

# Tris(hydridosilylethyl)boranes: highly reactive synthons for polymeric silicon compounds

Markus Weinmann <sup>a,\*</sup>, Thomas W. Kamphowe <sup>a</sup>, Peter Fischer <sup>b</sup>, Fritz Aldinger <sup>a</sup>

<sup>a</sup> Max-Planck-Institut für Metallforschung and Institut für Nichtmetallische Anorganische Materialien, Universität Stuttgart, Pulvermetallurgisches Laboratorium, Heisenbergstraße 5, D-70569 Stuttgart, Germany

<sup>b</sup> Institut für Organische Chemie und Isotopenforschung, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

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## Abstract

Two methods for the synthesis of tris(hydridosilylethyl)boranes  $B[C_2H_4Si(CH_3)_nH_{3-n}]_3$  ( $C_2H_4 = CHCH_3, CH_2CH_2$ ;  $n = 0, 1, 2$ ; **5a–c**) are reported. In the first route, tris(chlorosilylethyl)boranes  $B[C_2H_4Si(CH_3)_nCl_{3-n}]_3$  ( $n = 0, 1, 2$ ; **3a–c**) are reacted with  $LiAlH_4$  in diethyl ether solution. Compounds **3a–c** are prepared by hydroboration of the respective vinyl chlorosilanes  $(H_2C=CH)Si(CH_3)_nCl_{3-n}$  ( $n = 0, 1, 2$ ; **1a–c**) with borane dimethylsulfide,  $BH_3 \cdot S(CH_3)_2$ . Hydroboration of hydrido vinylsilanes  $(H_2C=CH)Si(CH_3)_nH_{3-n}$  ( $n = 0, 1, 2$ ; **6a–c**) with  $BH_3 \cdot S(CH_3)_2$  represents an alternative route, which produces **5a–c** in much higher yield. The intermediates **6a–c** are obtained from **1a–c** and  $LiAlH_4$  in diethyl ether solution and, because of their difficult handling, reacted in situ. Detailed NMR studies prove boron addition to the olefinic moieties to be not regioselective, since resonance signals for products formed by  $\alpha$ - and  $\beta$ -boron addition to the vinyl functions are observed. The elemental constitution of **5a–c** is established by high-resolution electron ionization mass spectrometry for both the molecular ion peak and a series of fragment ions. Major fragments arise from C–C bond formation in the gas phase between two of the boron side chains in the ion dipole complex. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Hydroboration; Vinylsilanes; Polysilazanes; NMR; EI-MS

## 1. Introduction

During the last two decades, enormous progress has been made in the synthesis of ceramic composite materials via precursor thermolysis, by which suitable polymeric networks are transformed into a wide variety of amorphous ceramics [1]. Silicon-containing polymeric compounds, e.g. polysilanes [2], polycarbosilanes [3], polysilazanes [4], and polysiloxanes [5], have proven to be especially promising precursors for technologically important ceramic components, such as fibers, coatings, infiltrated porous media, or complex-shaped bulk parts. Silicon-based ceramics with exceptional high-temperature and oxidation stability are obtained from organic

silicon polymers, which additionally incorporate boron, carbon, nitrogen and hydrogen, e.g. polyborosilazanes, borazine-modified polysilazanes, or boron-containing polysilylcarbodiimides [6–12].

The polymeric precursors specified above are either synthesized in solution or obtained by polycondensation reactions, with inevitable formation of by-products. Both aspects strongly limit the applicability of such polymeric systems for specific technological applications. We therefore searched for novel synthons that might be transformed into Si–B–C–N preceramic polymers, e.g. by polyaddition reactions, requiring neither catalysts nor solvents, and not producing any by-products. In this context, we now report the synthesis and detailed structural characterization, by NMR, IR, and mass spectrometry, of tris(hydridosilylethyl)boranes. These highly reactive species represent a novel educt type for the synthesis of Si–B–C–N preceramic compounds.

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\* Corresponding author. Tel.: +49-711-686-1231; fax: +49-711-686-1131.

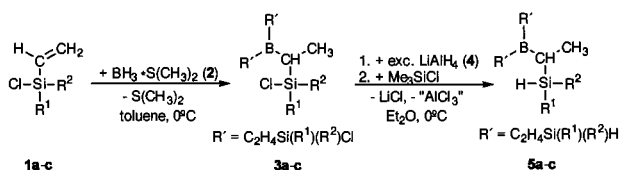
E-mail address: weinmann@aldix.mpi-stuttgart.mpg.de (M. Weinmann)

## 2. Results and discussion

### 2.1. Synthesis of tris(hydridosilylethyl)boranes from tris(chlorosilylethyl)boranes

The tris(hydridosilylethyl)boranes  $B[C_2H_4Si(CH_3)_nH_{3-n}]_3$  ( $n=0, 1, 2$ ; **5a–c**) were first synthesized by reaction of the corresponding chloro-substituted compounds  $B[C_2H_4Si(CH_3)_nCl_{3-n}]_3$  ( $n=0, 1, 2$ ; **3a–c**) with  $LiAlH_4$  (**4**) in diethyl ether solution. The tris(chlorosilylethyl)boranes **3a–c** themselves were prepared by hydroboration of chloro vinylsilanes  $(H_2C=CH)Si(CH_3)_nCl_{3-n}$  ( $n=0, 1, 2$ ; **1a–c**) with borane dimethylsulfide (**2**) as described previously [12a,13].

A 2 M  $BH_3 \cdot S(CH_3)_2$  solution in toluene was added dropwise at  $0^\circ C$  to a solution of the chloro vinylsilanes **1a–c**. The reaction mixture was allowed to warm to  $25^\circ C$ , and the volatile components were stripped off in vacuum. The spectroscopically pure colorless oils **3a–c** thus obtained were dissolved in diethyl ether, and a suspension of  $LiAlH_4$  (**4**, ~10% excess relative to Cl) in diethyl ether added dropwise at  $0^\circ C$ . The mixture was refluxed for 3 h, and excess  $LiAlH_4$  removed by treatment with  $(H_3C)_3SiCl$ .

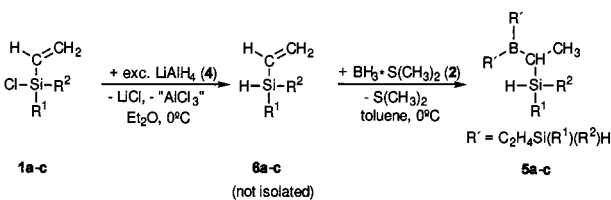


	R <sup>1</sup>	R <sup>2</sup>		R <sup>1</sup>	R <sup>2</sup>
<b>1a, 3a</b>	Cl	Cl	<b>5a</b>	H	H
<b>1b, 3b</b>	Cl	CH <sub>3</sub>	<b>5b</b>	H	CH <sub>3</sub>
<b>1c, 3c</b>	CH <sub>3</sub>	CH <sub>3</sub>	<b>5c</b>	CH <sub>3</sub>	CH <sub>3</sub>

After filtration and high-vacuum distillation, compounds **5a–c** were obtained as colorless oils. They are extremely sensitive to moisture and explode upon exposure to air (**CAUTION!**). While the intermediates **3a–c** are formed from **1a–c** in close to quantitative yield, the tris(hydridosilylethyl)boranes **5a–c** were obtained with at most 55% yield, due possibly to the formation of boron hydrides. This moderate yield motivated us to search for an alternative route to **5a–c**. By starting from hydrido vinylsilanes, formation of boron hydrides is indeed suppressed completely.

### 2.2. Synthesis of tris(hydridosilylethyl)boranes from hydrido vinylsilanes

Hydrido vinylsilanes of the general structure  $(H_2C=CH)Si(CH_3)_nH_{3-n}$  are difficult to handle in neat form; they were therefore synthesized from the corresponding chloro vinylsilanes **1a–c** with  $LiAlH_4$  (**4**) in diethyl ether and reacted in situ.



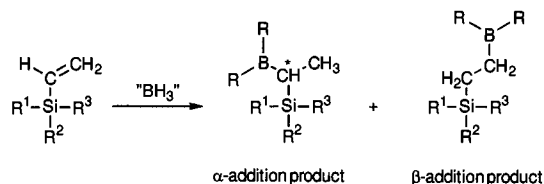
	R <sup>1</sup>	R <sup>2</sup>		R <sup>1</sup>	R <sup>2</sup>
<b>1a</b>	Cl	Cl	<b>5a, 6a</b>	H	H
<b>1b</b>	Cl	CH <sub>3</sub>	<b>5b, 6b</b>	H	CH <sub>3</sub>
<b>1c</b>	CH <sub>3</sub>	CH <sub>3</sub>	<b>5c, 6c</b>	CH <sub>3</sub>	CH <sub>3</sub>

The Schlenk reaction flask used for the hydrogenation of the chlorosilanes was connected directly, via distillation bridge and gas inlet tube, to a second flask containing the borane dimethylsulfide solution in toluene. The chloro vinylsilane was added dropwise to the  $LiAlH_4$  suspension, and the reaction mixture heated to  $50^\circ C$ . Approximately 80% of the diethyl ether–hydrido vinylsilane solution was distilled into the flask with the  $BH_3 \cdot S(CH_3)_2$  solution. From this mixture, all volatile components were removed at  $25^\circ C/10^{-1}$  mbar. Compounds **5a–c** were obtained by vacuum distillation as colorless oils (86–90% yield relative to borane dimethylsulfide).

### 2.3. Spectroscopic characterization

The tris(hydridosilylethyl)boranes  $B[C_2H_4Si(CH_3)_nH_{3-n}]_3$  **5a–c** were structurally characterized by various spectroscopic techniques,  $^1H$ -,  $^{11}B$ -,  $^{13}C$ -, and  $^{29}Si$ -NMR, IR, and electron ionization mass spectrometry (EI-MS). Their extreme sensitivity towards moisture and their explosive reaction upon exposure to air thwarted any attempts at elemental analysis.

Hydroboration of vinylsilanes is not regioselective as described previously [12a,13]. Rather, the boryl group may add, in each of the three successive hydroboration steps, at either the  $\alpha$ - or  $\beta$ -position of the vinyl function.



