1,1-Ethylboration of ethynyl(trimethyl)tin. (*E*)-1-Trimethylstannyl-2-diethylboryl-but-1-ene, isomerization and conversion into hydridoborates

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Dedicated to Rosalinda Contreras


Abstract

1,1-Ethylboration of ethynyl(trimethyl)tin affords quantitatively and selectively (*E*)-1-trimethylstannyl-2-diethylboryl-but-1-ene **1a**, which isomerizes fast at room temperature into the (*Z*)-isomer **2a**, followed by slow isomerization into the (*E/Z*)-1-diethylboryl-2-trimethylstannyl-but-1-enes **3a** and **4a**. These rearrangements are independent of the solvent (hexane, benzene, or benzene/THF) and take place at comparable rates at daylight or in the dark. A mechanism is proposed invoking hyperconjugation and three-membered cyclic structures, for which three-coordinate boron atoms as in **1a** - **2a** are a prerequisite. In order to prove this point, hydridoborates were prepared. The reaction of a mixture (80:20) of **1a** and **2a** with sodium hydride gives the corresponding hydridoborates **5a** and **6a**, respectively, which in contrast to the boranes do not undergo further rearrangements. An extended NMR data set of the compounds **1a** – **6a** was measured (^{1}H, ^{11}B, ^{13}C, ^{119}Sn NMR) and discussed. In addition, the synthesis of a mixture of the silicon analogues **1a(Si)** and **2a(Si)** was reproduced, the corresponding NMR data were obtained, the molecular structures were optimized by DFT methods [B3LYP/6-311+G(d,p)], and relevant chemical shifts were calculated at the same level of theory.

Keywords: Triethylborane, alkynes, alkenes, organotin, isomerization, multinuclear NMR, DFT calculations

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Introduction

Organometallic-substituted alkenylboranes are useful synthons for further transformations.[1-3] In this context, 1,1-organoboration of alkyn-1-ylmetal compounds has opened a convenient route to such alkenes.[4] Thus, triethylborane, BEt_3, reacts readily with numerous alkyn-1-yltin compounds below 0 °C in inert solvents by cleavage of the Sn-C≡ bond *via* a short-lived zwitterionic alkyn-

1-ylborate-like intermediate **A** to give alkenes of type **1**. In most cases, these organometallic-substituted alkenes are formed quantitatively and stereoselectively, bearing the boryl and the stannyl groups in *cis* positions at the C=C bond (Scheme 1).[4] The analogous reaction with alkyn-1-ylsilanes, although under much more severe reaction conditions (in boiling BEt$_3$ at ca. 100 °C), affords the corresponding alkenylsilanes **1(Si)**.[5] The mechanism is well established,[6,7] and after removing of readily volatile materials (solvent and the excess of BEt$_3$), the alkenes **1** can be used without further purification.
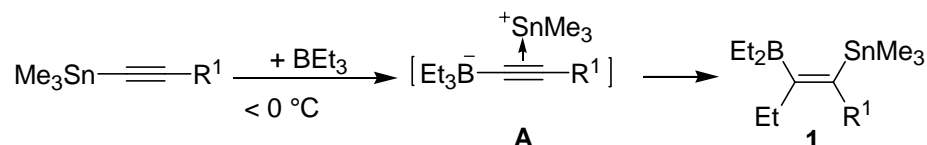
Scheme 1

For R^1 = alkyl or phenyl, the pure alkenes **1** are stable under Ar or N$_2$ atmosphere for several days at room temperature. However, in the case of R^1 = H (**1a**), it has been noted that (*E/Z*)-isomerization starts within minutes at room temperature (**2a**), followed more slowly by further rearrangements (**3a**, **4a**).[8] Since **1a** is one of the most simple 1,1-organoboration products of alkyn-1-yltin compounds, we have studied the formation of **1a** and its isomerization in greater detail, aiming for a more complete set of NMR data. It was also of interest to find out whether the three-coordinate boron atom in **1a** is a prerequisite for the isomerization. Furthermore, for comparison we have measured a complete NMR data set for the analogous isomers **1a(Si)** and **2a(Si)** which result from 1,1-ethylboration of ethynyl(trimethyl)silane.[5]

Results and Discussion

1,1-Ethylboration, isomerization, proposed mechanism and formation of hydridoborates
In the original report,[9] the 1,1-ethylboration of ethynyl(trimethyl)tin was carried out in THF, since this particular ethynyltin compound is most readily available as a THF solution.[10] In all other cases of 1,1-ethylboration of alkyn-1-yl(triorgano)tin derivatives, the solvents have been hexane, toluene, benzene or dichloromethane. This includes triethyl- and tributyl(ethynyl)tin, for which the 1,1-ethylboration products were found to be stable towards isomerization.[11] Therefore, *a priori* it could not be excluded that traces of THF catalyze the isomerization.
We have now prepared ethynyl(trimethyl)tin as a solution in hexane, using the reaction of freshly prepared Li$_2$C$_2$ in hexane with trimethyltin chloride in the presence of ethyne in excess. Although this leads mainly to bis(trimethylstannyl)ethyne, the desired ethynyl(trimethyl)tin (about 15-20 % yield) was found (δ^{119}Sn -68.3) in the hexane fraction which was removed from the reaction mixture in a vacuum and collected in a cold trap at -196 °C. The compound **1a** was then prepared by addition of BEt$_3$ at -78 °C to this hexane solution, warming to room

