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1,1-Organoboration of silylethynyltin compounds studied by multinuclear magnetic resonance spectroscopy: isomerization at the C=C bonds and electron-deficient Si–H–B bridges

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1,1-Organoboration, using triethyl-, triallyl- and triphenyl-borane (BEt_3, $BAll_3$, BPh_3), of dimethysilylethynyl(trimethyl)stannane, $Me_3Sn{-}C{\equiv}C{-}Si(H)Me_2$ (1), affords alkenes bearing three different organometallic groups at the C=C bond. For BEt_3 and BPh_3, the first products are the alkenes 4 with boryl and stannyl groups in cis-positions. These rearrange by consecutive 1,1-deorganoboration and 1,1-organoboration into the isomers 5 as the final products, where boryl and silyl groups are in cis-positions linked by an electron-deficient Si–H–B bridge. 1,1-Ethylboration of bis(dimethylsilylethynyl)dimethylstannane, $Me_2Sn[C{\equiv}C{-}Si(H)Me_2]_2$ (2), leads to the stannacyclopentadiene 6 along with non-cyclic di(alkenyl)tin compounds 7 and 8. 1,1-Ethylboration of ethynyl(trimethylstannylethynyl)methylsilane, $Me(H)Si(C{\equiv}C{-}SnMe_3)C{\equiv}C{-}H$ (3), leads selectively to a new silacyclopentadiene 13 as the final product. The reactions were monitored and the products were characterized by multinuclear magnetic resonance spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR). Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: boranes; silanes; stannanes; alkynes; siloles; stannoles; multinuclear magnetic resonance; NMR

INTRODUCTION

Owing to the reactivity of the polar Sn–C≡ bond, alkyn-1-yltin compounds are versatile reagents in organometallic chemistry.[1,2] It has been shown that triorganoboranes react with alkyn-1-yl tin compounds by 1,1-organoboration.[3] This reaction proceeds via cleavage of the Sn–C≡ bond and formation of alkyn-1-yl borate-like intermediates **A**,[3–5] where the positively charged tin fragment is coordinated side-on to the C≡C bond (Scheme 1). These intermediates **A** rearrange further to give selectively the alkenes **B**,[3] bearing stannyl and boryl groups in cis-positions at the C=C bond.

Frequently, the stereoselectivity of this 1,1-organoboration is lost if there is a second organometallic substituent attached to the C≡C bond.[3] In the case of trimethylsilylethynyl(trimethyl)stannane, $Me_3Sn{-}C{\equiv}C{-}SiMe_3$, the reaction with triethylborane (BEt_3) leads to the isomer **D** as the major product for all reaction conditions studied (Scheme 2).[6]

It is well known that facile 1,1-deorganoboration has to be considered for alkenes of the type **C** and **D**.[3] This raises questions as to whether the Me_3Si group causes a difference in the reaction mechanism or whether the stereochemistry in **D** is the result of facile cis/trans isomerization via 1,1-deorganoboration of the alkene **C** which might be formed in the beginning of the reaction. In order to address these points, we have prepared the alkyn-1-yltin compounds **1, 2** and **3** (Scheme 3a–c) which bear a dimethylsilyl or a methylsilyl group at the C≡C bonds. The reactions of **1** with BEt_3, triphenylborane (BPh_3), and triallylborane ($BAll_3$), and those of **2** and **3** with BEt_3 were studied.

RESULTS AND DISCUSSION

Synthesis of the silylethynyltin compounds 1, 2 and 3

The alkyne **1** was synthesized in two steps (Scheme 3a) by the reaction of bis(trimethylstannyl)ethyne[7] with one equivalent of BuLi,[8] followed by the reaction of the lithium alkynide with a slight excess of chloro(dimethyl)silane.

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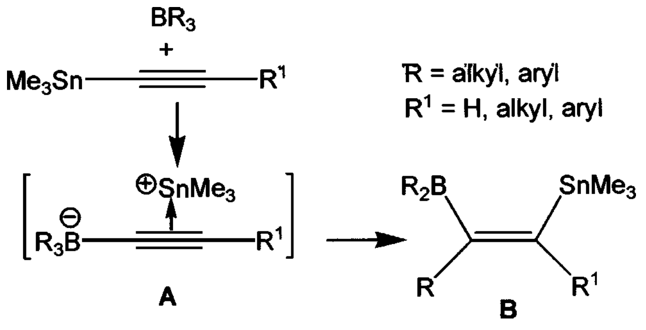
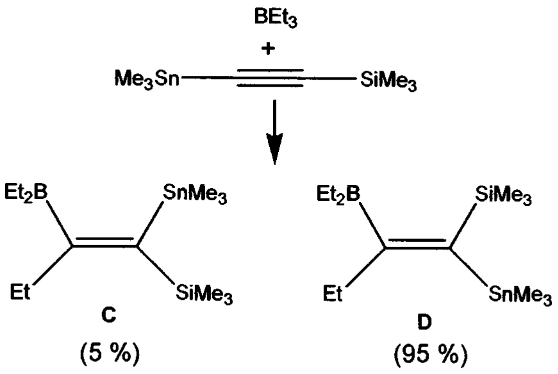
A different approach was required for the syntheses of **2** and **3** (Scheme 3b and c). The reaction of two equivalents of dimethylsilylethynylmagnesium bromide[9,10] with dimethyltin dichloride gave the dialkyn-1-yltin compound **2** (Scheme 3b). Diethynyl(methyl)silane was converted selectively into the mono-Grignard reagent,[9,10] when treated with one equivalent of ethylmagnesium bromide (Scheme 3c). Then, the reaction with trimethyltin chloride gave the alkyne derivative **3** in good yield. The compounds **1, 2** and **3** could be purified by distillation and were characterized by their ^{1}H, ^{13}C, ^{29}Si and ^{119}Sn NMR data.



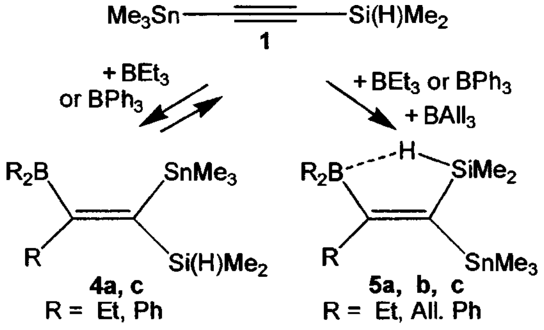
Scheme 1.



