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Synthesis and molecular structures of 1-boracyclopent-2-enes

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The reaction of 1-silyl-1-borylalkenes with alkyn-1-yltin compounds affords borol-2-enes, organometallic-substituted allenes, mixtures thereof or even more complex mixtures with buta-1,3-dienes, depending on the third substituent at the C=C bond (Bu or Ph), on the number of Si–Cl functions (two or three) and the nature of the alkyn-1-yltin compound. Six new borol-2-enes were isolated in pure state, and two of them were characterized by X-ray structural analysis. The solution-state structures of all major products were clearly established by multinuclear magnetic resonance methods (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{119}Sn NMR). Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: organoboration; silanes; stannanes; borol-2-enes; allenes; NMR; X-ray

Introduction

Organometallic-substituted alkenes offer numerous reactive sites that are inviting for further useful transformations. Thus, the presence of both boryl and silyl groups at the C=C bond is of particular interest.[1–5] We have shown that 1,2-hydroboration of alkyn-1-ylsilanes with 9-borabicyclo[3.3.1]nonane, 9-BBN, proceeds stereo- and regioselectively, independent of the nature of substitutens at the silicon atom, to give the 1-silyl-1-borylalkenes **A** (Scheme 1).[6–8] Such alkenes belong to the class of triorganoboranes and can be used in 1,1-organoboration reactions.[9] On the other hand, if Si–Cl functions are available, these can be substituted by numerous nucleophiles.[10] In the present work, aspects of 1,1-organoboration were studied, using alkyn-1-yltin compounds.

Previously, it was shown that the reactions of numerous alkenes of type **B** with bis(trimethylstannyl)ethyne afford allenes of type **C** as the major or even sole products, formed by 1,1-organoboration followed by an irreversible allylic rearrangement (Scheme 2).[11] In the course of a systematic study, we became interested in the influence of Si–Cl functions and other substituents on the product distribution arising from such reactions.

Therefore, the 1-silyl-1-borylalkenes **1**–**5** (Schemes 3–5) were used in reactions with bis(trimethylstannyl)ethyne **6**, and in two cases with trimethyl(propyn-1-yl)stannane **7**. The reactions were monitored by multinuclear magnetic resonance spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{119}Sn NMR), and the molecular structures of two new heterocycles were determined by X-ray crystallography.

Results and Discussion

In six cases (Scheme 3), the reactions of **1**–**5** with **6** give the borol-2-enes diastereoselectively in essentially quantitative yield. Two of these heterocycles were crystallized to study their molecular structure by X-ray diffraction, and all could be analyzed in solution by NMR spectroscopy of all NMR-suitable nuclei (^{1}H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn). Most of the data are collected in Table 1. It seems that either R = Ph is required to favor the borol-2-ene formation or the silyl group has to be SiCl$_3$ (R^1 = Cl).

We note that the substituent R = Bu (**a**) exerts a marked effect on the product distribution. Thus, the alkenes **2a**[8] and **3a** afford the borol-2-enes **9a** (5%) or **10a** (30%) as minor products, and the major products are the allenes **15a** (95%)and **16a** (70%), respectively (Scheme 4). The formation of the allenes is qualitatively readily evident from IR spectra [ν(C=C)$_{as}$ ≈ 1985 ± 10 cm^{-1}]. The NMR data of the allenes are listed in Table 2.

In addition to the influence of R and R^1, there is also a marked influence of the nature of the alkyn-1-yltin compound, as shown in the cases of the reactions of **2a** and **3a** with trimethyl(propyn-1-yl)stannane **7** (Scheme 5). In the complex reaction mixture, the borol-2-enes **13a, 14b**, the allenes **17a, 18b** as well as their potential precursors, the butadienes **19a** and **20b**, could be identified on the basis of some of their typical NMR data (Tables 2 and 3). The stereochemistry with respect to the positions of the stannyl- and the 4-phenyl group in **13a** and **14b** may differ from that of the other borol-2-enes, as indicated by the change in the ^{119}Sn chemical shifts (Table 1). The complex mixtures also contain other olefinic compounds which may result from further 1,1-organoboration reactions of the buta-1,3-dienes **19a** or **20b**, prior to rearrangements.[12] So far, it has not been possible to assign the structures of such products with certainty.

