Triethylborane: An "Old" Reagent with New Functions. 1,2-Hydroboration

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In contrast with previous findings, triethylborane, BEt_3, can act as a hydroborating reagent. Thus, the reactions of BEt_3 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 BEt_3 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^nPr_3, 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 (^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR).

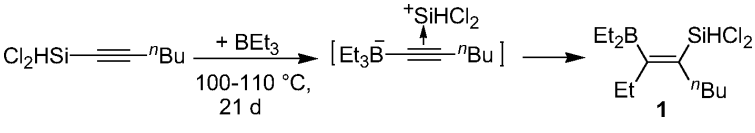
Key words: Alkynes, Alkenes, Triethylborane, Silanes, Hydroboration, NMR

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 BEt_3 into "Et_2BH", 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 BEt_3 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 BEt_3 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 Et_2B- 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**), $Cl_3Si–C{\equiv}C–R^1$ and $Cl_2Si(C{\equiv}C–R^1)_2$ with R^1 = ^{n}Bu (**a**) and Ph (**b**). Surprisingly, these reactions took a completely different course, when compared with Scheme 1, and BEt_3 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^nPr_3, instead of BEt_3. 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**.

	$\delta^{13}C$(Si–C≡); (≡C)	$\delta^{13}C$(Si–CH=); (=CH_2)	$\delta^{13}C(R^1)$	$\delta^{29}Si$
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*), 132.6(*o*), 128.6(*m*), 130.4(*p*)	−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 $J(^{29}Si,^{13}C)$ in Hz are given in brackets (±0.4 Hz).

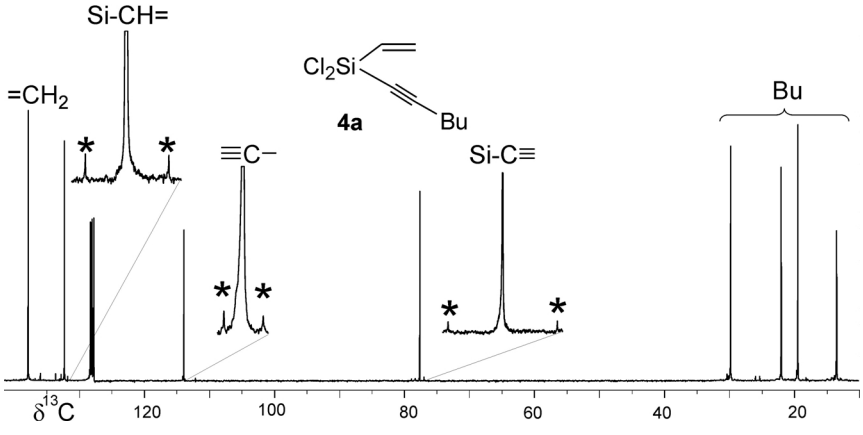
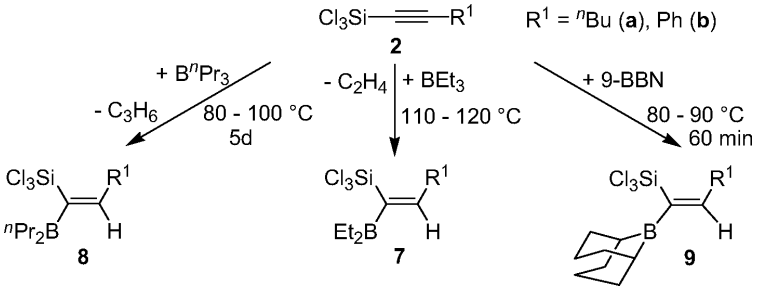


Fig. 1. 75.8 MHz $^{13}C\{^1H\}$ NMR spectrum of chloro (hexyn-1-yl)vinylsilane **4a** in C_6D_6. ^{29}Si satellites corresponding to $^1J(^{29}Si,^{13}C)$ and $^2J(^{29}Si,^{13}C)$ in expanded parts are marked by asterisks.



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 Cl_3Si–CH=CH_2 with the alkynyl lithium reagents Li–C≡C–^{n}Bu or Li–C≡C–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 C≡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).

