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1,1-Organoboration of bis(trimethylstannyl)ethyne with trimethylsilyl- and dimethylsilyl-dialkylboryl-substituted alkenes: organometallic-substituted allenes

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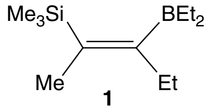
The reactions of bis(trimethylstannyl)ethyne, $Me_3Sn{-}C{\equiv}C{-}SnMe_3$ (4), with trimethylsilyl- or dimethylsilyl-dialkylboryl-substituted alkenes 1–3 afford organometallic-substituted allenes 5, 6 and 8, 9 in high yield. In the case of (*E*)-2-trimethylsilyl-3-diethylboryl-2-pentene (1), a butadiene derivative 7 could be detected as an intermediate prior to rearrangement into the allene. All reactions were monitored by ^{29}Si and ^{119}Sn NMR, and the products were characterized by an extensive NMR data set (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{119}Sn NMR).

KEYWORDS: boranes; silanes; organoboration; allenes; butadienes; multinuclear magnetic resonance

INTRODUCTION

Alkenes bearing a dialkylboryl group and an additional organometallic substituent at the C=C bond are attractive reagents for further transformations. Such compounds are readily available by various convenient routes. The reaction of triethyl(propyn-1-yl)borate with chloro(trimethyl)silane[1–3] or, alternatively, the 1,1-ethylboration of trimethyl(propyn-1-yl))silane[4,5] affords selectively the alkene **1** in high yield. Regiospecific 1,2-hydroboration of alkyn-1-yl(trimethyl)- or alkyn-1-yl(dimethyl)-silanes[6–13] by using 9-borabicyclo[3.3.1]nonane (9-BBN[14–16]) opens access to the alkenes **2**[17] and **3**.[18]

Previously, it was shown that treatment of alkenes of type **1**, where the $SiMe_3$ group is substituted by an $SnMe_3$ group, with bis(trimethylstannyl)ethyne, $Me_3Sn{-}C{=}C{-}SnMe_3$ (**4**), leads to allenes,[19–21] and these were subsequently also characterized by X-ray structural analysis.[22] Although 1,3-butadiene derivatives have been proposed as the most likely intermediates, these were never detected in the reaction solutions. Here, we extend this work to the reaction of the alkenes **1–3** with **4**, and in the case of **1** we present conclusive NMR spectroscopic evidence for a 1,3-butadiene derivative as an intermediate prior to allene formation. Although IR spectroscopy gives an immediate qualitative answer with respect to the question of allene formation ($\nu(C{=}C)_{as} = 1985 \pm 10\ cm^{-1}$), the elucidation of the substituent patterns



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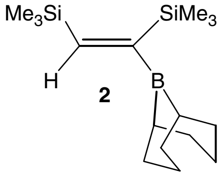

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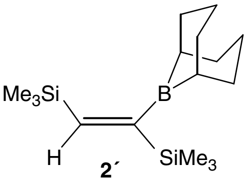

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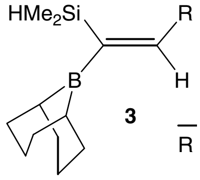

3

	a	b	c	d
R	Bu	ᵗBu	Ph	SiMe₃

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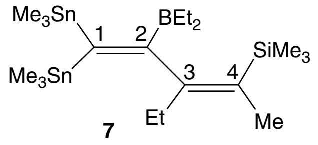
of the new allenes requires a careful multinuclear magnetic resonance study.

RESULTS AND DISCUSSION

Reaction of (*E*)-2-trimethylsilyl-2-diethylboryl-2-pentene (1) with $Me_3Sn-C\equiv C-SnMe_3$ (4)

When a mixture of the alkene **1** and the alkyne **4** (1 : 1.1 molar ratio; a slight excess of **4**), prepared in pentane at −78 °C, was brought to ambient temperature and kept stirring for several days, NMR spectra indicated the presence of two different allenes **5** and **6**, a butadiene **7**, and the starting materials **1** and **4**. After heating the mixture in benzene for 6 h at 80 °C the butadiene was no longer present, and a small amount of **1** was left along with the mixture of the allenes **5** and **6**. The reactions are summarized in Scheme 1. So far, it has not been possible to separate the allenes **5** and **6**. Apparently, the reaction of the 1,3-butadiene **7** with **4** to give **6** takes place at a rate comparable to those for the reaction of **1** with **4** and the rearrangement of **7** into **5**. This is the first time that the intermediacy of a 1,3-butadiene derivative in the course of allene formation by 1,1-organoboration is firmly established by a conclusive set of NMR data for **7** (Table 1). The presence of **7** in the reaction solution is already indicated by the ^{119}Sn NMR signals in the range of alkenyltin compounds[23,24] (Fig. 1) with their typical line shape as a result of partially relaxed scalar $^{119}Sn-^{11}B$ spin–spin coupling across three bonds.[23–25] The characterization of the allenes **5** and **6** in the mixture is also straightforward by NMR (Table 2). The number and relative intensities of the $^{117/119}Sn$ satellite signals in the ^{13}C NMR (Fig. 2) and ^{29}Si NMR spectra (Fig. 3) are diagnostic for distinguishing between **5** and **6**.

