

# Reactivity of Alkoxyethynyl(trimethyl)silane, -germane and -stannane towards Trialkylboranes. Organometallic-Substituted Enol Ethers

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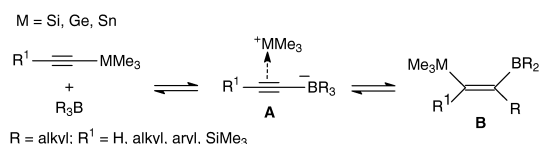
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Methoxyethynyl(trimethyl)silane (**1a**) reacts at 100 °C very slowly with triethylborane (**4**) to give a mixture of alkenes, one of which is the 1,1-organoboration product (Z)-1-methoxy-1-trimethylsilyl-2-diethylboryl-but-1-ene (**7a**). Methoxyethynyl(trimethyl)germane (**2a**) reacts within minutes at 60–70 °C with **4**, tripropylborane (**5**) and 9-ethyl-9-borabicyclo[3.3.1]nonane (**6**) by 1,1-organoboration in the usual regio- and stereospecific way to give the corresponding alkenes (**9a–11a**). The analogous reactions of the ethoxyethynyl(trimethyl)germane (**2b**) require longer heating and are accompanied by decomposition of **2b**. Ethoxyethynyl(trimethyl)stannane (**3b**) reacts with the trialkylboranes **4–6** already below room temperature by 1,1-organoboration to give the alkenes (**12b–14b**) in quantitative yield. The compound **3b** also reacts with the alkenes, e.g. **9a**, **13b**, **14b**, to give novel organometallic-substituted dienes. All products were characterised by multinuclear magnetic resonance spectroscopy (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>29</sup>Si, and <sup>119</sup>Sn NMR).

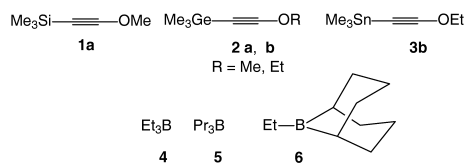
**Key words:** Silicon, Germanium, Tin, Enol Ethers, Boranes

## Introduction

Alkoxyethynyl derivatives of silicon, germanium and tin are attractive starting materials for numerous organic and organometallic transformations [1, 2]. The reaction of the silanes with dialkyl(allyl)boranes has been studied [3]. However, the reactivity of alkoxyethynyl trimethyl-Group 14 derivatives towards trialkylboranes has not been explored except for the reaction of the tin compound Me<sub>3</sub>Sn-C≡C-OEt **3b** with an excess of triethylborane [4]. The reactivity of other alkyne-1-yltin compounds towards triorganoboranes has been investigated in some detail [5], and it was found that in most cases 1,1-organoboration occurs, after cleavage of the Sn-C≡ bond (Scheme 1) via a borate-like intermediate **A**, to give stereoselectively the alkene of type **B**. The same appears to be true for the reaction of triorganoboranes with alkyne-1-ylgermanium compounds, although only a few reactions have been carried out so far [5]. The evidence available indicates that the reactivity of the Ge-C≡ bond is significantly lower than that of the Sn-C≡ bond in comparable compounds, and that alkyne-1-ylsilanes are even less reactive in this respect [5–7].



Scheme 1. Mechanism of 1,1-organoboration of alkyne-1-yl-Group 14 compounds.



Scheme 2. Alkoxyethynylsilane, -germanes, -stannane and trialkylboranes used in this work.

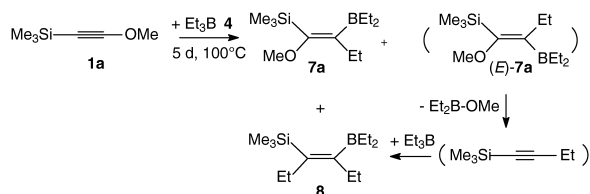
An alkoxy group linked to the C≡C bond, in addition to the organometallic group, could have a major influence on the reactivity of such alkynes towards trialkylboranes, because of changes in the electronic structure of the C≡C bond and in the intermediate of type **A**, and due to the Lewis base properties of the alkoxy group. In this work we report on the reactions of the silicon derivative **1a**, the ger-

manium compounds **2a,b** and the tin derivative **3b** with triethyl and tripropylborane **4, 5**, and 9-ethyl-9-borabicyclo[3.3.1]nonane **6** (Scheme 2).