Due to this lack of regioselectivity, the tris(hydridosilylethyl)boranes **5a–c** are formed as a mixture of four regioisomers, which can be characterized with the following abbreviations:  $\alpha\alpha\alpha$ ,  $\alpha\alpha\beta$ ,  $\alpha\beta\beta$ ,  $\beta\beta\beta$ . For the silylethyl functions, resulting from  $\alpha$ -addition, a further complication arises since a stereogenic center is generated at the boron-bonded 1-silylethyl carbon (indicated by an asterisk in the above reaction scheme).

### 2.3.1. NMR spectroscopy

Consequently, the  $^1\text{H}$ -NMR spectra of compounds **5a–c** present a complex appearance. The individual multiplet structures, which in part overlap, could be assigned unequivocally, however, by 2D NMR techniques. The  $^1\text{H},^1\text{H}$  COSY NMR spectrum (500.132 MHz) of  $\text{B}[\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{H}_2]_3$  (**5b**), obtained from  $(\text{H}_2\text{C}=\text{CH})\text{Si}(\text{CH}_3)\text{H}_2$  (**6b**) and  $\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$ , is shown as an example in Fig. 1.

On the basis of both relative chemical shift and coupling pattern, the tightly overlapping triplets at  $-0.07$  to  $0.05$  ppm are assigned, in a straightforward manner, to the  $\text{SiCH}_3$  groups in the various isomers. The dominant cross-peak in the  $^1\text{H},^1\text{H}$  COSY NMR links them with the respective  $\text{SiH}_2$  multiplets in the  $3.70$ – $4.00$  ppm range ( $^3J_{\text{H,H}}$   $4.1$ – $4.2$  Hz), which appear divided into three separate complex patterns. The low-field one is connected, via two pronounced cross-peaks, to two multiplets at  $0.50$  and  $0.64$  ppm, which represent  $\text{SiCH}_2$  groups, generated by  $\beta$ -addition of boron to the

vinylsilane. The two remaining  $\text{SiH}_2$  multiplets are connected by the respective cross-peaks to signals between  $1.15$  and  $1.23$  ppm. Both the relative position and the severely broadened lines prove these resonances to stem from the  $\text{B}-\text{CH}(\text{CH}_3)-\text{Si}$  functions resulting from  $\alpha$ -addition. Finally, there is a whole series of sharp  $\text{B}-\text{CH}(\text{CH}_3)-\text{Si}$  doublets ( $^3J_{\text{H,H}}$   $\sim 7$  Hz) for the various side chains with  $\alpha$ -addition structure at  $1.06$ – $1.13$  ppm. They are superimposed upon the  $\text{BCH}_2$  multiplets of the  $\beta$ -addition side chains, which in turn are marked clearly by the prominent cross-peak to the  $\text{SiCH}_2$  multiplets.

All compounds **5a–c** display  $^1\text{H}$ -NMR spectra with comparable appearance; thus, the assignments presented above exemplarily for **5b** (obtained from **6b**) are valid for the analysis of the  $^1\text{H}$ -NMR spectra of all compounds **5a–c** (see Table 1). The  $\text{SiH}$  protons appear as multiplets between  $3.3$  and  $4.1$  ppm. The respective  $\text{SiCH}_3$  multiplets (**5b,c**) are centered closely at  $0$  ppm and set off clearly from the  $\text{Si}-\text{CH}_2$  resonance

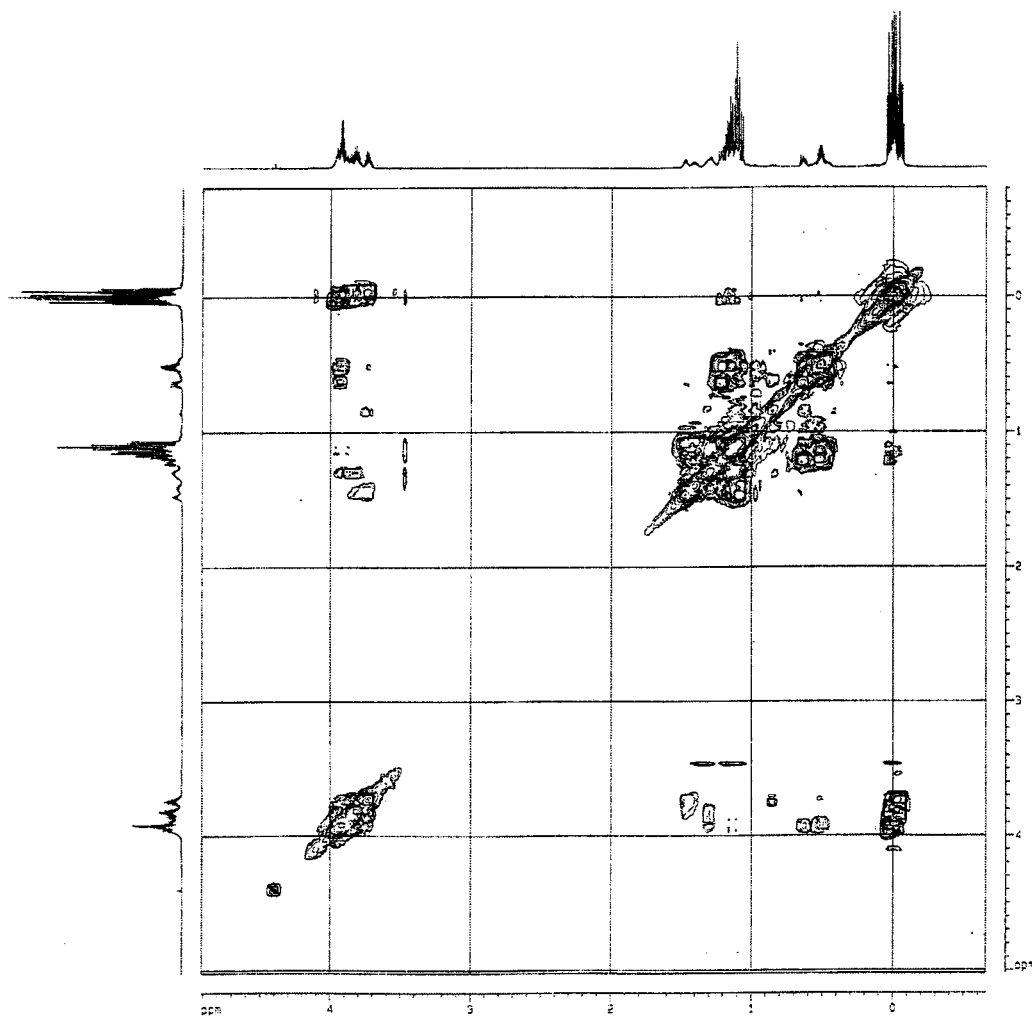


Fig. 1.  $^1\text{H},^1\text{H}$  COSY-NMR spectrum (500.132 MHz) of  $\text{B}[\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{H}_2]_3$  (**5b**, 0.01 M in  $\text{C}_6\text{D}_6$ ) obtained from  $(\text{H}_2\text{C}=\text{CH})\text{Si}(\text{CH}_3)\text{H}_2$  (**6b**) and  $\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$ .

Table 1  
<sup>1</sup>H-NMR chemical shift and integral values for the aliphatic C<sub>2</sub>H<sub>4</sub> units in tris(hydridosilylethyl)boranes **5a–c**

	<b>5a</b> from <b>3a</b>	<b>5b</b> from <b>3b</b> <sup>a</sup>	<b>5c</b> from <b>3d</b>	<b>5a</b> from <b>6a</b> <sup>a</sup>	<b>5b</b> from <b>6b</b> <sup>a</sup>	<b>5c</b> from <b>6c</b>
δ SiCH <sub>2</sub>	0.24–0.53	0.51–0.72	0.44–0.67	0.33–0.53	0.46–0.6	0.32–0.74
Int. SiCH <sub>2</sub>	0.8 H	2 H	2.8 H	1.4 H	2.2 H	3.2 H
δ CHCH <sub>3</sub>	0.66–0.72	1.08–1.26	1.05–1.13	0.69–1.08	1.04–1.23	1.05–1.12
Int. CHCH <sub>3</sub>	7.8 H	6 H	4.8 H	7 H	5.6 H	4.2 H
δ BCH <sub>2</sub>	1.21–1.40	1.08–1.26	1.14–1.22	0.69–1.08	1.04–1.23	1.13–1.25
Int. BCH <sub>2</sub>	0.8 H	2 H	2.8 H	1.4 H	2.2 H	3.2 H
δ CHCH <sub>3</sub>	0.89–1.12	1.32–1.52	1.42–1.46	1.20–1.32	1.26–1.49	1.28–1.46
Int. CHCH <sub>3</sub>	2.6 H	2 H	1.6 H	2.2 H	2.0 H	1.4 H
α:β ratio	6.5:1	2:1	1.2:1	3.3:1	1.7:1	0.9:1

<sup>a</sup> In this case, the resonance signals of CHCH<sub>3</sub> and BCH<sub>2</sub> overlap. The intensity of these signals was determined by subtracting the integrals of the SiCH<sub>2</sub> resonance signals from the sum of the integrals of the CHCH<sub>3</sub>+BCH<sub>2</sub> signals: Int. CHCH<sub>3</sub> = Int. (CHCH<sub>3</sub>+BCH<sub>2</sub>) – Int. SiCH<sub>2</sub>.

signals for the β-addition products (0.25–0.75 ppm). Both resonance signals for the CHCH<sub>3</sub> residues of the α-addition products and the broad B–CH<sub>2</sub> signals of the β-addition products are crowded together in the 1.0–1.5 ppm range. They are sufficiently set off from the SiCH<sub>2</sub> region, though, to allow for discrete integration for each compound. This is of crucial importance, since the SiCH<sub>2</sub> integral represents the share of 2-silyl-substituted ethyl side chains in all possible regioisomers. Subtracting this value from the bulk integral across the BCH<sub>2</sub> and CHCH<sub>3</sub> signals (see Table 1) gives an integral value for all 1-silyl-substituted side chains. The integrals for both regioisomeric functions correspond to four protons each, B–CH<sub>2</sub>CH<sub>2</sub>–Si or B–CH(CH<sub>3</sub>)–Si; thus, the α:β ratio can be read off directly (see Table 1, last line).