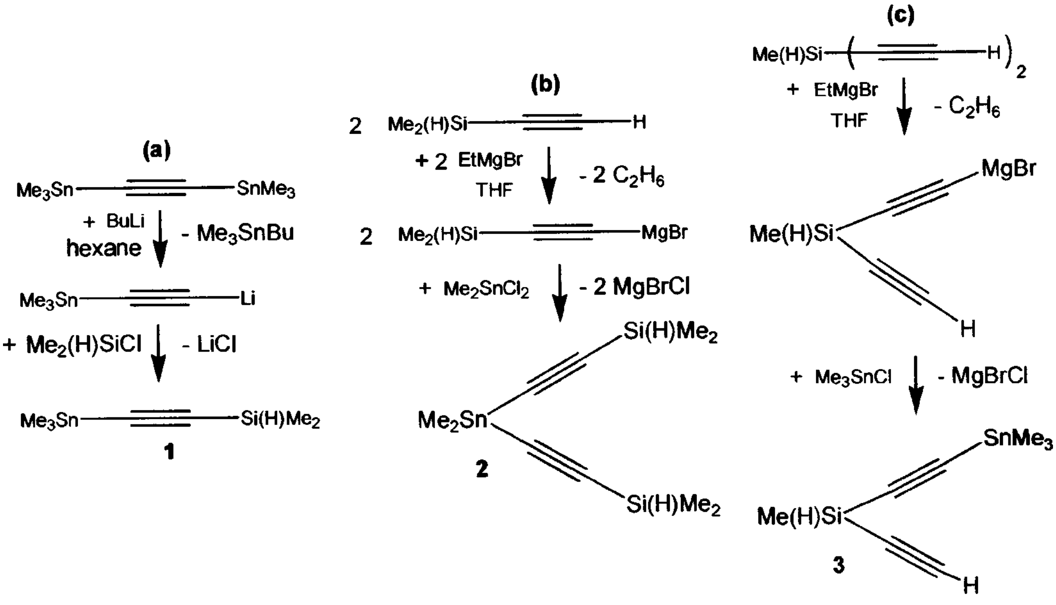
Scheme 2.

1,1-Organoboration of dimethylsilylethynyl (trimethyl)stannane (1)

Dimethylsilylethynyl(trimethyl)stannane (**1**) had already started to react with the triorganoboranes studied here at −70 °C to give alkenes (Scheme 4). In the beginning, the reactions with BEt_3 and BPh_3 gave only the isomers **4a** and **4c** respectively, with diorganoboryl and trimethylstannyl groups in cis positions. Upon warming the reaction solutions from −70 °C to room temperature, **4a** and **4c** rearranged quantitatively into the trans isomers **5a** and **5c** respectively. The rearrangement of **4c** into **5c** took less than 1 h at room temperature, whereas for **4a** the isomerization was



Scheme 4.



Scheme 3.

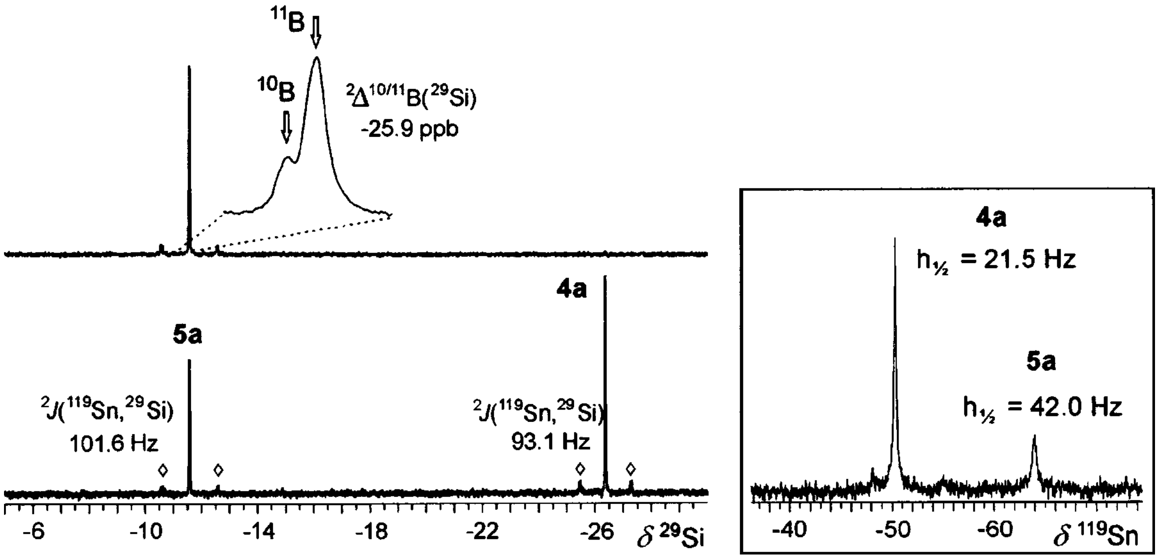


Figure 1. 99.4 MHz ^{29}Si{^{1}H} NMR spectrum (INEPT; acquisition time 5 s, repetition time 4 s) of the reaction solution containing first a mixture of the alkenes **4a** and **5a**, which after 24 h at room temperature contains only **5a** (upper trace). $^{117/119}$Sn satellites are marked. The expansion shows the isotope-induced chemical shift $^{2}\Delta^{10/11}$B(^{29}Si), typical of the electron-deficient Si–H–B bridge.[11–14] The 186.5 MHz ^{119}Sn{^{1}H} NMR spectrum is shown in the box. The line widths of the ^{119}Sn NMR signals are markedly different because of differential broadening owing to partially relaxed ^{119}Sn–^{11}B spin–spin coupling with $|^{3}J(^{119}\text{Sn},^{11}\text{B})_{\text{trans}}| > |^{3}J(^{119}\text{Sn},^{11}\text{B})_{\text{cis}}|$.[6]