## Results and Discussion

### Reaction of methoxyethynyl(trimethyl)silane **1a** with triethylborane **4**

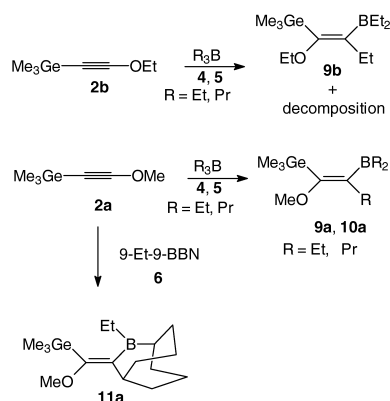
The reaction of **1a** with triethylborane **4** proceeds slowly at 100 °C in Et<sub>3</sub>B as the solvent and affords after heating the mixture for more than five days two products **7a** and **8** (Scheme 3). Compound **7a** with *Z*-configuration is the expected product of 1,1-organoboration. Compound **8** could be formed by MeO/Et exchange between **1a** and **4**, followed by 1,1-ethylboration of Me<sub>3</sub>SiC≡CEt, in the same way as has been described previously [7]. The MeO/Et exchange between **7a** and **4** is another possibility, although less likely, since **7a** is stable for many days in boiling Et<sub>3</sub>B. Yet another explanation of the intermediacy of Me<sub>3</sub>Si-C≡C-Et invokes that the 1,1-ethylboration of **1a** also affords the isomer (*E*)-**7a** which, under the harsh reaction conditions, eliminates Et<sub>2</sub>B-OMe leading to the formation of Me<sub>3</sub>Si-C≡C-Et. The latter undergoes immediately 1,1-ethylboration to give **8** (this route is depicted in Scheme 2). The mixture of **7a** and **8** (55 : 45) can be distilled and **8** is readily identified by its known [7] <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR data (see Figure 1 for the <sup>29</sup>Si NMR spectrum of the mixture).



Scheme 3. 1,1-Ethylboration of methoxyethynyl(trimethyl)silane **1a**; the products shown in parentheses were not detected.

### Reactions of methoxy- and ethoxyethynyl(trimethyl)germane **2a,b** with triethylborane **4**, tripropylborane **5**, and 9-ethyl-9-borabicyclo[3.3.1]nonane **6**

The reaction of **2a,b** with trialkylboranes requires heating to *ca.* 60–100 °C for several hours. In the case of **2b** and with a large excess of Et<sub>3</sub>B **4**, this reaction leads to **9b**. Since tripropylborane **5** is slightly less reactive than **4**, the reaction requires longer periods of heating and is therefore accompanied by ex-



Scheme 4. 1,1-Organoboration of alkoxyethynyl(trimethyl)germanes **2a, b**.

tensive decomposition of the alkyne **2b**, as has been described previously for the pure alkyne [8]. In contrast, **2a** is thermally much more stable than **2b**, and the 1 : 1 reaction with all three boranes **4, 5** and **6** affords the alkenes **9a, 10a** and **11a**, respectively, in essentially quantitative yield (Scheme 4) as colourless or yellowish, air-sensitive oils which can be distilled under reduced pressure.