temperature, and isolated.. It was dissolved in C_6D_6, and the isomerization of **1a** was studied without or with addition of a small amount of THF. The results were virtually identical (see Fig. 1). A sample of **1a** in hexane gave the same ^{119}Sn NMR spectra. Therefore, a significant influence of THF on the isomerization process can be excluded. There was also no appreciable difference in the type of products and rate of isomerization, when the samples were kept in the dark or at day light.
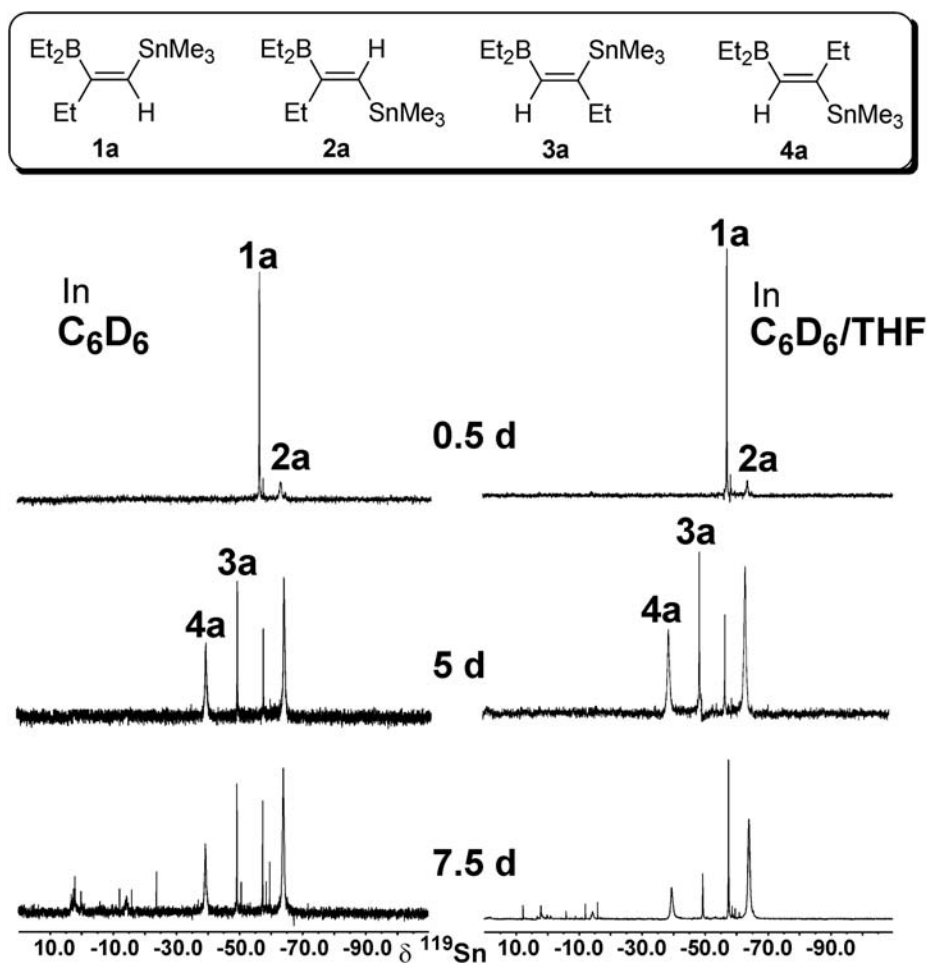

Figure 1. 149.2 MHz ^{119}Sn{^{1}H} NMR spectra of **1a**, dissolved in C_6D_6 (left) and C_6D_6/THF (1:1) (right) measured at room temperature at the times indicated. After 7 d, decomposition becomes apparent, and the product distribution is affected by the presence of THF.

The slow isomerization of other non-cyclic or cyclic alkenyltin compounds with a boryl group present at the C=C bond has been discussed,[12] and the general idea is lined out here for the isomerization of **1a** (Scheme 2). The contribution of the canonic structure **B** to the ground state is most likely negligible, although this type of structure is often invoked for vinylboranes. Clearly, **B** would in principle account for (*E/Z*)-isomerization (dashed arrows in Scheme 2). However, alkenylboranes, in general, do not exhibit such a pronounced tendency for (*E/Z*)-

