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Reactivity of some poly-1-alkynylsilicon and -tin compounds towards triallylborane—routes to novel heterocycles

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Abstract

Triallylborane reacts with most poly-1-alkynylsilanes (**1**–**5**), containing up to four C≡C units, or di(1-alkynyl)tin compounds (**6**) to give either siloles (**8**, **11**, **14**, **16**), as the result of an intermolecular 1,1-allylboration followed by an intramolecular 1,1-vinylboration, or the novel 2-alkylidene-1,3-silaborolene (**9**) or 2-alkylidene1,3-stannaborolene derivatives (**17**), as the result of intermolecular 1,1-allylboration followed by an intramolecular 1,2-allylboration. In the case of the borolene derivatives, a second intramolecular 1,2-allylboration takes place to give 1,7-borasila- or 1,7-borastannabicyclo[4.3.0]nona-5,8-diene derivatives (**10**, **12**, **13**, **15**, **18**). If the starting materials are di(1-alkynyl)methylsilicon hydrides (**2**), the latter reaction affords selectively only one diastereomer (**10(H)**). All products were characterised by extensive multinuclear magnetic resonance spectra (^{1}H-, ^{11}B-, ^{13}C-, ^{29}Si-, and ^{119}Sn-NMR). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organoboration; Alkynes; Siloles; Heterocycles; NMR; Multinuclear

1. Introduction

1,1-Organoboration of 1-alkynylmetal compounds [1,2] provides useful routes to numerous heterocycles. Among these, in particular the metalloles **C** are important examples [3], and the mechanism of their formation has been firmly established by isolating the intermediates of type **B** (formed in the reaction of di(1-alkynyl)metal compounds with triorganoboranes; Scheme 1), and characterising them by NMR in solution and in the solid state as well as by crystal structure analysis [2,4–7]. The zwitterionic intermediates of type **B** are precursors of the metalloles **C**, if an intramolecular vinylboration takes place. Although the product distribution depends on the groups R^1 and R, there are many combinations of R^1 and R for which the metalloles are formed selectively [1,2,4–8].

Triallylborane, All_3B, possesses unusual properties when compared with other triorganoboranes [9]. We have already shown that All_3B is extremely reactive, much more than Et_3B, towards 1-alkynylsilanes [10,11], -germanes and -stannanes [12]. For such alkynes it has become evident that 1,2-allylboration can compete with 1,1-allylboration, although the latter reaction appears to be dominant, at least in polar solvents [11,12]. In any case, these recent results prompted us to explore the reactivity of various poly-1-alkynylsilanes and -stannanes **1**–**6** (Scheme 2) towards triallylborane.

2. Results and discussion

2.1. Reactions of the bis(1-alkynyl)silanes *1a–d* and *2b–d* with triallylborane

The reaction of **1a**–**d** or **2b**–**d** with triethylborane requires prolonged heating at 100 °C, and siloles of type **C** have been reported as the final products [13,14].

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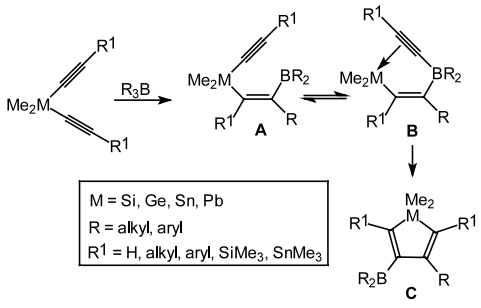
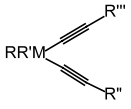
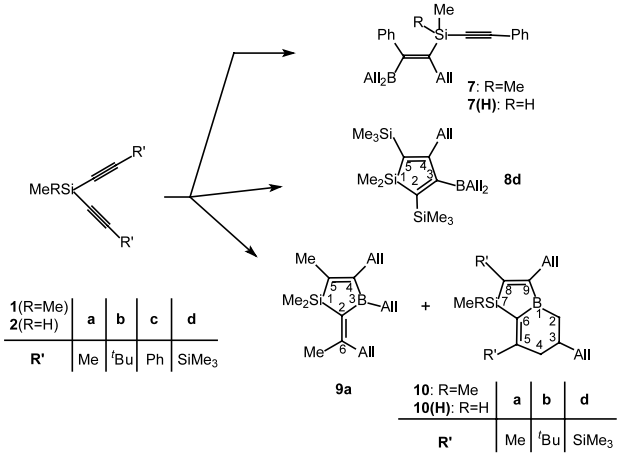


Scheme 1.



No	M	R	R'	R''	R'''
1a	Si	Me	Me	Me	Me
1b	Si	Me	Me	^{t}Bu	^{t}Bu
1c	Si	Me	Me	Ph	Ph
1d	Si	Me	Me	$SiMe_3$	$SiMe_3$
2b	Si	Me	H	^{t}Bu	^{t}Bu
2c	Si	Me	H	Ph	Ph
2d	Si	Me	H	$SiMe_3$	$SiMe_3$
3	Si	Me	Me	$SiMe_3$	$SiMe_2$-≡-$SiMe_3$
4	Si	Me_3Si-≡-	Me_3Si-≡-	$SiMe_3$	$SnMe_3$
5	Si	Me	Me	$SiMe_3$	$SiMe_3$
6a	Sn	Me	Me	Me	Me
6d	Sn	Me	Me	$SiMe_3$	$SiMe_3$

Scheme 2.



1(R=Me) 2(R=H)	a	b	c	d
R'	Me	^{t}Bu	Ph	$SiMe_3$

	a	b	d
R'	Me	^{t}Bu	$SiMe_3$

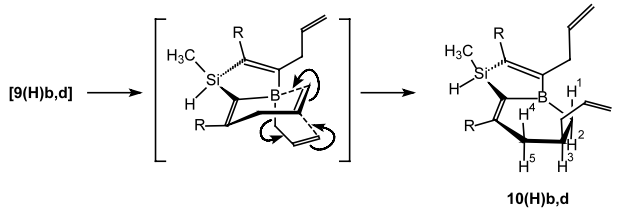
Scheme 3.

Scheme 3 summarises the results of the reactions of **1a**–**d** and **2b**–**d** with triallylborane All_3B. With **1a**, a new type of heterocycle **9a** was formed selectively when the reaction mixture was kept at room temperature for several days; the formation of a silole was not observed at all. After heating at 65 °C in $CDCl_3$ for 60 h, **9a** rearranged into **10a** by intramolecular 1,2-allylboration of one of the terminal C=C bonds. In order to induce any reaction of **1b** with All_3B prolonged heating at 65 °C was required, and therefore, **9b** was not observed; instead the bicyclic compound **10b** was formed selectively. In contrast, the reaction of **1c** with All_3B did not lead to any cyclic compound; the non-cyclic compound **7** was obtained selectively. The reaction of **1d** with All_3B afforded a 4:1 mixture of **8d** and **10d**. The formation of the silole **8d** can be understood as the result of an 1,1-allylboration followed by an intramolecular 1,1-vinylboration, as shown in Scheme 1. It is conceivable that the new heterocycles **9** are formed by a stereoselective intermolecular 1,1-allylboration in the initial step, as in **A** (Scheme 1), followed by an intramolecular 1,2-allylboration (instead of the intramolecular 1,1-vinylboration, **B** and **C** in Scheme 1). The intermediate **B** (Scheme 1) might be the same, both for 1,2-allylboration and 1,1-vinylboration (although, a six-membered transition state is proposed in general for the former type of reaction [9]). The conversion into the bicyclic compounds **10** is the result of another intramolecular 1,2-allylboration which requires more severe reaction conditions, a common reaction in the chemistry of allylboranes [9].