### Reactions of ethoxyethynyl(trimethyl)stannane **3b** with the trialkylboranes **4, 5** and **6**

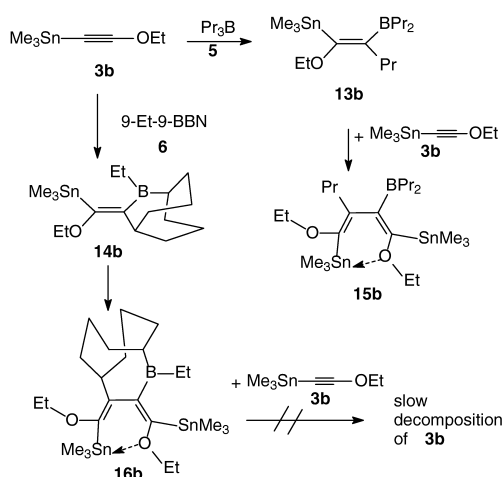
All three trialkylboranes **4–6** react with **3b** already below room temperature (Scheme 5). If an excess of Et<sub>3</sub>B **4** is present, the alkene **12b** is formed selectively, as has been reported previously [4]. The compound **12b** can be distilled under reduced pressure without decomposition. Monitoring of the reaction of **3b** with an excess of Pr<sub>3</sub>B **5** by <sup>119</sup>Sn NMR spectroscopy shows that the alkene **13b** is formed together with a second product **15b** (vide infra) which contains two tin atoms in different surroundings. If a large excess of **5** is used, **13b** can be obtained in pure state. However, decomposition takes place during distillation, and the main fraction contains **13b** together with the second product **15b**. Similarly, **3b** reacts with 9-Et-9-BBN (**6**) to give **14b**, in which the bicyclic system is enlarged by one olefinic carbon atom. However, the second product **16b** of this reaction contains again two tin atoms. Therefore, it appears that **3b** reacts even faster with the alkenylboranes **13b** and **14b** than with the trialkylboranes **5** and **6**. A large excess of the trialkylborane is required in order to obtain the alkenes as major products.

The side products **15b** and **16b** were identified (vide infra) as dienes with a preferred conformation

Table 1.  $^{11}\text{B}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data<sup>[a]</sup> of the alkenes **7a**, **9**–**13**.

	<b>7a</b>	<b>9a</b>	<b>9b</b>	<b>10a</b>	<b>11a</b>	<b>12b</b>	<b>13b</b>	<b>14b</b>
$\delta^{13}\text{C}(\text{SiC}=\text{C})$ (GeC=) (SnC=)	156.0 (80.7)	158.2	157.3	159.3	166.6	162.4	166.3 [580.8]	166.3 [577.8]
$\delta^{13}\text{C}(\text{BC}=\text{C})$ (14.0)	148.3 (br)	144.0 (br)	141.3 (br)	144.3 (br)	148.0 (br)	147.2 (br)	145.9 (br)	146.0 (br)
$\delta^{13}\text{C}(\text{SiMe})$ (GeMe) (SnMe)	0.2 (51.6)	0.3	0.5	0.8	2.1	−6.9	−6.3 [334.4]	−6.3 [334.7]
$\delta^{13}\text{C}(\text{BR}_2)$	22.3 (br)	21.3 (br)	21.1 (br)	33.7 (br)	241 (br)	21.7 (br)	[b]	[b]
	9.2	9.2	8.2	19.3, 18.0	9.7 (Et)	8.6		
$\delta^{13}\text{C}(\text{OMe})$ (OEt)	59.1	58.4	66.1, 15.8	58.3	58.0	66.2, 14.8	66.4 [21.6], 15.6	66.7 [21.0], 15.6
$\delta^{13}\text{C}(\text{R})$	20.5, 14.2	21.0, 14.8	21.4, 14.7	30.6, 23.9, 15.2,	32.9, 31.7, 30.6, 23.2	21.0	31.0 [41.9]	[b]
$\delta^{11}\text{B}$	83.0	83.6	84.0	83.2	82.3	83.6	84.0	84.0
$\delta^{29}\text{Si}$	−9.8							
$\delta^{119}\text{Sn}$						−59.0	−56.3	−60.4

<sup>[a]</sup> Measured in  $[\text{D}_8]\text{toluene}$  at 20 °C; coupling constants  $J(^{29}\text{Si}, ^{13}\text{C})$  ( $\pm 0.3$  Hz) are given in parentheses,  $J(^{119}\text{Sn}, ^{13}\text{C})$  ( $\pm 0.3$  Hz) in brackets; (br) denotes  $^{13}\text{C}$  NMR signals of carbon atoms linked to boron; <sup>[b]</sup> not assigned due to overlapping signals of mixture (see text).