The α:β ratio for B(C<sub>2</sub>H<sub>4</sub>SiH<sub>3</sub>)<sub>3</sub> (**5a**), obtained by hydroboration of vinyl trichlorosilane (**1a**) and subsequent reaction with LiAlH<sub>4</sub> (**4**), is 6.5:1; **5a** obtained from vinylsilane (**6a**) and BH<sub>3</sub>·S(CH<sub>3</sub>)<sub>2</sub> (**2**) in contrast shows an α:β ratio of 3.3:1. For the corresponding methyl derivatives the following α:β ratios are determined: 2:1 for the synthesis of **5b** from **3b**, 1.7:1 for the synthesis of **5b** from **6b**, 1.2:1 for synthesis of **5c** from **3d**, and 0.9:1 for the synthesis of **5c** from **6c**. This variance is caused by (i) steric effects and (ii) electronic, i.e. inductive effects. A schematic representation of the transition states (side-on B–H//C=C coordination) for the second α-hydroboration step is given in Fig. 2 for the reaction of H<sub>2</sub>B–CH(CH<sub>3</sub>)SiH<sub>3</sub> with (H<sub>2</sub>C=CH)SiH<sub>3</sub> (left) and of H<sub>2</sub>B–CH(CH<sub>3</sub>)Si(CH<sub>3</sub>)<sub>2</sub>H with (H<sub>2</sub>C=CH)Si(CH<sub>3</sub>)<sub>2</sub>H (right).

For the SiH<sub>3</sub> derivative, i.e. in the synthesis of **5a**, no interaction (steric hindrance) is apparent between the CHCH<sub>3</sub> moiety in the H<sub>2</sub>B–CH(CH<sub>3</sub>)SiH<sub>3</sub> intermediate and the silicon-bonded hydrogen atoms of vinylsilane (H<sub>2</sub>C=CH)SiH<sub>3</sub>. With the Si(CH<sub>3</sub>)<sub>2</sub>H derivative (synthesis of **5c**), in contrast, the B–H bond of the H<sub>2</sub>B–CH(CH<sub>3</sub>)Si(CH<sub>3</sub>)<sub>2</sub>H intermediate cannot approach the α-position of the C=C unit of vinyl dimethylsilane

(H<sub>2</sub>C=CH)Si(CH<sub>3</sub>)<sub>2</sub>H sufficiently for incipient bond formation because of steric repulsion between the CHCH<sub>3</sub> moiety and one of the SiCH<sub>3</sub> groups of the vinylsilane. Since for the third hydroboration step this spatial interaction is even more pronounced in HB[CH(CH<sub>3</sub>)Si(CH<sub>3</sub>)<sub>2</sub>H]<sub>2</sub>, β-addition is the more favored.

The influence of electronic effects upon the regioselectivity of hydroboration of vinylsilanes is more difficult to assess. Recent DFT (density functional theory) calculations indicate that electron-withdrawing substituents on silicon dramatically decrease the π-electron density around the terminal β-vinyl carbon, thus directing boron addition to the α-position [14].

The α:β ratio determined from the bulk integrals (see Table 1) neither gives an indication of the number of regioisomers which it represents, nor does it reflect upon their quantitative distribution. For this, the NMR spectra have to be analyzed in much more detail. In the following, such a spectral breakdown is represented

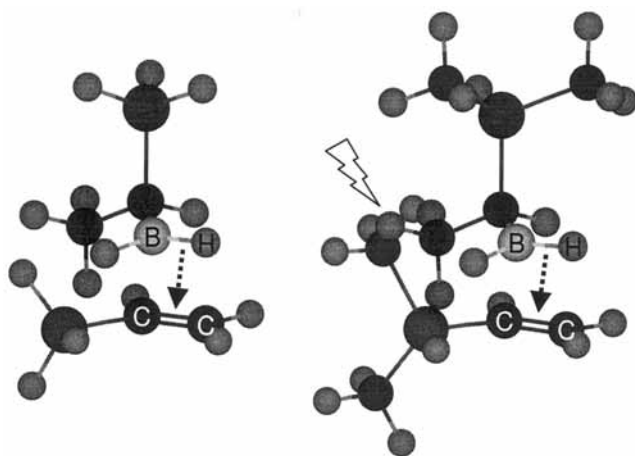


Fig. 2. Relative topology of the transition state for the second α-hydroboration step of H<sub>2</sub>B–CH(CH<sub>3</sub>)SiR<sub>2</sub>H + (H<sub>2</sub>C=CH)SiR<sub>2</sub>H (R = H, left; R = CH<sub>3</sub>, right; schematic representation: view parallel to the Si–C=C plane).

Table 2  
Possible stereoisomers of  $B[C_2H_4Si(CH_3)H_2]_3$  (**5b**;  $C_2H_4=CHCH_3$ ,  $CH_2CH_2$ ) and expected number of NMR signals for selected nuclei

Isomer <sup>a</sup>	Chiral centers <sup>b</sup>	Possible abs. configuration	Expected no. of $\alpha/\beta$ $SiCH_3$	Expected no. of $CHCH_3$	Expected no. of $\alpha/\beta$ $Si$	Expected no. of $SiCH_2$
$\alpha\alpha\alpha$	3 (8)	<i>RRR</i> , <i>SSS</i>	1( $\alpha$ )	1( $\alpha$ )	1( $\alpha$ )	–
		<i>RRS</i> , <i>RSR</i>	1( $\alpha$ )	–	1( $\alpha$ )	–
		<i>SRR</i> , <i>SSR</i>	1( $\alpha$ )	1( $\alpha$ )	1( $\alpha$ )	–
		<i>SRS</i> , <i>RSS</i>	1( $\alpha$ )	–	1( $\alpha$ )	–
$\alpha\alpha\beta$	2 (4)	<i>RR</i> , <i>SS</i>	1( $\alpha$ )+1( $\beta$ )	1( $\alpha$ )	1( $\alpha$ )+1( $\beta$ )	1( $\beta$ )
		<i>RS</i> , <i>SR</i>	1( $\alpha$ )+1( $\beta$ )	1( $\alpha$ )	1( $\alpha$ )+1( $\beta$ )	1( $\beta$ )
$\alpha\beta\beta$	1 (2)	<i>R</i> , <i>S</i>	1( $\alpha$ )+1( $\beta$ )	1( $\alpha$ )	1( $\alpha$ )+1( $\beta$ )	1( $\beta$ )
$\beta\beta\beta$	0	–	1( $\beta$ )	–	1( $\beta$ )	1( $\beta$ )
$\Sigma$		14	5( $\alpha$ )+4( $\beta$ )	5( $\alpha$ )	5( $\alpha$ )+4( $\beta$ )	4( $\beta$ )

<sup>a</sup> Regiochemistry for each successive hydroboration step.

<sup>b</sup> The number of configurational isomers given in parentheses.

exemplarily for  $B[C_2H_4Si(CH_3)H_2]_3$  (**5b**), obtained from  $(H_2C=CH)Si(CH_3)H_2$  (**6b**) and  $BH_3 \cdot S(CH_3)_2$  (**2**). The formula unit  $C_2H_4$  stands for both a  $CHCH_3$  and a  $CH_2CH_2$  moiety, representing the products of  $\alpha$ - and  $\beta$ -hydroboration, respectively.

In Table 2, all possible stereoisomers that may be produced by  $\alpha$ - or  $\beta$ -boron addition in each of the three successive hydroboration stages are listed. For each of these potential structures, the expected number of chemically non-equivalent, i.e. anisochorous  $^1H$ ,  $^{13}C$ , and  $^{29}Si$  positions is given.

The compilation in Table 2 shows that 14 stereoisomers can be formed in all. Triple  $\beta$ -addition yields a product with no stereogenic center, i.e. one isomer only, with a single set each of the various  $CH_2-CH_2-SiH_2-CH_3$  resonances. With double  $\beta$ -addition, i.e. with just one  $\alpha$ -addition, a pair of enantiomers is formed, though it is not differentiated in the NMR. The product of double  $\alpha$ -addition represents the classic case of a *meso* and a *DL* pair of diastereoisomers for which two signal sets are expected. Both of these sets, just as the single set for the  $\alpha\beta\beta$  isomer, each comprise resonance signals for  $\alpha$ - and  $\beta$ - $C_2H_4Si(CH_3)H_2$  moieties. Triple  $\alpha$ -addition produces three stereogenic centers. As a consequence, eight stereoisomers are expected. Due to the  $C_3$  symmetry of the molecular framework of compounds **5a–c**, two diastereoisomers can be distinguished by NMR: *RRR* and *SSS* on one hand, *RRS*, *RSR*, *SRR*, *RSS*, *SRS*, and *SSR* on the other hand.

The  $^{29}Si\{^1H\}$ -NMR spectrum (Fig. 3) of **5b** shows nine well-separated resonance signals between  $-28.8$  and  $-32.9$  ppm, indicating that all possible isomers are indeed formed (cf. Table 2). Assignment of these resonances to individual isomers failed since the  $^1H$ -coupled  $^{29}Si$ -NMR spectrum (Fig. 3, insert) appears highly complex. By  $^1J_{Si,H}$  coupling (186.2–190.8 Hz;  $SiH_2$ ) and  $^2J_{Si,H}$  coupling (7.0–7.2 Hz;  $SiCH_3$ ,  $SiCH_2$ ,  $SiCH$ ), each resonance is split either into a triplet of quartets of triplets ( $\beta$ -boron addition) or into a triplet of quartets

of doublets ( $\alpha$ -boron addition). Remarkably, the primary  $^1J(^1H, ^{29}Si)$  triplets represent a spectral splitting of  $\sim 380$  Hz, whereas the overall chemical shift range for the individual  $^{29}Si$  nuclei is only 160 Hz.

The  $^{13}C\{^1H\}$ -NMR spectrum of **5b** validates the findings from the  $^{29}Si$ -NMR. There are eight  $SiCH_3$  signals, in the range  $-8.5$  to  $-7.4$  ppm; the ninth line probably coincides with one of the other signals. The resonances for the  $SiCH_2$  groups (from  $\beta$ -boron addition) are observed at 3.7, 4.0, 4.2, and 5.2 ppm, the methyl carbons of the  $CHCH_3$  units (from  $\alpha$ -boron addition) appear as expected at 12.0–13.2 ppm. The boron-bonded carbon atoms are severely broadened by the neighboring quadrupolar nucleus ( $BCH_2$  at 18.5 ppm,  $BCH$  at 20.5, 21.7, and 22.2 ppm), and thus not resolved for the different regioisomers.