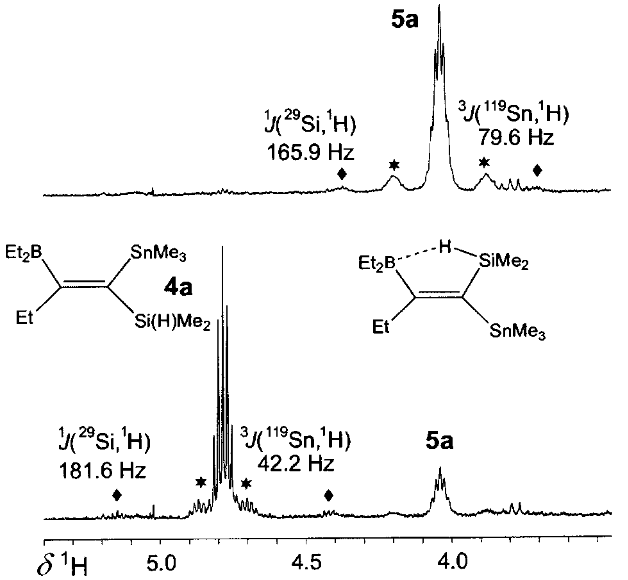


Figure 2. 500 MHz ^{1}H NMR spectra of the range for the Si–H functions of the mixture containing first **4a** and **5a** (lower trace), and after 24 h at room temperature only **5a** (upper trace). The electron-deficient Si–H–B bridge in **5a** is indicated by the shift of the ^{1}H(SiH) resonance to lower frequency, the smaller magnitude of ^{1}J(^{29}Si,^{1}H), the slight broadening of the line width, and, in this particular case, by the marked increase in the magnitude of ^{3}J(^{119}Sn,C,Si,^{1}H).

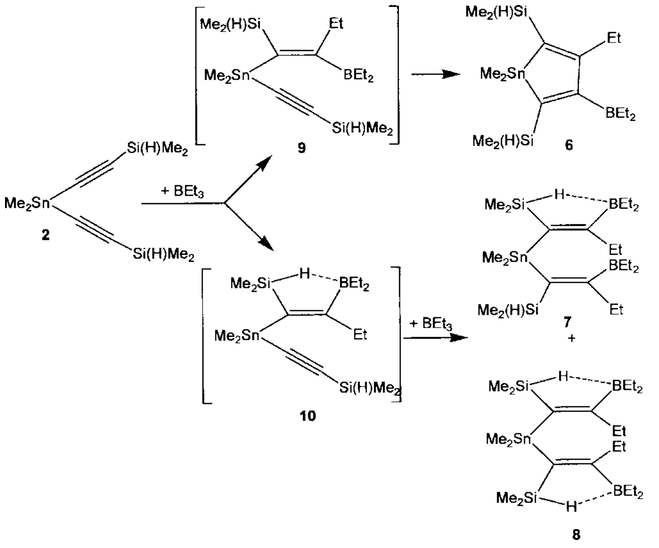
complete after 24 h (Figs 1 and 2). The isomerization of **4a,c** was not affected by light, but it was accelerated by gentle warming of the reaction solution above room temperature. This indicates that there is no direct way from **4** to **5**. Instead, 1,1-deorganoboration leads back to **1**, and eventually 1,1-organoboration takes place towards a thermodynamically more favoured configuration at the C=C bond. It has been shown previously that in alkenes bearing boryl and silyl groups with an Si–H function in cis positions, as in **5**, the formation of an electron-deficient Si–H–B bridge is possible.[11–14] NMR spectroscopic evidence (*vide infra* and Figs 1 and 2) clearly shows that such interactions are present in the alkenes **5a–c**.

In contrast with the behaviour of BEt$_3$ and BPh$_3$, the reaction of BAll$_3$ with **1** gave selectively the isomer **5b** even at low temperature, and the initial formation of **4b** was not observed. Since the basic mechanism of 1,1-allylboration is most likely the same as for other triorganoboranes, this indicates that isomerization occurs even under very mild conditions. Therefore, it is conceivable that 1,1-deallylboration involves the interaction of the boron atom with the C=C bond of the transferred allyl group. Such an interaction is not available for ethyl or phenyl groups. There was also no indication of 1,2-allylboration,[15,16] which in principle can compete with 1,1-allylboration.[17]

1,1-Ethylboration of bis(dimethylsilylethynyl) dimethylstannane (2)

The 1,1-ethylboration of bis(dimethylsilylethynyl)dimethylstannane (**2**) gave a mixture of three compounds, containing the stannacyclopentadiene **6** as the major component, along with the bis(alkenyl)tin compounds **7**, in a small amount, and **8** (Scheme 5 and Fig. 3).

The reaction starts at one of the Sn–C≡bonds, which are the most reactive sites in **2**. This leads to the intermediates **9** and **10**, which were not detected. In the case of **9**, the stereochemistry is favourable for the facile and irreversible intramolecular 1,1-vinylboration to the stannacyclopentadiene **6**. In contrast, in the case of **10** the second Sn–C≡bond is available for intermolecular 1,1-ethylboration, which affords the bis(alkenyl)tin compounds **7** and **8**. Although for both **7** and **8** it is conceivable that a series of 1,1-deethylboration and 1,1-ethylboration reactions may eventually give rise to the stereochemistry shown for the intermediate **9**, this route is rather long, and consecutive 1,1-deethylboration and 1,1-ethylboration can also transform the bis(alkenyl)tin compound **7** into **8** and vice versa. The stabilizing effect of Si–H–B bridges, which are clearly evident for **7** and **8** (*vide infra* and Fig. 3), has to be considered as another argument that the final rearrangement of **7** and in particular of **8** into **6** is hampered.



Scheme 5.

1,1-Ethylboration of ethynyl(trimethylstannylethynyl)(methyl)silane (3)

There is one reactive Sn–C≡bond in ethynyl(trimethylstannylethynyl)(methyl)silane (**3**), where 1,1-ethylboration is most likely to start (Scheme 6). It was found that this leads to the alkenylsilane **11**, with a stereochemistry analogous to that of **4**. Compound **11** could be identified unambiguously as the first product to be formed after mixing the reagents at low temperature (Fig. 4). The intermediate **12** (not detected) may be formed by slow isomerization at room temperature via 1,1-deethylboration and 1,1-ethylboration. The stereochemistry of **12** (compare with that of **9**) would be suitable for fast