isomerization and further rearrangements. In the case of **1a**, it is also necessary to consider the preferred perpendicular orientation of the Et$_2$B group with respect to the C=CB plane,[13,14] preventing efficient CB(pp)π interactions (see however **2a**, where this may play a role). On the other hand, this particular conformation around the boryl group of **1a** favors hyperconjugative C-B interactions represented in the structure **C**, where the stannyl group in β-position relative to the positively charged carbon atom exerts a stabilising effect.[15-20] Structure **C** helps to explain the observed fast isomerization of **1a** into **2a**. Migration of the stannyl group transforms **C** into **D**, which is of comparable energy or even more stable because of the additional ethyl group in β-position to the positive charge. The intermediacy of **D** explains the observed concomitant formation of **3a** and **4a**, of which **4a** appears to be preferred, most likely for steric reasons. It should be noted that other isomers bearing the boryl and the stannyl groups at the same olefinic carbon atom were not observed, and, indeed, neither **C** nor **D** provide an obvious route to such isomers. This also rules out 1,2-dehydroboration, conceivable at a first glance for **2a**, which should give rise to the formation of such alkenes.
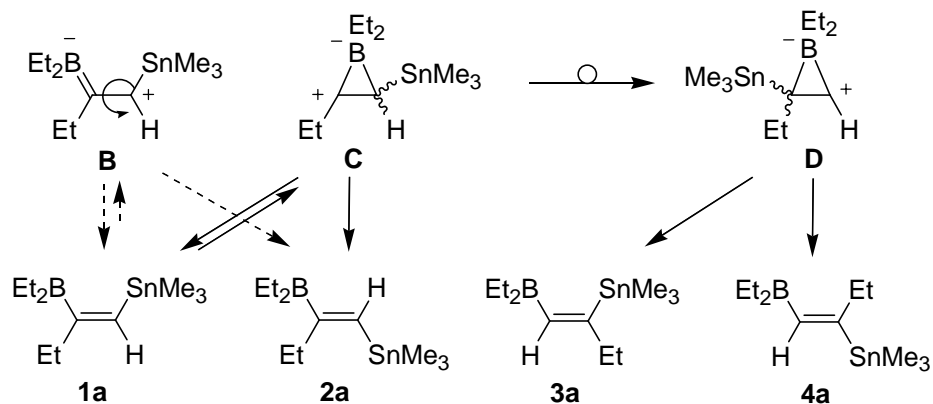
Scheme 2

If the arguments for **C** and **D** (Scheme 2) are relevant, the isomerization of **1a** as well as further rearrangements of **2a** will be suppressed when the boron atom becomes tetra-coordinate as in borates. Therefore, the reaction of **1a** with sodium hydride (NaH) was studied. Since the heterogeneous reaction with NaH was slow and isomerization of **1a** occurred before significant amounts of hydridoborates were formed, NaH was activated [21] in boiling hexane with BEt$_3$ prior to its reaction with **1a**. By this, a mixture of **1a/2a** (80:20) was converted completely into the hydridoborates **5a** and **6a** (Scheme 3). The isolated materials were redissolved in C$_6$D$_6$, and NMR spectra indicated the presence of the desired hydridoborates in an unchanged 80:20 ratio. The C$_6$D$_6$ solution was monitored over several weeks by ^{1}H, ^{11}B and ^{119}Sn NMR spectroscopy, and further isomerization was not detected.
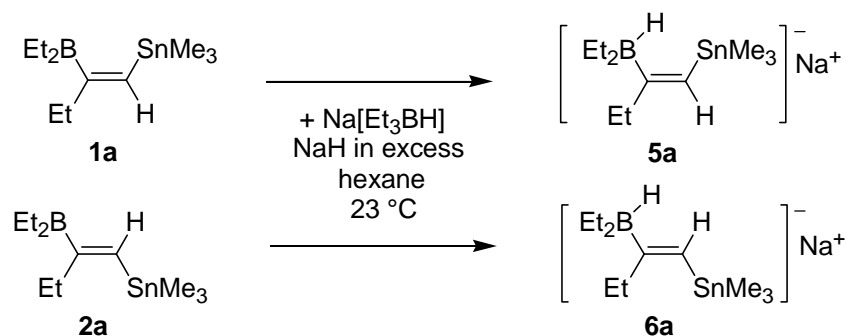
Scheme 3

NMR spectroscopic results

The consistent set of NMR data leaves no doubt on the proposed solution state structures of the compounds **1a** – **6a**, and their ^{11}B, ^{13}C and ^{119}Sn NMR parameters are given in Table 1 (see the Experimental Section for ^{1}H NMR data), together with data for the silicon analogues **1a(Si)** and **2a(Si)**.