Table 1. ^{13}C, ^{29}Si and ^{119}Sn NMR data[a] of the 1,3-butadiene derivative **7**



7

$\delta^{13}C(1)$	144.0 [312.0, 312.0]; −5.5 [307.0, 11.4] ($SnMe_3$), −5.0 [307.8, 8.2] ($SnMe_3$)
$\delta^{13}C(2)$	187.3 (br); 21.7 (br), 9.4 (BEt_2)
$\delta^{13}C(3)$	159.2 [123.0 (*trans*), 80.1 (*cis*)]; 28.1 [12.4], 13.9 (Et)
$\delta^{13}C(4)$	128.1 [8.0]; 21.4 (Me); 0.8 (51.3) ($SiMe_3$)
$\delta^{29}Si$	−6.7 [6.2]
$\delta^{119}Sn$	−47.8 [984.8[b]] (*cis* to BEt_2); −49.5 (*trans* to BEt_2)

[a] In mixture with the allenes **5** and **6**; coupling constants $J(^{119}Sn,X)$ ($X = {}^{13}C$, ^{29}Si, ^{119}Sn) are given in brackets [±0.5 Hz], and $J(^{29}Si,^{13}C)$ in parentheses (±0.5 Hz); (br) denotes a broad ^{13}C NMR signal owing to partially relaxed scalar $^{13}C-^{11}B$ spin–spin coupling.

[b] Measured as $^2J(^{119}Sn, ^{117}Sn) = 941$ Hz (Fig 1); given as $^2J(^{119}Sn, ^{119}Sn)$ by multiplication with the factor 1.0465 for $\gamma(^{119}Sn)/\gamma(^{117}Sn)$.

Reactions of the alkenes 2 and 3 with $Me_3Sn-C\equiv C-SnMe_3$ (4)

Since the reaction of **1** with **4** afforded a mixture of allenes, we decided to use the 9-BBN derivatives **2** and **3** instead

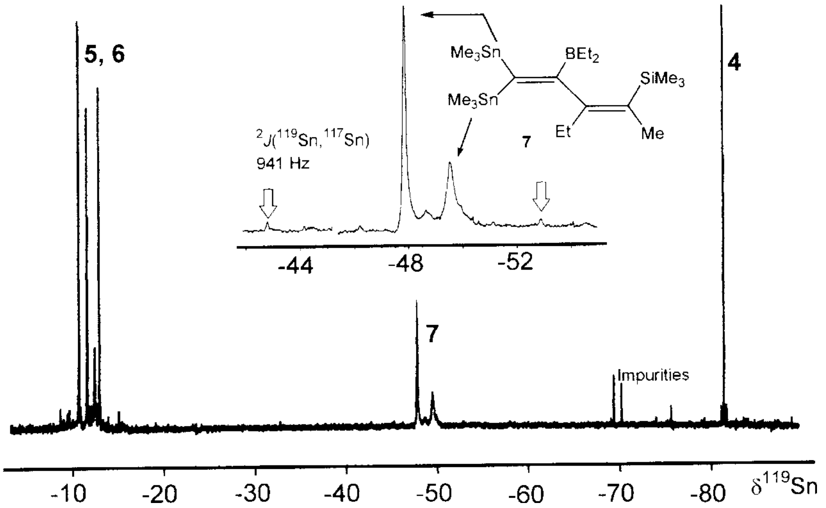
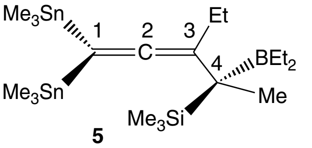


Figure 1. The 93.3 MHz $^{119}Sn\{^1H\}$ NMR spectrum of the reaction solution containing **1**, **4**, **5**, **6** and **7**, recorded after stirring the mixture for 7 days at room temperature. The ^{119}Sn NMR signals of the 1,3-butadiene derivative **7** cannot be mistaken, because of the characteristic $\delta^{119}Sn$ values, the line shapes and the large magnitude of the geminal coupling constant $^2J(^{119}Sn,^{119}Sn)$ (in the expansion, the ^{117}Sn satellites are indicated by arrows).

Table 2. ^{13}C, ^{29}Si and ^{119}Sn NMR data[a] of the allenes **5** and **6**



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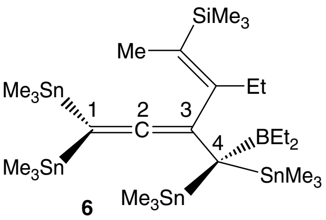


6

	5	**6**
δ^{13}C(1)	82.7 [298.6, 290.2]; −7.7 [311.0], −7.6 [310.6] ($SnMe_3$)	80.2 [287.4, 5.3]; −5.4 [324.0, 5.2] [=C($SnMe_3$)$_2$]
δ^{13}C(2)	207.7 [39.7]	205.5 [41.0]
δ^{13}C(3)	91.0 [75.3, 72.6]; 25.9 [25.8], 13.6 [6.6] (Et)	92.2 [72.4, 17.2]; 152.4 [27.5], 30.3 [14.5, 10.3], 14.3 (=C–Et); 130.2 [18.5, 2.3] (66.5) (=C–Si); 18.2 [5.0] (Me)
δ^{13}C(4)	40.2 (br); 18.6 (br), 8.5 (BEt_2); 19.1 [24.0, 21.2] (Me); −0.1 (51.0) ($SiMe_3$)	n.o. (br); 18.3 (br), 10.2 (BEt_2); −2.9 [311.0]
δ^{29}Si	−0.3 [7.4]	−7.1 [2.4]
δ^{119}Sn	−13.0 [406.6[b]], −10.8 [406.8[b]]	−11.7 [438.8[c]] [=CSn(Me_3)$_2$], −12.5[d] [C($SnMe_3$)$_2$]