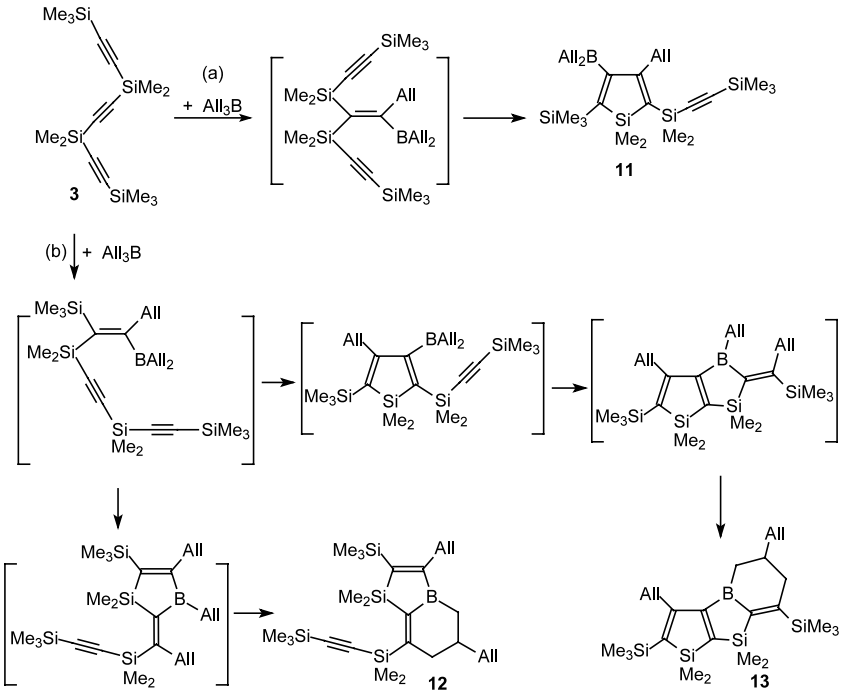
In the case of the silanes **2b**–**d**, the reactions with triallylborane proceeds mainly in the same way as for **1** (Scheme 3). Thus, the only product from the reaction of **2c** with All_3B is the non-cyclic **7(H)**, whereas the new heterocycles **10(H)b** and **10(H)d** were obtained selectively by starting from **2b** to **2d**. Interestingly, only one of the possible diastereomers of both **10(H)b** and **10(H)d** is formed, in which, according to ^1H–^1H NOESY spectra, the C(3)-allyl and the SiMe groups are in *cis*-positions. The proposed route to **10(H)** is shown in Scheme 4. Presumably, this can be traced to steric interactions in the transition state.

2.2. Reactions of the triyne 3 and of tetrakis(trimethylsilylethynyl)silane 4 with triallylborane

Compound **3** contains three reactive C≡C bonds. Depending on the attack of All_3B either at a Me_3Si–C≡ or a Me_2Si–C≡ bond, different products can be expected [15,16]. The NMR analysis of the reaction mixture revealed the presence of three products (1:3:3 ratio), the silole **11** and the heterocycles **12** and **13**



Scheme 4.



Scheme 5.

(Scheme 5). This mixture is best analysed by ^{29}Si-NMR (Fig. 1). If one of the Me_2Si–C≡ bonds is attacked (Scheme 5a; intermediate not isolated or detected), the silole **11** can be formed, and there is no easy way for **11** to undergo further intramolecular reactions. However, if the reaction starts at one of the Me_3Si–C≡ bonds (Scheme 5b) intermediates as shown (not isolated or detected) can be formed, and further intramolecular reactions can lead either to **12** or to **13**.

The reaction of **4** with triallylborane afforded a mixture consisting mainly of two compounds (Scheme 6), the silole **14**, corresponding to type **C**, and the bicyclic compound **15**, in a molar ratio of 1:5. An excess of All_3B did not induce further reactions with the remaining C≡C bonds even upon prolonged heating. Surprisingly, considering the high reactivity of triallylborane, this is in contrast with the reaction of Et_3B with **4** [17].

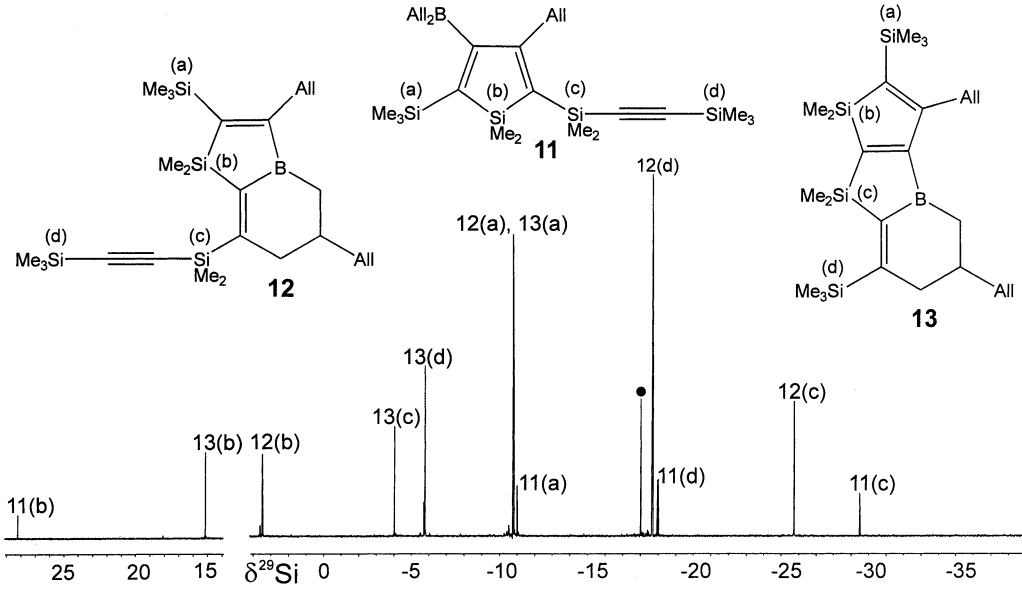
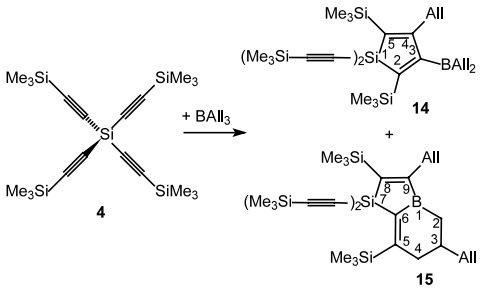


Fig. 1. ^{29}Si{^{1}H}-NMR spectrum (99.4 MHz) (refocused INEPT [23] with ^{1}H decoupling) of the reaction mixture containing **11**, **12** and **13** in $CDCl_3$ solution. The signals of the starting triyne **3** are marked by full circles. The assignment is based on characteristic chemical shifts δ^{29}Si and on ^{29}Si satellites (not shown) due to $^nJ(^{29}Si, ^{29}Si)$.