Despite the inherent complexity of the proton NMR spectrum of **5b** (cf. Fig. 1), the  $SiCH_3$  and  $CHCH_3$  resonances are sufficiently set off from the remaining signals. Resolution enhancement (by Gaussian multiplication), however, reveals once again eight triplets for the  $SiCH_3$  protons (Fig. 4) centered at 0.038, 0.037, 0.014, 0.001,  $-0.006$ ,  $-0.014$ ,  $-0.042$ , and  $-0.063$  ppm with  $^3J_{H,H}$  4.1–4.2 Hz. For the  $CHCH_3$  moiety, five doublets appear resolved at 1.070, 1.097, 1.098, 1.112, and 1.114 ppm ( $^3J_{H,H}$  6.7 Hz).

Other than  $^1H$ -,  $^{13}C$ -, and  $^{29}Si$ -NMR spectra, the  $^{11}B$ -NMR spectrum shows only one single resonance around 80 ppm without any fine structure.

In combination, the results of the various NMR techniques have shown that in the synthesis of  $B[C_2H_4Si(CH_3)H_2]_3$  (**5b**) from  $(H_2C=CH)Si(CH_3)H_2$  (**6b**) and  $BH_3 \cdot S(CH_3)_2$ , all possible regioisomers in fact are formed. The bulk  $\alpha:\beta$  ratio, summed up over the three side chains of all isomers, is determined unequivocally as 1.7:1. The relative percentage of the different regio- and stereoisomers cannot be determined with sufficient precision, though. The complete sets of NMR data for all compounds **5a–c** are given in Section 4.

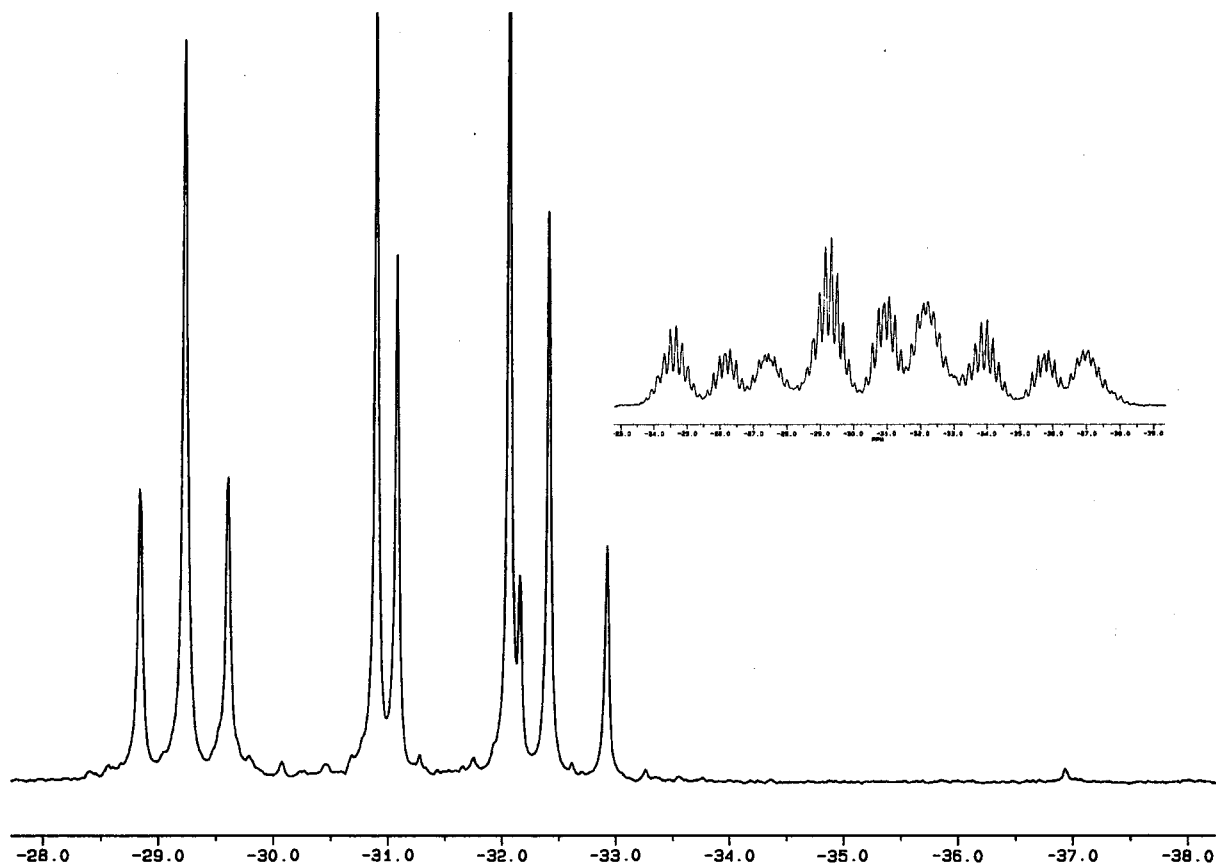


Fig. 3.  $^{29}\text{Si}\{^1\text{H}\}$ -NMR (39.761 MHz) and  $^{29}\text{Si}$ -NMR spectrum (insert, 39.761 MHz) of  $\text{B}[\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{H}_2]_3$  (**5b**, 0.2 M in  $\text{C}_6\text{D}_6$ ) obtained from  $(\text{H}_2\text{C}=\text{CH})\text{Si}(\text{CH}_3)\text{H}_2$  (**6b**) and  $\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$ .

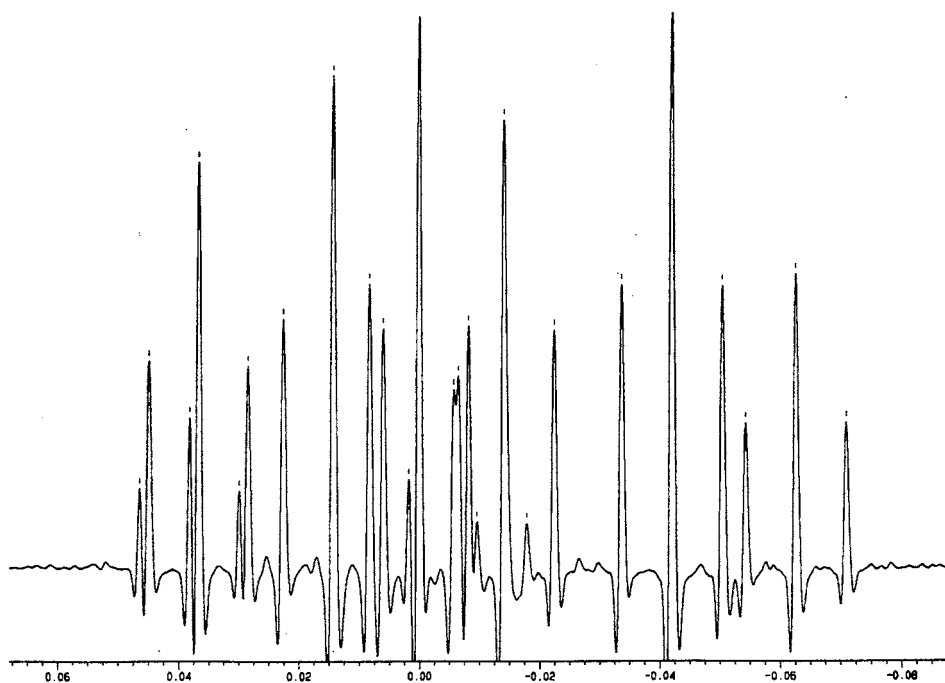


Fig. 4.  $\text{SiCH}_3$  resonance signals (resolution-enhanced by Gaussian multiplication) in the  $^1\text{H}$ -NMR spectrum of  $\text{B}[\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{H}_2]_3$  (**5b**) obtained from  $(\text{H}_2\text{C}=\text{CH})\text{Si}(\text{CH}_3)\text{H}_2$  (**6b**) and  $\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$  (500.133 MHz, 0.01 M in  $\text{C}_6\text{D}_6$ ; digital resolution 0.04 Hz/Pt).

Table 3  
IR spectroscopic data of compounds **5a–c**

	<b>5a</b>	<b>5b</b>	<b>5c</b>
$\nu(\text{C–H})$	2949 m, 2931 m, 2870 m	2962 m, 2908 m, 2873 m	2958 s, 2908 m, 2871 m
$\nu \text{ Si–H}$	2146 vs	2133 vs	2111 s
$\delta_{\text{a}}(\text{C–}) \text{CH}_3$	1462 m	1483 m	1467 m
$\delta_{\text{s}}(\text{C–}) \text{CH}_3$	1378 m	1408 s	1396 s
$\delta_{\text{s}}(\text{Si–}) \text{CH}_3$	–	1253 s	1252 s
$\nu_{\text{a}} \text{ C–C}$	1144 m	1182 s	1151 m
$\nu_{\text{a}} \text{ C–B–C}$	1081 w	1053 m	1093 m
$\delta \text{ CH}_3 \text{ rock.}$	937 m	944 s	n.o. <sup>a</sup>

<sup>a</sup> n.o., not observed.

### 2.3.2. IR spectroscopy

The IR spectra of compounds  $\text{B}[\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)_n\text{H}_{3-n}]_3$ , **5a–c**, clearly show the characteristic group frequencies (Table 3). Apart from the C–H stretching absorptions at 2870–2962  $\text{cm}^{-1}$ , characteristic bands observed are  $\delta_{\text{a}}(\text{C–CH}_3)$  1462–1483 (m);  $\delta_{\text{s}}(\text{C–CH}_3)$  1387–1408 (m),  $\delta_{\text{s}}(\text{Si–CH}_3)$  1252 or 1253 (m, only **5b** and **5c**),  $\nu_{\text{a}} \text{ C–B–C}$  1053–1093 (w–m) and the  $\text{CH}_3$  rocking vibration at 937–944  $\text{cm}^{-1}$  (m–s). The most remarkable feature in the IR spectra of compounds **5** is the very strong Si–H valence at 2111–2146  $\text{cm}^{-1}$ ; its frequency decreases with the number of silicon-bonded methyl groups (see Table 3), i.e. from 2146  $\text{cm}^{-1}$  (**5a**) to 2111  $\text{cm}^{-1}$  (**5c**). The relative signal intensity is attenuated in the same order. The spectra show no indication of B–H vibrations, which would indicate incomplete hydroboration.