[a] Mixture of the allenes **5** and **6** with the butadiene derivative **7** (Table 1); coupling constants $J(^{119}\text{Sn},X)$ ($X = {}^{13}$C, ^{29}Si, ^{119}Sn) are given in brackets [±0.5 Hz], and $J(^{29}\text{Si},^{13}\text{C})$ in parentheses (±0.5 Hz); (br) denotes a broad ^{13}C NMR signal owing to partially relaxed scalar ^{13}C–^{11}B spin–spin coupling; n.o. means not observed.

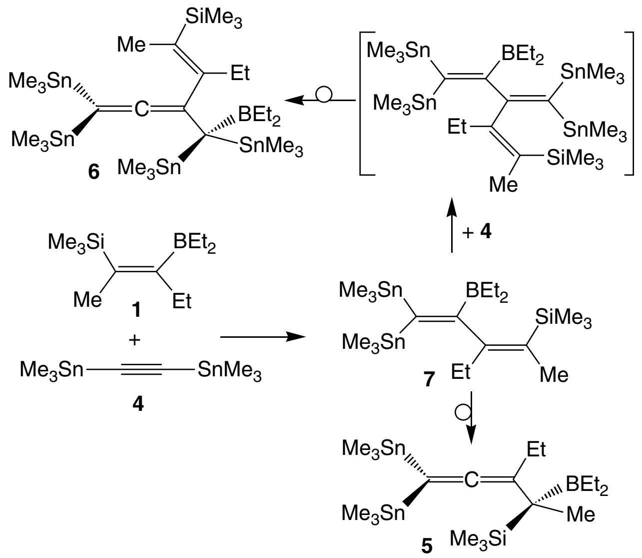
[b] Measured as $^2J(^{119}\text{Sn},^{117}\text{Sn}) = 388.5$ Hz; given as $^2J(^{119}\text{Sn},^{119}\text{Sn})$ by multiplication with the factor 1.0465 for $\gamma(^{119}\text{Sn})/\gamma(^{117}\text{Sn})$.

[c] Measured as $^2J(^{119}\text{Sn},^{117}\text{Sn}) = 419.3$ Hz; given as $^2J(^{119}\text{Sn},^{119}\text{Sn})$ by multiplication with the factor 1.0465 for $\gamma(^{119}\text{Sn})/\gamma(^{117}\text{Sn})$; $^{117/119}$Sn satellites due to ^5J(Sn,Sn) overlap with other signals and were not resolved.

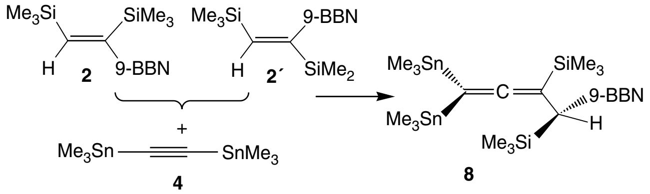
[d] Signal is broad owing to hindered rotation about the =C–C bond; $^{119/117}$Sn satellites were not assigned.

of diethylboryl-substituted alkenes. It was expected that the reactivity of the B–C=bond in the 9-BBN derivatives would be somewhat reduced. In the case of **2**, a mixture of **2** and **2′**[17] was used, whereas compounds **3** were available in the pure state.[18] Although 1,3-butadienes analogous to **7** were not detected in the reaction mixtures, the clean formation of the allenes **8** and **9** suggests that short-lived 1,3-butadienes are intermediates, from which irreversible allylic rearrangement leads to the allenes (Schemes 2 and 3).

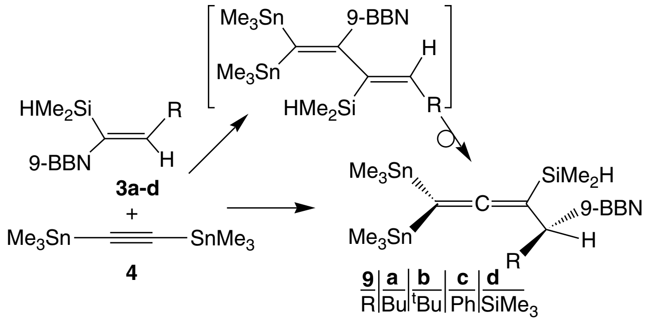
The allenes **9** are the first examples of allenes prepared by 1,1-organoboration, in which the silicon atom bears the hydride as a functional group and which is promising for the introduction of other functions at silicon. All allenes **8** and **9** are fully characterized by NMR spectroscopy in solution



Scheme 1.



