹)	$\delta^{13}\text{C}$ (R ¹)	$\delta^{13}\text{C}$ (BR ₂ or BBN)	$\delta^{11}\text{B}$	$\delta^{29}\text{Si}$
7a	145.1(br) [88.2] ^b	154.9	35.5, 31.3, 22.6, 14.3	21.7 (br), 8.9	82.8	−7.8
7a'	n. o. (br)	164.8	33.6, 31.0, 22.5, 14.1	n.o. (br), 9.0	82.8	−5.8
7b	147.0 (br) [90.5] ^b	151.6	138.2(<i>i</i>), 129.6(<i>o</i>), 128.5(<i>m</i>), 129.3(<i>p</i>)	21.3 (br), 8.9	83.0	−8.5
7b'	147.8 (br)	161.1	137.9(<i>i</i>), 129.6(<i>o</i>), 128.7(<i>m</i>) 130.4(<i>p</i>)	21.6 (br), 8.9	83.0	−6.9
8a	145.6 (br)	155.2	35.5, 31.3, 22.6, 14.1	32.8 (br), 18.7, 17.6	82.8	−7.4
8b	148.2 (br)	151.5	137.9(<i>i</i>), 130.9(<i>o</i>), 128.7(<i>m</i>), 130.1(<i>p</i>)	31.2(br), 18.4, 17.9	83.8	−8.5
9a^c	141.8 (br)	167.0	35.4, 31.1, 22.8, 14.1	34.5, 31.6 (br), 23.4	81.5	−3.9
9b^c	143.0 (br) [95.7]	160.8	138.0(<i>i</i>), 130.4(<i>o</i>), 129.8(<i>m</i>), 128.4(<i>p</i>)	34.7, 31.9 (br), 23.4	81.3	−4.8

^a In C₆D₆ at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C - ^{11}B scalar coupling [25]; some coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ in Hz are given in brackets (± 0.4 Hz); ^b measured from ^{13}C satellites in the ^{29}Si NMR spectra (Fig. 2); ^c data taken from [13].

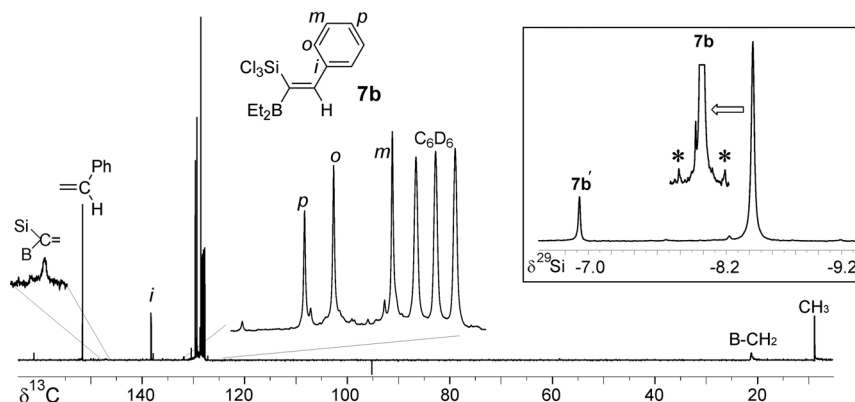
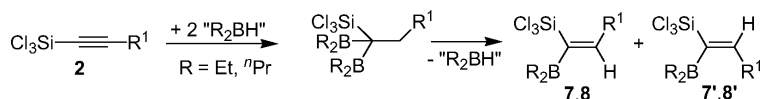


Fig. 2. 100.5 MHz $^{13}\text{C}\{^1\text{H}\}$ and 59.6 MHz $^{29}\text{Si}\{^1\text{H}\}$, (insert) NMR spectra of diethyl-[(*Z*)-2-phenyl-1-trichlorosilyl-vinyl] borane **7b** in C₆D₆. The (*E*)-isomer **7b'** is present as is evident from weak additional ^{13}C NMR signals and from the additional ^{29}Si NMR signals as marked. The magnitude of the coupling constant $^1J(^{29}\text{Si}, ^{13}\text{C})$ cannot readily be determined from the ^{13}C NMR spectrum (weak and broad signal!). However, from the ^{13}C satellites in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum, marked by asterisks in the insert, $^1J(^{29}\text{Si}, ^{13}\text{C}) = 90.5$ Hz can be determined.



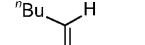
Scheme 3. Loss of stereoselectivity of hydroboration of alkynes as a consequence of double hydroboration and dehydroboration.

It is well known that dehydroboration of tri-*n*-propylborane B^{*n*}Pr₃ starts slowly at 100 °C [3,4]. After 5 d at this temperature, the alkyne **2** is completely converted into the alkene **8** which also contains a small amount of the (*E*)-isomer **8'**. The NMR data for **7–9** (Table 2 and Experimental Section) leave no doubt about the substituent pattern at the C=C bonds. It is therefore concluded that BEt₃ also undergoes dehydroboration, although less readily than B^{*n*}Pr₃, to give “Et₂BH” and ethene, and can be used as a hydroborating reagent. This is of interest, since BEt₃ is commercially available, whereas “Et₂BH” has to be prepared from the reaction of BEt₃ with diborane(6), and can be obtained only as a mixture containing various amounts of Et₂BH₂BEt₂, Et₂BH₂B(H)Et and BEt₃ [14], for which the content