Scheme 6.

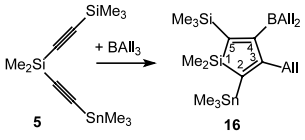
2.3. Reaction of the bis(1-alkynyl)silane **5** with triallylborane

In the compound **5**, the silicon atom bears two different 1-alkynyl groups: the one with the terminal Me_3Sn group is known to react readily with triorganoboranes [16]. Therefore, the reaction with All_3B followed the mechanism outlined in Scheme 1, starting by 1,1-allylboration of the C≡C–$SnMe_3$ unit. After this first step, fast intramolecular 1,1-vinylboration took place (products from 1,2-allylboration were not observed), and the silole **16** was formed selectively (Scheme 7). The finding that the Me_3Sn group is linked to C-2, the boryl group to C-4, and the Me_3Si group to C-5 strongly supports the proposed mechanism.

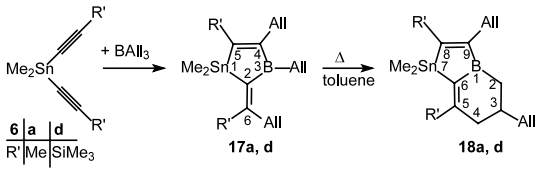
2.4. Reaction of the bis(1-alkynyl)dimethyltin compounds **6a** and **6d** with triallylborane

The 1-alkynyltin compounds reacted with triallylborane already at low temperature (< -20 °C), and the reactions were complete at room temperature. In the case of **6a**, the heterocycle **17a** was formed selectively (Scheme 8). Heating of **17a** in boiling toluene induced further intramolecular 1,2-allylboration to give the bicyclic compound **18a** (see Fig. 3 for the change in the ^{13}C-NMR signals of the ring carbon atoms) which corresponds to the silicon compounds **9a**, **10a**,**b**, **13** and **15**.

The reaction of **6d** with triallylborane gives at first **17d** (see Fig. 2 for the ^{29}Si-NMR spectrum) together with small amounts of unidentified products (apparently as a result of exchange reactions, similar to those observed for the reaction of All_3B with Me_3Sn–C≡C–$SiMe_3$ [12]). Compound **17d** rearranges slowly at room temperature into **18d**. By monitoring the reaction of **6d** with All_3B, using ^{119}Sn-, ^{29}Si- and ^{13}C-NMR, starting from -40 °C in $CDCl_3$ solution, it proved possible to identify an

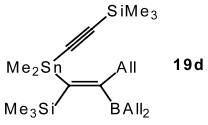


Scheme 7.



Scheme 8.

intermediate **19d**. The structure of **19d** results from 1,1-allylboration, and **19d** has a reasonably long lifetime, because, its stereochemistry is wrong for cyclisation. By warming the reaction solution to room temperature, the signals for **19d** vanished and the signals for **17d** and **18d** became dominant. This finding indicates that indeed 1,1-allylboration (reversible!) is the preferred initial step, followed by intramolecular 1,2-allylboration. The intermediate **A** with M = Sn in Scheme 1 appears to have a favourable disposition for 1,2-allylboration which may take place before the intermediate **B** is really formed.



Formula **19d**

3. NMR spectroscopic results

The ^{11}B-, ^{13}C-, ^{29}Si- and ^{119}Sn-NMR data listed in the Tables 1–3 (^{1}H-NMR data are given in the Section 5) strongly support the proposed structures. In most cases it was possible to determine the coupling constants $^1J(^{29}Si, ^{13}C)$ either from ^{29}Si satellite signals in the ^{13}C-NMR spectra or from ^{13}C satellites in the ^{29}Si-NMR spectra, and the same applies to $^nJ(^{119}Sn, ^{13}C)$ for $n = 1$ (for $n > 1$, the ^{13}C-NMR spectra are more reliable, since the ^{13}C satellites in the ^{119}Sn-NMR spectra close to the central line are not always well resolved). Together with the broadened ^{13}C-NMR signals, characteristic for carbon atoms linked to boron [18], the structural assignments are confirmed. Typical examples are shown in the Fig. 2. The siloles show one broad and three sharp ^{13}C-NMR signals for the ring carbon atoms. Two of the sharp signals are accompanied by ^{29}Si satellites corresponding to one-bond ^{29}Si–^{13}C coupling. In the case of the 2-alkylidene-1,3-silaborole (**9a**) or related bicyclic derivatives **10** and the 2-alkylidene-1,3-stannaborolenes, there are two broad and two sharp signals for the ring carbon atoms. Only one of the sharp signals is accompanied by ^{29}Si or $^{117/119}$Sn satellites corresponding to the relevant one-bond ^{29}Si–^{13}C or $^{117/119}$Sn–^{13}C coupling. ^{29}Si-NMR spectra help to analyse complex or simple mixtures as shown in the Figs. 1 and 4, respectively. In

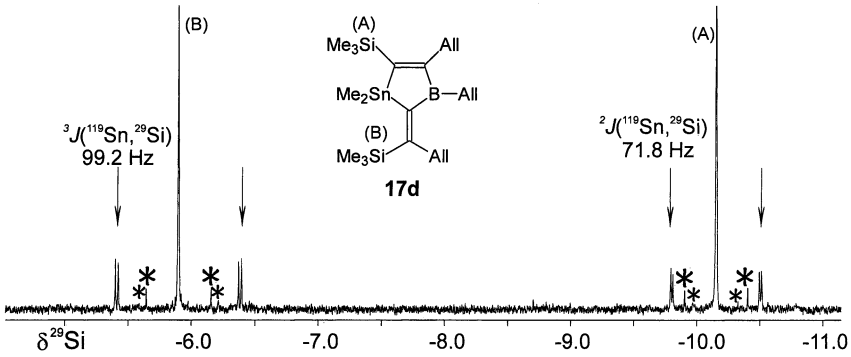


Fig. 2. 99.4 MHz ^{29}Si (refocused INEPT [23] with ^{1}H decoupling) NMR spectrum of **17d** in $CDCl_3$ at 303 K. The assignment of Si(A) and Si(B) is based on the magnitude of the coupling constants $|^{1}J(^{29}Si, ^{13}C=)|$ which is smaller for Si(A) than for Si(B), confirmed by the information from ^{13}C-NMR spectra. The $^{117/119}$Sn satellites are marked by arrows, and the ^{13}C satellites (Me, and C=) by asterisks.