Scheme 2.



Scheme 3.

(Table 3). Again, the $^{117/119}$Sn satellites in ^{13}C, ^{29}Si (Fig. 4) and ^{119}Sn NMR spectra (Fig. 5) provide convincing indirect structural information. The $SnMe_3$ groups at the terminal allenic carbon atom, and the methyl groups of the $SiMe_2H$ unit in **9** become diastereotopic because of the presence of a chiral centre, further confirming the proposed structures.

The remarkable potential of ^{119}Sn NMR in the analysis of mixtures and structural assignment is due to the sensitivity of tin chemical shifts towards small structural changes four or even five bonds away from the tin

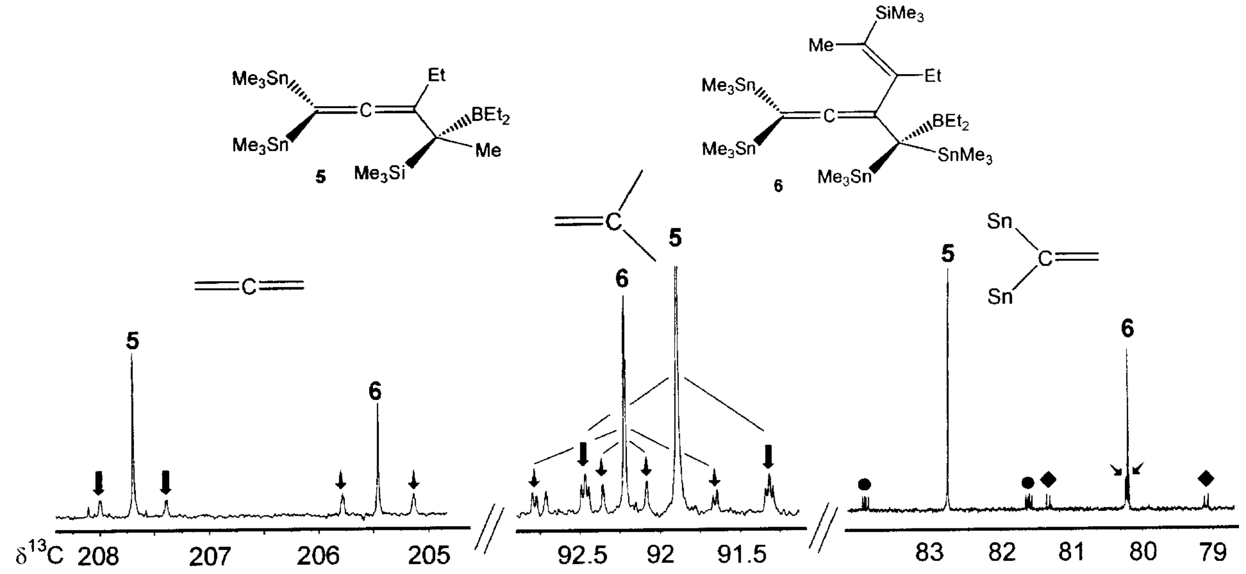


Figure 2. The 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the mixture (in C_6D_6, after keeping a pentane solution for 7 days at room temperature) containing the allenes **5**, **6** and the 1,3-butadiene **7**. The ^{13}C NMR signals of the central and terminal allenic carbon atoms are shown. The various $^{117/119}Sn$ satellites are marked by filled circles and rhombs for $^1J(Sn,^{13}C)$, and by arrows for $^nJ(Sn,^{13}C)$ ($n = 2, 3, 4$). The number and relative intensities of the $^{117/119}Sn$ satellites confirm the assignment of the signals to **5** and **6**.

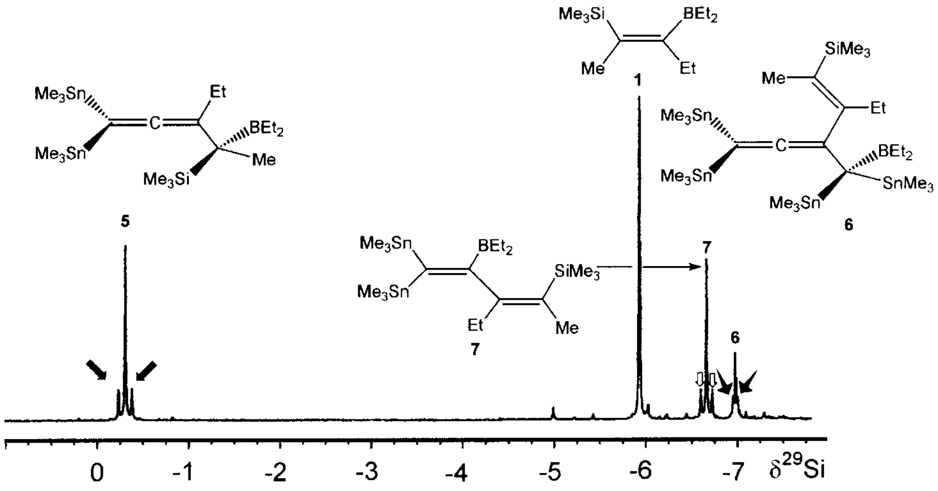
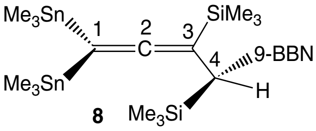