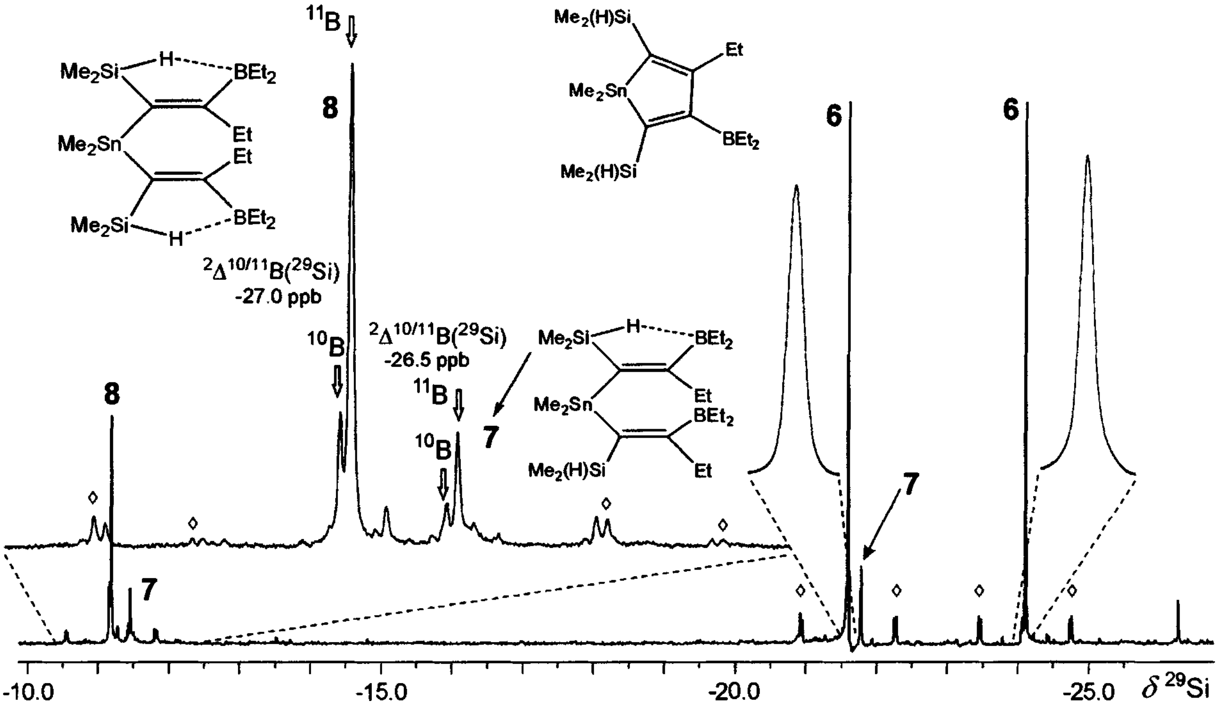
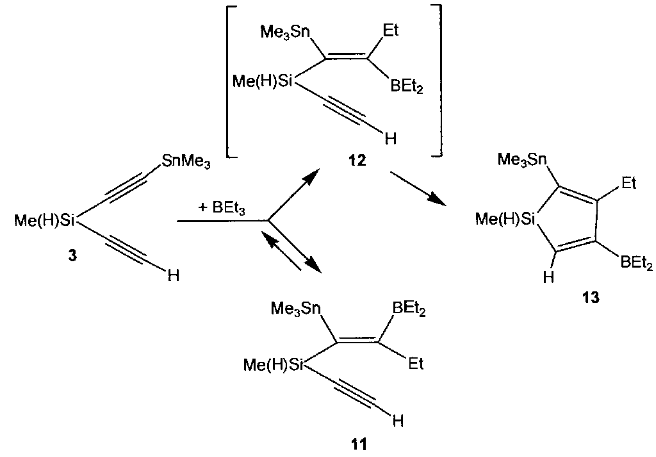


Figure 3. 99.4 MHz ^{29}Si{^{1}H} NMR spectrum (INEPT; acquisition time 5 s, repetition time 4 s) of the reaction mixture containing the products **6, 7** and **8** of the 1,1-ethylboration of **2**. The species with Si–H–B bridges are readily identified by the isotope-induced chemical shifts $^{2}\Delta^{10/11}$B(^{29}Si) (see also Fig. 1). Note the typical large shift difference for the ^{29}Si nuclei involved or not involved in Si–H–B bridges, as in **7**. Apparently, potential Si–H–B bridging plays a minor role in the stannacyclopentadiene derivative **6**. $^{117/119}$Sn satellites are marked with open rhombs.

intramolecular 1,1-vinylboration, leading selectively to the silacyclopentadiene **13** as the final product of this reaction. Stepwise 1,1-organoboration aiming for the synthesis of siloles has already been successful for alkynes of the type $Me_2Si(C{\equiv}C{-}SnMe_3)C{\equiv}C{-}R$ (R = alkyl, aryl, $SiMe_3$).[18] However, in the case of the reaction of **3** with BEt_3, an intermediate (**11**) could be clearly identified for the first time prior to the formation of the silacyclopentadiene **13**. This silole **13** is the first example bearing six different substituents.



Scheme 6.

NMR spectroscopic results

Table 1 lists the relevant NMR data for the alkenes, and other NMR data are given in the Experimental section. Representative ^{29}Si, ^{119}Sn and ^{1}H NMR spectra are shown in Figs 1 to 4. The ^{11}B NMR spectra show broad signals ($h_{1/2} > 500$ Hz) in the region typical for triorganoboranes[19] without significant BC(pp)π interactions.

The Si–H–B bridge in **5a** is weak, since the ^{11}B chemical shift is almost the same as for **4a**. In the case of **5c**, the shift to low frequencies, when compared with **4c**, is larger, possibly because of the BPh_2 group in **5c** being more Lewis acidic than the BEt_2 group in **5a**. The ^{11}B resonance of **5b** is also shifted to lower frequencies when compared with derivatives without Si–H–B bridges.[17] As can be seen by inspection of Figs 1 and 3, the ^{29}Si NMR signals are most useful for detecting the Si–H–B bridges, since the relevant signals show the isotope-induced chemical shifts $^{2}\Delta^{10/11}B(^{29}Si)$, a property that appears to be unique for this particular structural feature.[11–14] ^{1}H NMR spectra in the Si–H region are also instructive if a direct comparison is possible with species for which the Si–H–B bridge is absent, as shown in Fig. 2. The magnitude of $^{3}J(^{119}Sn,C,Si,^{1}H)$ in the isomer **5a** with the Si–H–B bridge is much larger than that for **4a**. This difference can be explained