Reaction Mechanism

The reaction mechanism for the two possible routes to borol-2-enes or to allenes is proposed in Scheme 6. First the zwitterionic intermediate **I** is formed, typical of 1,1-organoboration reactions.[9] From this intermediate two routes are open for intramolecular rearrangements leading to two other intermediates (**II** and **III**). Intermediate **I** is converted by migration of the olefinic group from boron to carbon into the intermediate **II**, a butadiene derivative (see also **19** and **20** in Scheme 5). An alternative is the activation of one of the B-C(9-BBN) bonds leading to expansion of the bicyclic system in the intermediate **III**, which is a dialkenylborane. In the next step, both intermediates **II** and **III**

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Table 1. ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR data[a] of 1-boracyclopent-2-enes **8–14**

	Si–R^1	4-R	δ^{13}C (C-2)	δ^{13}C (C-3)	δ^{13}C (C-4)	δ^{13}C (C-5)	δ^{11}B	δ^{29}Si	δ^{119}Sn
8b[b]	H	Ph	172.0 br	179.6 [393.7, 13.6]	68.4 [70.2, 9.8]	51.9 br [50.4, 30.1]	75.4	−0.4 {32.8, 5.5}	24.6 (37.6), −60.9
9a[c]	Me	Bu	170.0 br	180.2 [403.0, 12.2]	61.9 [69.5, 12.4]	53.5 br	72.2	24.2 {37.2, 8.9}	31.2 (49.6), −65.8
9b[d]	Me	Ph	171.3 br	179.4 [398.9, 14.0]	68.9 [71.4, 10.2]	55.1 br	71.4	23.3 {35.6, 7.8}	23.6 (40.7), −61.1
10a[e]	Ph	Bu	169.9 br	180.5 [402.5, 12.3]	62.2 [69.6, 13.0]	53.8 br	72.3	12.4 {40.6, 8.6}	33.7(48.7), −66.1
10b[f]	Ph	Ph	170.3 br	180.2 [401.7, 13.1]	68.8 [70.7, 11.7]	56.2 br [35.8]	73.8	12.4 {41.9, 7.2}	29.8 (41.8), −61.0
11a[g]	Cl	Bu	170.1 br	180.8 [397.8, 10.9]	61.9 [69.6, 10.7]	55.0 br [46.9, 36.3] [[83.1]]	72.5	2.7 {35.9, 10.7}	37.4 (42.0), −64.5
11b[h]	Cl	Ph	170.8 br	180.5 [394.3, 12.2]	68.9 [71.0, 8.6]	56.2 br [44.0, 31.5]	70.2	0.2 {37.5, 7.1}	31.6 (37.4), −59.9
12b[i]	Ph	Ph	165.9 br	185.0 [401.0, 12.3]	66.9 [66.5, 14.2]	14.0 br	69.3	12.6 {44.3, 8.6}	23.1 (46.3), −59.7
13a	Me	Bu	153.6 br	169.9 [9.6]	58.1 [15.4]	48.5 br	75.3	23.6 {31.2}	−1.2 (31.2)
14b	Ph	Ph	156.9 br	168.9 [12.2]	64.3 [12.7]	48.7 br	78.2	10.5 {32.2}	−8.7 (33.5)