Scheme 5. 1,1-Organoboration of ethoxyethynyl(trimethyl)stannane **3b**.

as shown in Scheme 5. Apparently weak intramolecular coordinative O–Sn interactions prevent further rearrangements which are known to take place for similar dienes [5, 9], at least for those in which the *cis*-conformation is not enforced [10] by the constraints exerted by a fairly rigid bicyclic system. Treatment of **16b** with an excess of **3b** did not induce any further reaction at room temperature. After heating to 100 °C for 28 h, complete decomposition of **3b** [11] was observed as the only change. In contrast, **15b** reacts with an excess of **3b** to give a complex mixture of compounds, some of which must contain the allene structural unit

(bands in the IR spectra:  $\nu_{\text{as}}(\text{C}=\text{C})$  around 1980  $\text{cm}^{-1}$ ; and several  $^{13}\text{C}$  NMR signals around  $\delta$  205 for the central carbon atom of the allene unit). More work is necessary to clarify this behaviour. A “mixed” diene **17ab** (see Scheme 6), analogous to **16b**, can be obtained from the reaction of **11a** with **3b**. In this case, weak coordinative O–Ge interactions are proposed in order to account for the stability of the diene **17ab**.

#### NMR spectroscopic results

The structures proposed for the alkenes **7**–**14** in solution are based on a consistent set of NMR data (Table 1). Although  $^{11}\text{B}$  NMR spectra are not particularly conclusive with respect to the overall structure of the alkenes, the  $\delta^{11}\text{B}$  values are typical of three-coordinate boron atoms, surrounded by three carbon atoms, and negligible  $\text{BC}(\text{pp})\pi$  interactions [12]. The  $\delta^{11}\text{B}$  values also exclude intermolecular coordinative O–B interactions, and they do not support a structure with the alkoxy and the boryl groups in *cis*-positions (see (*E*)-**7a** in Scheme 3), where intramolecular coordinative O–B bonding might have to be considered.

The inspection of the  $^{13}\text{C}$  NMR spectra is particularly instructive with respect to the structure of the products. In the cases of the silicon derivative **7a** and the tin compounds **12**–**14**, the coupling constants  $^1J(^{29}\text{Si}, ^{13}\text{C}=\text{C})$  and  $^1J(^{119}\text{Sn}, ^{13}\text{C}=\text{C})$ , respectively, measured from satellites of sharp  $^{13}\text{C}$  resonance signal in each case, and the appearance of a broad  $^{13}\text{C}$  resonance

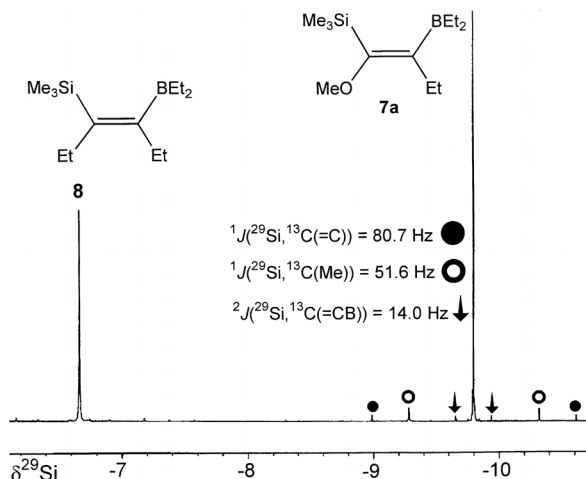


Fig. 1. 49.7 MHz  $^{29}\text{Si}$  NMR spectrum (refocused INEPT [15] with  $^1\text{H}$  decoupling) of the distilled mixture containing the alkenylsilanes **7a** and **8** (15% V/V in  $\text{C}_6\text{D}_6$ ; result of 256 transients; acquisition time 7 s; repetition time 10 s; FT with line broadening of 0.05 Hz). The  $^{13}\text{C}$  satellites observed for the  $^{29}\text{Si}$  NMR signal of **7a** are marked.

signal [13] of an olefinic carbon atom indicate the particular substituent pattern at the  $\text{C}=\text{C}$  bond. The analogous  $\delta^{13}\text{C}$  data of the germanium compounds **9–11** suggest the same stereochemistry as in **7a** and **12–14**. The *cis*-position of the boryl group with respect to the silyl-, germyl- or stannyl groups follows from  $^1\text{H}/^1\text{H}$  NOE difference spectra [14]. Apparently, the presence of the alkoxy group in **1–3** does not change the stereochemistry of the 1,1-organoboration [with the possible exception of **1a** (see Scheme 3)] when compared with alkyl or aryl groups.