The chemical shifts δ^{11}B for **1a** – **4a** are in the typical range for three-coordinate boron atoms bearing three organyl groups without or with weak BC(pp)π interactions, whereas those for **5a** and **6a** are characteristic for borates.[22] The slight increase in ^{11}B nuclear shielding observed for **2a** (δ^{11}B 78.9) relative to that for **1a**, **3a** and **4a** indicates that the mean angle formed between the C_2B plane of the Et_2B group and the C=CB plane in **2a** deviates markedly from 90° and allows for CB(pp)π interactions. The reduced line width of the ^{11}B NMR signal of **2a** indicates longer relaxation times $T^Q(^{11}B)$, most likely as a result of a more freely rotating Et_2B group in **2a** when compared with the situation in **1a**. CB(pp)π interactions in **2a** and **2a(Si)** are supported by the δ^{13}C(SnC=) and δ^{13}C(SiC=) data for the pairs **1a**/**2a** and **1a(Si)**/**2a(Si)**. Typically, the possibility for extended π interactions between the C=C bond and an appropriate π acceptor orbital at a neighbored atom induces deshielding of the olefinic ^{13}C nucleus in β-position relative to the π acceptor [23] (here by 12.5 and 10.2 ppm). Such a difference in the δ^{13}C(SnC=) values is absent for the pair **3a**/**4a**, and one can conclude that the preferred conformation of the Et_2B group is similar in these isomers. The enforced absence of an extended π system in the borates **5a** and **6a** is mirrored by the shielding of the ^{13}C(SnC=) nuclei, which is very similar to that in **1a**, for which the arrangement of the Et_2B group is unfavorable for CB(pp)π interactions.

The assignment of all ^{13}C NMR signals is straightforward, using the information from $^{117/119}$Sn and ^{29}Si satellites [J(Sn^{13}C) (Fig. 2) or J(^{29}Si,^{13}C)], the typically broad lines for ^{13}C nuclei linked directly to boron (scalar relaxation of the second kind owing to ^{13}C-^{11}B spin-spin coupling [24,25]). The mutual positions of substituents at the C=C bond are further confirmed by ^{1}H/^{1}H NOE difference spectra.[26]

Table 1. ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR parameters [a] of the alkenes **1 – 6**

	δ^{13}C					δ^{119}Sn	δ^{11}B
	Me$_3$Sn	Sn-C=	=C-B	BEt$_2$	Et	(h$_{1/2}$) [Hz]	(h$_{1/2}$) [Hz]
	Me$_3$Si	Si-C=				δ^{29}Si	
1a	-8.5	124.9	173.9	21.6, 8.8	32.7, 13.3	-57.3	84.9
	[338.0]	[502.1]	(br)	(br)	[96.3]	(13)	(480)
1a(Si)	0.6	125.2	171.4	22.1, 9.7	31.3, 13.3	-9.7	84.4
	{51.2}	{69.7}	(br)	(br)	{9.4}	(0.8)	(390)
2a	-8.3	137.4	173.1	18.8, 9.7	32.7, 15.9	-63.9 br	78.9
	[336.1]	[441.8]	(br)	(br)	[63.9]	(90)	(380)
2a(Si)	1.1	135.4	173.7	19.4, 9.2	29.4, 16.1	-11.0	80.2
	{50.8}	{64.0}	(br)	(br)	{5.6}	(1.3)	(320)
3a	-7.4	162.3	148.2	21.6, 9.1	38.4, 14.8	-49.3	86.5
	[328.6]	[448.9]	(br)	(br)	[62.0]	(16)	(n.m.[b])
4a	-9.0	161.9	149.1	21.6, 9.0	33.3, 15.9	-39.3	81.0
	[325.8]	[466.6]	(br)	(br)	[63.1]	(81)	(n.m.[b])
5a	-6.4	124.9	192.4	13.8, 12.4	33.4, 9.7	-68.8	-12.1
	[330.2]	[521.1]	(br)	(br)	[100.6]	(43)	(160)
6a	-8.0	126.9	193.8	16.5, 13.6	34.2, 10.8	-72.9	-10.1
	[325.6]	[444.8]	(br)	(br)	[65.5]	(174)	(n.m.[b])

[a] Samples (5-10 %) in C$_6$D$_6$ at 296 K; coupling constants J(^{119}Sn,^{13}C) are given in brackets [± 0.5 Hz], and J(^{29}Si,^{13}C) in braces {± 0.5 Hz}; (br) denotes ^{13}C NMR signals broadened by partially relaxed scalar ^{13}C-^{11}B spin-spin coupling;[25] h$_{1/2}$ means full line width at half height.
[b] n.m. = not measured, because of overlapping ^{11}B NMR signals.

The ^{119}Sn NMR parameters [27] of **1a – 6a** are instructive in several respects. ^{119}Sn nuclear shielding increases in the borates **5a** and **6a** by 11.5 and 9.0 ppm, when compared with the boranes **1a** and **2a**, respectively. This fairly constant change means that CB(pp)π interactions in **2a** have little influence on δ^{119}Sn. It appears that the δ^{119}Sn data of **1a – 6a** depend on substituent effects exerted by the proximity and the respective nature of the substituent rather than on small changes in the bonding situation of the C=C bond. There are also changes in the magnitude of ^1J(^{119}Sn,^{13}C$_{(SnC=)}$) depending on the other substituents. This parameter may change readily with the bond angle at the olefinic carbon SnC= as a function of the bulkiness of other substituents in geminal or *cis* positions relative to the stannyl group. In contrast to changes in ^1J(^{119}Sn,^{13}C$_{(SnC=)}$), the magnitude of ^1J(^{119}Sn,^{13}C$_{(SnMe)}$) remains fairly constant throughout the series of compounds **1a – 6a**. The magnitude of the coupling constants ^3J(^{119}Sn,^{13}C$_{(Et)}$) across the C=C bond is expectedly greater for the *trans* (**1a**) than for the *cis* coupling-pathway (**2a**).[27,28] A similar behavior is expected for ^{119}Sn-^{11}B spin-spin coupling.[8] Although splitting due to this coupling is not resolved, the comparison of the line widths (Fig. 3) of the ^{119}Sn NMR signals shows that