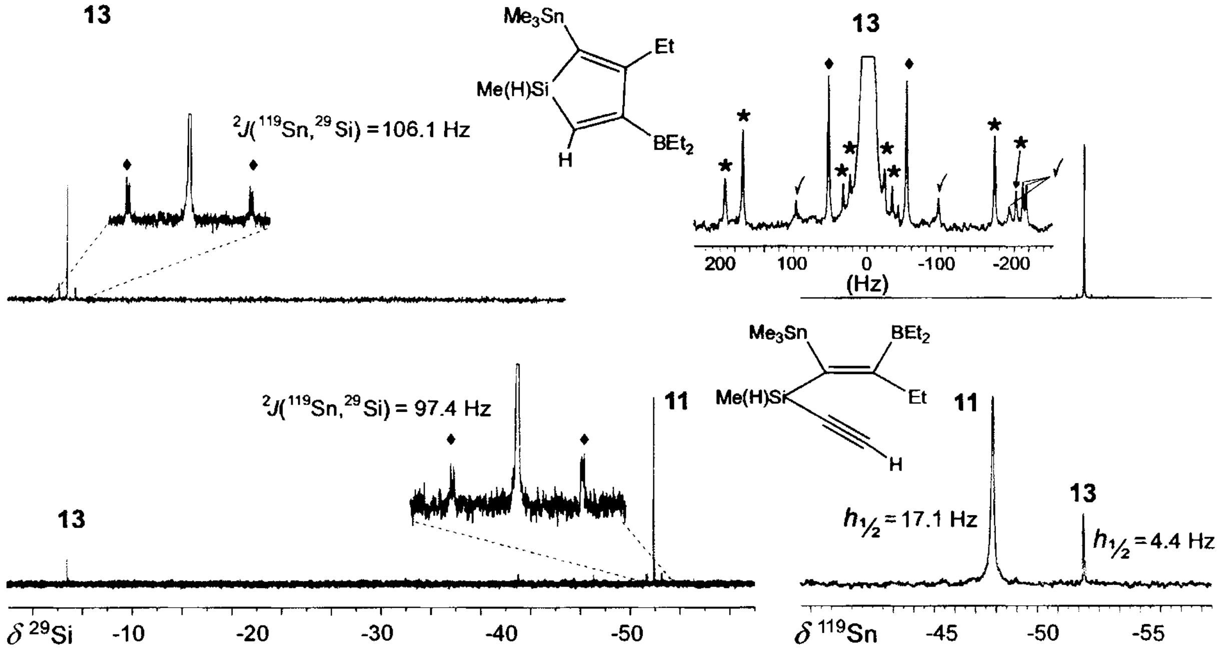


Figure 4. 99.4 MHz ^{29}Si{^{1}H} NMR (INEPT; acquisition time 5 s, repetition time 4 s) and 186.5 MHz ^{119}Sn{^{1}H} NMR spectra, monitoring the 1,1-ethylboration of **3**. The first product **11** is readily identified by its typical ^{29}Si resonance at low frequencies and its fairly broad ^{119}Sn NMR signal (unresolved ^{119}Sn–^{11}B coupling across three bonds; see also Fig. 1). Complete rearrangement (upper traces) to the silacyclopentadiene derivative **13** is indicated by the ^{29}Si resonance at high frequency and the sharp ^{119}Sn NMR signal (^{11}B nucleus is now separated by four bonds). $^{117/119}$Sn satellites are marked, and the ^{119}Sn NMR signal of **13** is accompanied by ^{29}Si (rhombs) and ^{13}C satellites asterisks), in agreement with data from ^{29}Si and ^{13}C NMR spectra. Weak intensities in the ^{119}Sn NMR spectrum due to impurities are also marked.

Table 1. ^{1}H, ^{29}Si, ^{13}C, ^{11}B and ^{119}Sn NMR data[a] of the alkenes **4** and **5**

	$\delta^{119}Sn$	$\delta^{29}Si$ $\{^{2}J(^{119}Sn,^{29}Si)\}$ $\langle^{2}\Delta^{10/11}B(^{29}Si)\rangle$	$\delta^{11}B$	$\delta^{1}H_{(SiH)}$ $[^{1}J(^{29}Si,^{1}H)]$ $\{^{3}J(^{119}Sn,^{1}H)\}$	$\delta^{13}C_{(Si-C=)}$ $\{^{1}J(^{119}Sn,^{13}C)\}$ $[^{1}J(^{29}Si,^{13}C)]$	$\delta^{13}C_{(B-C=)}$ $\{^{2}J(^{119}Sn,^{13}C)\}$
4a[b]	−50.3	−26.4 {93.1}	82.6	4.78 [181.6] {42.2}	135.8 {307.6} [58.8]	187.1 br
4c[c]	−47.0	−21.4 {83.7}	71.0	4.73 [188.0] {30.7}	153.4 {323.3} [52.6]	182.3 br {29.3}
5a[d]	−64.0	−11.6 {101.1} ⟨−25.9⟩	80.6	4.04 [165.9] {79.6}	135.7 {324.0} [58.6]	188.4 br
5b[e]	−61.7	−6.1 {99.4} ⟨−63.1⟩	71.4	3.77 [158.6] {73.8}	138.9 {323.2} [56.6]	183.2 br
5c[f]	−53.4	−13.2 {88.6} ⟨−19.6⟩	68.1	4.60 [177.0] {63.8}	149.6 {303.0} [55.7]	183.9 br {37.4}

[a] In C_6D_6 at room temperature; isotope-induced chemical shifts $\langle^{2}\Delta^{10/11}B(^{29}Si)\rangle$ are given in ppb; br denotes broad ^{13}C NMR signals as a result of partially relaxed one-bond $^{13}C-^{11}B$ scalar spin–spin coupling.

[b] Other ^{13}C NMR data: $\delta = -6.0$ {310.7} ($SnMe_3$), −0.5 {9.8} [49.7] ($SiMe_2$), 22.2 br, 9.8 (BEt_2), 32.0 {126.3} [12.3], 15.0 {9.8} (=C–Et).

[c] Other ^{13}C NMR data: $\delta = -6.1$ {319.5} ($SnMe_3$), −1.1 {10.0} [50.3] ($SiMe_2$), 126.6, 128.1, 128.2, 146.8 {119.2} [8.6] (=C–Ph), 128.0, 132.2, 139.3, 140.3 br (BPh_2).

[d] Other ^{13}C NMR data: $\delta = -5.9$ {311.1} ($SnMe_3$), −1.1 {1.2} [50.6] ($SiMe_2$), 21.7 br, 10.4 (BEt_2), 35.7 {101.3} [14.5], 14.6 {8.5} (=C–Et).

[e] Other ^{13}C NMR data: $\delta = -6.1$ {318.1} ($SnMe_3$), −0.9 [50.5] ($SiMe_2$), 35.9 br, 114.1, 137.9 ($BAll_2$), 47.2 {92.3}, [14.5], 117.2, 136.6 (=C–All).