	$\delta^{13}C$ (Si(B)C=)	$\delta^{13}C$ (=C(H)R^1)	$\delta^{13}C$ (R^1)	$\delta^{13}C$ (BR$_2$ or BBN)	$\delta^{11}B$	$\delta^{29}Si$
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*), 129.6(*o*), 128.5(*m*), 129.3(*p*)	21.3 (br), 8.9	83.0	−8.5
7b′	147.8 (br)	161.1	137.9(*i*), 129.6(*o*), 128.7(*m*) 130.4(*p*)	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*), 130.9(*o*), 128.7(*m*), 130.1(*p*)	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*), 130.4(*o*), 129.8(*m*), 128.4(*p*)	34.7, 31.9 (br), 23.4	81.3	−4.8

[a] In C_6D_6 at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling [25]; some coupling constants $^1J(^{29}Si,^{13}C)$ 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].

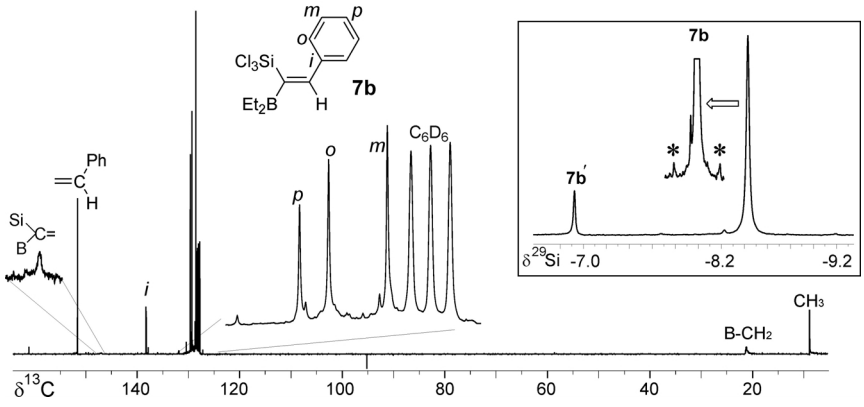
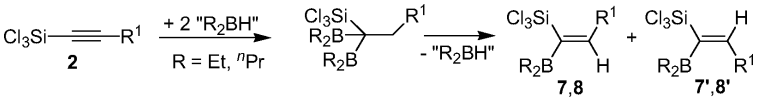


Fig. 2. 100.5 MHz $^{13}C\{^1H\}$ and 59.6 MHz $^{29}Si\{^1H\}$, (insert) NMR spectra of diethyl-[(*Z*)-2-phenyl-1-trichlorosilyl-vinyl] borane **7b** in C_6D_6. The (*E*)-isomer **7b′** is present as is evident from weak additional ^{13}C NMR signals and from the additional ^{29}Si NMR signals as marked. The magnitude of the coupling constant $^1J(^{29}Si,^{13}C)$ cannot readily be determined from the ^{13}C NMR spectrum (weak and broad signal!). However, from the ^{13}C satellites in the $^{29}Si\{^1H\}$ NMR spectrum, marked by asterisks in the insert, $^1J(^{29}Si,^{13}C)$ = 90.5 Hz can be determined.

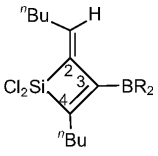


Scheme 3. Loss of stereoselectivity of hydroboration of alkynes as a consequence of double hydroboration and dehydroboration.