[a] Measured in C_6D_6 at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{11}B–^{13}C scalar coupling;[17] coupling constants $J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$, $J(^{29}\mathrm{Si}, ^{13}\mathrm{C})$, $J(^{119}\mathrm{Sn}, ^{29}\mathrm{Si})$ and $J(^{119}\mathrm{Sn}, ^{119}\mathrm{Sn})$ are given in brackets, double brackets, braces and parenthesis, respectively. [b] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$] = −5.7 [343.5, $SnMe_3$], −8.5 [338.2, $SnMe_3$], 40.0 [30.8], 33.9, 32.8, 29.2, 27.9, 25.3 br, 25.1, 23.5 (9-BBN), 140.0 [11.9, 3.4], 131.9, 128.7, 128.6, 128.6, 127.8 (Ph). [c] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$] = 40.6 [33.8, C-2′], other carbons are not assigned owing to low concentration *ca* 5%; [d] Other ^{13}C data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$], [[$J(^{29}\mathrm{Si}, ^{13}\mathrm{C})$]] = −8.5 [337.9, $SnMe_3$], −4.6 [341.7, $SnMe_3$], 10.3 [[68.7, Si–Me]], 40.0 [31.9], 33.8, 33.0, 29.2, 28.3, 25.5 br, 24.9, 23.7 (9-BBN), 140.7 [13.6, 4.3, *i*], 132.5, 129.4, 128.5, 128.4, 127.8 (Ph). [e] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$] = −7.7 [337.4, $SnMe_3$], −3.3 [333.9, $SnMe_3$], 40.7 [34.6], 34.3, 32.8, 28.9, 25.5 br, 23.8, 23.4 (9-BBN), 36.3 [16.2], 32.3, 25.0, 14.3 (Bu), 137.2 [10.8], 133.6, 128.1, 130.9 (*i*, *o*, *m*, *p*, Si–Ph); [f] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$], [[$J(^{29}\mathrm{Si}, ^{13}\mathrm{C})$]] = −8.6 [337.8, $SnMe_3$], −3.5 [340.1, $SnMe_3$], 40.2 [31.4], 33.6, 32.8, 29.2, 28.6, 25.5 br, 24.9, 23.6 (9-BBN), 136.4 [[93.4]] [9.4], 134.1 [5.7], 127.4, 128.2 (*i*, *o*, *m*, *p*, Si–Ph), 139.8 [14.8, 4.5, *i*], 133.5, 130.3, 129.8, 129.0, 128.2 (Ph). [g] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$] = −7.5 [338.0, $SnMe_3$], −4.1 [345.8, $SnMe_3$], 40.6 [33.9], 35.0, 31.9, 28.7, 28.4, 25.6 br, 23.6, 23.2 (9-BBN), 35.8 [15.5], 30.5, 25.4, 14.3 (Bu). [h] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$] = 0.7 [343.7, $SnMe_3$], 0.8 [374.6, $SnMe_3$], 40.0 [30.8], 33.3, 29.0, 28.2, 25.6 br, 24.5, 24.0 (9-BBN), 139.1 [12.6, 4.2, *i*], 133.3, 129.7, 128.2, 128.1, 127.9 (Si–Ph); [i] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$] = −8.3 [337.3, $SnMe_3$], −3.9 [340.1, $SnMe_3$], 26.8 [33.8], 16.8 [6.9] (Et), 30.2 br, 9.0 (BEt), 138.9 [19.4, 4.5, *i*], 133.4, 132.2, 129.3, 128.0, 127.8 (Si–Ph), 136.1 [12.4], 133.7, 130.2, 128.7 (Ph).

Table 2. ^{11}B, ^{13}C ^{29}Si and ^{119}Sn NMR data[a] of allene derivatives **15–18** and **B** for comparison

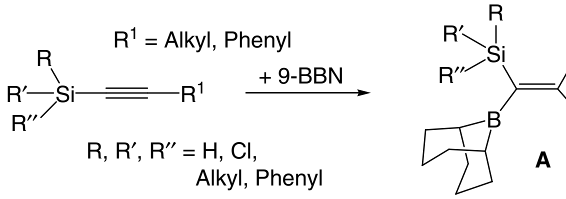
	15a[b]	16a[c]	17a	18b	B[d]
δ^{13}C(C-1)	74.4 [227.9, 226.8]	74.2 [235.2, 224.5]	93.5	93.5 [462.7, 19.5]	70.0 [268.4, 262.1]
δ^{13}C(C-2)	200.1 [24.2]	200.4 [23.8]	202.4 [36.9]	202.2 [38.7, 8.7]	201.5 [28.2]
δ^{13}C(C-3)	70.5 [48.5] [[94.2]]	70.4 [48.6] [[96.6]]	104.1 [57.1], [35.4]	109.9 [52.6, 35.8]	67.4 [55.5]
δ^{13}C(C-4)	35.2 br	35.5 br	n. a.	n. a.	45.5 br [20.0]
δ^{11}B	84.0	82.9	82.9	84.8	78.6
δ^{29}Si	21.7 {34.1}	10.0 {34.5}	13.5	6.3	−14.7 {29.8}
δ^{119}Sn	6.4, −0.3 (161.7, 151.5)	7.1, 0.8 (157.1, 148.9)	22.8	6.1.	−2.3, 1.2(238.8)

[a] Measured in C_6D_6 at 23 °C; br. indicates a broad NMR signal owing to partially relaxed ^{13}C–^{11}B spin–spin coupling;[17] n. a. means not assigned due to small intensity and overlapping of other signals belonging to aliphatic carbons. [b] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$], [[$J(^{29}\mathrm{Si}, ^{13}\mathrm{C})$]] = −7.1 [349.4, $SnMe_3$], −7.1 [347.3, $SnMe_3$], 5.9 [[73.9, Si–Me]], 14.5, 19.5, 22.1, 30.0 (Bu), 34.3, 34.1, 30.9 br, 23.8 (9-BBN). [c] Other ^{13}C NMR data: δ [$J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$] = −7.2 [349.1 $SnMe_3$], −7.3 [347.8, $SnMe_3$], 32.8, 31.6, 23.3, 14.5 (Bu), 34.3, 34.1, 30.9 br, 23.8 (9-BBN), 134.8, 134.6, 131.2, 128.1 (*i*, *o*, *p*, *m*, Si–Ph). [d] Data taken from Wrackmeyer *et al.*[11] for comparison.