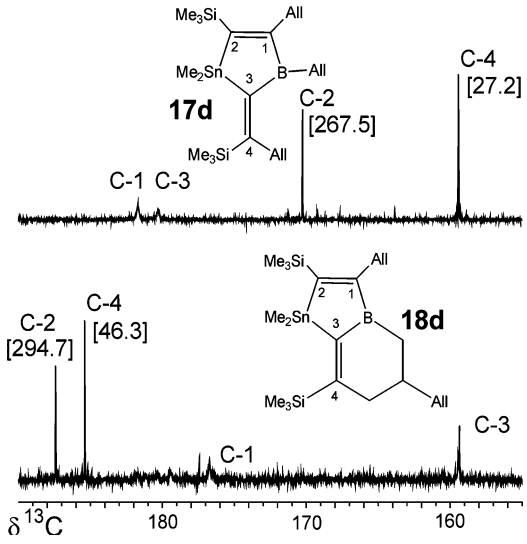


Fig. 3. Changes in $^{13}C\{^{1}H\}$-NMR spectrum (125.8 MHz, $CDCl_3$, low field region) of monocyclic compound **17d** after heating at 60 °C overnight with the formation of bicyclic compound **18d**. The numbering of carbon atoms was changed from nomenclature for simplicity; values $^{1}J(^{119}Sn, ^{13}C)$ are given in brackets.

the case of pure compounds, ^{29}Si-NMR spectra provide convincing evidence, because of their simplicity, if they are recorded with sufficient signal-to-noise ratio in order to detect satellite signals (Fig. 2).

The ^{11}B-NMR spectra show broad signals either in the range typical [19] of triorganoboranes without significant CB(pp)π interactions, as in the case of the 3-boryl substituted siloles ($\delta^{11}B = 82 \pm 1.5$), or shifted to markedly lower frequencies, because, the boron atom is part of a ring system allowing for CB(pp)π interactions, as in the 2-alkylidene-1,3-stannaborolenes ($\delta^{11}B = 63 \pm 1.5$). The ^{29}Si nuclear shielding is typically low for siloles with Me_3Si groups in 2,5-positions [13–16] (see Table 1), whereas the ^{29}Si nuclei in 2-alkylidene-1,3-silaborolenes are better shielded (> 20 ppm), irrespective of alkyl or $SiMe_3$ substituents.

4. Conclusions

There is competition between 1,1- and 1,2-allyboration. In the case of **1c** and **2c**, 1,2-allylboration is preferred already in the initial intermolecular step, and this suggests that the phenyl group at the C≡C bond exerts a specific effect. In all the other cases, it appears that intermolecular 1,1-allylboration dominates, followed by intramolecular 1,1-vinylboration, leading to siloles, or intramolecular 1,2-allylboration, leading to the novel 2-alkylidene-1,3-stannanborolenes. At present, the factors directing the course of these reactions are not clear or predictable, although, the di(1-alkynyl)tin compounds seem to react exclusively by the combination of 1,1- and 1,2-allylboration [20]. In the course of the transformations of the silanes **2**, the silicon atom becomes a chiral centre, and the diastereoselective formation of the bicyclic compounds **10(H)** is certainly promising for future work.

5. Experimental

5.1. General and starting materials

All compounds were handled under dry argon, observing all necessary conditions to exclude air and moisture, and by using carefully dried solvents. Starting materials such as triallylborane [21], di- and polyalkynyl silanes and stannanes [13,22] were prepared according to literature procedures. The synthesis of silicon hydrides **2b–d** was achieved by the reaction of the respective chlorosilanes with lithium alkynides in the usual way [22]. Details will be described elsewhere [14]. NMR measurements: Bruker ARX 250 and DRX 500 [^{1}H, ^{11}B, ^{13}C, ^{119}Sn, ^{29}Si-NMR (refocused INEPT [23] based on $^{2}J(^{29}Si, ^{1}H_{Me}) = 7$ Hz)]. Chemical shifts are given with respect to Me_4Si [$\delta^{1}H$ ($CHCl_3$–$CDCl_3$) = 7.24; $\delta^{13}C$ ($CDCl_3$) = 77.0; $\delta^{29}Si = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz], BF_3-Et_2O [$\delta^{11}B = 0$; $\Xi(^{11}B) = 32.083971$ MHz],

Table 1
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data [a] of the siloles **8d**, **11**, **14** and **16**

	δ^{29}Si	δ^{11}B	δ^{13}C			
			C(2)	C(3)	C(4)	C(5)
8d [b]	27.3	82.9	148.0 (62.4, 43.8)	182.1 br	164.2 (11.4, 8.9)	141.4 (61.5, 48.9)
11 [c]	28.2	83.2	149.4	179.0 br	165.8	135.2
14 [d]	n.o.	81.4	142.1	184.9 br	167.8	134.9
16 [e]	26.0 [f]	83.7	144.7 (55.6)[375.7]	163.4 (11.0, 9.3) [3.5]	181.4 [72.3] br	148.0 (13.7)

[a] In $CDCl_3$ at 30 °C; $^nJ(^{29}Si, ^{13}C)$ ($\pm$0.1 Hz) are given in parentheses; $^nJ(^{119}Sn, ^{13}C)$ [$\pm$0.2 Hz] in brackets; br denotes broad signals due to partially relaxed $^{13}C-^{10/11}B$ coupling; n.o., not observed.
[b] $\delta^{13}C = 136.4, 113.9, 40.5$ (All); 136.4, 117.6, 37.2 (br) (All_2B); 1.4 (50.7), 1.1 (51.1) (Me_3Si); −2.2 (47.2) (Me_2Si). $\delta^{29}Si = -10.6$ (10.4), −11.2 (10.3) (Me_3Si).
[c] $\delta^{13}C = 137.1, 114.0, 40.5$ (All); 136.4, 114.9, 37.3 (br) (All_2B); 115.3, 114.3 ($Me_3Si-C\equiv C$); 0.29, 0.31 (Me_2Si); 0.21, 0.19 (Me_3Si). $\delta^{29}Si = -11.1$ (10.0) (Me_3Si), −19.0 ($Me_3Si-C\equiv$), −30.5 (11.2) ($Me_2Si-C\equiv$).
[d] $\delta^{13}C = 136.1, 114.2, 41.2$ (All); 135.6, 116.9, 29.7 (br) (All_2B); 118.2 ($Si-C\equiv$); 106.8 ($\equiv C-SiMe_3$); 1.4, 1.0, −0.6 (Me_3Si). $\delta^{29}Si = -8.9$ (9.5), −9.1 (9.4) (Me_3Si); −18.0 (1.8) ($\equiv C-SiMe_3$). ^{29}Si-NMR signal was not observed by standard INEPT pulse sequence.
[e] $\delta^{13}C = 136.4, 114.0, 42.5$ [44.1] (All); 136.35, 117.2, 37.1 (br) (All_2B); 1.4 (51.2) (Me_3Si); −2.8 (47.2) (Me_2Si); −8.2 [342.2] (Me_3Sn). $\delta^{29}Si = -11.0$ (10.1) [2.1] (Me_3Si). $\delta^{119}Sn = -48.1$.
[f] $^2J(^{119}Sn, ^{29}Si) = 101.4$ Hz.