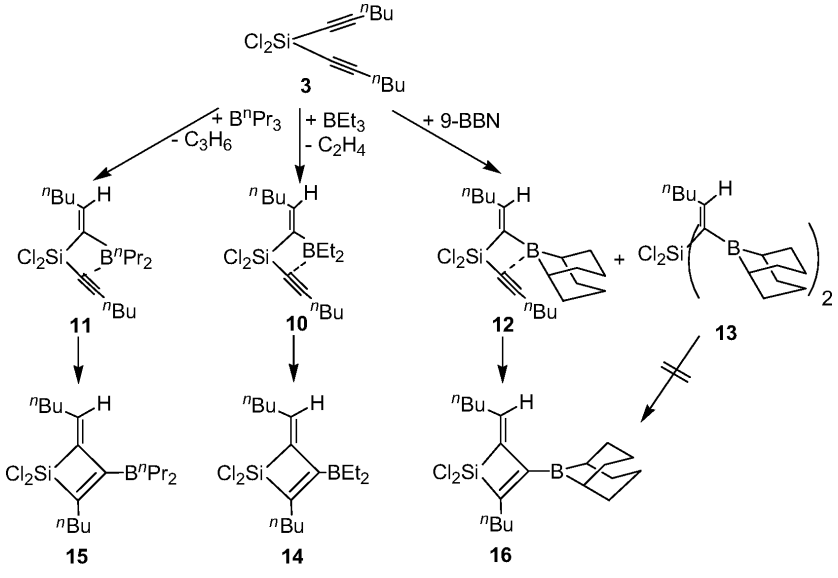
It is well known that dehydroboration of tri-*n*-propylborane B^{n}Pr$_3$ starts slowly at 100 °C [3, 4]. After 5 d at this temperature, the alkyne **2** is completely converted into the alkene **8** which also contains a small amount of the (*E*)-isomer **8′**. The NMR data for **7** – **9** (Table 2 and Experimental Section) leave no doubt about the substituent pattern at the C=C bonds. It is therefore concluded that BEt_3 also undergoes dehydroboration, although less readily than B^{n}Pr$_3$, to give "Et_2BH" and ethene, and can be used as a hydroborating reagent. This is of interest, since BEt_3 is commercially available, whereas "Et_2BH" has to be prepared from the reaction of BEt_3 with diborane(6), and can be obtained only as a mixture containing various amounts of $Et_2BH_2BEt_2$, $Et_2BH_2B(H)Et$ and BEt_3 [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≡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.* $Me_2Si(C{\equiv}C{-}R^1)_2$) are treated with BEt_3 [9]. The results found here for the reaction of **3** with BEt_3, B^{n}Pr$_3$ 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**
	$\delta^{13}C(^n\mathrm{Bu}\mathbf{C}H=)$	129.3	130.5 [12.3]	131.1 [11.8]
	$\delta^{13}C(\mathbf{C}2)$	147.8 [67.5]	148.1 [67.2]	148.0 [66.5]
	$\delta^{13}C(\mathbf{C}3)$	179.4 (br)	179.5 (br)	176.5 (br)
	$\delta^{13}C(\mathbf{C}4)$	158.3 [70.0]	158.4 [69.3]	163.1 [67.9]
	$\delta^{13}C(BR_2/9\text{-BBN})$	21.7 (br), 9.3	32.8 (br), 18.5, 17.7	33.3, 31.5 (br), 23.2
	$\delta^{13}C(^n\mathrm{Bu})$	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]
	$\delta^{29}Si$	−10.9	−10.7	−9.2
	$\delta^{11}B$	87.5	86.8	86.3

[a] In C_6D_6 at 23 °C; coupling constants $J(^{29}Si,^{13}C)$ 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] $^{13}C(^n\mathrm{Bu})$ 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.

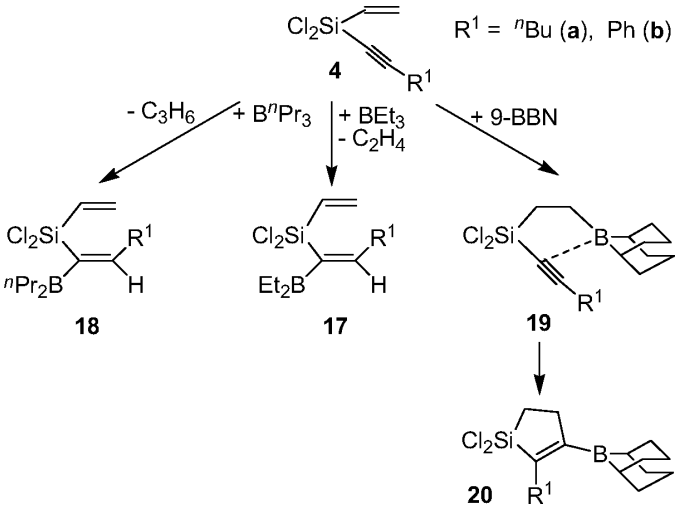
ilar, except for the reaction conditions required to start the transformations. The first step is the 1,2-hydroboration leading to the intermediates **10** – **12**, as is well known for other dialkyn-1-ylsilanes in the presence of "Et_2BH" [15] or 9-BBN [15, 16]. In the case of 9-BBN it proved possible 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 R^1 = Ph and ^{n}Bu) 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 C≡C bonds are more reactive than all types of C=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).