$\left|^3J(^{119}Sn,^{11}B)_{trans}\right| > \left|^3J(^{119}Sn,^{11}B)_{cis}\right|$. In the borates **5a** and **6a**, the times $T^Q(^{11}B)$ are longer than in the boranes. Therefore, the life time of the ^{11}B nuclear spin states increases, and the residual broadening of the ^{119}Sn NMR signals as a result of scalar ^{119}Sn-^{11}B coupling is larger in **5a** and **6a** when compared with the boranes **1a** and **2a**, respectively.
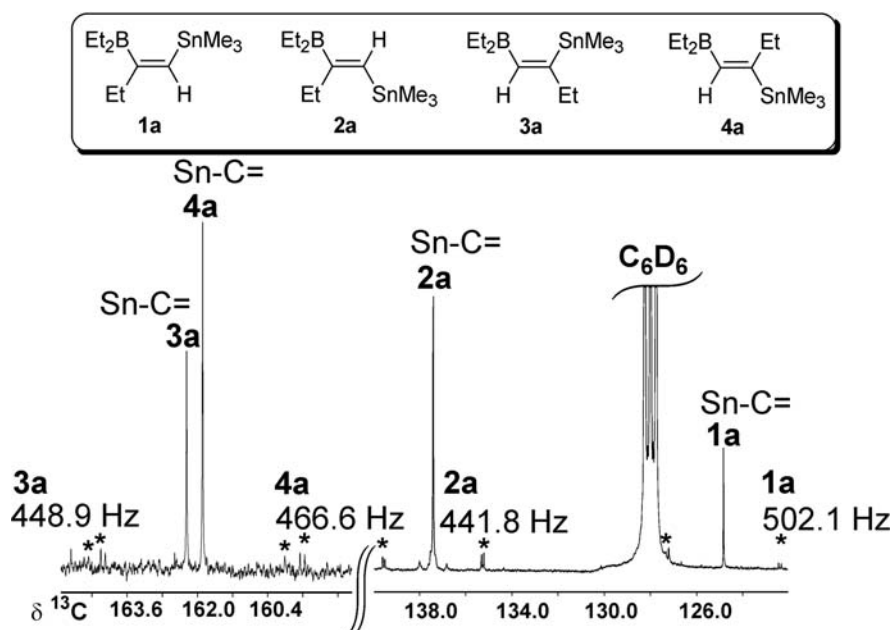

Figure 2. Parts of the 100 MHz $^{13}C\{^1H\}$ NMR spectrum of the mixture of isomers **1a** – **4a** in C_6D_6 (10 % v/v; at 296 K) showing the $^{13}C(Sn-C=)$ NMR signals with the $^{117/119}Sn$ satellites (marked by asterisks) corresponding to $^1J(Sn,^{13}C)$, and the data $^1J(^{119}Sn,^{13}C)$ are given.
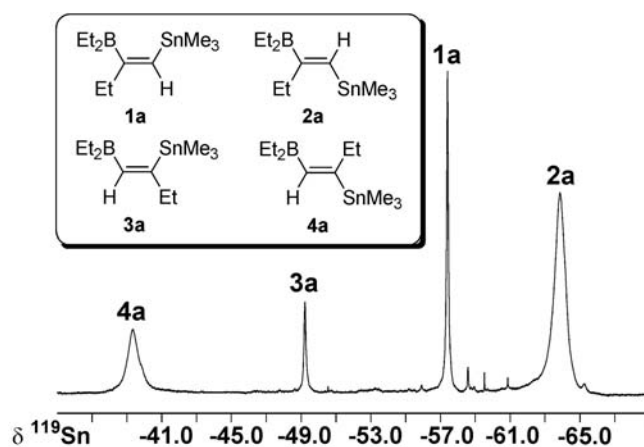

Figure 3. 149.2 MHz $^{119}Sn\{^1H\}$ NMR spectrum of the mixture of isomers **1a** – **4a** showing the different line widths owing to partially relaxed scalar ^{119}Sn-^{11}B spin-spin coupling for $\left|^3J(^{119}Sn,^{11}B)_{trans}\right| > \left|^3J(^{119}Sn,^{11}B)_{cis}\right|$.