Me_4Sn [$\delta^{119}Sn = 0$; $\Xi(^{119}Sn) = 37.290665$ MHz]. Assignments in ^{1}H and ^{13}C-NMR spectra are based on appropriate 2D $^1H-^1H$ COSY, $^1H-^1H$ NOESYTP, $^1H-^{13}C$ and $^1H-^{29}Si$ HETCOR experiments.

5.2. Reaction of the di- and polyalkynylsilanes *1a–d, 2b–d, 3, and 5* with triallylborane

5.2.1. General procedure

To a solution of about 2 mmol of **1a**–**d**, **2b**–**d**, **3**, or **5** in $CDCl_3$ or pentane (2 ml) the equimolar amount of All_3B was added in one portion at room temperature (r.t.); the mixture was heated several hours at 50–60 °C. The progress of the reaction was monitored by ^{1}H and ^{29}Si-NMR spectroscopy.

7: ^{1}H-NMR (500 MHz, $CDCl_3$, J, Hz): $\delta = 0.06$ (s, 6H, Me_2Si), 2.52 (d, 4H, CH_2B, 7.5), 3.01 (d, 2H, CH_2, 7.0), 5.0–5.1 (m, 6H, $=CH_2$), 5.77 (ddt, 1H, =CH–, 17.5, 9.4, 7.0), 6.21 (ddt, 2H, =CH–{B}, 17.2, 10.2, 7.5), 7.2–7.5 (m, 6H, Ph), 7.51 (dd, 2H, Ph, 7.8, 2.0), 7.59 (dd, 2H, Ph, 7.9, 2.1). ^{13}C-NMR (125 MHz, $CDCl_3$, $J(^{13}C-^{29}Si)$, Hz); $\delta = 0.8$ (Me_2Si, 57.5), 36.4 (br, CH_2B), 48.0 (CH_2); 94.4 ($\equiv C-Si$, 81.4), 106.3 ($\equiv C-Ph$, 15.2), 123.1; 127.7; 128.2; 128.3; 128.55, 128.61, 131.7 (Ph; not assigned), 144.5 ($=C-Si$, 66.7); 148.2 (br, $=C-B$); 150.5 (Ph). ^{29}Si-NMR (99.6 MHz, $CDCl_3$): $\delta = -33.4$. ^{11}B-NMR (160 MHz, $CDCl_3$): $\delta = 81.2$.

7(H): ^{1}H-NMR (500 MHz, $CDCl_3$, J, Hz): $\delta = 0.04$ (d, 3H, MeSi, 3.8), 2.56 (d, 4H, CH_2B, 7.6), 3.11 (dd, 1H, CH_2, 15.3, 7.0), 3.22 (dd, 1H, CH_2, 15.3, 7.0), 4.45 (q, 1H, SiH, 3.8, $^1J(^{29}Si, ^1H) = 213.5$ Hz), 5.1–5.2 (m, 6H, $=CH_2$), 5.89 (ddt, 1H, =CH–, 17.0, 10.0, 7.0), 6.26 (ddt, 2H, =CH–, 16.8, 10.3, 7.6), 7.4–7.6 (m, 10H, Ph). ^{13}C-NMR (125.8 MHz, $CDCl_3$, $J(^{13}C-^{29}Si)$, Hz): $\delta = -3.5$ (MeSi, 57.7); 36.3 (br., CH_2B); 46.9 (CH_2, 8.1); 90.9 ($\equiv C-Si$, 83.9); 107.1 ($\equiv C-Ph$, 14.8); 113.6 ($=CH_2$); 118.6 ($=CH_2$); 127.0, 127.93, 127.95, 128.2; 128.7 (Ph; not assigned); 135.2 (=CH–); 136.8 (=CH–). ^{29}Si-NMR (99.6 MHz, $CDCl_3$): $\delta = -53.2$. ^{11}B-NMR (160 MHz, $CDCl_3$): $\delta = 81.0$.

Table 2
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data [a] of the 2-(but-3-en-1-ylidene)-1,3-silaborolene **9a** and -1,3-stannaborolene derivatives **17a**,**d**

	δ^{13}C				δ^{119}Sn	δ^{11}B
	C(2)	C(4)	C(5)	C(6)		
9a [b]	142.3 br	163.2 br	174.2 (65.3)	163.8		64.0
17a [c]	152.4 br	162.4 br	172.3 [446.0]	156.6	−38.9	62.4
17d [d]	180.3 br [108.7]	181.7 br	170.2 [267.5] (55.7)	159.4 [27.2] (61.8)	−78.8	64.4

[a] In $CDCl_3$ at 23 °C; $^nJ(^{29}Si, ^{13}C)$ ($\pm$0.1 Hz) are given in parentheses; $^nJ(^{119}Sn, ^{13}C)$ [$\pm$0.2 Hz] in brackets; br denotes broad signals due to partially relaxed $^{13}C-^{10/11}B$ coupling.
[b] $\delta^{13}C = 137.0, 136.7, 115.0, 114.1, 44.1, 33.4$ (All); 135.1, 116.1, 29.3 (br) (AllB); 27.6, 15.7 (Me); −2.5 (48.2) (Me_2Si); $\delta^{29}Si = -2.3$.
[c] $\delta^{13}C = 137.6$ [9.7], 137.0, 116.0, 114.2, 45.0 [76.3], 34.1 [64.9] (All); 136.3, 114.3 (br), 30.8 (br) (AllB); 31.7 [58.2], 21.1 [62.8] (Me); −8.3 [303.1] (Me_2Sn).
[d] $\delta^{13}C = 137.6$ [9.6], 136.5, 116.3, 115.6, 48.3 [78.5], 43.2 [111.8], (All); 137.8, 113.5, 32.5 (br) (AllB); 1.4 (50.9) [12.3], 0.6 (50.9) (Me_3Si); −4.7 [285.9] (Me_2Sn). $\delta^{29}Si = -5.9$ [99.1], −10.2 [71.8].