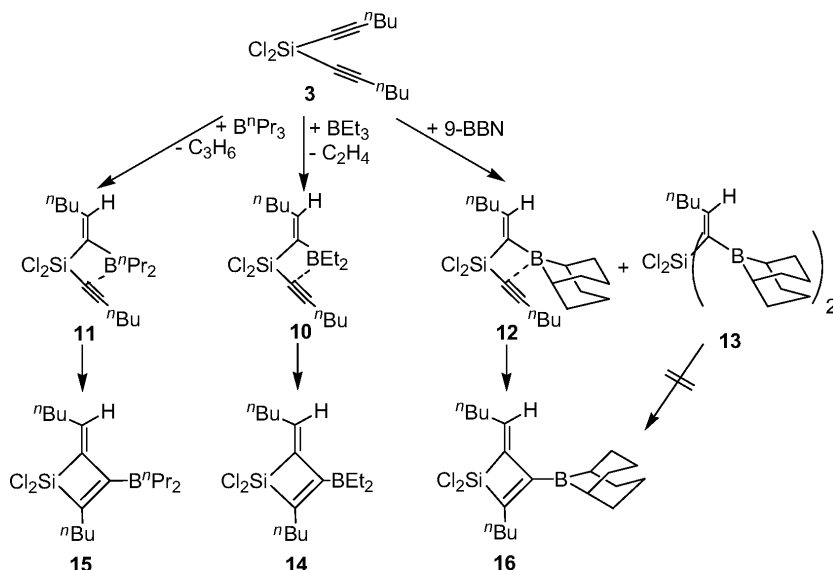
of hydride has to be determined accurately prior to use.

The comparison of the results in Scheme 2 with those in Scheme 1 indicates the influence of substituents upon the ease of cleaving the Si–C≡ bond. Apparently, the Si–Cl functions stabilise the Si–C≡ bond, in contrast to the Si–H functions, and 1,2-hydroboration (Scheme 2) becomes an alternative to 1,1-ethylboration (Scheme 1). Therefore, it was of interest to study the influence of a second Si–C≡^{*n*}Bu function as in **3** (Scheme 4). If hydroboration does not take place, one expects the clean formation of siloles (silacyclopentadienes) which usually are obtained when dialkyn-1-ylsilanes (*e. g.* Me₂Si(C≡C–R¹)₂) are treated with BEt₃ [9]. The results found here for the reaction of **3** with BEt₃, B^{*n*}Pr₃ and 9-BBN are very sim-

Table 3. ^{11}B , ^{13}C , ^{29}Si NMR data^a of the silacyclobutenes **14**–**16** (Scheme 4).

	Compound	14	15	16
	$\delta^{13}\text{C}(\text{}^n\text{BuCH=})$	129.3	130.5 [12.3]	131.1 [11.8]
	$\delta^{13}\text{C}(\text{C2})$	147.8 [67.5]	148.1 [67.2]	148.0 [66.5]
	$\delta^{13}\text{C}(\text{C3})$	179.4 (br)	179.5 (br)	176.5 (br)
	$\delta^{13}\text{C}(\text{C4})$	158.3 [70.0]	158.4 [69.3]	163.1 [67.9]
	$\delta^{13}\text{C}(\text{BR}_2/9\text{-BBN})$	21.7 (br), 9.3	32.8 (br), 18.5, 17.7	33.3, 31.5 (br), 23.2
	$\delta^{13}\text{C}(\text{}^n\text{Bu})$	34.2, 32.3, 31.7, 30.7, 22.9, 22.7, 14.2, 13.1 ^b	34.3, 32.4, 31.8, 30.7, 23.0, 22.6, 14.2, 14.0 ^b	34.5, 32.5, 31.9, 31.1, 23.0, 22.7, 14.2, 14.1 ^b
	$\delta^{29}\text{Si}$	−10.9	−10.7	−9.2
	$\delta^{11}\text{B}$	87.5	86.8	86.3

^a In C_6D_6 at 23 °C; coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ in Hz are given in brackets (± 0.4 Hz); (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{13}C – ^{11}B coupling [25]; ^b $^{13}\text{C}(\text{}^n\text{Bu})$ signals without assignment.



Scheme 4. Triethylborane, BEt_3 , as a hydroborating agent towards dichloro(dialkyn-1-yl)silane, in comparison with B^nPr_3 and 9-BBN.

ilar, except for the reaction conditions required to start the transformations. The first step is the 1,2-hydroboration leading to the intermediates **10**–**12**, as is well known for other dialkyn-1-ylsilanes in the presence of “ Et_2BH ” [15] or 9-BBN [15, 16]. In the case of 9-BBN it proved possible to detect intermediates analogous to **12** in the reaction solutions by NMR spectroscopy [16]. In the case of the reaction of **3** with 9-BBN, the hydroboration of the second alkynyl group cannot be completely suppressed, and **13** is a side product which does not undergo further rearrangements. The next step is an intramolecular 1,1-vinylboration by which the silacyclobutene derivatives **14**–**16** are formed. The NMR data (Table 3) compare well with those reported previously for derivatives containing the SiMe_2 or SiPh_2 instead of the SiCl_2 unit [15, 16]. The molecular structure of a four-membered ring analogous to **16** (with a SiPh_2