	$\delta^{13}C$ (Si(B)C=)	$\delta^{13}C$ (=C(H)R^1)	$\delta^{13}C$ (R^1)	$\delta^{13}C$ (BEt$_2$ / BPr$_2$)	$\delta^{11}B$	$\delta^{29}Si$
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*), 136.8(*o*), 128.4(*m*), 130.4(*p*)	21.4 (br), 9.0	84.2	−2.5
18b[d]	150.9 (br)	148.4	139.9(*i*), 129.2(*o*), 128.4(*m*), 128.9(*p*)	29.2 (br), 18.3, 17.7	81.2	−8.4

[a] In C_6D_6 at 23 °C; coupling constants $J(^{29}Si,^{13}C)$ 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 (=CH$_2$); [c] other ^{13}C data: 132.7 [89.7] (Si–CH=), 138.6 (=CH$_2$); [d] other ^{13}C data: 132.2 (Si–CH=), 136.3 (=CH$_2$).



Scheme 5. Triethylborane, BEt_3, as a hydroborating agent towards alkyn-1-yl(dichloro)vinylsilanes, in comparison with B^nPr_3 and 9-BBN.

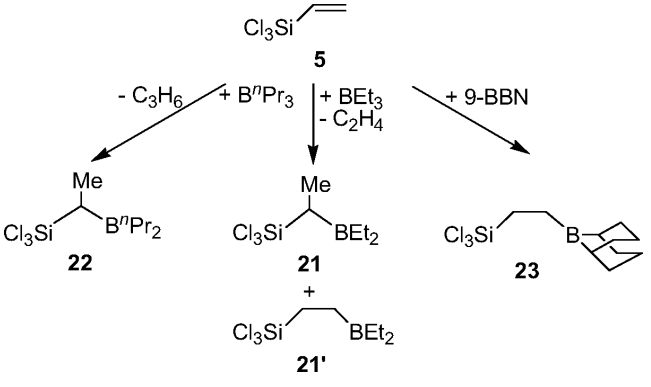
dicyclohexyl- and disiamylborane [17]. We note the selective formation of **17** from the reaction of **4** with BEt_3, leaving the Si-vinyl group untouched. The same is true for **18**, when B^nPr_3 is used. The consistent NMR data are listed in Table 4. Therefore, we conclude that the preference noted previously in a different context [17] is also valid for sterically less hindered dialkylboranes such as "Et_2BH" or "$^nPr_2BH$" 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 $SiMe_2$ or $SiPh_2$ 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 necessary to use heating up to 120 – 130 °C under pressure to induce the reaction with BEt_3. 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 ^{13}C NMR spectra (Table 5). The analogous result was found for B^nPr_3 to give **22** under less harsh reaction conditions. Whereas **22** is the preferred product of the reaction of **5** with B^nPr_3, BEt_3 affords slightly more of the isomer **21′** than of **21**. However, the results for BEt_3 and B^nPr_3 are not strictly comparable, since the reaction of BEt_3 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 B^nPr_3.

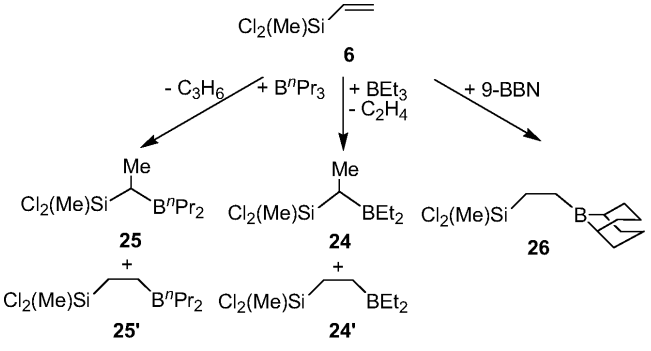
Table 5. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of hydroboration products **21** – **26** of vinylsilanes (Schemes 6 and 7).