[f] Other ^{13}C NMR data: $\delta = -5.3$ {320.9} ($SnMe_3$), −1.4 {2.0} [50.6] ($SiMe_2$), 127.7, 128.5, 129.2, 147.6 {78.3} (=C–Ph), 128.6, 132.1, 138.6, 141.8 br (BPh_2).

by considering the dihedral dependence of vicinal couplings. The Si–H–B bridge in **5a** holds the Si–H bond in trans position relative to the =C–Sn bond; in **4a**, however, essentially free rotation about the =C–Si bond can be assumed. Therefore, the value of $^{3}J(^{119}Sn,C,Si,^{1}H)$ for **4a** represents the average of all orientations. Reliable information from IR spectra on Si–H–B bridges can be gained only in those cases, where isomers such as **4** and **5** can be studied independently. Thus, the difference in the ν(Si–H) data for **4a** (2102 cm^{-1}) and **5a** (2072 cm^{-1}) is rather small and the bands are fairly broad. Therefore, the most reliable source for detecting Si–H–B bridges is ^{29}Si NMR with the strong effect of the bridge on ^{29}Si chemical shifts (^{29}Si nuclear deshielding), the decrease in the magnitude of $^{1}J(^{29}Si,^{1}H)$, and the pronounced isotope-induced chemical shifts $^{2}\Delta^{10/11}B(^{29}Si)$. The absence of such effects in the case of the stannacyclopentadiene **13**, where the Si–H–B bridge cannot be present, points towards a strong dependence of the Si–H–B interactions on steric conditions.

^{13}C NMR spectra are particularly instructive in the range for olefinic carbon atoms. The broad ^{13}C NMR signals, typical of carbon atoms bonded to boron,[20] and the observation of ^{29}Si and $^{117/119}Sn$ satellites help with the structural assignments. This is expectedly straightforward in the case of the alkenes **4, 5** and **11**, and very useful in the case of the silacyclopentadiene **6** and the stannacyclopentadiene **13**. The substituent pattern of **13**, clearly evident from the ^{13}C NMR signals in the olefinic region, proves that the 1,1-ethylboration starts at the Sn–C≡bond of **3**, fully in agreement with previous assumptions[18] and with the proposed structure of the intermediate **11**.

CONCLUSIONS

Novel alkenes bearing three different organometallic substituents are available by 1,1-organoboration of dimethylsilylethynyl(trimethyl)stannane, $Me_3Sn-C\equiv C-Si(H)Me_2$ (**1**). For BEt_3 and BPh_3, it could be established that the 1,1-organoboration gives the products **4** with boryl and stannyl groups in cis positions in the beginning. Isomerization of **4** takes place via 1,1-deorganoboration and 1,1-organoboration to give **5** as the final products, where boryl and silyl groups are in cis positions and an electron-deficient Si–H–B bridge is present. This is further supported by the structure of the products from the 1,1-ethylboration of bis(dimethylsilylethynyl)dimethylstannane, $Me_2Sn[C\equiv C-Si(H)Me_2]_2$ (**2**), and ethynyl(trimethylstannylethynyl)methylsilane, $Me(H)Si(C\equiv C-SnMe_3)C\equiv C-H$ (**3**). In the case of the latter, a new silacyclopentadiene **13** was formed selectively, bearing four different substituents in 2–5-postions and two different substituents at the silicon atom.

EXPERIMENTAL

General and starting materials

All compounds were handled under dry argon, and air and moisture excluded, using carefully dried solvents and oven-dried glassware throughout. Starting materials such as chlorosilanes, trimethyltin chloride, dimethyltin dichloride, BuLi (1.6 M in hexane) were commercially available and used without further purifications. Bis(trimethylstannyl)ethyne, $Me_3Sn-C\equiv C-SnMe_3$, was prepared as described.[7,21,22] Ethnyl(dimethyl)silane, $Me_2(H)Si-C\equiv C-H$, and diethynyl(methyl)silane, $Me(H)Si(C\equiv C-H)_2$, were prepared by the Grignard route as described for $Me_3Si-C\equiv C-H$,[22] and the solutions of the alkynes in tetrahydrofuran (THF) were used for further reactions. NMR measurements at 23 °C in 5 mm (o.d.) tubes in C_6D_6 (concentration 5–10%): Bruker ARX 250, DRX 500 and Varian Inova 400 (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{119}Sn NMR, refocused INEPT,[23,24] based on $^{2}J(^{29}Si,^{1}H_{Me}) \approx 7$ Hz or $^{1}J(^{29}Si,^{1}H) \approx 180$ Hz and $^{2}J(^{119}Sn,^{1}H_{Me}) \approx 52$ Hz respectively). Chemical shifts are given relative to Me_4Si ($\delta^{1}H$ (C_6D_5H) =

7.15 (±0.01) δ^{13}C (C_6D_6) = 128.0 ± 0.05; δ^{29}Si = 0 ± 0.01 for $\Xi(^{29}$Si) = 19.867184 MHz), BF_3–OEt_2 (δ^{11}B = 0 ± 0.3 for $\Xi(^{11}$B) = 32.083971 MHz) and Me_4Sn (δ^{119}Sn = 0 ± 0.05 for $\Xi(^{119}$Sn) = 37.290665 MHz). Coupling constants are given in hertz with a precision of at least ±0.2 Hz or higher (e.g. in the ^{29}Si NMR spectra for determination of isotope-induced chemical shifts). IR spectra were measured using a Perkin Elmer Spectrum 2000 FTIR instrument.

Dimethylsilylethynyl(trimethyl)stannane (1)

A solution of bis(trimethylstannyl)ethyne (1.74 g, 4.95 mmol) in pentane (5 ml) was cooled to 0 °C, and an equimolar amount of BuLi (1.6 M in hexane) was added. The mixture was kept stirring for 30 min, cooled again to 0 °C before an excess of $Me_2Si(H)Cl$ was added. After 1 h at room temperature, the insoluble materials were filtered off, the solvents were removed *in vacuo*, and the residue was distilled at reduced pressure to give the alkyne **1** as a colourless liquid (1.08 g (88%), b.p. 50–53 °C/18 Torr). ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.22 {61.3} (s, 9H, $SnMe_3$), 0.27 (d, 6H, $SiMe_2$, $^{3}J(^{1}$H,^{1}H) = 3.8 Hz), 4.43 (sp, 1H, SiH, $^{3}J(^{1}$H,^{1}H) = 3.8 Hz, $^{1}J(^{29}$Si,^{1}H) = 199.8 Hz). ^{13}C NMR: δ {$J(^{119}$Sn,^{13}C)} [$J(^{29}$Si,^{13}C)] = −7.6 {402.6} ($SnMe_3$), −2.1 {7.5} [55.7] ($SiMe_2$), 114.6 {62.9} [79.8] (Si–C≡), 116.0 {390.2} [12.0] (Sn–C≡). ^{29}Si NMR: δ {$J(^{119}$Sn,^{29}Si)} = −39.1 {11.0}. ^{119}Sn NMR: δ = −71.2. IR (toluene, cm^{-1}): ν(Si–H) = 2158, ν(C≡C) = 2085–2087.