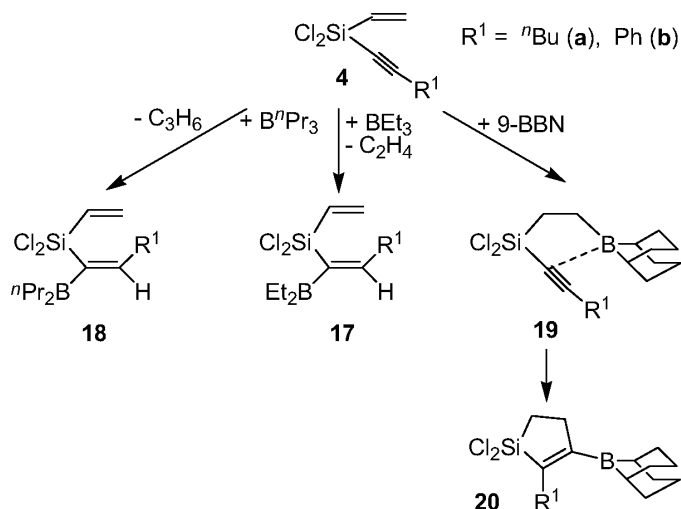
unit and $\text{R}^1 = \text{Ph}$ and ^nBu) has already been determined [16]. Thus, the formation of **14** and **15** is a rare example of combining 1,2-hydroboration and 1,1-organoboration, accomplished here without using a boron hydride reagent. The straightforward access to **14** and **15** opens the way to novel silacyclobutenes taking advantage of the reactivity of the Si – Cl functions.

Having established the potential hydroborating activity of BEt_3 , we became interested in the question whether a Si -vinyl or a Si -alkynyl group is preferably attacked by hydroboration with the “ Et_2BH ” species generated *in situ*. For this purpose the reaction of alkyn-1-yl(dichloro)vinylsilane **4** with BEt_3 was studied (Scheme 5). The result reminds of the findings by H. C. Brown *et al.* that $\text{C}\equiv\text{C}$ bonds are more reactive than all types of $\text{C}=\text{C}$ bonds towards 1,2-hydroboration, using sterically hindered dialkylboranes such as

Table 4. ^{11}B , ^{13}C and ^{29}Si NMR data^a of the alkenes **17** and **18** (Scheme 5).

	$\delta^{13}\text{C}$ (Si(B)C=)	$\delta^{13}\text{C}$ (=C(H)R ¹)	$\delta^{13}\text{C}$ (R ¹)	$\delta^{13}\text{C}$ (BEt ₂ / BPr ₂)	$\delta^{11}\text{B}$	$\delta^{29}\text{Si}$
17a ^b	145.4 (br)	151.9	35.8, 31.6, 22.6, 14.2	21.7 (br), 9.0	83.0	−2.0
17b ^c	149.5 (br) [74.1]	148.4	139.7(<i>i</i>), 136.8(<i>o</i>), 128.4(<i>m</i>), 130.4(<i>p</i>)	21.4 (br), 9.0	84.2	−2.5
18b ^d	150.9 (br)	148.4	139.9(<i>i</i>), 129.2(<i>o</i>), 128.4(<i>m</i>), 128.9(<i>p</i>)	29.2 (br), 18.3, 17.7	81.2	−8.4

^a In C₆D₆ at 23 °C; coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ in Hz are given in brackets (± 0.4 Hz); (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{13}C - ^{11}B coupling [25]; ^b other ^{13}C data: 134.9 [88.9](Si-CH=), 136.7 (=CH₂); ^c other ^{13}C data: 132.7 [89.7](Si-CH=), 138.6 (=CH₂); ^d other ^{13}C data: 132.2 (Si-CH=), 136.3 (=CH₂).

Scheme 5. Triethylborane, BEt₃, as a hydroborating agent towards alkyn-1-yl(dichloro)vinylsilanes, in comparison with BⁿPr₃ and 9-BBN.

dicyclohexyl- and disiamylborane [17]. We note the selective formation of **17** from the reaction of **4** with BEt₃, leaving the Si-vinyl group untouched. The same is true for **18**, when BⁿPr₃ is used. The consistent NMR data are listed in Table 4. Therefore, we conclude that the preference noted previously in a different context [17] is also valid for sterically less hindered dialkylboranes such as “Et₂BH” or “ⁿPr₂BH” generated *in situ*. It has been found that 9-BBN behaves differently when compared with other dialkylboranes, since it prefers terminal C=C bonds over C≡C bonds, at least if it is used in THF solution [18]. In the case of **4**, we have found that with 9-BBN indeed the attack at the Si-vinyl group is preferred (> 80 % according to NMR spectra of reaction solutions), leading to **19** which rearranges *via* intramolecular 1,1-organoboration into the 1-silacyclopent-2-ene **20**. This particular reaction sequence has already been found for silanes analogous to **4** containing SiMe₂ or SiPh₂ units, and molecular structures of such silacyclopent-2-enes have been determined [19].