### 2.3.3. Mass spectrometry

The mass spectra of compounds **5a–c** each show the molecular ion peak  $\text{M}^{+\bullet}$ , though with very low intensity and with a highly analogous fragmentation pattern. It is observed that due to the elimination of  $\text{H}^\bullet$ ,  $\text{CH}_3^\bullet$ ,  $\text{H}^\bullet\text{–SiR}_2\text{H}_2$ ,  $\text{CH}_2\text{SiR}_2\text{H}^\bullet$  and  $\text{C}_2\text{H}_4\text{SiR}_2\text{H}^\bullet$  (**5a**,  $\text{R}_2 = \text{H}_2$ ; **5b**,  $\text{R}_2 = \text{H}(\text{CH}_3)$ ; **5c**,  $\text{R}_2 = (\text{CH}_3)_2$ ) the corresponding cations are formed. For **5a** and **5b**, the base peak at  $m/z = 129$  and 157, respectively, arises from straightforward elimination of one hydridosilylethyl sidechain as a radical species  $\text{C}_2\text{H}_4\text{SiR}_2\text{H}^\bullet$ . In the case of **5c**, the respective fragment  $[\text{M} - \text{C}_2\text{H}_4\text{Si}(\text{CH}_3)_2\text{H}]^+$  ( $m/z = 185$ ) has only 79% relative intensity; here, the silaethylene radical cation  $\text{H}_2\text{C}^\bullet\text{=SiH}(\text{CH}_3)^{+\bullet}$  ( $m/z = 58$ ) constitutes the base peak. Fragments with higher  $m/z$  ratio than  $[\text{M} - \text{C}_2\text{H}_4\text{SiR}_2\text{H}]^+$  are observed in at most 13% relative intensity. Loss of  $\text{CH}_3^\bullet$  from the molecular ion of **5a** is possible only from a  $\text{CHCH}_3\text{SiH}_3$  side chain formed by  $\alpha$ -addition. In contrast, the fragment ions at  $m/z = 155$  (**5a**), 183 (**5b**), and 211 (**5c**) can only be formed from  $\beta$ -hydroboration products, via the fragmentation process  $\text{M}^{+\bullet} - \text{CH}_2\text{SiR}_2\text{H}^\bullet$  (see Fig. 5).

The cations observed at  $m/z = 129$  (**5a**), 157 (**5b**), and 185 (**5c**) are further stabilized by either elimination of

$\text{H}_2$  to  $m/z = 127$  (**5a**), 155 (**5b**), 183 (**5c**), or by dehydro-silylation to  $m/z = 97$  (**5a**, elimination of  $\text{SiH}_4$ ), 111 (**5b**, elimination of  $\text{H}_3\text{CSiH}_3$ ), and 125 (**5c**, elimination of  $(\text{H}_3\text{C})_2\text{SiH}_2$ ). For the allylic-type cations species thus formed, various structural alternatives exist (Scheme 1).

Remarkably, there is also a series of three boron-free fragment cations each with severely high intensity at  $m/z = 87$ , 101, 115 (**5a**), 115, 129, 143 (**5b**), 143, 157, and 171 (**5c**). Their elemental constitution was established unequivocally by dynamic high-resolution mass spectrometry ( $\Delta m$  in each case  $< 0.6$  mmu). These boron-free fragment ions cannot be formed by an elimination process directly from  $\text{M}^{+\bullet}$ ; rather, they represent products of hydrogen or alkyl transfer in the ion dipole complex as shown schematically in Scheme 2.

We propose that C–C bond formation takes place by the transfer of either a methyl group or a hydrogen atom from the  $\text{C}_2\text{H}_4\text{SiR}_2\text{H}^\bullet$  fragment to the boron center. Following B–C bond cleavage produces  $\text{HR}_2\text{Si}(\text{H})\text{C–C}(\text{CH}_2)\text{SiR}_2\text{H}^+$  ( $m/z = 101$ , **5a**; 129, **5b**; 157, **5c**; route 1) or  $\text{HR}_2\text{Si}(\text{CH}_3)\text{C–C}(\text{CH}_2)\text{SiR}_2\text{H}^+$  ( $m/z = 115$ , **5a**; 143, **5b**; 171, **5c**; route 2). Moreover, the EI-MS of **5a–c** delivers boron-free species with  $m/z = 87$  (**5a**), 115 (**5b**), and 143 (**5c**), which must also have been produced from the ion–dipole complex. In contrast to the mechanism proposed in Scheme 2, the boryl cation must have been delivered with a  $\text{CH}_2\text{CH}_3$  fragment of the radical species  $\text{C}_2\text{H}_4\text{SiR}_2\text{H}^\bullet$  (after isomerization of the radical fragment). Finally, also the expected ‘light weight’ fragments  $\text{SiH}_2\text{R}^+$  (31, 45) and  $\text{CH}_2\text{SiH}_2\text{R}^+$  (45, 59) are detected.

## 3. Outlook

First orienting studies have already shown a remarkable potential of the title compounds **5a–c** for the synthesis of novel precursors for Si–B–C–N ceramic composites [15,16]. Until now, Si–B–C–N polymers were usually obtained by salt elimination reactions [10,11], reaction of borazine with polysilazanes [7,8], or from bis(trimethylsilyl)carbodiimide and boron-

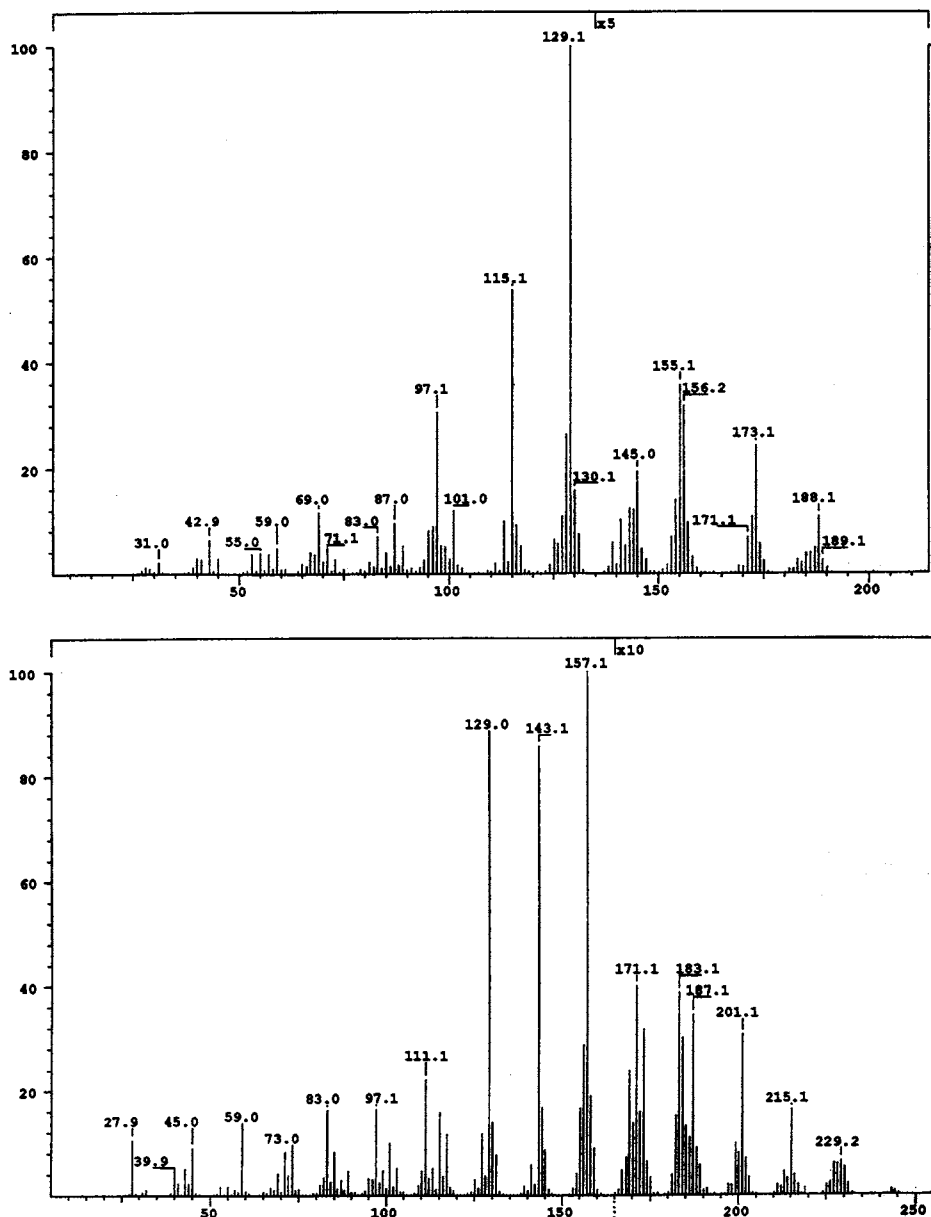
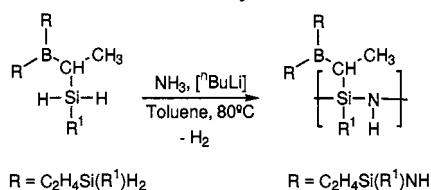


Fig. 5. EI mass spectra (70 eV) of  $B(C_2H_4SiH_3)_3$  (**5a**, top) and  $B[C_2H_4Si(CH_3)H_2]_3$  (**5b**, bottom).

modified chlorosilanes [12] with elimination of chlorotrimethylsilane. The novel precursors, derived from **5a–c**, are obtained either by base-catalyzed dehydrogenative coupling with ammonia or primary amines, or by hydrosilylation of vinyl- or alkynyl-substituted polysilazanes.