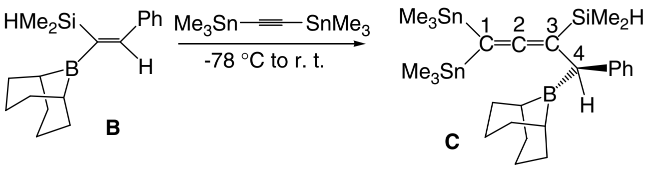
lead to different products: **II** undergoes allylic rearrangement into the allene derivatives and **III** gives the borol-2-enes.[13] In both cases, the stereochemistry appears to be controlled by the sreic requirements of R in the =C(R)H moiety, and both intermediates (**II** and **III**) are notoriously unstable[13–16] and could not be detected in the reaction solutions. The diastereoselectivity is shown by selective formation of the borol-2-enes (Scheme 3) and by the fact that only one of the two conceivable diastereomers **17a** or **18b** (Scheme 5) was formed.

NMR Spectroscopic Studies

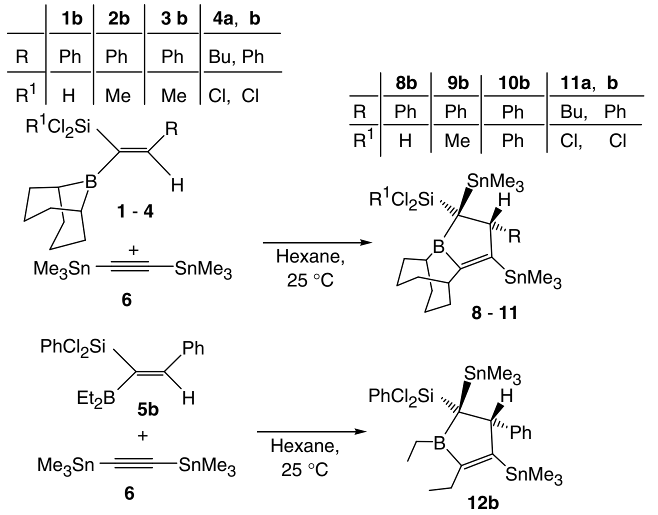
The NMR data (^{11}B, ^{13}C, ^{29}Si and ^{119}Sn) for borol-2-enes (**8–14**), allenes (**15–18**) and butadienes (**19,20**) are listed in Tables 1–3,



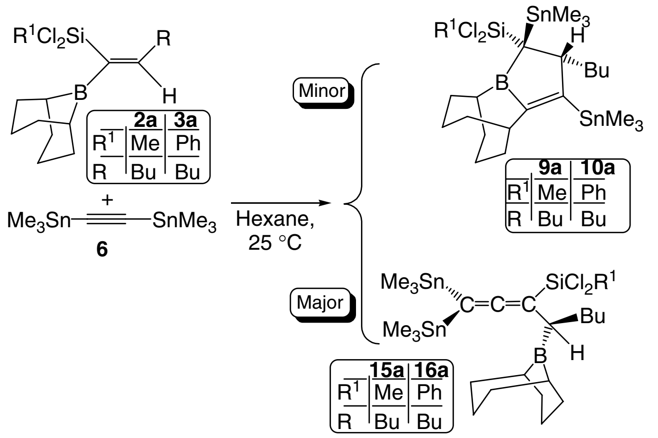
Scheme 1. 1,2-Hydroboration of alkyn-1-ylsilanes.



Scheme 2. Reaction of 1-silyl-1-borylalkenes and bis(trimethylstannyl)ethyne to afford allenes quantitatively.

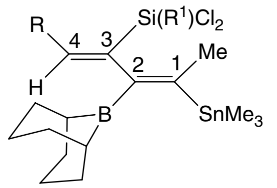


Scheme 3. Reactions of the alkenes **1**–**5** leading diastereoselctively to borol-2-enes in high yield.



Scheme 4. Reactions of the 1-silyl-1-borylalkenes **2a** and **3a** with **6** lead to the borol-2-enes **9a, 10a** as minor and to the allene derivatives **15a, 16a** as major products.