Table 3
^{13}C-, ^{29}Si- and ^{119}Sn-NMR data [a] of the 1-bora-7-sila- (**10a**, **10b**, **10d**, **12**, **13**, **15**) and 1-bora-7-stannabicyclo[4.3.0]nona-5,8-dienes (**18a**, **d**)

	δ^{13}C							δ^{29}Si	δ^{119}Sn
	C(2)	C(3)	C(4)	C(5)	C(6)	C(8)	C(9)		
10a [b]	26.9 br	34.0	36.0 (7.4)	174.9	159.4 br	169.4 (44.8)	136.3 br	−2.1	
10b [c]	26.5 br	36.5	36.6 (6.8)	184.9	159.4 br	182.9 (66.5)	133.2 br	−1.5	
10d [d]	26.7 br	35.2	42.0 (7.6)	182.2 (64.1)	157.7 br	183.0 (63.2, 51.4)	177.8 br	2.7 (10.1, 5.3)	
12 [e]	26.7 br	35.2	40.6 (9.7)	176.7 (70.1)	159.7 br	193.8 (60.0, 46.7)	177.6 br	3.4 (10.3, 5.6)	
13 [f]	28.7 br	35.1	39.3 (8.8)	181.7 (63.5)	160.8 br	183.3 (55.1, 52.0)	183.7 br	−4.1 (12.3, 5.6)	
15 [g]	26.5 br	34.9	42.1 (8.9)	188.7 (60.3)	150.4 br	176.0 (65.3, 54.8)	180.1	n.o.	
18a [h]	26.5 br	34.2	42.3 [62.3]	170.9 [14.5]	158.6 br	178.5 [446.8]	190.2 br	–	−28.5
18d [i]	28.4 br	35.2 [9.5]	41.9 [86.8]	187.1 [46.3]	159.4 br	189.1 [294.7]	178.4 br	–	−7.6
10(H)b [k]	26.3 br	36.38	36.39 (8.4)	182.8 (< 4)	159.9 br	184.5 (66.3)	129.7 br	−21.5	
10(H)d [l]	26.6 br	35.1	40.9 (8.1)	179.9 (52.2)	154.3 br	184.0 (62.5)	179.5 br	−16.7 (9.8, 5.0)	

[a] In $CDCl_3$ at 30 °C; $^nJ(^{29}Si, ^{13}C)$ (±0.1 Hz) are given in parentheses; $^nJ(^{119}Sn, ^{13}C)$ [±0.2 Hz] in brackets; br denotes broad signals due to partially relaxed $^{13}C-^{10/11}B$ coupling.

[b] $\delta^{13}C = 137.8, 137.1, 115.4, 113.8, 43.5, 42.6$ (All); 28.3, 15.6 (Me); −2.9 (48.2), −2.9 (48.6) (Me_2Si). $\delta^{11}B = 66.2$.

[c] $\delta^{13}C = 138.1, 137.8, 116.2, 115.3, 43.4, 39.7$ (All); 41.4, 41.2, 31.6, 29.9 (*t*-Bu); 3.3 (49.3), 2.7 (49.3) (Me_2Si). $\delta^{11}B = 67.5$.

[d] $\delta^{13}C = 137.6, 137.6, 115.4, 115.1, 43.3, 40.6$ (All); 1.3 (50.7), −0.5 (50.7) (Me_3Si); 0.4 (43.0), −0.2 (43.0) (Me_2Si). $\delta^{29}Si = -5.9, -11.0$ (Me_3Si). $\delta^{11}B = 63.7$.

[e] $\delta^{13}C = 137.7, 137.6, 115.5, 115.1, 43.3, 41.5$ (All); 116.6 (76.3, 11.9), 112.8 (78.9, 12.3) ($Me_3Si-C\equiv C-$); 1.3 (50.3), 0.2 (51.2) (Me_2Si); −0.16 (56.4), −0.4 (54.7) (Me_3Si); −0.4 (50.8), −3.5 (48.5) (Me_2Si). $\delta^{29}Si = -10.9$ (Me_3Si); −18.7 (1.8) ($Me_3Si-C\equiv$); −26.8 (1.8) ($Me_2Si-C\equiv$). $\delta^{11}B = 63.8$.

[f] $\delta^{13}C = 167.1$ (All-*C*=); 143.7 (61.3, 49.0) ($Me_3Si-C=$); 137.6, 137.1, 115.5, 115.4, 43.2, 41.4 (All); 1.1 (51.2), −0.4 (52.0) (Me_3Si); 0.8 (48.5), 0.5 (48.5), −0.6 (50.3), −3.3 (51.2) (Me_2Si). $\delta^{29}Si = 15.1$ (12.3, 9.7) (Me_2Si); −5.9, −10.8 (Me_3Si). $\delta^{11}B = 63.8$.

[g] $\delta^{13}C = 137.4, 136.9, 115.6, 115.6, 43.21\ 40.8$ (All); 117.1, 116.9 (≡C–Si); 110.5 (11.8), 110.1 (12.2) (≡C–$SiMe_3$); 1.1 (51.1), −0.4 (56.4), −0.5 (56.2), −0.7 (51.3) (Me_3Si). $\delta^{29}Si = -2.2$ (5.7), −8.9 (9.4) ($SiMe_3$); −18.3 (1.8), −18.4 (1.8) (≡C–$SiMe_3$). $\delta^{11}B = 64.0$.

[h] $\delta^{13}C = 137.9, 137.6, 115.3, 113.6, 43.5$ [5.0], 36.0 [6.0] (All); 32.6 [52.9], 21.3 [62.3] (Me); −9.3 [302.7], −9.41 [298.7]. $\delta^{11}B = 61.8$.

[i] $\delta^{13}C = 138.4$ [9.5], 137.6, 115.4, 114.9, 43.3 [7.6], 42.2 [87.8] (All); 1.4 (50.5), 1.3 (51.0) (Me_3Si); −4.7 [289.4], −5.2 [290.4] (Me_2Sn). $\delta^{29}Si = -5.1$ [53.5], −8.7 [84.6]. $\delta^{11}B = 62.9$.

[k] $\delta^{13}C = 137.8, 134.8, 115.4, 114.9, 42.4, 38.6$ (All); 38.5, 37.4 (9.1) (*C*Me_3); 31.3, 29.6 (C*Me*$_3$); 0.1 (50.1) (MeSi). $\delta^{11}B = 71.0$.

[l] $\delta^{13}C = 137.5, 137.3, 115.5, 115.2, 42.7, 41.0$ (7.6) (All); 0.9 (50.8), −0.9 (50.7) (Me_3Si); −2.2 (46.2) (MeSi). $\delta^{11}B = 64.9$. $\delta^{29}Si = -3.9$ (5.0), −10.3 (9.8) (Me_3Si).

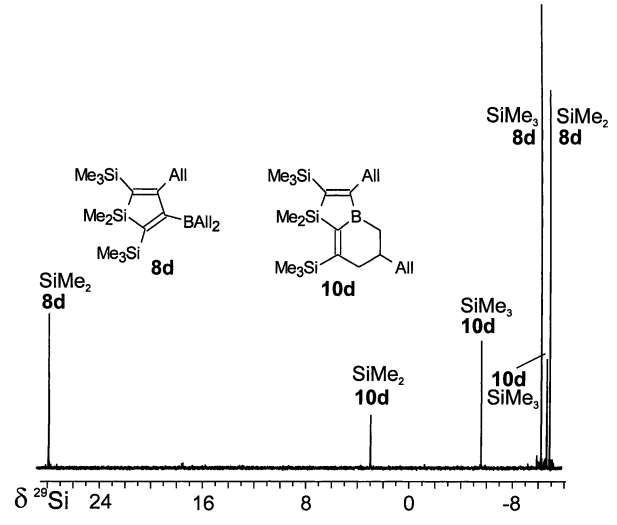


Fig. 4. ^{29}Si-NMR (99.4 MHz) (refocused INEPT [23] with ^{1}H decoupling) spectrum of the product mixture (**8d** and **10d**) obtained from the reaction of **1d** with triallylborane in $CDCl_3$ at room temperature.