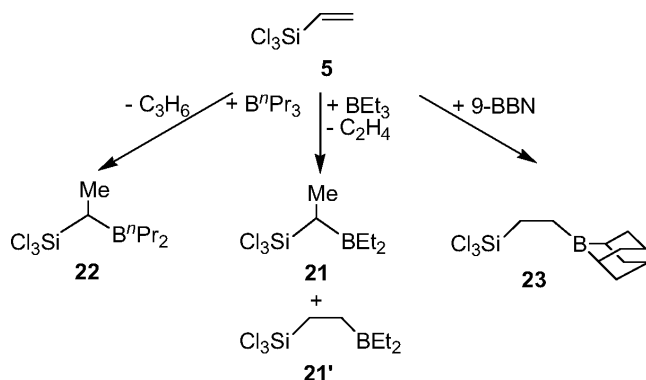
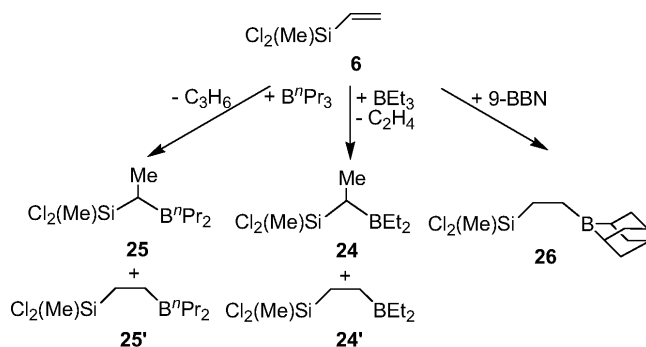
Finally, the hydroborating potential of triethylborane was studied in reactions with the chloro(vinyl)silanes **5** and **6** (Schemes 6 and 7). Here it proved nec-

essary to use heating up to 120–130 °C under pressure to induce the reaction with BEt₃. Mixtures of the hydroboration products **21** and **21'** were obtained which could not be separated by distillation. The structural assignment follows unambiguously from the ¹H and ¹³C NMR spectra (Table 5). The analogous result was found for BⁿPr₃ to give **22** under less harsh reaction conditions. Whereas **22** is the preferred product of the reaction of **5** with BⁿPr₃, BEt₃ affords slightly more of the isomer **21'** than of **21**. However, the results for BEt₃ and BⁿPr₃ are not strictly comparable, since the reaction of BEt₃ with **5** or **6** is accompanied by decomposition either of **5** or **6** or of the products. The nature of the black solid materials formed under these conditions is currently being studied. Using 9-BBN, one observes the hydroboration products **23** and **26** almost exclusively (> 96 % according to NMR data), in agreement with the literature report for **23** [20]. Prolonged heating of **23** at 120 °C does not induce significant isomerisation. Previous attempts at the hydroboration of trichloro(vinyl)silane [21, 22] using other hydroborating reagents gave mainly products analogous to **21** and **22**, similar to our results, in particular to those for BⁿPr₃.

Table 5. ^{11}B , ^{13}C and ^{29}Si NMR data^a of hydroboration products **21**–**26** of vinylsilanes (Schemes 6 and 7).

	$\delta^{13}\text{C}$ (Si–C)	$\delta^{13}\text{C}$ (CH ₂ –B)	$\delta^{13}\text{C}$ (BR ₂)	$\delta^{13}\text{C}$ (Me)	$\delta^{13}\text{C}$ (SiMe)	$\delta^{29}\text{Si}$	$\delta^{11}\text{B}$
21	31.2 (br)	–	19.9 (br), 8.2	10.0	–	9.1	86.0
21'	18.5	19.5 (br)	20.5 (br), 8.1	–	–	14.8	86.0
22	31.8 (br)	–	30.6 (br), 18.2, 17.6	9.9	–	9.1	86.1
23	18.7 [85.7]	19.0 (br)	33.5, 31.3 (br), 23.5	–	–	14.7	87.4
24	29.8 (br)	–	19.4 (br), 8.2	10.0	5.4	29.2	86.2
24'	15.3	18.2 (br)	19.4 (br), 8.3	–	4.2	34.3	86.2
25	30.3 (br)	–	31.2 (br), 18.4, 17.8	10.0	4.3	29.0	86.0
25'	15.5 [69.1]	23.9 (br)	30.7 (br), 18.1, 17.7	4.4 [66.5]	4.0	34.2	86.0
26	15.4 [69.6]	18.8 (br)	33.5, 31.3 (br), 23.5	4.5 [66.4, SiMe]	5.0	34.4	87.5

^a Measured in C₆D₆ at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C – ^{11}B scalar coupling [25]; some coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ in Hz are given in brackets (± 0.4 Hz).

Scheme 6. Triethylborane, BEt_3 , as a hydroborating agent towards trichloro(vinyl)silane, in comparison with B^nPr_3 and 9-BBN.Scheme 7. Triethylborane, BEt_3 , as a hydroborating agent towards dichloro(methyl)vinylsilane, in comparison with B^nPr_3 and 9-BBN.

Conclusions

Triethylborane, BEt_3 , undergoes slow dehydroboration at temperatures > 100 °C, generating diethylborane “ Et_2BH ” and C_2H_4 and, therefore, can be used *in situ* as a promising simple, commercially available hydroborating agent for thermally stable unsaturated compounds. There appears to be a high selectivity for $\text{C}\equiv\text{C}$ relative to $\text{C}=\text{C}$ bonds.

Experimental Section

All preparative work was carried out by observing necessary precautions to exclude traces of oxygen and moisture.

Tetrachlorosilane, trichloro(vinyl)silane, dichloro(methyl)vinylsilane, 1-hexyne, ethynylbenzene, *n*-butyllithium in hexane (1.6 M), triethylborane (BEt_3), and 9-borabicyclo [3.3.1]nonane (9-BBN) were used as commercial products without further purification. Tri-*n*-propylborane (B^nPr_3) was prepared by hydroboration of propene using NaBH_4 and $\text{BF}_3\cdot\text{OEt}_2$ in Et_2O [23].