Frequently, the measurement of  $^1J(^{29}\text{Si}, ^{13}\text{C}=\text{C})$  from  $^{29}\text{Si}$  satellites accompanying  $^{13}\text{C}$  NMR signals of quaternary carbon atoms in  $^{13}\text{C}$  NMR spectra can be time-consuming. An alternative is offered by the observation of  $^{13}\text{C}$  satellites in  $^{29}\text{Si}$  NMR spectra which can be recorded with a sufficient signal-to-noise ratio within a few minutes using the INEPT technique [14]. An example is shown in Fig. 1 for **7a**. In this particular case it proved also possible to observe satellites for  $^2J(^{29}\text{Si}, ^{13}\text{C}(\text{=CB})) = 14$  Hz, and this value is not accessible at all from normal  $^{13}\text{C}$  NMR spectra owing to the broad and weak  $^{13}\text{C}(\text{=CB})$  resonance signals. The assignment of these satellites can be made on the basis of their intensity and on the fact that all sharp and intense  $^{13}\text{C}$  NMR signals of **7a** do not show  $^{29}\text{Si}$  satellites separated by 14.0 Hz.

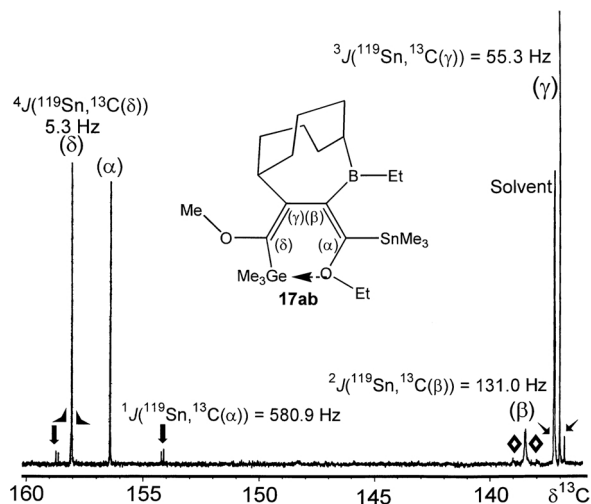
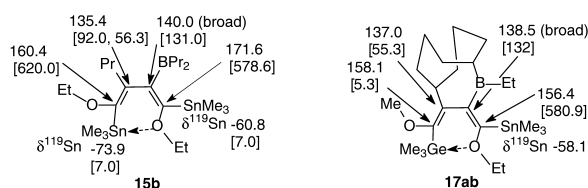


Fig. 2. 125.8 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the diene **17ab** in toluene- $[\text{D}_8]$ , showing the range of the olefinic carbon atoms.  $^{117}/^{119}\text{Sn}$  satellites are marked. Note the typically broad [13]  $^{13}\text{C}$  NMR signal of the carbon atom  $\text{C}(\beta)$  which is linked to boron.



Scheme 6.  $^{13}\text{C}$  (olefinic carbon atoms) and  $^{119}\text{Sn}$  NMR data of two dienes. Coupling constants  $J(^{119}\text{Sn}, ^{13}\text{C})$  and  $J(^{119}\text{Sn}, ^{119}\text{Sn})$  are given in brackets.

The structures of the dienes **15–17** are best assigned referring to the  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra (Scheme 6). An instructive example of a  $^{13}\text{C}$  NMR spectrum of the olefinic region of **17ab** is shown in Figure 2 with the typical signals, three sharp and one broad, all accompanied by  $^{117}/^{119}\text{Sn}$  satellites.