Figure 3. The 49.7 MHz $^{29}Si\{^1H\}$ NMR spectrum (refocused INEPT[26–29]) of the reaction mixture containing **1**, **4**, **5**, **6** and **7**, recorded after stirring the mixture for 7 days at room temperature. The assignments of the ^{29}Si NMR signals to **5**, **6** and **7** are confirmed by the presence of $^{117/119}Sn$ satellites and their relative intensities.

atom.[23,24] Coupling constants involving the ^{119}Sn nuclei provide a second set of valuable information. In the present study, the geminal coupling constants $^2J(^{119}Sn,^{119}Sn)$ deserve particular interest. Apparently, the magnitude of $^2J(^{119}Sn,^{119}Sn)$ across sp^3- or sp^2-hybridized carbon atoms changes significantly depending on the other substituents.[23,24] In the case of the 1,1-bis(trimethylstannyl)allenes, substituents that affect $^2J(^{119}Sn,^{119}Sn)$ are much more distant than in corresponding alkanes or alkenes. Nevertheless, there are changes in the magnitude of $^2J(^{119}Sn,^{119}Sn)$ from +165 Hz, in $(Me_3Sn)_2C{=}C{=}CH_2$,[30] to +443.6 Hz, in $(Me_3Sn)_2C{=}C{=}C(Et)C(SnMe_3)_2BEt_2$.[22]

^{11}B NMR spectroscopy is not helpful for monitoring the reactions described here, because the broad ^{11}B NMR signals of the starting alkenylboranes are in the same range as those of the products. However, it is noteworthy that the $\delta^{11}B$ values for such allenes[19–22] cover a rather large range ($\delta^{11}B$ 73 to 88 ppm), considering the apparently similar surroundings of the boron atoms. In the allenes, an increase in the magnetic shielding of the ^{11}B nuclei

Table 3. ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR data[a] of the allenes **8** and **9**



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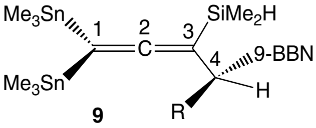

9

	8	**9a** (R = Bu)	**9b** (R = ^{t}Bu)	**9c**[c] (R = Ph)	**9d** (R = SiMe$_3$)
δ^{13}C(1)	70.3 [299.5, 290.4]; −7.1 [332.2, 4.5] (SnMe$_3$)	68.7 [273.6, 261.1]; −7.38 [337.5], −7.35 [344.9] (SnMe$_3$)	67.7 [280.9, 270.7]; −6.7 [338.7], −6.3 [334.9] (SnMe$_3$)	70.0 [268.4, 262.1]; −8.2 [342.4], −7.9 [343.4] (SnMe$_3$)	70.4 [290.0, 283.2]; −7.4 [334.0], −6.6 [333.3] (SnMe$_3$)
δ^{13}C(2)	203.5 [33.3, 30.2]	202.4 [29.1]	202.5 [31.7, 25.8]	201.5 [28.2]	203.1 [30.7]
δ^{13}C(3)	69.7 [59.1] (63.0); −0.3 [6.0] (52.1) (SiMe$_3$)	65.8 [53.2] (64.9); −2.91 (52.8), −2.89 (52.4) (SiMe$_2$)	64.8 [55.0] (64.3); −2.9 (52.8), −2.7 (52.0) (SiMe$_2$)	67.4 [55.8] (65.4); −3.4 (52.5), −3.3 (52.7) (SiMe$_2$)	67.5 [58.4] (65.0); −3.20 (52.4), −3.15 (52.0) (SiMe$_2$)
δ^{13}C(4)	35.4 [20.0]; 31.8 (br), 33.6, 34.0, 23.6 (9-BBN); 1.9 (51.0) (SiMe$_3$)	37.8 (br); 30.4 (br), 34.0, 33.9, 23.7 (9-BBN); 31.4 [12.6], 33.0, 23.5, 14.5 (Bu)	50.7 (br) [17.0]; 33.0 (br), 34.4, 34.1, 23.8 (9-BBN); 37.4 [17.8], 31.8 (^{t}Bu)	45.5 (br) [20.0]; 31.2 (br), 33.5, 33.5, 23.6 (9-BBN); 142.6 [18.0], 129.3, 127.7, 125.1 (Ph)	36.5 (br) [17.0]; 31.9 (br), 33.7, 33.3, 23.6 (9-BBN); 1.5 (51.1) (SiMe$_3$)
δ^{29}Si	−2.4 [32.9, 32.1] (2.9) (=C–SiMe$_3$); 2.1 [29.9, 26.3] (2.9) (C–SiMe$_3$)	−16.9 [30.4]	−13.3 [32.6]	−14.7 [29.8]	−12.9 [33.3] (3.0) (=C–SiMe$_2$); 2.3 [27.4, 24.2] (2.0) (C–SiMe$_3$)
δ^{119}Sn	−9.7 [332.1^b], −1.2 [332.1^b]	−4.2 [239.4^b], 0.0 [239.4^b]	−5.6 [256.8^b], 6.9 [256.8^b]	−2.3 [238.8^b], 1.2 [238.8^b]	−7.1 [313.7^b], 0.0 [313.7^b]
δ^{11}B	88.5	80.5	84.1	82.6	86.7

[a] Coupling constants $J(^{119}\text{Sn},X)$ ($X = {}^{13}$C, ^{29}Si, ^{119}Sn) are given in brackets [±0.5 Hz], and $J(^{29}\text{Si},^{13}\text{C})$ and $J(^{29}\text{Si},^{29}\text{Si})$ in parentheses (±0.5 Hz); (br) denotes a broad ^{13}C NMR signal owing to partially relaxed scalar ^{13}C–^{11}B spin–spin coupling.