8d: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.08$ (s, 9H, Me_3Si) 0.16 (s, 9H, Me_3Si), 0.23 (s, 6H, Me_2Si); 2.32 (dd, 4H, CH_2B, 17.4, 7.5), 3.08 (dd, 2H, CH_2, 5.5, 2.4), 4.89–5.05 (m, 6H, CH_2=); 5.90 (m, 3H, CH=).

9a: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.19$ (s, 6H, Me_2Si); 1.98 (s, 3H, Me); 2.03 (s, 3H, Me); 2.45 (dt, 2H, CH_2B, 7.4, 1.6); 3.17 (dt, 2H, CH_2, 5.9, 1.8); 3.26 (dt, 2H, CH_2, 6.5, 1.5); 4.8–5.1 (m, 6H, =CH_2); 5.8–6.0 (m, 3H, –CH=).

10a: ^{1}H-NMR (250 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.14$, 0.15 (s,s 6H, Me_2Si), 0.67 (dd, 1H, H-1, 17.1, 12.1), 1.58 (ddd, 1H, H-2, 17.1, 4.1, 1.2), 1.7–2.1 (m, 4H, H-3,4,6,7), 1.97 (s, 3H, Me), 1.99 (s, 3H, Me), 2.27 (ddd, 1H, H-5, 16.9, 3.6, 1.0), 3.08 (dt, 2H, H-11,12, 6.3, 1.5), 4.87 (ddt, 2H, =CH_2-*trans*, 13.7, 2.0, 1.8), 5.02 (ddt, 2H, =CH_2-*cis*, 6.8, 2.0, 1.3); 5.79 (m, 2H, –CH=).

10b: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.32$, 0.42 (s,s, 6H, Me_2Si), 0.69 (dd, 1H, H-1, 17.7, 12.9), 1.17 (s, 9H, *t*-Bu), 1.28 (s, 9H, *t*-Bu), 1.59 (ddd, 1H, H-2, 17.7, 3.8, 1.5), 1.60 (m, 1H, H-3), 1.85 (dd, 1H, H-4, 16.8, 10.5), 2.06 (m, 2H, H-6,7), 2.55 (ddd, 1H, H-5, 16.8, 3.5, 1.7), 3.38 (dt, 2H, H-11,12, 6.2, 1.5), 4.8–5.1 (m, 4H, =CH_2), 5.81 (ddt, 1H, H-8, 17.5, 10.4, 6.5), 5.84 (ddt, 1H, H-13, 16.6, 10.1, 6.2).

10(H)b: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.42$ (d, 3H, MeSi, 3.4), 0.96 (dd, 1H, H-1, 16.8, 10.2), 1.22 (s,

9H, *t*-Bu), 1.32 (s, 9H, *t*-Bu), 1.54 (dd, 1H, H-2, 16.8, 4.0), 1.81 (m, 1H, H-3), 2.05 (dd, 1H, H-4, 16.8, 9.0), 2.08 (m, 2H, H-6,7), 2.55 (dd, 1H, H-5, 16.8, 3.8), 3.33 (ddt, 1H, H-8, 15.2, 5.8, 1.6), 3.40 (ddt, 1H, H-9, 15.2, 5.6, 1.8), 4.55 (q, 1H, SiH, 3.4, $^1J(^{29}Si,^1H) = 201.3$ Hz), 4.9–5.0 (m, 4H, $=CH_2$), 5.8–6.0 (m, 2H, =CH).

10d: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.18$ (s, 9H, Me_3Si); 0.26 (s, 9H, Me_3Si); 0.29, 0.30 (s,s, 3H, Me_2Si), 0.78 (dd, 1H, H-1, 17.3, 12.2), 1.65 (m, 1H, H-3), 1.68 (dd, 1H, H-2, 17.3, 4.0), 1.93 (dd, 1H, H-4, 17.5, 10.4); 2.07 (m, 2H, H-6,7), 2.65 (dd, 1H, H-5, 17.5, 3.8), 3.31 (m, 2H, H-11,12), 4.90–5.05 (m, 3H, $=CH_2$), 5.09 (d, 1H, $=CH_2$, 10.2); 5.77 (m, 2H, –CH=).

10(H)d: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.25$ (s, 9H, Me_3Si), 0.29 (s, 9H, Me_3Si), 0.34 (d, 3H, MeSi, 3.5), 1.03 (dd, 1H, H-1, 16.3, 10.1), 1.67 (dd, 1H, H-2, 16.3, 3.7), 1.82 (m, 1H, H-3), 2.10 (m, 2H, H-6,7), 2.13 (dd, 1H, H-4, 17.5, 9.0), 2.67 (dd, 1H, H-5, 17.5, 3.7), 3.36 (m, 2H, H-11,12), 4.83 (q, 1H, SiH, 3.5, $^1J(^{29}Si, ^1H) = 187.0$ Hz), 4.9–5.0 (m, 4H, $=CH_2$), 5.8–6.0 (m, 2H, =CH).

11: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.19$ (s, 9H, Me_3Si); 0.21 (s, 9H, Me_3Si), 0.29, 0.31 (s,s 6H, Me_2Si), 2.33 (dd, 2H, CH_2B, 17.7, 7.6), 2.40 (dd, CH_2B, 17.7, 7.5), 3.20 (dt, 2H, CH_2, 5.8, 1.8), 4.8–5.1 (m, 6H, $=CH_2$), 5.8–6.0 (m, 3H, –CH=).

12: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.18$ (s, 9H, Me_3Si), 0.20 (s, 9H, Me_3Si), 0.26, 0.27 (s,s, 6H, Me_2Si), 0.33 (s, 6H, Me_2Si), 1.02 (dd, 1H, H-1, 17.4, 12.0), 1.68 (m, 1H, H-3), 1.90 (d, 1H, H-4, 17.2), 1.97 (ddd, 1H, H-2, 17.4, 2.6, 1.5), 2.08 (m, 2H, H-6,7), 2.62 (ddd, 1H, H-5, 17.2, 3.7, 1.4), 3.28 (ddt, 1H, H-11(12), 14.5, 6.0, 1.8), 3.33 (ddt, 1H, H-12(11), 14.5, 6.2, 1.7), 4.8–5.1 (m, 4H, $=CH_2$), 5.8–6.0 (m, 2H, H-8, 13).