NMR spectra were recorded at 23 °C on Varian Inova 300 and 400 spectrometers, both equipped with multinuclear units, using C_6D_6 solutions (*ca.* 5–10 % V/V) in 5 mm tubes. Chemical shifts are given with respect to SiMe_4 [$\delta^1\text{H}$ ($\text{C}_6\text{D}_5\text{H}$) = 7.15, $\delta^{13}\text{C}$ (C_6D_6) = 128.0, $\delta^{29}\text{Si}$ = 0 for SiMe_4 with $\Xi(^{29}\text{Si})$ = 19.867187 MHz], and $\delta^{11}\text{B}$ = 0 for $\text{BF}_3\cdot\text{OEt}_2$ with $\Xi(^{11}\text{B})$ = 32.083971 MHz. ^{29}Si NMR spectra were

recorded using the refocused INEPT pulse sequence with ^1H decoupling [24], based on $^3J(^{29}\text{Si}-\text{C}=\text{C}^1\text{H}) \approx 15$ Hz or 25–35 Hz (after optimisation of the refocusing delay according to the number of protons). Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for ^1H , ^{11}B , ^{12}C , ^{35}Cl , ^{28}Si).

Synthesis of silanes **2**, **3** and **4**

A suspension of $\text{R}^1\text{C}\equiv\text{CLi}$ ($\text{R}^1 = n\text{Bu}$, Ph; 19.5 mmol) in hexane (60 mL) was freshly prepared, and the solution was cooled to -78°C . Then the respective chlorosilane (6–8 fold excess) was added slowly with constant stirring. The reaction mixture was warmed to r.t. and kept stirring for 3–4 h. Insoluble materials were filtered off, and volatiles were removed in a vacuum. The colourless oily residue was identified as a mixture of $\text{Cl}_3\text{Si}-\text{C}\equiv\text{C}-\text{R}^1$ (**2**) [13], $\text{Cl}_2\text{Si}(\text{C}\equiv\text{C}-\text{R}^1)_2$ (**3**) and $\text{Cl}_2\text{Si}(\text{CH}=\text{CH}_2)\text{C}\equiv\text{C}-\text{R}^1$ (**4**), the desired silanes, together with $\text{ClSi}(\text{C}\equiv\text{C}-\text{R}^1)_3$, $\text{Si}(\text{C}\equiv\text{C}-\text{R}^1)_4$, and $\text{ClSi}(\text{C}\equiv\text{C}-\text{R}^1)_2\text{CH}=\text{CH}_2$, respectively. Pure samples of **2**, **3** and **4** were obtained (yield ca. 25 %) by fractional distillation. **2a**: b.p. $30^\circ\text{C}/0.3$ Torr. – ^1H NMR (300 MHz, C_6D_6): $\delta = 1.88$, 1.20, 0.66 (t, m, t, 9H, $n\text{Bu}$). **3a**: b.p. $85^\circ\text{C}/0.15$ Torr. – ^1H NMR (300 MHz, C_6D_6): $\delta = 1.77$, 1.04, 0.66 (t, m, t, 18 H, $n\text{Bu}$). **4a**: b.p. = $38-42^\circ\text{C}/0.3$ Torr. – ^1H NMR (400 MHz, C_6D_6): $\delta = 1.8$, 1.1, 0.7 (t, m, t, 9H, $n\text{Bu}$), 5.8 (dd, $^2J(^1\text{H}, ^1\text{H}) = 3.6$ Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{cis}} = 13.4$ Hz, 1H, $=\text{CH}_2$), 6.0 (dd, $^3J(^1\text{H}, ^1\text{H})_{\text{cis}} = 13.4$ Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{trans}} = 19.8$ Hz, 1H, Si–CH), 6.1 (dd, $^2J(^1\text{H}, ^1\text{H}) = 3.7$ Hz, $^3J(^1\text{H}, ^1\text{H}) = 19.9$ Hz, 1H, $=\text{CH}_2$). – MS: m/z (%) = 207 (17) [M^+], 192 (5) [$\text{M}^+ - \text{CH}_3$], 180 (10) [$\text{M}^+ - \text{C}_2\text{H}_3$], 171 (25) [$\text{M}^+ - \text{Cl}$], 81 (73) [C_6H_9^+], 43 (98) [C_3H_7^+], 41 (100). – **4b**: b.p. = $54-55^\circ\text{C}/0.075$ Torr. – ^1H NMR (400 MHz, C_6D_6): $\delta = 6.8$, 7.1 (m, m, 5H, Ph), 5.8 (dd, $^2J(^1\text{H}, ^1\text{H}) = 3.5$ Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{cis}} = 13.5$ Hz, 1H, $=\text{CH}_2$), 6.0 (dd, $^2J(^1\text{H}, ^1\text{H})_{\text{cis}} = 13.5$ Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{trans}} = 19.8$ Hz, 1H, Si–CH), 6.1 (dd, $^2J(^1\text{H}, ^1\text{H}) = 3.5$ Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{trans}} = 19.4$ Hz, 1H, $=\text{CH}_2$).