The  $^{119}\text{Sn}$  NMR spectra of the dienes **15b** or **16b** show two NMR signals each, accompanied by  $^{117}/^{119}\text{Sn}$  satellites owing to  $^5J(\text{Sn}, \text{Sn}) = 8.5$  Hz. This proves that the tin atoms are in the same molecule. The signal at lower frequency is somewhat sharper than the other one; however the lineshape depends markedly on temperature gradients in the sample, and  $^{119}\text{Sn}$  nuclear shielding increases or decreases (by a few ppm, independent of concentration) upon cooling or heating the samples below or above room temperature. This

is typical of weak intramolecular association of tin compounds [16].

## Conclusion

1,1-Organoboration of alkoxyethynyl(trimethyl)-Group 14 compounds opens the way to novel enol ethers bearing organometallic substituents at the C=C bond. Very few of such compounds have been described previously [3, 17], and for the majority it was reported that elimination of dialkyl(alkoxy)boranes is fast at room temperature [3]. In contrast, the enol ether derivatives reported in the present work are fairly stable towards elimination reactions, and can be used for numerous further transformations taking advantage of the reactive B-C bonds, and of the Ge-C and in particular of the Sn-C bonds.

## Experimental Section

All preparative work and handling of samples for NMR measurements were carried out by observing necessary precautions to exclude traces of oxygen and moisture. Solvents were dried by standard methods. The alkyne derivatives **1**, **2** and **3** [8, 17–19] and the trialkylboranes **5** [20] and **6** [21] were prepared following literature procedures, and **4** was used as a commercial product without further purification.

NMR spectra were recorded at 25 °C on Bruker ARX 250 or DRX 500 spectrometers, both equipped with multinuclear units, using toluene[D<sub>8</sub>] solutions if not mentioned otherwise (*ca.* 15–20% V/V) in 5 mm tubes. Chemical shifts are given with respect to Me<sub>4</sub>Si [ $\delta^1\text{H}$  (C<sub>6</sub>D<sub>5</sub>CD<sub>2</sub>H) = 2.03,  $\delta^{13}\text{C}$  (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>) = 20.4],  $\delta^{29}\text{Si}$  = 0 for Me<sub>4</sub>Si with  $\chi(^{29}\text{Si})$  = 19.867187 MHz], and  $\delta^{119}\text{Sn}$  = 0 for Me<sub>4</sub>Sn with  $\chi(^{119}\text{Sn})$  = 37.290665 MHz. <sup>29</sup>Si and <sup>119</sup>Sn NMR spectra were recorded using the refocused INEPT pulse sequence with <sup>1</sup>H decoupling [15] (see Fig. 1 for conditions for <sup>29</sup>Si NMR spectra). Mass spectra (EI, 70 eV, Finnigan MAT 8500 with direct inlet) did not give meaningful and consistent information. IR spectra were measured using a Perkin-Elmer Spectrum 2000 FTIR.

### (Z)-1-Methoxy-1-trimethylsilyl-2-diethylboryl-but-1-ene **7a**

A solution of **1** (0.8 g, 6.2 mmol) in triethylborane **4** (5 ml) was heated at reflux (*ca.* 100 °C) for 5 d, using IR and <sup>29</sup>Si NMR spectroscopy for monitoring the progress of the reaction. Then, the excess of Et<sub>3</sub>B was removed *in vacuo*, and the yellowish oily residue was distilled (60–65 °C/1 Torr) to give a mixture of **7a** and **8** (ratio 55 : 45) which could not be further separated. **7a**: <sup>1</sup>H NMR (500.13 MHz; C<sub>6</sub>D<sub>6</sub>):  $\delta^1\text{H}$  = 0.12 (s, 9H, SiMe<sub>3</sub>), 1.25, 1.05 (m, t, 10H, BEt<sub>2</sub>), 2.00, 0.93 (q, t, 5H, =CEt), 3.42 (s, 3H, OMe).