[b] Measured as $^2J(^{119}\text{Sn},^{117}\text{Sn})$; given as $^2J(^{119}\text{Sn},^{119}\text{Sn})$ by multiplication with the factor 1.0465 for $\gamma(^{119}\text{Sn})/\gamma(^{117}\text{Sn})$.

[c] In CDCl$_3$.

in comparison with trialkylboranes (δ^{11}B 87 ± 1 ppm[31]) can be traced to hyperconjugative interactions (σ conjugation)[32] between boron and neighbouring C–C and M–C (M=Si, Sn) bonds. These interactions require a preferred conformation of the C$_2$B plane of the 9-BBN or the Et$_2$B group, which depends on steric repulsion exerted by other substituents, in particular on C-3 and C-4.

CONCLUSIONS

Consecutive 1,1-organoboration of alkyn-1-yl-metal compounds, and, probably even more versatile in future applications, the combination of 1,2-hydroboration and 1,1-organoboration[33] have been used to prepare new organometallic-substituted allenes. Firm evidence is available now that 1,3-butadiene derivatives are intermediates prior to allene formation. Multinuclear magnetic resonance methods serve for monitoring the progress of the reactions, as well as for the characterization of the products.

EXPERIMENTAL

General and starting materials

All compounds were handled under dry argon, observing all necessary precautions to exclude air and moisture, and carefully dried solvents and oven-dried glassware were used throughout. Starting materials, such as (*E*)-2-trimethylsilyl-3-diethylboryl-2-pentene (**1**),[34] the alkenylsilanes **2**[17] and **3**,[18] and bis(trimethylstannyl)ethyne (**4**)[35,36] were prepared according to literature procedures. NMR measurements: Bruker ARX 250 and DRX 500 [^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{119}Sn NMR (refocused INEPT[26–29] based on $^2J(^{29}\text{Si}, ^1\text{H}_{\text{Me}}) = 7$ Hz and $^2J(^{119}\text{Sn}, ^1\text{H}_{\text{Me}}) = 52$ Hz respectively]. Chemical shifts (ppm) are given with respect to Me$_4$Si [δ^1H (CHCl$_3$–CDCl$_3$) = 7.24; δ^{13}C (CDCl$_3$) = 77.0, (C$_6$D$_6$) = 128.0; δ^{29}Si = 0 for $\Xi(^{29}\text{Si}) =$ 19.867 184 MHz], BF$_3$–OEt$_2$ [δ^{11}B = 0 for $\Xi(^{11}\text{B}) = 32.083$ 971 MHz] and Me$_4$Sn [δ^{119}Sn = 0 for $\Xi(^{119}\text{Sn}) = 37.290$ 665 MHz]. IR spectra were measured using a Perkin Elmer Spectrum 2000 FTIR instrument; all allenes gave the characteristic band for $\nu(\text{C=C})_{\text{as}}$ close to 1985 ± 10 cm^{-1}.