In the case of the silanes **1a(Si)** and **2a(Si)**, the residual broadening of the ^{29}Si NMR signals is much less pronounced (Fig. 4), since the magnitude of $^3J(^{29}\text{Si},^{11}\text{B})$ is expectedly markedly smaller than that of $^3J(^{119}\text{Sn},^{11}\text{B})$ and, at the same time, the quadrupolar relaxation of the ^{11}B nuclei is similarly efficient in the stannanes and silanes, as can be seen from the line widths of the ^{11}B NMR signals (Table 1). However, the ^{29}Si NMR spectra, if measured by using the refocused INEPT pulse sequence with ^{1}H decoupling,[29] serve for measuring ^{13}C satellites corresponding to coupling constants $J(^{29}\text{Si},^{13}\text{C})$, some of which may be difficult to obtain from ^{13}C NMR spectra.
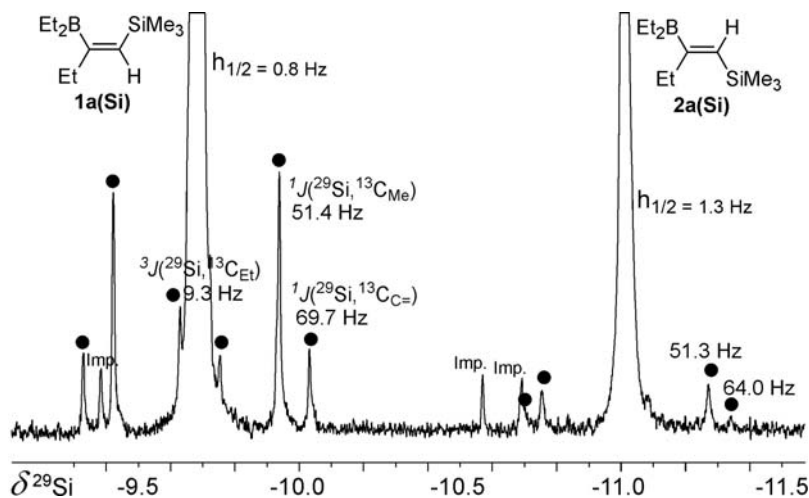

Figure 4. 99.4 MHz ^{29}Si$\{^1\text{H}\}$ NMR spectrum of the mixture of the silanes **1a(Si)** and **2a(Si)** refocused INEPT ^{29}) showing the ^{13}C satellites (marked by filled circles) in agreement with the information from ^{13}C NMR spectra.

DFT Calculations

The assumption of a significant conformational difference between **1a** and **2a** concerning the Et$_2$B-group is supported by optimizing the geometry of the silicon analogues **1a(Si)** and **2a(Si)** using DFT methods [B3LYP/6-311G(d,p)],[30] and the result is shown in Fig. 5. Relevant chemical shifts, calculated (GIAO [31]) at the same level of theory, show reasonable agreement with the experimental data. The calculated orientation of the ethyl groups may not represent exactly the preferred structures in solution. This appears to affect in particular some of the calculated δ^{13}C values. The experimental trend, however, is correctly reproduced.
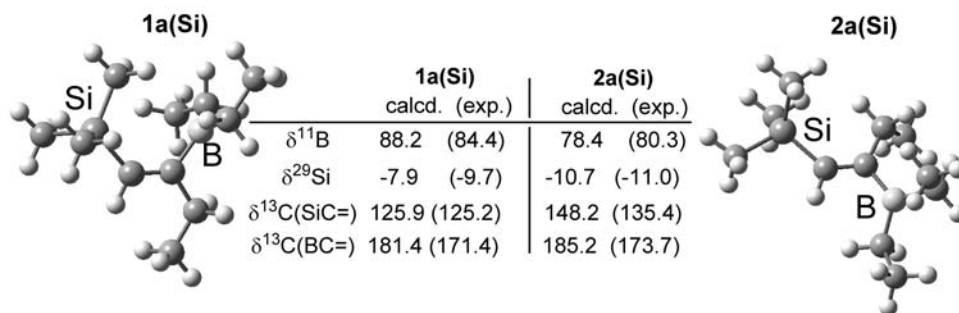
	1a(Si) calcd. (exp.)	2a(Si) calcd. (exp.)
$\delta^{11}B$	88.2 (84.4)	78.4 (80.3)
$\delta^{29}Si$	-7.9 (-9.7)	-10.7 (-11.0)
$\delta^{13}C(SiC=)$	125.9 (125.2)	148.2 (135.4)
$\delta^{13}C(BC=)$	181.4 (171.4)	185.2 (173.7)

Figure 5. Optimized molecular structures of **1a(Si)** and **2a(Si),** and comparison of calculated (GIAO [31]) and experimental chemical shifts [B3LYP/6-311+G(d,p)]. It shows the almost perpendicular arrangement of the BC_2 plane of the BEt_2 group relative to the $BC=C$ plane in **1a(Si)** (mean angle 85°), in contrast to the analogous much less twisted conformation in **2a(Si)** (mean angle 38°).