Hydroboration of the alkyn-1-yl(trichloro)silanes **2** with BEt_3 and B^nPr_3

Pure **2a** (1 g, 4.7 mmol) was given into a pressure-safe Schlenk tube and an excess of BEt_3 (2 mL, 16 mmol) was added. The tube was closed, and the reaction mixture was heated at 120°C in an oil bath for 28 d, when the reaction was found to be complete (^{29}Si NMR spectra). All volatiles were removed *in vacuo*, the colourless residue was identified as a mixture of **7a** and **7a'** (ca. 9 : 1 according to NMR analysis). The procedure for the preparation of **7b** was the same as for **7a**, except of the heating period of 24 d. Hydroboration of **2b** with B^nPr_3 was carried out at 120°C in a sealed NMR tube, C_6D_6 was used as solvent. The reaction was complete after 2 d at $80-90^\circ\text{C}$ the product is the same but it takes 5–

6 d in order to convert **2** into **8b**. **7a**: ^1H NMR (400 MHz, C_6D_6): $\delta = 2.30$, 1.80, 1.10, 1.00 (t, m, m, t, 9H, $n\text{Bu}$), 1.30, 0.70 (m, t, 10H, BEt_2), 6.0 (t, $^3J(^1\text{H}, ^1\text{H}) = 7.4$ Hz, 1H, $=\text{CH}$, $^3J(^{29}\text{Si}, ^1\text{H}) = 35.3$). **7a'**: ^1H NMR (400 MHz, C_6D_6): $\delta = 2.4$, 1.8, 1.1, 1.0 (t, m, m, t, $n\text{Bu}$), 1.30, 0.80 (m, t, BEt_2), 6.60 (t, $^3J(^1\text{H}, ^1\text{H}) = 7.5$ Hz, 1H, $=\text{CH}$). – MS: m/z (%) = 285 (10) [M^+], 207 (20), 115 (20), 92 (100), 27 (95). **7b**: ^1H NMR (400 MHz, C_6D_6): $\delta = 1.30$, 0.90 (q, t, 10H, BEt_2), 6.9–7.3 (m, 6H, Ph, $=\text{CH}$, $^3J(^{29}\text{Si}, ^1\text{H}) = 35.8$ Hz). **7b'**: ^1H NMR (400 MHz, C_6D_6): $\delta = 1.20$, 0.80 (q, t, BEt_2), 7.70 (s, $=\text{CH}$, $^3J(^{29}\text{Si}, ^1\text{H}) = 32.9$ Hz), 6.9–7.3 (m, Ph). – MS: m/z (%) = 304 (9) [M^+], 275 (35) [$\text{M}^+ - \text{C}_2\text{H}_5$], 269 (6) [$\text{M}^+ - \text{Cl}$], 265 (100), 240 (16), 236 (31), 199 (29), 133 (13). **8a**: ^1H NMR (400 MHz, C_6D_6): $\delta = 1.44$, 1.21–1.33, 0.90 (m, m, t, 14H, B^nPr_2), 2.36, 1.21–1.33, 0.8 (q, m, t, 9H, $n\text{Bu}$), 6.07 (t, $^3J(^1\text{H}, ^1\text{H}) = 7.4$ Hz, 1H, $=\text{CH}$, $^3J(^{29}\text{Si}, ^1\text{H}) = 35.0$ Hz). **8a'**: ^1H NMR: $\delta = 1.45$, 1.21–1.33, 0.9 (m, m, t, B^nPr_2), 2.43, 1.21–1.33, 0.8 (q, m, t, $n\text{Bu}$), 5.96 (t, $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz, $=\text{CH}$). **8b**: ^1H NMR (400 MHz, C_6D_6): $\delta = 1.4$, 1.1, 0.9 (m, t, t, 14H, B^nPr_2), 6.9–7.4 (m, 6H, Ph, $=\text{CH}$). **8b'**: ^1H NMR (C_6D_6): $\delta = 1.5$, 0.9, 0.8 (m, t, t, B^nPr_2), 6.9–7.4 (m, Ph, $=\text{CH}$).

Hydroboration of the dialkyn-1-yl(dichloro)silane **3a** with BEt_3 and B^nPr_3

The mixture of the silane $\text{Cl}_2\text{Si}(\text{C}\equiv\text{C}-n\text{Bu})_2$ (280 mg, 1.1 mmol) and BEt_3 (0.21 mL, 1.5 mmol, slight excess) was heated in a sealed NMR tube and kept at 110°C in an oil bath. The progress of the reaction was monitored by ^{29}Si NMR, and after 24 d the reaction was found complete. The NMR tube was cooled in liquid N_2 before opening, excess of BEt_3 and other volatiles were removed *in vacuo*, and the product was obtained as a colourless oil, identified by NMR spectra as pure **14**. The synthetic procedure for **15** was similar to that of **14** except that the reaction was almost complete (ca. 90 %) within 6 d. **14**: ^1H NMR (400 MHz, C_6D_6): $\delta = 0.86$, 0.95, 1.2–2.1 (t, t, m, 18H, $n\text{Bu}$, $n\text{Bu}$), 1.0, 2.2 (t, m, 10H, Et_2B), 5.4 (t, $^3J(^1\text{H}, ^1\text{H}) = 7.0$ Hz, 1H, $=\text{CH}$). – MS: m/z (%) = 331 (6) [M^+], 260 (76), 254 (100), 211 (45), 69 (45), 41 (76). **15**: ^1H NMR: $\delta = 2.1$, 1.3, 0.9 (m, m, t, 18H, $n\text{Bu}$, $n\text{Bu}$), 1.4, 1.1 (m, t, 14H, B^nPr_2), 5.4 (t, $^3J(^1\text{H}, ^1\text{H}) = 7.0$ Hz, 1H, $=\text{C}-\text{H}$).