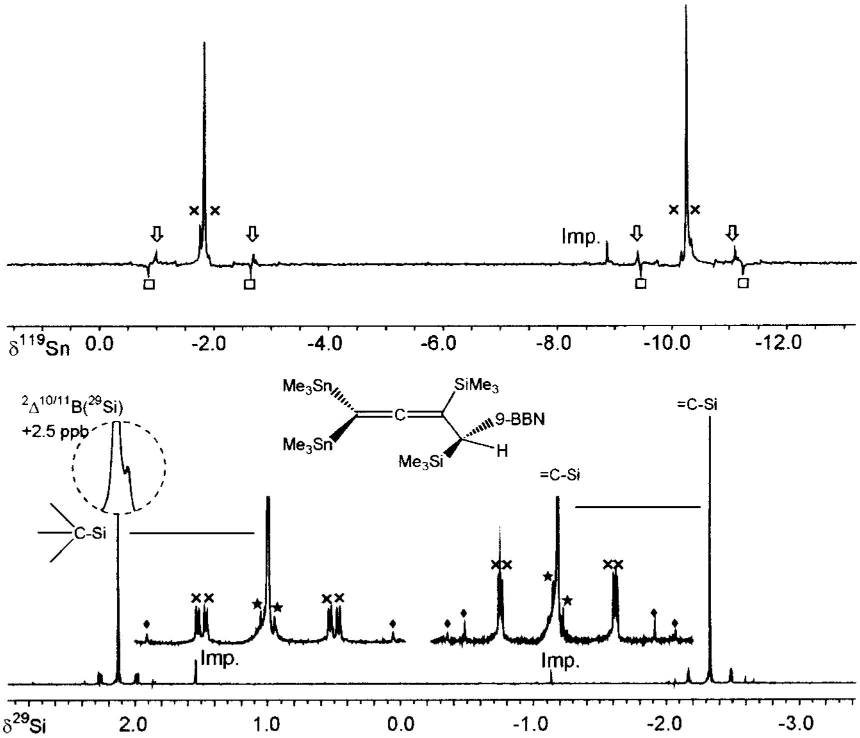

Figure 4. The 186.5 MHz ^{119}Sn{^{1}H} and 99.4 MHz ^{29}Si NMR spectra (refocused INEPT$^{26-29}$) of the allene **8** (impurities are marked). In the ^{29}Si NMR spectrum, $^{117/119}$Sn satellites are marked with crossed bars, ^{29}Si satellites with stars and ^{13}C satellites with filled rhombs. One pair of ^{13}C satellites due to $^1J(^{29}\text{Si}, ^{13}\text{C})$ is missing; it lies underneath the Sn satellites. The SnMe$_3$ groups are diastereotopic, as shown in the ^{119}Sn NMR spectrum; ^{117}Sn satellites (arrows), ^{119}Sn satellites (open squares), and ^{29}Si satellites (crossed bars; in agreement with data from the ^{29}Si NMR spectrum) are indicated. Note the distorted phase of the ^{119}Sn satellites (see also Fig 5), typical of an AB spin system in the INEPT pulse sequence, where effects arising from homonuclear spin–spin couplings are not refocused.

Mass spectra (EI MS at 70 eV; Finnigan MAT 8500 instrument with direct inlet) gave the molecular ions only in weak intensity, showing mainly fragments containing only one tin atom, and, therefore, did not provide reliable information on the composition of the allenes. Because of the extremely air- and moisture-sensitivity of the compounds, other mass spectrometric techniques were not applied.

Reaction of 1 with 4: mixture of the allenes 5, 6 and the 1,3-butadiene derivative 7

A solution of **1** (0.95 g, 4.5 mmol) in pentane (10 mL) was cooled to −78 °C and **4** (1.61 g, 4.6 mmol) was added as a solid in one portion. The mixture was kept stirring for several days at room temperature, and the progress of the reaction was monitored by ^{119}Sn and ^{29}Si NMR spectroscopy (see Figs 1 and 3). After removing the pentane *in vacuo*, the oily residue was dissolved in benzene. The NMR signals for the 1,3-butadiene derivative **7** vanished after heating at 80 °C for several hours. The mixture of the allenes **5** and **6** could not be separated. The ^{1}H NMR signals of the compounds **5**, **6** and **7** overlap in all regions. Therefore, the analysis of the mixture was carried out using ^{13}C, ^{29}Si and ^{119}Sn NMR spectroscopy (see Tables 1 and 2).

4-(9-Borabicyclo[3.3.1]non-9-yl)-3,4-bis(trimethylsilyl)-1,1-bis(trimethylstannyl)-1,2-butadiene (8) and 4-(9-borabicyclo[3.3.1]non-9-yl)-3-dimethylsilyl-1,1-bis(trimethylstannyl)-1,2-butadiene derivatives (9a–d): general procedure

A solution of **4** (0.84 g, 2.4 mmol) in pentane (10 mL) was cooled to −78 °C, and an equimolar amount of the respective alkene **2** or **3** was added in one portion. After warming the mixture to room temperature, stirring was continued for 3 h. Then, all volatile materials were removed *in vacuo*, leaving viscous oils, some of which became waxy solids after several months. Attempts at further purification by crystallization were not successful. Chromatography on silica or Al$_2$O$_3$ was accompanied by extensive decomposition. The oils isolated without purification were pure (>95%) according to ^{1}H NMR spectra, indicating essentially quantitative conversion of the alkenes **2** or **3** into the allenes **8** and **9** respectively.

8: ^{1}H NMR (C$_6$D$_6$; 250.1 MHz): δ [$J(^{119}\text{Sn}, ^1\text{H})$] = 0.09 (s, 9H, SiMe$_3$), 0.18 (s, 9H, SiMe$_3$), 0.19 [53.2] (s, 9H, SnMe$_3$), 0.22 [53.2] (s, 9H, SnMe$_3$), 1.20–1.90 (m, 15H, 9-BBN, 4-H).