### (Z)-1-Methoxy-1-trimethylgermyl-2-diethylboryl-but-1-ene **9a**

Triethylborane **3** (1.1 g, 11.2 mmol) was added at room temperature in one portion to a solution of **2a** (1.65 g, 9.28 mmol) in toluene (15 ml), and the mixture was heated at 100 °C for 20 h. Then IR spectra showed the absence of  $\nu(\text{C}\equiv\text{C})$  of **2a**. The excess of Et<sub>3</sub>B and the solvent were removed *in vacuo*. The fractional distillation of the yellowish, oily residue gave pure **9a** (1.75 g; 68%; b.p. 48–49 °C/10<sup>-2</sup> Torr). The synthesis of **10a** (75%; b.p. 80–82 °C/10<sup>-2</sup> Torr) and **11a** (70%; b.p. 102–105 °C/10<sup>-2</sup> Torr) was carried out in the same way. **9a**: <sup>1</sup>H NMR (500.13 MHz):  $\delta^1\text{H}$  = 0.22 (s, 9H, GeMe<sub>3</sub>), 1.25, 1.05 (m, t, 10H, BEt<sub>2</sub>), 2.22, 0.98 (q, t, 5H, =CEt), 3.38 (s, 3H, OMe). **10a**: <sup>1</sup>H NMR (500.13 MHz; C<sub>6</sub>D<sub>6</sub>):  $\delta^1\text{H}$  = 0.26 (s, 9H, SiMe<sub>3</sub>), 1.50, 1.30, 1.02 (m, m, t, 14H, BPr<sub>2</sub>), 2.28, 1.40, 0.98 (m, m, t, 7H, =CPr), 3.27 (s, 3H, OMe). **11a**: <sup>1</sup>H NMR (250.13 MHz; C<sub>6</sub>D<sub>6</sub>):  $\delta^1\text{H}$  = 0.33 (s, 9H, GeMe<sub>3</sub>), 1.75–1.00 (m, 19H, BEt, BBN), 2.00, 0.93 (q, t, 5H, =CEt), 3.27 (s, 3H, OMe).

### (Z)-1-Ethoxy-1-trimethylstannyl-2-diproylboryl-but-1-ene **13b**

Tripropylborane **5** (1.3 g, 9.2 mmol) was added in one portion at –78 °C to a solution of **3b** (1.44 g, 6.2 mmol) in toluene (10 ml). After warming to room temperature, the excess of **5** and the solvent were removed *in vacuo*, and the residue was distilled (b. p. 75–85 °C/10<sup>-1</sup> Torr) to give 1.49 g of a mixture containing **13b** and some (*ca.* 20 %) **15b**. The compounds could not be separated by distillation. Compound **14b** as a mixture with **16b** was obtained in the same way; distillation led to decomposition. **13b**: <sup>1</sup>H NMR (250.13 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta^1\text{H}$  [ $J(^{119}\text{Sn}, ^1\text{H})$ ] = 0.09 [51.0] (s, 9H, SnMe<sub>3</sub>), 1.40, 1.10, 0.93 (m, m, t, 14H, BPr<sub>2</sub>), 2.31, 1.14, 0.92 (m, m, t, 7H, =CPr), 3.52, 0.94 (q, t, 5H, OEt).

### Synthesis of the diene **17ab**

The solution of **11a** (80 mg, 0.25 mmol) in toluene[D<sub>8</sub>] (0.6 ml) was cooled to –78 °C and ethoxyethynyl(trimethyl)stannane **3b** (60 mg, 0.26 mmol) was added in one portion. The mixture was warmed to room temperature, heated to 80 °C for 1 h. NMR spectra indicated that all of **11a** was converted into **17ab**. **17ab**: <sup>13</sup>C NMR (125.8 MHz; C<sub>7</sub>D<sub>8</sub>):  $\delta^{13}\text{C}$  [ $J(^{119}\text{Sn}, ^{13}\text{C})$ ] = –6.9 [333.8] (SnMe<sub>3</sub>), 2.2 (GeMe<sub>3</sub>), 24.6 (br), 9.1 (BEt), 32.1 (br) (BCH), 30.3, 30.1, 27.0, 26.2, 22.1 (CH<sub>2</sub>), 34.9 [3.2] (=CCH), 58.2 (OMe), 66.3 [28.0], 15.8 (OEt), 137.0 [55.3] (CH-C=), 138.6 (br) [131.9] (B-C=), 156.4 [580.9] (Sn-C=), 158.1 [5.3] (Ge-C=).

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