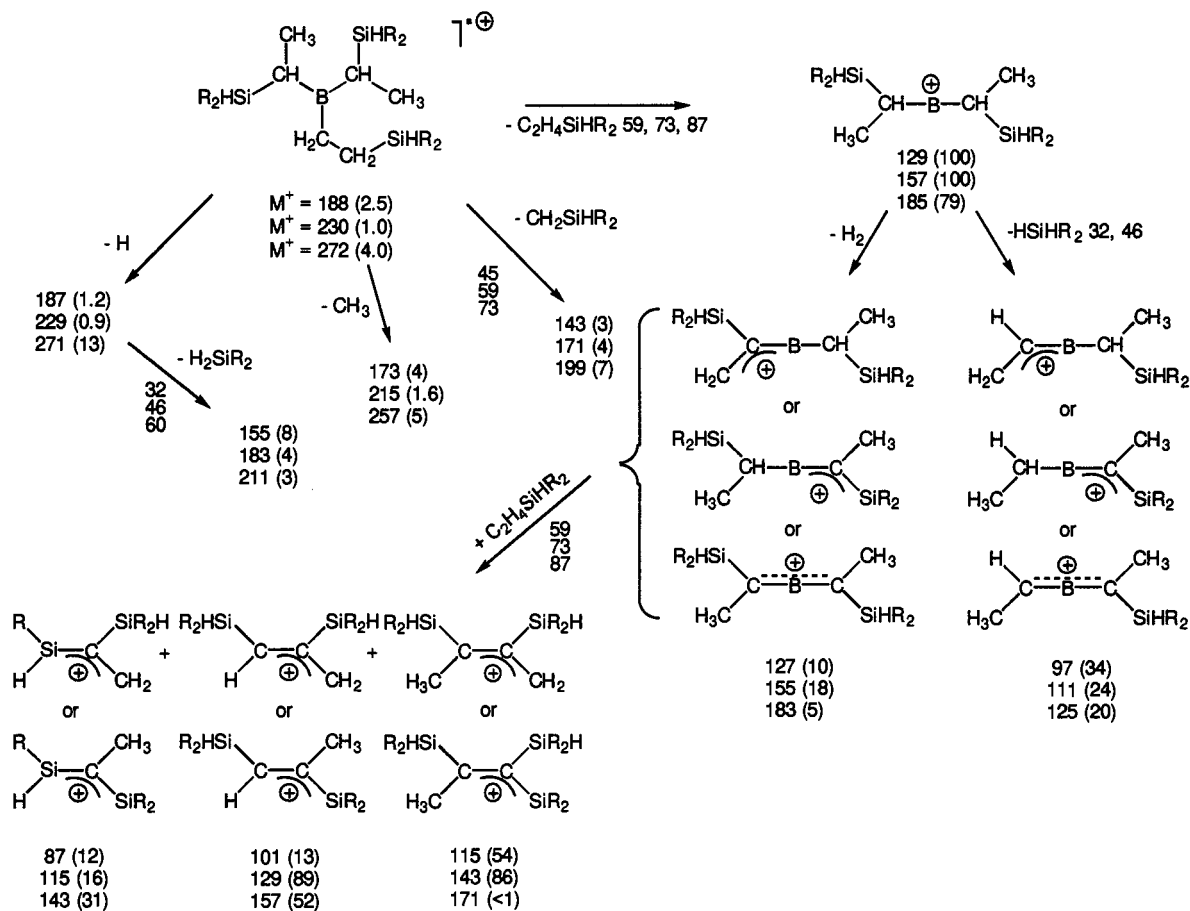
In the first case, compounds **5a–c** are dissolved in toluene and reacted with ammonia at elevated temperature with in most cases *n*-butyl lithium as a catalyst [15].



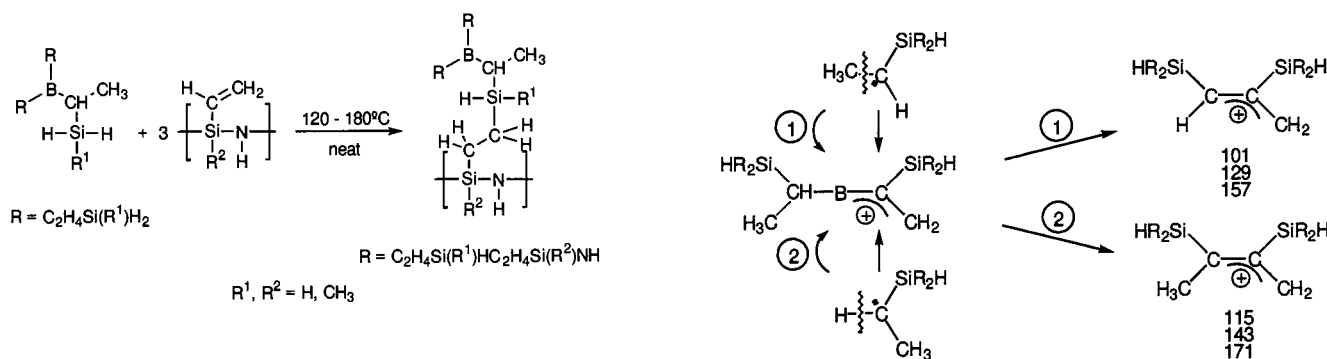
The polymer is precipitated directly from the solution; it can be separated from the solvent, soluble oligomers and catalyst simply by filtration. The only byproduct is molecular hydrogen.

The transformation of tris(hydrosilylethyl)-boranes into Si–B–C–N precursors by reaction with vinyl- or alkynyl-substituted polysilazanes also is a very promising reaction. Both components which are colorless oils are either mixed stoichiometrically or with excess polysilazane and reacted, without solvent or catalyst, at elevated temperature [16]. The Si–B–C–N precursors thus are obtained, directly and without any by-products, as glass-like polymers in quantitative yield.





Scheme 1. MS fragmentation of  $B[C_2H_4Si(R)_2H]_3$  (5a–c;  $R = H, CH_3$ ) obtained from vinylsilanes  $(H_2C=CH)Si(CH_3)_nH_{3-n}$  and  $BH_3 \cdot S(CH_3)_2$ . Top values are  $m/z$  for  $R_2 = H_2$ , bottom values are  $m/z$  for  $R_2 = (CH_3)_2$ , values in the middle are for  $R_2 = H(CH_3)$ . Relative intensities are given in parentheses.



## 4. Experimental

### 4.1. General comments

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques.  $LiAlH_4$  (95%) was obtained from Merck AG and used as a powder. Borane dimethylsulfide was obtained from Sigma Aldrich GmbH and used as a 2 M solution in toluene. Diethyl ether was purified by distillation from  $CaH_2$ ; toluene was purified by distillation from potas-

Scheme 2. Possible mechanism for the C–C bond formation in the ion–dipole complex  $H(R)_2SiC_2H_4BC(CH_2)Si(R)_2H^+ \cdot H_3CCHSi(R)_2H^+$  in the EI-MS (70 eV) of  $B[C_2H_4Si(R)_2H]_3$  by either (1) alkyl or (2) hydrogen transfer onto boron.

sium. FT-IR spectra were obtained with a Bruker IFS66 spectrometer as film in KBr cells.  $^1H$ - and  $^{13}C$ -NMR spectra were recorded on a Bruker ARX500 spectrometer (nominal frequency 500.133 and 125.77 MHz, respectively).  $^{11}B$ - and  $^{29}Si$ -NMR spectra were recorded on a Bruker AC250 spectrometer operating at 80.253 MHz ( $^{11}B$ -NMR), 39.761 or 49.694 MHz ( $^{29}Si$ -

Table 4  
Experimental details for the synthesis of tris(hydridosilylethyl)boranes (**5a–c**) from tris(chlorosilylethyl)boranes (**3a–c**)

Educt	B(C <sub>2</sub> H <sub>4</sub> SiCl <sub>3</sub> ) <sub>3</sub> ( <b>3a</b> )	B[C <sub>2</sub> H <sub>4</sub> Si(CH <sub>3</sub> )Cl <sub>2</sub> ] <sub>3</sub> ( <b>3b</b> )	B[C <sub>2</sub> H <sub>4</sub> Si(CH <sub>3</sub> ) <sub>2</sub> Cl] <sub>3</sub> ( <b>3c</b> )
Weight g (mmol)	29.2 (58.6)	40.7 (93)	28 (75)
Dissolved in Et <sub>2</sub> O (ml)	200	400	200
LiAlH <sub>4</sub> g (mmol)	5.11 (135)	5.48 (145)	2.27 (60)
Suspended in Et <sub>2</sub> O (ml)	200	200	50
(H <sub>3</sub> C) <sub>3</sub> SiCl g (mmol)	2.2 (20)	2.2 (20)	1.5 (14)
<i>n</i> -Pentane (ml)	250	300	100
Product	B(C <sub>2</sub> H <sub>4</sub> SiH <sub>3</sub> ) <sub>3</sub> ( <b>5a</b> )	B[C <sub>2</sub> H <sub>4</sub> Si(CH <sub>3</sub> )H <sub>2</sub> ] <sub>3</sub> ( <b>5b</b> )	B[C <sub>2</sub> H <sub>4</sub> Si(CH <sub>3</sub> ) <sub>2</sub> H] <sub>3</sub> ( <b>5c</b> )
Elemental composition	C <sub>6</sub> H <sub>21</sub> BSi <sub>3</sub>	C <sub>9</sub> H <sub>27</sub> BSi <sub>3</sub>	C <sub>12</sub> H <sub>33</sub> BSi <sub>3</sub>
Molecular mass (g mol <sup>-1</sup> )	188.32	230.39	272.64
B.p.	44°C/10 <sup>-1</sup> mbar	55°C/5 × 10 <sup>-2</sup> mbar	80°C/10 <sup>-1</sup> mbar
Yield g (mmol)	6.4 (34)	10.5 (46)	10.5 (46)
Yield (%)	58	49	49

Table 5  
<sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}-, <sup>11</sup>B{<sup>1</sup>H}-, and <sup>29</sup>Si{<sup>1</sup>H}-NMR chemical shifts or shift ranges (ppm) of tris(hydridosilylethyl)boranes (**5a–c**), obtained from tris(chlorosilylethyl)boranes (**3a–c**)