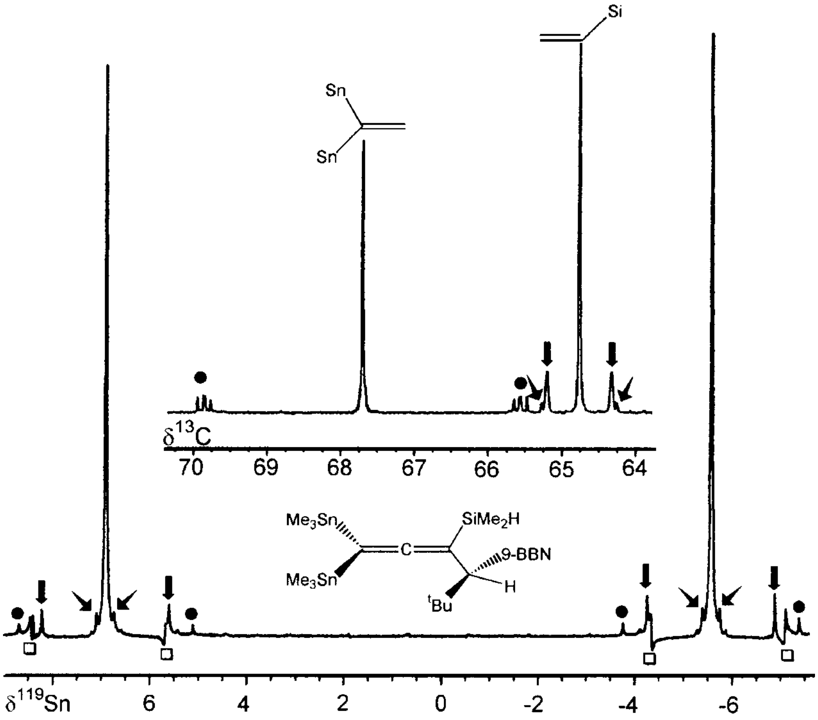

Figure 5. The 93.3 MHz $^{119}Sn\{^{1}H\}$ (refocused INEPT[26–29]) and 62.9 MH_3 $13C\{^{1}H\}$ NMR spectra of the allene **9b**. The ^{119}Sn signals are accompanied by ^{13}C satellites (filled circles; for the methyl groups), ^{117}Sn satellites (arrows; AX spin systems), ^{119}Sn satellites (open squares; AB systems with a distorted phase, as in Fig. 4), and ^{29}Si satellites (filled, tilted arrows). The ^{13}C NMR signals of the terminal allenic carbon atoms are shown with their $^{117/119}Sn$ [filled circles for $^{1}J(Sn, ^{13}C)$, and filled arrows for $^{3}J(Sn, ^{13}C)$] and ^{29}Si satellites [filled, tilted arrows for $^{1}J(^{29}Si, ^{13}C)$].

9a: ^{1}H NMR (C_6D_6; 250.1 MHz): δ [$J(^{119}Sn, ^{1}H)$] = 0.15, 0.16 (d, d, 3H, 3H,$^{3}J(^{1}H,C,Si, ^{1}H) = 3.5$ Hz, $SiMe_2$), 0.22 [52.5] (s, 9H, $SnMe_3$), 0.23 [53.3] (s, 9H, $SnMe_3$), 4.5 (sp, 1H, $^{3}J(^{1}H,C,Si, ^{1}H) = 3.5$ Hz, SiH; $^{1}J(^{29}Si, ^{1}H) = 186.6$ Hz); various overlapping multiplets for the butyl group, 9-BBN, and 4-CH corresponding to 24H.

9b: ^{1}H NMR (C_6D_6; 250.1 MHz): δ [$J(^{119}Sn, ^{1}H)$] = 0.15, 0.17 (d, d, 3H, 3H, $^{3}J(^{1}H,C,Si, ^{1}H) = 3.6$ Hz, $SiMe_2$), 0.19 [53.5] (s, 9H, $SnMe_3$), 0.22 [53.3] (s, 9H, $SnMe_3$), 1.12 (s, 9H, ^{t}Bu), 1.30–1.90 (m, 15H, 9-BBN, 4-CH), 4.30 (sp, 1H, $^{3}J(^{1}H,C,Si, ^{1}H) = 3.6$ Hz, SiH; $^{1}J(^{29}Si, ^{1}H) = 188.0$ Hz).

9c: ^{1}H NMR ($CDCl_3$; 250.1 MHz): δ [$J(^{119}Sn, ^{1}H)$] = 0.00, 0.03 (d, d, 3H, 3H, $^{3}J(^{1}H,C,Si, ^{1}H) = 3.5$ Hz, $SiMe_2$), 0.07 [54.1] (s, 9H, $SnMe_3$), 0.18 [53.9] (s, 9H, $SnMe_3$), 1.30–1.70 (m, 14H, 9-BBN), 3.25 [21.9] (s, 1H, 4-H), 4.10 (sp, 1H, $^{3}J(^{1}H,C,Si, ^{1}H) = 3.5$ Hz, SiH; $^{1}J(^{29}Si, ^{1}H) = 187.8$ Hz), 7.05, 7.20 (m, m, 2H, 3H, Ph).

9d: ^{1}H NMR (C_6D_6; 250.1 MHz): δ [$J(^{119}Sn, ^{1}H)$] = 0.18, 0.20 (d, d, 3H, 3H, $^{3}J(^{1}H,C,Si, ^{1}H) = 3.2$ Hz, $SiMe_2$), 0.22 (s, 9H, $SiMe_3$), 0.23 [53.2] (s, 9H, $SnMe_3$), 0.24 [53.4] (s, 9H, $SnMe_3$), 1.30–1.70 (m, 15H, 9-BBN, 4-H), 4.30 (sp, 1H, $^{3}J(^{1}H,C,Si, ^{1}H) = 3.2$ Hz, SiH; $^{1}J(^{29}Si, ^{1}H) = 187.1$ Hz).

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