Bis(dimethylsilylethynyl)dimethylstannane (2)

To the solution of $Me_2HSiC{\equiv}CMgBr$ (6.12 mmol) in THF (freshly prepared from $Me_2(H)SiC{\equiv}CH$ and EtMgBr at 0 °C) a solution of Me_2SnCl_2 (3.06 mmol) in THF (10 ml) was added at 0 °C. The reaction mixture was kept stirring for 12 h, and then THF was removed *in vacuo*. The residue, a colourless, oily solid, was taken up in pentane (40 ml), insoluble materials were filtered off, and pentane was removed *in vacuo*. The resulting white solid consisted of ca 95% of the stannane **2** (according to ^{1}H NMR spectra) and was used without further purification. ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.11(d, 12H, $SiMe_2$, $^{3}J(^{1}$H, ^{1}H) = 3.8 Hz), 0.17 {64.3} (s, 6H, $SnMe_2$), 4.33 (sp, 1H, SiH, $^{3}J(^{1}$H,^{1}H) = 3.8 Hz, $^{1}J(^{29}$Si, ^{1}H) = 201.1 Hz). ^{13}C NMR: δ {$J(^{119}$Sn,^{13}C)} [$J(^{29}$Si,^{13}C)] = −6.3 {479.7} ($SnMe_2$), −2.5 {9.1} [50.5] ($SiMe_2$), 112.2 {538.0} [13.2] (Sn–C≡), 116.1 {88.1} [79.8] (Si–C≡). ^{29}Si NMR: δ {$J(^{119}$Sn,^{29}Si)} = −39.8 {11.0}. ^{119}Sn NMR: δ = −156.4. IR (toluene, cm^{-1}): ν(Si–H) = 2160; ν(C≡C), not assigned.

Ethynyl(trimethylstannylethynyl)methylsilane (3)

The solution of $Me(H)Si(C{\equiv}CH)_2$ (26 mmol) in THF was cooled to 0 °C and EtMgBr (26 mmol) was added. The mixture was stirred for 1 h before a solution of Me_3SnCl (5.22 g, 26 mmol) in THF (10 ml) was added. After stirring for 12 h, the solvent was removed *in vacuo*, pentane (40 ml) was added, insoluble materials were filtered off, and the resulting oil was distilled to give the alkyne **3** as a colourless liquid (64%; b.p. 49–50 °C/0.1 Torr). ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.03 {60.8} (s, 9H, $SnMe_3$), 0.21 (d, 3H, SiMe, $^{3}J(^{1}$H,^{1}H) = 4.0 Hz), 2.07 (d, 1H, ≡C–H, $^{4}J(^{1}$H,^{1}H) = 1.2 Hz), 4.48 (qd, 1H, SiH, $^{3}J(^{1}$H,^{1}H) = 4.0 Hz, $^{4}J(^{1}$H,^{1}H) = 1.2 Hz, $^{1}J(^{29}$Si,^{1}H) = 222.7 Hz). ^{13}C NMR: δ {$J(^{119}$Sn,^{13}C)} [$J(^{29}$Si,^{13}C)] = −7.7 {403.0} ($SnMe_3$), −2.1 {2.2} [61.7] (SiMe); 84.4 {3.1} [96.2] (Si–C≡CH), 96.5 [19.1] (≡C–H), 109.7 {56.7} [92.9] (Si–C≡C–Sn), 119.0 {345.3}, [14.2] (Sn–C≡). ^{29}Si NMR: δ {$J(^{119}$Sn,^{29}Si)} = −64.5 {11.8}. ^{119}Sn NMR: δ = −74.7. IR (cm^{-1}): ν = 2165 (Si–H), 2089 (C≡C), 2042 (C≡ C).

Organoboration of the alkynes 1–3

To a frozen solution of the boranes (2–3 mmol) in C_6D_6, or to a toluene solution of the boranes, an equimolar amount of the respective alkyne **1, 2** or **3** was added at −78 °C. The mixtures were allowed to warm up slowly and the progress of the reactions was monitored by NMR. The pure alkenes **5a–c** as the final products of the 1,1-organoboration of **1**, and the silacyclopentadiene **13** as the final product of the 1,1-ethylboration of **3**, remained as colourless oily liquids after all volatile materials had been removed *in vacuo*. The mixture resulting from 1,1-ethylboration of **2**, containing **6, 7** and **8**, could not be separated further.

4a. ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.28 {50.7} (s, 9H, $SnMe_3$), 0.40 (d, 6H, $SiMe_2$, $^{3}J(^{1}$H,^{1}H) = 3.9 Hz), 2.39 {7.6} 1.03 (q, t, 5H, =C–Et); 1.35, 1.11 (q, t, 10H, BEt_2). IR (cm^{-1}): ν(Si–H) = 2102.

4c. ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.35 {52.1} (s, 9H, $SnMe_3$), 0.37 (d, 6H, $SiMe_2$, $^{3}J(^{1}$H,^{1}H) = 3.9 Hz), 7.4–8.2 (m, 15H, Ph, BPh_2).

5a. ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.29 (d, 6H, $SiMe_2$, $^{3}J(^{1}$H,^{1}H) = 3.5 Hz), 0.38 {51.5} (s, 9H, $SnMe_3$); 2.25 {10.8}, 1.02 (q, t, 5H, =C–Et), 1.36, 1.16 (q, t, 10H, BEt_2). IR (cm^{-1}): ν(Si–H) = 2072.

5b. ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.14 {51.4} (s, 9H, $SnMe_3$), 0.24 (d, 6H, $SiMe_2$, $^{3}J(^{1}$H,^{1}H) = 3.3 Hz), 6.00, 4.9–5.1, 2.18 (ddt, m, d, 2H, 4H, 4H, $BAll_2$), 5.75, 4.9–5.1, 3.01 {11.0} (ddt, m, d, 1H, 2H, 2H, =C–All). IR (cm^{-1}): ν(Si–H) = 2071.

5c. ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.21 {51.1} (s, 9H, $SnMe_3$), 0.25 (d, 6H, $SiMe_2$, $^{3}J(^{1}$H,^{1}H) = 3.5 Hz), 7.0–8.0 (m, 15H, =C–Ph, BPh_2).