13: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.19$ (s, 9H, Me_3Si), 0.23 (s, 9H, Me_3Si), 0.27, 0.37 (s,s, 6H, Me_2Si), 0.36 (s, 6H, Me_2Si), 0.80 (dd, 1H, H-1, 17.2, 13.4), 1.69 (ddd, 1H, H-2, 17.2, 3.8, 1.5), 1.70 (m, 1H, H-3), 1.96 (d, 1H, H-4, 17.5), 2.08 (m, 2H, H-6,7), 2.75 (ddd, 1H, H-5, 17.5, 3.6, 1.4), 3.46 (ddt, 1H, H-11(12), 16.0, 5.2, 2.0), 3.53 (ddt, 1H, H-12(11), 16.0, 5.0, 2.0), 4.8–5.1 (m, 4H, $=CH_2$), 5.8–6.0 (m, 2H, H-8, 13).

14: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.18$ (s, 9H, Me_3Si), 0.20 (s, 9H, Me_3Si), 0.22 (s, 18H, Me_3Si), 2.32 (dd, 2H, $CH_2\{B\}$, 18.1, 7.5), 2.39 (dd, 2H, $CH_2\{B\}$, 18.1, 7.5), 3.28 (d, 2H, CH_2, 6.3), 4.9–5.0 (m, 6H, $=CH_2$), 5.7–6.0 (m, 3H, –CH=).

15: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.16$ (s, 9H, Me_3Si), 0.16 (s, 9H, Me_3Si), 0.31 (s, 9H, Me_3Si), 0.33 (s, 9H, Me_3Si), 0.80 (dd, 1H, H-1, 17.4, 12.5), 1.67 (dd, 1H, H-2, 17.4, 4.0), 1.72 (m, 1H, H-3), 1.98 (dd, 1H, H-4, 17.8, 10.4), 2.07 (m, 2H, H-6,7), 2.69 (dd, 1H, H-5, 17.8, 4.0), 3.31 (m, 2H, H-11,12), 4.85–5.05 (m, 4H, H-9,10,14,15), 5.79 (m, 1H, H-8), 5.83 (m, 1H, H-13).

5.3. Reaction of the di(1-alkynyl)silane (**4**) and the di(1-alkynyl)stannanes **6a,d** with triallylborane

5.3.1. General procedure

To a solution of **4** or **6a,d** (2 mmol) in $CDCl_3$ or pentane (2 ml) the equimolar amount of All_3B was added in one portion at −78 °C; the mixture was warmed to r.t. The progress of the reaction was monitored by ^{1}H-, ^{29}Si- and ^{119}Sn-NMR spectroscopy.

16: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.08$ (s, 9H, Me_3Si), 0.18 (s, 9H, Me_3Sn, $^2J(^{119}Sn, ^1H) = 54.2$Hz); 0.23 (s, 6H, Me_2Si), 2.33 (dd, 2H, CH_2B, 17.5, 7.5), 2.40 (dd, 2H, CH_2B, 17.5, 7.5), 3.01 (dt, 2H, CH_2, 5.7, 1.9), 4.90 (m, 4H, $=CH_2$), 5.00 (ddd, 1H, $=CH_2$-*trans*, 17.2, 3.8, 1.9), 5.08 (ddd, 1H, $=CH_2$-*cis*, 10.2, 3.7, 1.8), 5.78 (m, 1H, –CH=), 5.92 (m, 2H, –CHB).

17a: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.33$ (s, 6H, Me_2Sn, $^2J(^{119}Sn, ^1H) = 53.8$ Hz), 2.01 (s, 3H, Me, $^4J(^{119}Sn, ^1H) = 8.8$ Hz), 2.17 (s, 3H, Me, $^3J(^{119}Sn, ^1H) = 48.7$ Hz), 2.41 (d, 2H, CH_2, 7.5), 3.16 (d, 2H, CH_2, 6.7), 3.19 (dt, 2H, CH_2, 5.8, 1.5), 4.8–5.2 (m, 6H, $=CH_2$), 5.8–5.9 (m, 3H, –CH=).

17d: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.11$ (s, 9H, Me_3Si), 0.16 (s, 9H, Me_3Si), 0.35 (s, 9H, Me_2Sn, $^2J(^{119}Sn, ^1H) = 53.9$ Hz), 2.27 (dt, 2H, CH_2B, 7.8, 1.4), 3.04 (dt, 2H, CH_2, $^4J(^{119}Sn, ^1H) = 15.7$ Hz, 6.2, 1.5), 3.29 (dt, 2H, CH_2, $^4J(^{119}Sn, ^1H) = 14.5$ Hz, 6.6, 1.7), 4.79 (ddt, 1H, $=CH_2$-*cis*, 10.1, 2.1, 1.5), 4.85 (ddt, 1H, $=CH_2$-*trans*, 16.9, 2.2, 1.5), 4.99 (ddt, 1H, $=CH_2$-*cis*, 10.1, 2.0, 1.4), 5.0–5.1 (m, 3H, $=CH_2$), 5.72 (m, 2H, =CH–), 5.84 (ddt, 1H, =CH–, 16.9, 10.1, 6.7).

18a: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.27$ (s, 6H, Me_2Sn, $^2J(^{119}Sn, ^1H) = 53.5$ Hz), 0.72 (dd, 1H, H-1, 17.1, 12.0), 1.63 (dd, 1H, H-2, 17.1, 3.8), 1.80 (m, 1H, H-3), 1.94 (dd, 1H, H-4, 17.2, 10.4), 2.04 (s, 3H, Me, $^4J(^{119}Sn, ^1H) = 9.3$ Hz), 2.10 (m, 2H, H-6,7), 2.20 (s, 3H, Me, $^3J(^{119}Sn, ^1H) = 44.0$ Hz), 2.36 (dd, 1H, H-5, 17.2, 4.0), 3.13 (d, 2H, H-11,12, 6.1), 4.9–5.1 (m, 4H, $=CH_2$), 5.8–5.9 (m, 2H, –CH=).

18d: ^{1}H-NMR (500 MHz, $CDCl_3$, *J*, Hz): $\delta = 0.11$ (s, 3H, MeSn), 0.12 (s, 3H, MeSn); 0.21 (s, 9H, Me_3Si), 0.39 (s, 9H, Me_3Si), 0.84 (dd, 1H, H-1, 17.2, 12.0), 1.66 (m, 1H, H-3), 1.75 (ddd, 1H, H-2, 17.2, 3.7, 1.2), 1.95 (dd, 1H, H-4, 17.2, 10.5), 2.07 (m, 2H, H-6,7), 2.67 (ddd, 1H, H-5, 17.2, 3.8, 1.4), 3.28 (ddt, 1H, H-11, 14.5, 5.9, 1.6), 3.35 (ddt, 1H, H-12, 14.5, 6.1, 1.7), 4.8–5.1 (m, 4H, $=CH_2$), 5.7–5.9 (m, 2H, =CH–).

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