Hydroboration of the dialkyn-1-yl(dichloro)silane **3a** with 9-BBN

The pure silane **3a** (0.277 g, 1.07 mmol) was dissolved in C_6D_6 (1.5 mL), given into an NMR tube, and 9-BBN (0.13 g, 1.07 mmol) was added as a solid in one portion. The mixture was heated to 80°C for 20 min. In this time 9-BBN was completely consumed (^{11}B NMR spectra). By analysing the product, two intermediates, **12** and **13**, were identified by their NMR data. The mixture was heated again, now in toluene at 120°C (oil bath), for 4 d. Then, NMR spectra in-

indicated the formation of the product **16**, with **13** remaining as a side product. **12**: ^1H NMR (400 MHz, C_6D_6): δ = 0.6, 0.8, 1.1, 1.3, 1.8, 2.7 (t, m, m, m, q, 18H, ^nBu , ^nBu), 1.3–2.1 (m, 14H, BBN), 7.1 (t, $^3J(^1\text{H}, ^1\text{H})$ = 7.5 Hz, 1H, =CH). – ^{13}C NMR (100.5 MHz, C_6D_6): δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 165.8 [< 3] (=CH), 141.8 (br, B–C=), 112.5 [26.9] ($\equiv\text{C}$), 81.3 [132.1] ($\text{SiC}\equiv$), 34.5, 31.7 br, 23.5 (BBN), 35.2, 31.3, 29.9, 22.8, 22.1, 19.7, 13.6, 14.2 (^nBu). – ^{29}Si NMR (74.8 MHz, C_6D_6): δ = –24.4. – ^{11}B NMR (128.4 MHz, C_6D_6): δ = 81.7. **13**: ^1H NMR (400 MHz, C_6D_6): δ = 0.8, 1.3, 2.5 (t, m, q, 18H, =C– ^nBu), 1.3–2.1 (m, 28H, BBN), 6.9 (t, $^3J(^1\text{H}, ^1\text{H})$ = 7.5 Hz, 2H, =CH). – ^{13}C NMR (100.5 MHz, C_6D_6): δ = 161.5 (=CH), 146.4 (br, B–C=), 34.5, 31.4 br, 23.6 (BBN), 35.7, 33.8, 31.4, 14.2 (^nBu). – ^{29}Si NMR (74.8 MHz, C_6D_6): δ = 0.5. **16**: ^1H NMR (400 MHz, C_6D_6): δ = 2.3, 2.2, 1.2–1.5, 0.8, 0.7 (t, q, m, t, t, 18H, ^nBu , ^nBu), 1.7–2.1 (m, 14H, BBN), 5.8 (t, $^3J(^1\text{H}, ^1\text{H})$ = 7.0 Hz, 1H, =C–H).

Hydroboration of the alkyn-1-yl(dichloro)vinylsilanes **4** with BEt_3 and B^nPr_3

Pure **4a** (1.3 g, 6 mmol) was dissolved in an excess of BEt_3 (2.5 mL, 18 mmol) and the solution was heated at 120 °C for 7 d. After the reaction was almost complete all volatiles were removed *in vacuo*, and the residue was identified as **17a**. The procedure for the preparation of **17b** and **18b** was the same, except that heating lasted for 10 and 8 d, respectively. **17a**: ^1H NMR (400 MHz, C_6D_6): δ = 2.2, 1.9, 1.3, 0.9 (m, t, m, t, 9H, ^nBu), 5.9 (dd, $^2J(^1\text{H}, ^1\text{H})$ = 3.9 Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{cis}}$ = 13.1 Hz, 1H, =CH₂), 6.0 (dd, $^3J(^1\text{H}, ^1\text{H})_{\text{cis}}$ = 13.1 Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{trans}}$ = 19.5 Hz, 1H, Si–CH), 6.1 (dd, $^2J(^1\text{H}, ^1\text{H})$ = 4.0 Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{trans}}$ = 19.5 Hz, 1H, =CH₂), 1.2, 0.7 (m, t, 10H, BEt_2). **17b**: ^1H NMR (400 MHz, C_6D_6): δ = 6.8–7.1 (m, 5H, Ph), 5.4 (dd, $^2J(^1\text{H}, ^1\text{H})$ = 3.1 Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{cis}}$ = 14.1 Hz, 1H, =CH₂), 5.5 (dd, $^3J(^1\text{H}, ^1\text{H})_{\text{cis}}$ = 14.0 Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{trans}}$ = 19.6 Hz, 1H, Si–CH), 5.6 (dd, $^2J(^1\text{H}, ^1\text{H})$ = 3.1 Hz, $^3J(^1\text{H}, ^1\text{H})_{\text{trans}}$ = 19.6 Hz, 1H, =CH₂), 1.2, 0.8 (q, t, 10H, BEt_2). **18b**: ^1H NMR (400 MHz, C_6D_6): δ = 1.4–1.5, 0.9 (m, t, B^nPr_2), 5.6–6.0 (m, Si–CH, =CH₂), 6.9–7.2 (m, Ph).