	$\delta^{13}C$ (Si–C)	$\delta^{13}C$ (CH_2–B)	$\delta^{13}C$ (BR_2)	$\delta^{13}C$ (Me)	$\delta^{13}C$ (SiMe)	$\delta^{29}Si$	$\delta^{11}B$
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 C_6D_6 at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling [25]; some coupling constants $^1J(^{29}Si,^{13}C)$ 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 C≡C relative to C=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 $BF_3 \cdot OEt_2$ 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 $SiMe_4$ [δ^1H (C_6D_5H) = 7.15, $\delta^{13}C$ (C_6D_6) = 128.0, $\delta^{29}Si$ = 0 for $SiMe_4$ with $\Xi(^{29}Si)$ = 19.867187 MHz], and $\delta^{11}B$ = 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 [24], based on $^3J(^{29}SiC{=}C^1H) \approx 15$ 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 ^{1}H, ^{11}B, ^{12}C, ^{35}Cl, ^{28}Si).

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

A suspension of $R^1C{\equiv}CLi$ (R^1 = ^{n}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 $Cl_3Si{-}C{\equiv}C{-}R^1$ (**2**) [13], $Cl_2Si(C{\equiv}C{-}R^1)_2$ (**3**) and $Cl_2Si(CH{=}CH_2)C{\equiv}C{-}R^1$ (**4**), the desired silanes, together with $ClSi(C{\equiv}C{-}R^1)_3$, $Si(C{\equiv}C{-}R^1)_4$, and $ClSi(C{\equiv}C{-}R^1)_2CH{=}CH_2$, respectively. Pure samples of **2**, **3** and **4** were obtained (yield *ca.* 25 %) by fractional distillation. **2a**: b. p. 30 °C/0.3 Torr. – ^{1}H NMR (300 MHz, C_6D_6): δ = 1.88, 1.20, 0.66 (t, m, t, 9H, ^{n}Bu). **3a**: b. p. 85 °C/0.15 Torr. – ^{1}H NMR (300 MHz, C_6D_6): δ = 1.77, 1.04, 0.66 (t, m, t, 18 H, ^{n}Bu). **4a**: b. p. = 38 – 42 °C/0.3 Torr. – ^{1}H NMR (400 MHz, C_6D_6): δ = 1.8, 1.1, 0.7 (t, m, t, 9H, ^{n}Bu), 5.8 (dd, $^2J(^1H,^1H)$ = 3.6 Hz, $^3J(^1H,^1H)_{cis}$ = 13.4 Hz, 1H, =CH_2), 6.0 (dd, $^3J(^1H,^1H)_{cis}$ = 13.4 Hz, $^3J(^1H,^1H)_{trans}$ = 19.8 Hz, 1H, Si–CH), 6.1 (dd, $^2J(^1H, ^1H)$ = 3.7 Hz, $^3J(^1H,^1H)$ = 19.9 Hz, 1H, =CH_2). – MS: *m/z* (%) = 207 (17) [M^+], 192 (5) [M^+–CH_3], 180 (10) [M^+–C_2H_3], 171 (25) [M^+–Cl], 81 (73) [$C_6H_9^+$], 43 (98) [$C_3H_7^+$], 41 (100). – **4b**: b. p. = 54 – 55 °C/0.075 Torr. – ^{1}H NMR (400 MHz, C_6D_6): δ = 6.8, 7.1 (m, m, 5H, Ph), 5.8 (dd, $^2J(^1H,^1H)$ = 3.5 Hz, $^3J(^1H,^1H)_{cis}$ = 13.5 Hz, 1H, =CH_2), 6.0 (dd, $^2J(^1H,^1H)_{cis}$ =13.5 Hz, $^3J(^1H,^1H)_{trans}$ = 19.8 Hz, 1H, Si–CH), 6.1 (dd, $^2J(^1H, ^1H)$ = 3.5 Hz, $^3J(^1H, ^1H)_{trans}$ = 19.4 Hz, 1H, =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 °C the product is the same but it takes 5 – 6 d in order to convert **2** into **8b**. **7a**: ^{1}H NMR (400 MHz, C_6D_6): δ = 2.30, 1.80, 1.10, 1.00 (t, m, m, t, 9H, ^{n}Bu), 1.30, 0.70 (m, t, 10H, BEt_2), 6.0 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 1H, =CH, $^3J(^{29}Si,^1H)$ = 35.3). **7a′**: ^{1}H NMR (400 MHz, C_6D_6): δ = 2.4, 1.8, 1.1, 1.0 (t, m, m, t, ^{n}Bu), 1.30, 0.80 (m, t, BEt_2), 6.60 (t, $^3J(^1H, ^1H)$ = 7.5 Hz, 1H, =CH). – MS: *m/z* (%) = 285 (10) [M^+], 207 (20), 115 (20), 92 (100), 27 (95). **7b**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1.30, 0.90 (q, t, 10H, BEt_2), 6.9 – 7.3 (m, 6H, Ph, =CH, $^3J(^{29}Si,^1H)$ = 35.8 Hz). **7b′**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1,20, 0.80 (q, t, BEt_2), 7.70 (s, =CH, $^3J(^{29}Si,^1H)$ = 32.9 Hz), 6.9 – 7.3 (m, Ph). – MS: *m/z* (%) = 304 (9) [M^+], 275 (35) [M^+–C_2H_5], 269 (6) [M^+–Cl], 265 (100), 240 (16), 236 (31), 199 (29), 133 (13). **8a**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1.44, 1.21 – 1.33, 0.90 (m, m, t, 14H, B^{n}Pr$_2$), 2.36, 1.21 – 1.33, 0.8 (q, m, t, 9H, ^{n}Bu), 6.07 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 1H, =CH,$^3J(^{29}Si,^1H)$ = 35.0 Hz). **8a′**: ^{1}H NMR: δ = 1.45, 1.21 – 1.33, 0.9 (m, m, t, B^{n}Pr$_2$), 2.43, 1.21 – 1.33, 0.8 (q, m, t, ^{n}Bu), 5.96 (t, $^3J(^1H,^1H)$ = 7.3 Hz, =CH). **8b**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1.4, 1.1, 0.9 (m, t, t, 14H, B^{n}Pr$_2$), 6.9 – 7.4 (m, 6H, Ph, =CH). **8b′**: ^{1}H NMR (C_6D_6): δ = 1.5, 0.9, 0.8 (m, t, t, B^{n}Pr$_2$), 6.9 – 7.4 (m, Ph, =CH).