	<b>5a</b>	<b>5b</b> <sup>a</sup>	<b>5c</b>
<sup>1</sup> H-NMR (C <sub>6</sub> D <sub>6</sub> )			
δ SiCH <sub>3</sub>	–	–0.03–0.09 (9 H)	–0.07–0.06 (18 H)
δ SiCH <sub>2</sub>	0.24–0.53 (0.8 H)	0.51–0.72 (2 H)	0.44–0.67 (2.8 H)
δ CHCH <sub>3</sub>	0.66–0.72 (7.8 H)	1.08–1.26 (6 H)	1.05–1.13 (4.8 H)
δ BCH <sub>2</sub>	1.21–1.40 (0.8 H)	1.08–1.26 (2 H)	1.14–1.22 (2.8 H)
δ CHCH <sub>3</sub>	0.89–1.12 (2.6 H)	1.32–1.52 (2 H)	1.42–1.46 (1.6 H)
δ SiH	3.28–3.43 (6.5 H)	3.74–4.02 (6 H)	3.92–3.98 (1.5 H) 4.00–4.11 (1.5 H)
	3.48–3.59 (2.5 H)		
<sup>13</sup> C{ <sup>1</sup> H}-NMR (C <sub>6</sub> D <sub>6</sub> )			
δ SiCH <sub>3</sub>	–	–8.41, –8.39, –8.37, –8.34, –8.28, –8.27, –7.86, –7.76, –7.74	–5.83, –5.65, –5.15, –5.08, –4.88, –4.70, –4.23, –3.95, –0.21
δ SiCH <sub>2</sub>	–0.02, 0.8	3.77, 4.24, 5.19	5.35, 6.20, 6.31, 7.65
δ BCH <sub>2</sub>	14.8 (br)	17.8, 18.6 (br)	14.9, 18.2 (br)
δ CHCH <sub>3</sub>	13.7, 13.8, 14.0	12.00, 12.23, 12.25, 12.31, 12.78, 13.22	9.65, 9.73, 9.87, 10.04, 10.07, 10.61
δ CHCH <sub>3</sub>	16.5 (br)	20.3, 20.7 (br)	21.8, 24.1, 25.0 (br)
<sup>11</sup> B{ <sup>1</sup> H}-NMR (C <sub>6</sub> D <sub>6</sub> )	n.d. <sup>b</sup>	80.2	n.d.
<sup>29</sup> Si{ <sup>1</sup> H}-NMR (C <sub>6</sub> D <sub>6</sub> )	–57.8, –53.2, –47.1, –46.3	–32.9, –32.4, –32.0, –31.1, –30.9, –29.6, –29.2, –28.8	n.d.

<sup>a</sup> In this case, the resonance signals of CHCH<sub>3</sub> and BCH<sub>2</sub> overlap. The intensity of these signals was determined by subtracting the integrals of the SiCH<sub>2</sub> resonance signals from the sum of the integrals of the CHCH<sub>3</sub>+BCH<sub>2</sub> signals: Int. CHCH<sub>3</sub> = Int. (CHCH<sub>3</sub>+BCH<sub>2</sub>) – Int. SiCH<sub>2</sub>.

<sup>b</sup> n.d., not determined.

NMR). Chemical shifts are reported in δ units (parts per million) downfield from TMS (δ = 0) with the solvent as the reference signal): <sup>1</sup>H-NMR, C<sub>6</sub>D<sub>6</sub> δ = 7.17; <sup>13</sup>C-NMR, C<sub>6</sub>D<sub>6</sub> δ = 127.0; <sup>29</sup>Si-NMR: standard extern rel. TMS (δ = 0), <sup>11</sup>B-NMR: standard rel. BF<sub>3</sub>·OEt<sub>2</sub>. EI mass spectra (70 eV) were recorded on a MAT 8230 (Finnigan) mass spectrometer operating in the positive ion mode at the Institut für Organische Chemie der Universität Stuttgart.

**Caution:** Tris(hydridosilylethyl)boranes are highly reactive and may explode spontaneously upon exposure to air.

#### 4.2. Synthesis of tris(hydridosilylethyl)boranes (**5a–c**) from tris(chlorosilylethyl)boranes (**3a–c**)

In a typical experiment, a tris(chlorosilylethyl)borane B[C<sub>2</sub>H<sub>4</sub>Si(CH<sub>3</sub>)<sub>n</sub>Cl<sub>3–n</sub>]<sub>3</sub> (*n* = 0, 1, 2; **3a–c**) was dis-

solved in diethyl ether and a suspension of  $\text{LiAlH}_4$  (used in a slight excess) in diethyl ether added dropwise at  $0^\circ\text{C}$  to. The reaction mixture was then warmed to  $25^\circ\text{C}$  over night and refluxed for 3 h. After adding *n*-pentane and chlorotrimethylsilane,  $(\text{H}_3\text{C})_3\text{SiCl}$ , the mixture was refluxed again for 30 min and then filtered through a plug of Celite. All volatile components were removed in vacuum ( $10^{-1}$  mbar,  $25^\circ\text{C}$ ) and the oily colorless residue distilled in vacuum. For experimental details (scale, yields, b.p.) see Table 4; for NMR data see Table 5.

#### 4.2.1. IR spectra (KBr cells, $[\text{cm}^{-1}]$ )

**5a:**  $\nu(\text{C-H})$  2949 m, 2931 m, 2870 m;  $\nu(\text{Si-H})$  2146 vs;  $\delta_{\text{a}}(\text{C-CH}_3)$  1462 m;  $\delta_{\text{s}}(\text{C-CH}_3)$  1378 m;  $\nu(\text{C-C})$  1144 m;  $\delta(\text{CH}_3 \text{ rocking})$  937 m;  $\delta_{\text{s}}(\text{SiH}_3)$  901 s.

**5b:**  $\nu(\text{C-H})$  2962 m, 2908 m, 2873 m;  $\nu(\text{Si-H})$  2133 vs;  $\delta_{\text{a}}(\text{C-CH}_3)$  1483 m;  $\delta_{\text{a}}(\text{C-CH}_3)$  1408 s;  $\delta_{\text{s}}(\text{Si-CH}_3)$  1253 s;  $\nu(\text{C-C})$  1182 s;  $\nu_{\text{a}}(\text{C-B-C})$  1053 m;  $\delta(\text{CH}_3 \text{ rocking})$  944 s;  $\gamma(\text{SiH}_2)$  889 vs,  $\delta(\text{Si-C rocking})$  762 m.

**5c:**  $\nu(\text{C-H})$  2958 s, 2908 m, 2871 m;  $\nu(\text{Si-H})$  2111 s;  $\delta_{\text{a}}(\text{C-CH}_3)$  1467 m;  $\delta_{\text{s}}(\text{C-CH}_3)$  1396 m;  $\delta_{\text{s}}(\text{Si-CH}_3)$  1252 s;  $\nu(\text{C-C})$  1151 m;  $\nu_{\text{a}}(\text{C-B-C})$  1093 m;  $\gamma(\text{Si-H})$  879 vs;  $\delta(\text{Si-C rocking})$  766 m.

#### 4.2.2. EI-MS [70 eV; $m/z$ (rel. int.)]

**5b:**  $[\text{M}^+]$  230 (6);  $[\text{M}^+ - \text{H}]$  229 (22);  $[\text{M}^+ - \text{CH}_3]$  215 (9);  $[\text{M}^+ - \text{C}_2\text{H}_5]$  201 (10);  $[\text{M}^+ - \text{H} - \text{Si}(\text{CH}_3)_3]$  183 (10);  $[\text{M}^+ - \text{CH}_2\text{Si}(\text{CH}_3)_2]$  171 (23);  $[\text{M}^+ - \text{C}_2\text{H}_4\text{Si}(\text{CH}_3)_2]$  157 (94);  $[\text{M}^+ - \text{C}_2\text{H}_4\text{Si}(\text{CH}_3)_2 - \text{H}_2]$  155 (17);  $[\text{Si}_2\text{C}_6\text{H}_{15}^+]$  143 (94);  $[\text{Si}_2\text{C}_5\text{H}_{13}^+]$  129 (100);  $[\text{Si}_2\text{C}_5\text{H}_{11}^+]$  125 (19);  $[\text{BSiC}_5\text{H}_{12}^+]$  111 (24);  $[\text{SiC}_2\text{H}_6^+]$  58 (29).

### 4.3. Synthesis of tris(hydridosilylethyl)boranes (**5a-c**) from hydrido vinylsilanes (**6a-c**)

A chloro vinylsilane  $(\text{H}_2\text{C}=\text{CH})\text{Si}(\text{CH}_3)_n\text{Cl}_{3-n}$  ( $n = 0, 1, 2$ ; **1a-c**) was dissolved in diethyl ether and added dropwise at  $0^\circ\text{C}$  to a suspension of  $\text{LiAlH}_4$  (**4**) in diethyl

ether. The reaction flask was equipped with a reflux condenser cooled at  $-30^\circ\text{C}$  to avoid the loss of partly hydrogenated products. At the top of the reflux condenser a glass tube was installed, which was connected to a second reaction flask in which borane dimethylsulfide was dissolved in toluene. After addition of the chloro vinylsilane to the  $\text{LiAlH}_4$  suspension was completed, the reaction mixture was slowly warmed to  $25^\circ\text{C}$ . Cooling of the reflux condenser was stopped and the reaction mixture was heated further to slowly distil all volatile components into the borane dimethylsulfide solution which was cooled to  $0^\circ\text{C}$ . When the addition was completed the solvents, by-product dimethylsulfide as well as excess vinylsilane were carefully removed at  $25^\circ\text{C}/5 \times 10^{-1}$  mbar. The crude products were then purified by vacuum distillation to yield the title compounds as colorless oils. For experimental details (scale, yields, b.p.) see Table 6; for NMR data see Table 7.

#### 4.3.1. IR spectra (KBr cells, $[\text{cm}^{-1}]$ )

**5a:**  $\nu(\text{C-H})$  2949 m, 2931 m, 2870 m;  $\nu(\text{Si-H})$  2146 vs;  $\delta_{\text{a}}(\text{C-CH}_3)$  1457 m;  $\delta_{\text{s}}(\text{C-CH}_3)$  1378 m;  $\nu(\text{C-C})$  1144 m;  $\nu_{\text{a}}(\text{C-B-C})$  1081 w;  $\delta(\text{CH}_3 \text{ rocking})$  937 m;  $\delta_{\text{s}}(\text{SiH}_3)$  901 s.

**5b:**  $\nu(\text{C-H})$  2958 m, 2927 m, 2873 m;  $\nu(\text{Si-H})$  2129 vs;  $\delta_{\text{a}}(\text{C-CH}_3)$  1461 m;  $\delta_{\text{s}}(\text{C-CH}_3)$  1386 m;  $\delta_{\text{s}}(\text{Si-CH}_3)$  1253 m;  $\nu(\text{C-C})$  1180 s;  $\nu_{\text{a}}(\text{C-B-C})$  1072 w;  $\delta(\text{CH}_3 \text{ rocking})$  944 m;  $\gamma(\text{SiH})$  889 vs,  $\delta(\text{Si-C rocking})$  763 m.