Conclusions

The fast (*E/Z*)-isomerization of the title compound **1a** into **2a** was found to be independent of the solvent or day light. Isomerization was not observed when the boron atom became tetra-coordiante in the case of the hydridoborate **5a**. Therefore, the electron-deficient character of the boron atom in the Et_2B group plays a decisive role. The selective further rearrangement of **2a** into the isomers **3a** and **4a**, again not observed for the hydridoborate **6a**, points towards a three-membered cyclic transition state, in which the stannyl- and the boryl groups can readily migrate from one olefinic carbon to the other. Application of multinuclear NMR serves for the unambiguous structural assignment of the compounds studied and ^{119}Sn NMR spectroscopy, in particular, allows for monitoring of the isomerization process.

Experimental Section

General Procedures. The preparations and all handling of samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware and dry solvents were used throughout. BuLi in hexane (1.6 M), trimethyltin chloride, ethynyl(trimethyl)silane, triethylborane, sodium hydride in mineral oil (Aldrich), and ethyne (purified by passing it through a trap at -78 °C, followed by washing it with concentrated H_2SO_4) were commercial products. NMR measurements in C_6D_6 (concentration ca. 5 – 15 %) were carried out with samples in 5 mm tubes at 23 ± 1 °C, using a Bruker DRX 500 and Varian Inova 300 and 400 spectrometers for ^1H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR; 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 $\Xi(^{29}Si)$ = 19.867184 MHz];

external BF_3-OEt_2 [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz], and $\delta^{119}Sn = 0$ for neat $SnMe_4$ with $\Xi(^{119}Sn) = 37.290665$ MHz. Chemical shifts δ^1H are given to ± 0.03 ppm, $\delta^{13}C$, $\delta^{29}Si$, and $\delta^{119}Sn$ to ± 0.1 ppm, and $\delta^{11}B$ to ± 0.3 ppm. ^{29}Si and most of the ^{119}Sn NMR spectra were measured by using the refocused INEPT pulse sequence,[29] based on $^2J(^{29}Si, ^1H_{Me})$ (ca. 7 Hz) and $^2J(^{119}Sn, ^1H_{Me})$ (ca. 52 Hz), respectively. Calculations for optimization of the structures and nuclear shielding were carried out using the Gaussian 03 program package.[30] Calculated. $\sigma(^{13}C)$ data were converted to $\delta^{13}C$ data by $\delta^{13}C = \sigma(^{13}C)$ [$SiMe_4$] - $\sigma(^{13}C)$, with $\sigma(^{13}C)$ [$SiMe_4$] = 184.0, $\delta^{13}C$ [$SiMe_4$] = 0; $\sigma(^{11}B)$ data to $\delta^{11}B$ data by $\delta^{11}B = \sigma(^{11}B)$ [B_2H_6] - $\sigma(^{11}B)$ + 18, with $\sigma(^{11}B)$ [B_2H_6] = 84.1, $\delta^{11}B$ [B_2H_6] = 18.0 and $\delta^{11}B$ [BF_3-OEt_2] = 0; $\sigma(^{29}Si)$ data to $\delta^{29}Si$ data by $\delta^{29}Si = \sigma(^{29}Si)$ [$SiMe_4$] - $\sigma(^{29}Si)$, with $\sigma(^{29}Si)$ [$SiMe_4$] = 340.1, $\delta^{29}Si$ [$SiMe_4$] = 0.

Ethynyl(trimethyl)tin as a hexane solution. Under an Ar atmosphere butyllithium (1.6 M in hexane; 85.5 mL, 136.8 mmol) was further diluted with hexane (100 mL) and cooled at 0 °C. Purified ethyne was slowly bubbled into the stirred solution for 90 min. Immediately, a white precipitate was formed. Then trimethyltin chloride (27.2 g, 136.55 mmol) was added as a solid, when the suspension was cooled at -78 °C. The cooling bath was taken away, und the reaction solution stirred for 12 h. Insoluble materials were filtered off, and all volatiles were collected in a cold trap. The remaining solid was bis(trimethylstannyl)ethyne ($\delta^{119}Sn$ -81.1 in hexane) which can be purified by sublimation or used directly for further syntheses. The cold trap contained a hexane solution of ethynyl(trimethyl)tin (20 mmol in 185 mL) as indicated by ^1H and ^{119}Sn NMR spectra ($\delta^{119}Sn$ -68.3).

(E)-1-Trimethylstannyl-2-diethylboryl-but-1-ene 1a and isomerization into 2a, 3a and 4a. The hexane solution of ethynyl(trimethyl)tin (20 mmol in 185 mL) was cooled at -78 °C, and triethylborane (5 mL, 35 mmol) was added in one portion. The stirred mixture was warmed to 0 °C within 10 min, and the solvent and excess of BEt_3 were removed in a vacuum, leaving the pure compound **1a** in quantitative yield as extremely air-sensitive colorless oil. The pure sample of **1a** can be kept under Ar at -80 °C for prolonged periods without isomerization.