6. ^{1}H NMR: δ {$J(^{119}$Sn,^{1}H)} = 0.10 (d, 6H, $SiMe_2$, $^{3}J(^{1}$H,^{1}H) = 3.1 Hz), 0.17 (d, 6H, $SiMe_2$, $^{3}J(^{1}$H,^{1}H) = 3.2 Hz), 0.35 {51.5} (s, 6H, $SnMe_2$), 2.30, 1.02 (q, t, 5H, =C–Et); 1.19, 0.92 (q, t, 10H, BEt_2), 4.14 {70.4} (sp, 1H, SiH, $^{3}J(^{1}$H,^{1}H) = 3.2 Hz, $^{1}J(^{29}$Si,^{1}H) = 177.8 Hz), 4.50 {53.3} (sp, 1H, SiH, $^{3}J(^{1}$H,^{1}H) = 3.1 Hz, $^{1}J(^{29}$Si,^{1}H) = 183.2 Hz). ^{13}C NMR: δ {$J(^{119}$Sn,^{13}C)} [$J(^{29}$Si,^{13}C)] = −6.1 {268.6} ($SnMe_2$), −1.1 [52.5], −0.9 {3.6} [52.5] ($SiMe_2$), 22.5 br, 9.4 (BEt_2), 31.7 {85.4} [6.4], 16.0 {9.9} (=C–Et), 137.8 {274.1} [64.4] (C-5), 141.6 {209.1} [65.0] (C-2), 168.5 {85.4} [12.6] (C-4), 184.5 (br, C-3). ^{29}Si NMR: δ {$J(^{119}$Sn,^{29}Si)} = −24.1 {104.9} (Si-5), −21.6 {107.9} (Si-2). ^{119}Sn NMR: δ = 125.9.

7. The concentration of **7** in the mixture with **6** and **8** was too small for the assignment of relevant ^{1}H and ^{13}C NMR signals; for the ^{29}Si NMR signals, see Fig. 3.

8. ^{1}H NMR: δ $\{J(^{119}\text{Sn},^{1}\text{H})\} = 0.09$ (d, 12H, SiMe$_2$, $^{3}J(^{1}\text{H},^{1}\text{H}) = 3.8$ Hz), 0.26 {52.4} (s, 6H, SnMe$_2$), 0.9–1.4 (m, 26H, BEt$_2$, =C–Et), 2.27 (q, 4H, =C–Et), 3.81 {78.4} (m, 2H, SiH, $^{1}J(^{29}\text{Si},^{1}\text{H}) = 171.4$ Hz). ^{13}C NMR: δ $\{J(^{119}\text{Sn},^{13}\text{C})\}$ $[J(^{29}\text{Si},^{13}\text{C})] = -4.9$ {289.3} (SnMe$_2$), −1.3 [50.2] (SiMe$_2$), 21.5 br, 10.0 (BEt$_2$), 36.4 {107.3} [14.4], 13.7 (=C–Et), 137.9 {297.0} [58.6] (Sn–C=), 187.3 (br, B–C=). ^{29}Si NMR: δ $\{J(^{119}\text{Sn},^{29}\text{Si})\}$ $\langle ^{2}\Delta^{10/11}\text{B}(^{29}\text{Si})\rangle = -11.2$ {102.8} ⟨−28.0 ppb⟩. ^{119}Sn NMR: $\delta = -132.9$.

11. ^{1}H NMR: δ $\{J(^{119}\text{Sn},^{1}\text{H})\} = 0.12$ {51.6} (s, 9H, SnMe$_3$), 0.27 (d, 3H, SiMe, $^{3}J(^{1}\text{H},^{1}\text{H}) = 3.9$ Hz), 1.04, 0.83 (q, t, 10H, BEt$_2$); 2.23, 0.88 (q, t, 5H, =C–Et), 2.07 (s, 1H, ≡C–H), 4.77 {45.0} (q, 1H, SiH, $^{3}J(^{1}\text{H},^{1}\text{H}) = 3.9$ Hz, $^{1}J(^{29}\text{Si},^{1}\text{H}) = 201.1$ Hz). ^{13}C NMR: δ $\{J(^{119}\text{Sn},^{13}\text{C})\}$ $[J(^{29}\text{Si},^{13}\text{C})] = -5.6$ {320.1} (SnMe$_3$), −0.7 {6.9} [54.6] (SiMe), 22.2 br, 9.7 (BEt$_2$), 32.1 {114.5} [14.0], 14.8 {9.3} (=C–Et), 88.6 {11.2} [82.8] (Si–C≡), 96.5 [15.0] (≡C–H), 131.4 {354.9} [62.5] (=C–Sn), 189.4 (br, =C–B). ^{29}Si NMR: δ $\{J(^{119}\text{Sn},^{29}\text{Si})\} = -51.9$ {97.4}. ^{11}B NMR: $\delta = 83.1$. ^{119}Sn NMR: $\delta = -47.4$.

13. ^{1}H NMR: δ $\{J(^{119}\text{Sn},^{1}\text{H})\} = 0.15$ (d, 3H, SiMe, $^{3}J(^{1}\text{H},^{1}\text{H}) = 4.3$ Hz), 0.16 {54.0} (s, 9H, SnMe$_3$), 2.30 {4.0}, 0.81 (q, t, 5H, =C–Et), 1.25, 0.89 (q, t, 10H, BEt$_2$), 4.62 (q, 1H, SiH, $^{3}J(^{1}\text{H},^{1}\text{H}) = 4.3$ Hz, $^{1}J(^{29}\text{Si},^{1}\text{H}) = 187.4$ Hz), 5.90 {5.7} (s, 1H, =C–H, $^{2}J(^{29}\text{Si},^{1}\text{H}) = 15.3$ Hz). ^{13}C NMR: δ $\{J(^{119}\text{Sn},^{13}\text{C})\}$ $[J(^{29}\text{Si},^{13}\text{C})] = -7.5$ {342.1} (SnMe$_3$), −6.1 {1.7} [43.9] (SiMe), 21.6 br, 9.7 (BEt$_2$), 33.5 {46.6} [9.6], 15.3 (=C–Et), 132.9 {22.2} [60.0] (=C–H), 134.3 {396.3} [53.1] (=C–Sn), 173.0 {3.4} [5.4] (=C–Et), 178.0 (br, =C–B). ^{29}Si NMR: δ $\{J(^{119}\text{Sn},^{29}\text{Si})\} = -4.8$ {106.1}. ^{11}B NMR: $\delta = 82.8$. ^{119}Sn NMR: $\delta = -51.8$.

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