Hydroboration of the alkyn-1-yl(dichloro)vinylsilanes **4** with 9-BBN

The silane **4a** (0.368 g, 1.78 mmol) or **4b** (0.6867 g, 3.02 mmol) was dissolved in toluene and 9-BBN (0.2239 and 0.2235 g, respectively) was added as a solid in one portion. The reaction mixture was stirred at r. t. for 8 h. Then all volatiles were removed in a vacuum, and the colourless oily products, in both cases **20a** and **20b** along with intermediate **19b**, were identified by NMR spectroscopy. Pure products were obtained in THF. **19b**: ^{13}C NMR (100.5 MHz, C_6D_6): δ = 121.0, 132.7, 128.6, 130.4 (*i*, *o*, *m*, *p*, Ph), 109.0 ($\equiv\text{C}$), 87.0 ($\text{SiC}\equiv$), 33.5, 31.4 (br), 23.5 (BBN), 16.2 (SiCH_2), 18.7

(br, B–CH₂). **20a**: ^1H NMR (400 MHz, C_6D_6): δ = 1.2–1.9 (m, 14H, BBN), 2.4, 1.3, 0.8 (m, m, t, 9H, ^nBu), 2.4 (m, 2H, CH₂), 1.1 (m, 2H, CH₂). – ^{13}C NMR (100.5 MHz, C_6D_6): δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 144.9 [70.0] (C2), 170.5 (br, C3), 32.0 [7.2] (C4), 12.7 [61.1] (C5), 33.8, 32.3 br, 23.3 (BBN), 33.5, 31.0, 29.9, 14.1 (^nBu). – ^{29}Si NMR (74.8 MHz, C_6D_6): δ = 38.2. – ^{11}B NMR (128.4 MHz, C_6D_6): δ = 85.8. – MS: m/z (%) = 328 (44) [M^+], 286 (8) [$\text{M}^+ - \text{C}_3\text{H}_7$], 271 (32) [$\text{M}^+ - \text{C}_4\text{H}_8$], 244 (89), 208 (9) [$\text{M}^+ - \text{BBN}$], 122 (100), 110 (31). **20b**: ^1H NMR (400 MHz, C_6D_6): δ = 1.1, 2.3 (m, m, 4H, SiCH_2 , CH₂), 1.2–1.5 (m, 14H, 9-BBN), 6.6–7.0 (m, 5H, Ph). – ^{13}C NMR (100.5 MHz, C_6D_6): δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 146.4 [69.8] (C2), 174.6 (br, C3), 33.1 (C4), 13.3 [60.7] (C5), 34.4, 32.5 (br), 23.4 (BBN), 139.0, 128.7, 128.4, 127.4 (*i*, *o*, *m*, *p*, Ph). – ^{29}Si NMR (74.8 MHz, C_6D_6): δ = 37.4. – ^{11}B NMR (128.4 MHz, C_6D_6): δ = 85.2. – MS: m/z (%) = 349 (49), 348 (100) [$\text{M}^+ - \text{H}$], 313 (15) [$\text{M}^+ - \text{Cl}$], 239 (61), 228 (86) [$\text{M}^+ - \text{BBN}$], 192 (72) [$\text{M}^+ - \text{BClC}_8\text{H}_{14}$].

Hydroboration of the chloro(vinyl)silanes **5** and **6** with BEt_3 , B^nPr_3 and 9-BBN

Trichloro(vinyl)silane, **5** (6 g, 36 mmol) was given into a pressure-safe Schlenk tube, an excess of BEt_3 (6 mL, 44 mmol) was added, and the mixture was heated at 120 °C for 3 d. A dark colour developed and black solid materials were formed. After removing the volatiles in a vacuum, the remaining liquid (yield 25 %) was separated from the solid and analysed by NMR spectroscopy as a mixture of **21** and **21'**, with the latter in slight excess. The same procedure was applied to the synthesis of **24** and **24'**, and the analogous behaviour was observed in the course of heating. The reaction for the synthesis of **22** and **25**, **25'** starting from B^nPr_3 and **5** and **6**, respectively, was carried out at 100 °C for 5 d, and decomposition was not observed. 9-BBN in THF reacts at r. t. after 2 h with **5** and **6** to give selectively **23** and **26** [20]. **21**: ^1H NMR (400 MHz, C_6D_6): δ = 0.9, 1.2 (t, m, 10H, BEt_2), 1.9 (q, 1H, Si–CH), 1.1 (d, 3H, CH₃). **22**: b. p. 38 °C/0.1 Torr (*ca.* 90 % pure). – ^1H NMR (400 MHz, C_6D_6): δ = 0.9, 1.5 (t, m, CH₃, CH₂, BPr_2), 1.2 (d, CH₃, $^3J(^1\text{H}, ^1\text{H})$ = 7.0 Hz), 1.9 (q, CH). **23**: ^1H NMR (400 MHz, C_6D_6): δ = 1.1–1.8 (m, 14H, BBN), 1.40, 1.20 (m, m, 4H, CH₂, Si–CH₂). **24**, **24'**: ^1H NMR (400 MHz, C_6D_6): δ = 0.44 (s, SiMe), 0.42 (s, SiMe), 1.30, 0.90 (m, t, BEt_2 , CH₃, CH₂CH₂), 1.70 (q, $^3J(^1\text{H}, ^1\text{H})$ = 7.4 Hz, 1H, CH).

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