Compound **1a** was dissolved in C_6D_6 and in a mixture of C_6D_6/THF (1:1), and the time-dependent isomerization was studied by ^{119}Sn NMR spectroscopy (Fig. 1). Daylight does neither affect the rate of isomerization nor the product distribution. **1a**: ^1H NMR (300 MHz): δ^1H [$J(^{119}Sn, ^1H)$] = 0.09 [52.5] (s, 9H, Me_3Sn), 1.27, 0.99 (q, t, $J = 7.5$ Hz, 10H, Et_2B), 2.12, 0.99 (q, t, $J = 7.3$ Hz, 5H, Et-C=), 6.12 [92.1] (s, 1H, H-C=). **2a**: ^1H NMR (300 MHz): δ^1H [$J(^{119}Sn, ^1H)$] = 0.19 [53.0] (s, 9H, Me_3Sn), 1,27, 0.99 (q, t, $J = 7.5$ Hz, Et_2B), 2.32, 0.90 (q, t, $J = 7.3$ Hz, 5H, Et-C=), 6.34 [98.6] (s, 1H, H-C=). **3a**: ^1H NMR (300 MHz): δ^1H [$J(^{119}Sn, ^1H)$] = 0.13 [52.5] (s, 9H, Me_3Sn), 1.27, 0.99 (q, t, $J = 7.5$ Hz, Et_2B), 2.32, 098 (q, t, $J = 7.3$ Hz, 5H, Et-C=), 6.86 [190.6] (s, 1H, H-C=). **4a**: ^1H NMR (300 MHz): δ^1H [$J(^{119}Sn, ^1H)$] = 0.16 [52.5] (s, 9H, Me_3Sn), 1.27, 0.99 (q, t, $J = 7.6$ Hz, Et_2B), 2.32, 0.97 (q, t, $J = 7.3$ Hz, Et-C=), 6.26 [109.4] (s, 1H, H-C=).

Mixture (80:20) of (E)- and (Z)-1-trimethylsilyl-2-diethylboryl-but-1-ene 1a(Si) and 2a(Si). A mixture of ethynyl(trimethyl)silane (2.4 g, 24.4 mmol) and an excess of triethylborane (4 mL,

29 .mmol) were heated in a closed Schlenk tube under Ar at 120 °C (oil bath) for 100 h. The reaction was monitored by ^{29}Si NMR (see Table 1 and Fig. 4) until about 40 % conversion of the alkyne was achieved. The excess of BEt$_3$ and unreacted alkyne were removed in a vacuum, and the products were left as air-sensitive colorless oil. In one of these experiments, the mixture contained a small amount (< 10 %) of a third compound (δ^{29}Si -7.4), most likely a hydroboration product,[32] not mentioned in the first report.[5] **1a(Si)**: ^{1}H NMR (400 MHz): δ^{1}H = 0.00 (s, 9H, Me$_3$Si), 1.21, 0.93 (q, t, J = 7.5 Hz 10H, Et$_2$B), 1.91, 0.90 (dq, t, J = 0.8 Hz, J = 7.3 Hz, 5H, Et-C=). 5.67 (t, J = 0.8 Hz, 1H, H-C=). **2a(Si)**: ^{1}H NMR (300 MHz): δ^{1}H = 0.13 (s, 9H, Me$_3$Si), 1.21, 0.93 (q, t, J = 7.3 Hz. 10H, Et$_2$B), 2.36, 0.92 (q, t, 5H, Et-C=), 5.85 (s, 1H, H-C=).

Sodium 2-[(*E*)-1-trimethylstannyl-but-1-enyl]diethylhydridoborate 5a and the (*Z*)-isomer 6a. Sodium hydride was filtered off from a suspension in mineral oil, washed repeatedly with pentane and dried in a vacuum. Then the powder of NaH (2.5 g) was given into a Schlenk tube, suspended in hexane, BEt$_3$ (0.5 mL) was added, and the mixture was heated to reflux for 90 min. At room temperature, a small amount of an 80:20 mixture of **1a** and **2a** (0.86 g, 3 mmol) was added, and the mixture was kept stirring for 90 min. The supernatant solution was decanted, and volatiles were removed in a vacuum, leaving a colorless oily material which was dissolved in C$_6$D$_6$ and characterized by NMR spectroscopy (Table 1). **5a**: ^{1}H NMR (300 MHz): δ^{1}H [^{2}J(^{119}Sn,^{1}H)] = 0.22 [51.2] (s, 9H, Me$_3$Sn), 0.17, 0.95 (q, t, J = 7.6 Hz, 10H, Et$_2$B), 2.25, 0.84 (q, t, J = 7.3 Hz, Et-C=), 6.02 [110.3] (s, 1H, H-C=). **6a**: ^{1}H NMR (300 MHz): δ^{1}H [^{2}J(^{119}Sn,^{1}H)] = 0.24 [51.2] (s, 9H, Me$_3$Sn), 0.17, 0.95 (q, t, J = 7.6 Hz, Et$_2$B), 2.19, 1.09 (q, t, J = 7.3 Hz, Et-=), 5.76 [115.9] (s, 1H, H-C=).

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