**5c:**  $\nu(\text{C-H})$  2958 s, 2906 m, 2873 m;  $\nu(\text{Si-H})$  2113 s;  $\delta_{\text{a}}(\text{C-CH}_3)$  1459 m;  $\delta_{\text{s}}(\text{C-CH}_3)$  1396 m;  $\delta_{\text{s}}(\text{Si-CH}_3)$  1251 s;  $\nu_{\text{a}}(\text{C-C})$  1180 w;  $\gamma(\text{Si-H})$  883 vs.

#### 4.3.2. EI-MS [70 eV; $m/z$ (rel. Int.)]

**5a:**  $[\text{M}^+]$  188 (2.5);  $[\text{M}^+ - \text{CH}_3]$  173 (4);  $[\text{M}^+ - \text{CH}_3 - \text{H}_2]$  171 (2);  $[\text{M}^+ - \text{SiH}_3]$  157 (7);  $[\text{M}^+ - \text{H} - \text{SiH}_4]$  155 (8);  $[\text{M}^+ - \text{CH}_2\text{SiH}_3]$  143 (3);  $[\text{M}^+ - \text{C}_2\text{H}_4\text{SiH}_3]$  129 (100);  $[\text{M}^+ - \text{C}_2\text{H}_4\text{SiH}_3 - \text{H}_2]$  127 (10);  $[\text{Si}_2\text{C}_4\text{H}_{11}^+]$  115 (54);  $[\text{Si}_2\text{C}_3\text{H}_9^+]$  101 (13);  $[\text{BSiC}_4\text{H}_{10}^+]$  97 (34);  $[\text{Si}_2\text{C}_2\text{H}_7^+]$  87 (12);  $[\text{C}_2\text{H}_4\text{SiH}_3^+]$  59 (8);  $[\text{SiH}_3^+]$  31 (5).

Table 6

Experimental details for the synthesis of tris(hydridosilylethyl)boranes (**5a-c**) from chloro vinylsilanes (**1a-c**)

Educt	$(\text{H}_2\text{C}=\text{CH})\text{SiCl}_3$ ( <b>1a</b> )	$(\text{H}_2\text{C}=\text{CH})\text{Si}(\text{CH}_3)\text{Cl}_2$ ( <b>1b</b> )	$(\text{H}_2\text{C}=\text{CH})\text{Si}(\text{CH}_3)_2\text{Cl}$ ( <b>1c</b> )
Weight g (mmol)	100.0 (620)	53.5 (380)	48.3 (400)
Dissolved in $\text{Et}_2\text{O}$ (ml)	250	200	200
$\text{LiAlH}_4$ g (mmol)	22.8 (600)	9.5 (250)	4.5 (118)
Suspended in $\text{Et}_2\text{O}$ (ml)	200	150	100
2 M $\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$ ml (mmol)	82 (164)	60 (120)	60 (120)
Product	$\text{B}(\text{C}_2\text{H}_4\text{SiH}_3)_3$ ( <b>5a</b> )	$\text{B}[\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)\text{H}_2]_3$ ( <b>5b</b> )	$\text{B}[\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)_2\text{H}]_3$ ( <b>5c</b> )
Elemental composition	$\text{C}_6\text{H}_{21}\text{BSi}_3$	$\text{C}_9\text{H}_{27}\text{BSi}_3$	$\text{C}_{12}\text{H}_{33}\text{BSi}_3$
Molecular weight ( $\text{g mol}^{-1}$ )	188.32	230.39	272.64
B.p.	$32-40^\circ\text{C}/5 \times 10^{-2}$ mbar	$70^\circ\text{C}/5 \times 10^{-1}$ mbar	$80^\circ\text{C}/10^{-1}$ mbar
Yield g (mmol)	27.2 (145)	24.9 (108)	28.1 (103)
Yield (%)	88	90	86

Table 7  
 $^1\text{H}$ -,  $^{13}\text{C}\{^1\text{H}\}$ -,  $^{11}\text{B}\{^1\text{H}\}$ -, and  $^{29}\text{Si}\{^1\text{H}\}$ -NMR chemical shifts or shift ranges (ppm) of tris(hydridosilylethyl)boranes (**5a–c**), obtained from chloro vinylsilanes (**3a–c**)

	<b>5a</b> <sup>a</sup>	<b>5b</b> <sup>a</sup>	<b>5c</b>
$^1\text{H}$ -NMR			
(C <sub>6</sub> D <sub>6</sub> )			
$\delta$ SiCH <sub>3</sub>	–	–0.07–0.05 (9 H)	–0.12–0.05 (18 H)
$\delta$ SiCH <sub>2</sub>	0.33–0.53 (1.4 H)	0.46–0.6 (2.2 H)	0.32–0.74 (3.2 H)
$\delta$ CHCH <sub>3</sub>	0.69–1.08 (7 H)	1.04–1.23 (5.6 H)	1.05–1.12 (4.2 H)
$\delta$ BCH <sub>2</sub>	0.69–1.08 (1.4 H)	1.04–1.23 (2.2 H)	1.13–1.25 (3.2 H)
$\delta$ CHCH <sub>3</sub>	1.20–1.32 (2.2 H)	1.26–1.49 (2 H)	1.28–1.46 (1.4 H)
$\delta$ SiH	3.42–3.63 (9 H)	3.70–4.00 (6 H)	3.94–4.03 (1.5 H), 4.05–4.13 (1.5 H)
$^{13}\text{C}\{^1\text{H}\}$ -NMR			
(C <sub>6</sub> D <sub>6</sub> )			
$\delta$ SiCH <sub>3</sub>	–	–8.49, –8.42, –8.40, –8.37, –8.29, –7.88, –7.76, –7.38	–1.83, –1.77, –1.70, –1.64, –1.13, –0.94, –0.80, –0.28, 0.0
$\delta$ SiCH <sub>2</sub>	0.00, 0.8	3.77, 4.00, 4.22, 5.17	9.29, 10.27, 10.38, 11.62
$\delta$ BCH <sub>2</sub>	16.1 (br)	17.9, 18.5 (br)	18.8, 22.2
$\delta$ CHCH <sub>3</sub>	13.3, 13.7, 13.8, 14.3, 14.7, 14.8	11.99, 12.22, 12.25, 12.77, 12.88, 13.21	13.68, 13.81, 14.03, 14.58
$\delta$ CHCH <sub>3</sub>	21.9 (br)	20.5, 21.7, 22.2 (br)	25.8, 28.0, 28.9
$^{11}\text{B}\{^1\text{H}\}$ -NMR			
(C <sub>6</sub> D <sub>6</sub> )			
	79.7	80.3	81.1
$^{29}\text{Si}\{^1\text{H}\}$ -NMR			
(C <sub>6</sub> D <sub>6</sub> )			
	–56.6, –56.3, –56.1, –55.8, –55.3,	–32.9, –32.4, –32.2, –32.1, –31.1,	–14.9, –14.4, –13.2, –12.4, –11.3,
	–55.2, –54.6, –54.3, –53.9	–30.9, –29.6, –29.3, –28.9	–10.3, –9.8, –9.4

<sup>a</sup> In this case, the resonance signals of CHCH<sub>3</sub> and BCH<sub>2</sub> overlap. The intensity of these signals was determined by subtracting the integrals of the SiCH<sub>2</sub> resonance signals from the sum of the integrals of the CHCH<sub>3</sub>+BCH<sub>2</sub> signals: Int. CHCH<sub>3</sub> = Int. (CHCH<sub>3</sub>+BCH<sub>2</sub>) – Int. SiCH<sub>2</sub>.

**5b**: [M<sup>+</sup>] 230 (1); [M<sup>+</sup> – H] 229 (0.9); [M<sup>+</sup> – CH<sub>3</sub>] 215 (1.6); [M<sup>+</sup> – C<sub>2</sub>H<sub>5</sub>] 201 (3); [M<sup>+</sup> – H – Si(CH<sub>3</sub>)H<sub>3</sub>] 183 (4); [M<sup>+</sup> – CH<sub>2</sub>Si(CH<sub>3</sub>)H<sub>2</sub>] 171 (4); [M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>Si(CH<sub>3</sub>)H<sub>2</sub>] 157 (100); [M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>Si(CH<sub>3</sub>)H<sub>2</sub> – H<sub>2</sub>] 155 (18); [Si<sub>2</sub>C<sub>6</sub>H<sub>15</sub><sup>+</sup>] 143 (86); [Si<sub>2</sub>C<sub>5</sub>H<sub>13</sub><sup>+</sup>] 129 (89); [Si<sub>2</sub>C<sub>4</sub>H<sub>11</sub><sup>+</sup>] 115 (16); [BSiC<sub>5</sub>H<sub>12</sub><sup>+</sup>] 111 (24); [C<sub>2</sub>H<sub>4</sub>Si(CH<sub>3</sub>)H<sub>2</sub><sup>+</sup>] 73 (10); [CH<sub>2</sub>Si(CH<sub>3</sub>)H<sub>2</sub><sup>+</sup>] 59 (13); [Si(CH<sub>3</sub>)H<sub>2</sub><sup>+</sup>] 45 (9).

**5c**: [M<sup>+</sup>] 272 (4); [M<sup>+</sup> – H] 271 (13); [M<sup>+</sup> – CH<sub>3</sub>] 257 (5); [M<sup>+</sup> – H – Si(CH<sub>3</sub>)<sub>2</sub>H<sub>2</sub>] 211 (3); [M<sup>+</sup> – CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>H] 199 (7); [M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>Si(CH<sub>3</sub>)<sub>2</sub>H] 185 (79); [Si<sub>2</sub>C<sub>7</sub>H<sub>17</sub><sup>+</sup>] 157 (52); [Si<sub>2</sub>C<sub>6</sub>H<sub>15</sub><sup>+</sup>] 143 (31); [BSiC<sub>6</sub>H<sub>14</sub><sup>+</sup>] 125 (20); [C<sub>2</sub>H<sub>4</sub>Si(CH<sub>3</sub>)<sub>2</sub>H<sup>+</sup>] 87 (15); [CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>H<sup>+</sup>] 73 (23); [C<sub>2</sub>H<sub>6</sub>Si<sup>+</sup>] 58 (100).

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