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

The mixture of the silane $Cl_2Si(C{\equiv}C{-}^nBu)_2$ (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**: ^{1}H NMR (400 MHz, C_6D_6): δ = 0.86, 0.95, 1.2 – 2.1 (t, t, m, 18H, ^{n}Bu, ^{n}Bu), 1.0, 2.2 (t, m, 10H, Et_2B), 5.4 (t, $^3J(^1H, ^1H)$ = 7.0 Hz, 1H, =CH). – MS: *m/z* (%) = 331 (6) [M^+], 260 (76), 254 (100), 211 (45), 69 (45), 41 (76). **15**: ^{1}H NMR: δ = 2.1, 1.3, 0.9 (m, m, t, 18H, ^{n}Bu, ^{n}Bu), 1.4, 1.1 (m, t, 14H, B^{n}Pr$_2$), 5.4 (t, $^3J(^1H, ^1H)$ = 7.0 Hz, 1H, =C–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-

dicated the formation of the product **16**, with **13** remaining as a side product. **12**: ^{1}H NMR (400 MHz, C_6D_6): δ = 0.6, 0.8, 1.1, 1.3, 1.8, 2.7 (t, t, m, m, m, q, 18H, ^{n}Bu, ^{n}Bu), 1.3 – 2.1 (m, 14H, BBN), 7.1 (t, $^3J(^1H,^1H)$ = 7.5 Hz, 1H, =CH). – ^{13}C NMR (100.5 MHz, C_6D_6): δ [$J(^{29}Si,^{13}C)$] = 165.8 [< 3] (=CH), 141.8 (br, B–C=), 112.5 [26.9] (≡C), 81.3 [132.1] (SiC≡), 34.5, 31.7 br, 23.5 (BBN), 35.2, 31.3, 29.9, 22.8, 22.1, 19.7, 13.6, 14.2 (^{n}Bu). – ^{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**: ^{1}H NMR (400 MHz, C_6D_6): δ = 0.8, 1.3, 2.5 (t, m, q, 18H, =C–^{n}Bu), 1.3 – 2.1 (m, 28H, BBN), 6.9 (t, $^3J(^1H,^1H)$ = 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 (^{n}Bu). – ^{29}Si NMR (74.8 MHz, C_6D_6): δ = 0.5. **16**: ^{1}H 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, ^{n}Bu,^{n}Bu), 1.7 – 2.1 (m, 14H, BBN), 5.8 (t, $^3J(^1H,^1H)$ = 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**: ^{1}H NMR (400 MHz, C_6D_6): δ = 2.2, 1.9, 1.3, 0.9 (m, t, m, t, 9H, ^{n}Bu), 5.9 (dd, $^2J(^1H,^1H)$ = 3.9 Hz, $^3J(^1H,^1H)_{cis}$ = 13.1 Hz, 1H, =CH_2), 6.0 (dd, $^3J(^1H,^1H)_{cis}$ = 13.1 Hz, $^3J(^1H,^1H)_{trans}$ = 19.5 Hz, 1H, Si–CH), 6.1 (dd, $^2J(^1H,^1H)$ = 4.0 Hz, $^3J(^1H,^1H)_{trans}$ = 19.5 Hz, 1H, =CH_2), 1.2, 0.7 (m, t, 10H, BEt_2). **17b**: ^{1}H NMR (400 MHz, C_6D_6): δ = 6.8 – 7.1 (m, 5H, Ph), 5.4 (dd, $^2J(^1H,^1H)$ = 3.1 Hz, $^3J(^1H,^1H)_{cis}$ = 14.1 Hz, 1H, =CH_2), 5.5 (dd, $^3J(^1H,^1H)_{cis}$ = 14.0 Hz, $^3J(^1H,^1H)_{trans}$ = 19.6 Hz, 1H, Si–CH), 5.6 (dd, $^2J(^1H,^1H)$ = 3.1 Hz, $^3J(^1H,^1H)_{trans}$ = 19.6 Hz, 1H, =CH_2), 1.2, 0.8 (q, t, 10H, BEt_2). **18b**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1.4 – 1.5, 0.9 (m, t, B^{n}Pr$_2$), 5.6 – 6.0 (m, Si–CH, =CH_2), 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 (≡C), 87.0 (SiC≡), 33.5, 31.4 (br), 23.5 (BBN), 16.2 ($SiCH_2$), 18.7 (br, B–CH_2). **20a**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1.2 – 1.9 (m, 14H, BBN), 2.4, 1.3, 0.8 (m, m, t, 9H, ^{n}Bu), 2.4 (m, 2H, CH_2), 1.1 (m, 2H, CH_2). – ^{13}C NMR (100.5 MHz, C_6D_6): δ [$J(^{29}Si,^{13}C)$] = 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 (^{n}Bu). – ^{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) [M^+–C_3H_7], 271 (32) [M^+–C_4H_8], 244 (89), 208 (9) [M^+–BBN], 122 (100), 110 (31). **20b**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1.1, 2.3 (m, m, 4H, $SiCH_2$, CH_2), 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 [$J(^{29}Si,^{13}C)$] = 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) [M^+–H], 313 (15) [M^+–Cl], 239 (61), 228 (86) [M^+–BBN], 192 (72) [M^+–$BClC_8H_{14}$].

*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**: ^{1}H 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, CH_3). **22**: b. p. 38 °C/0.1 Torr (*ca.* 90 % pure). – ^{1}H NMR (400 MHz, C_6D_6): δ = 0.9, 1.5 (t, m, CH_3, CH_2, BPr_2), 1.2 (d, CH_3, $^3J(^1H,^1H)$ = 7.0 Hz), 1.9 (q, CH). **23**: ^{1}H NMR (400 MHz, C_6D_6): δ = 1.1 – 1.8 (m, 14H, BBN), 1.40, 1.20 (m, m, 4H, CH_2, Si–CH_2). **24**, **24′**: ^{1}H NMR (400 MHz, C_6D_6): δ = 0.44 (s, SiMe), 0.42 (s, SiMe), 1.30, 0.90 (m, t, BEt_2, CH_3, CH_2CH_2), 1.70 (q, $^3J(^1H,^1H)$ = 7.4 Hz, 1H, CH).

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