Table 3. NMR data[a] (^{13}C, ^{29}Si and ^{119}Sn) of 1,3-butadiene derivatives **19a** and **20b**



	19a	20b
δ^{13}C (C-1)	159.5 [478.0]	165.0 [473.2]
δ^{13}C (C-2)	162.2 br	161.7 br
δ^{13}C (C-3)	141.0 [77.5], [[84.2]]	144.2 [76.6] [[85.8]]
δ^{13}C (C-4)	148.4 [11.3]	147.0 [11.6]
δ^{29}Si	12.5 {6.6}	−1.3 {6.4}
δ^{119}Sn	−44.3	−41.7

[a] Measured in C_6D_6 at 23 °C, coupling constants are given in square brackets; br. means a broad ^{13}C resonance owing to partially relaxed ^{13}C–^{11}B scalar coupling.[17] Values in brackets corresponding to $J(^{119}$Sn, ^{13}C), those in double brackets to $J(^{29}$Si, ^{13}C) and in braces to $J(^{119}$Sn, ^{29}Si) spin–spin coupling constants.

respectively. The ^{1}H NMR data and other relevant data are collected in the Experimental section. The NMR data sets are consistent with the proposed structures. The assignment is strongly supported by various NMR parameters such as coupling constants $J(^{29}$Si, ^{13}C), $J(^{119/117}$Sn, ^{13}C), $J(^{119/117}$Sn, $^{119/117}$Sn) and $J(^{119/117}$Sn, ^{29}Si). In the ^{13}C NMR spectra, the typically broadened signals of ^{13}C nuclei adjacent to boron[17] are readily assigned. In the case of allenes, the high frequency shift of the ^{13}C NMR signal of the central carbon atom C(2) is characteristic. ^{13}C NMR spectra of the borol-2-ene (Fig. 1) and of the mixture containing the borol-2-ene **10a** and the allene **16a** (Fig. 2) are representative.

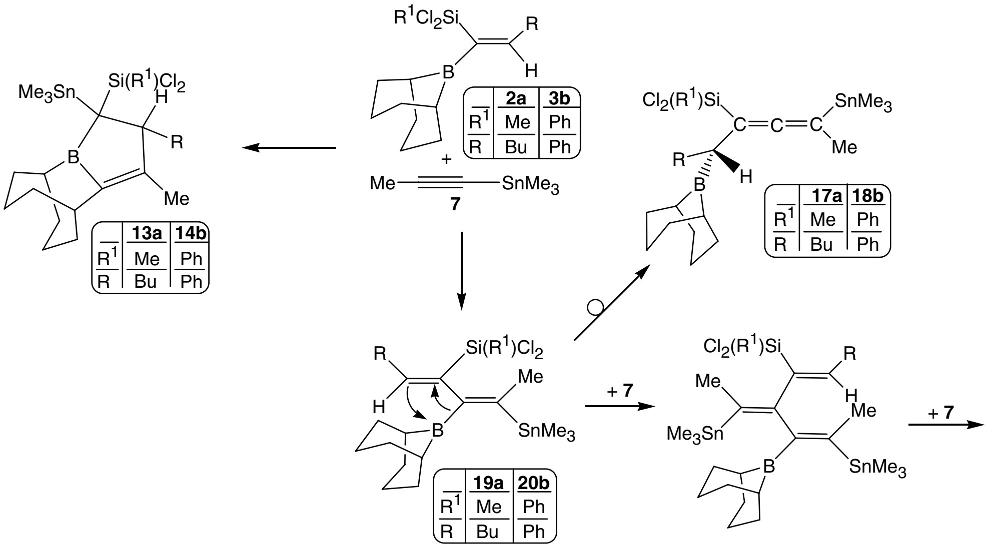
The carbon atom C(5) in the borol-2-enes is linked to three-coordinate boron and to one of the $SnMe_3$ groups. This situation should give rise to $\sigma-\pi$ interactions (hyperconjugation) between the Sn–C(5) bond and the formally empty boron p_z orbital. We note the rather small coupling constant $|^1J(^{119/117}$Sn, ^{13}C(5))| (see e.g. Fig. 1) in the order of 40–50 Hz as evidence for this bonding situation. The inspection of the structural parameters reveals a marked elongation of the Sn–C(5) bond, when compared with other Sn–C bond lengths.

The application of ^{29}Si[18] and ^{119}Sn NMR spectra[19] for studying reaction solutions is shown in Fig. 3 for the borol-2-ene **11b** and in Fig. 4 for the mixture containing the borol-2-ene **10a** and the allene **16a**. The complementary information is evident from the observation of the relevant satellite signals in both ^{29}Si and ^{119}Sn NMR spectra.

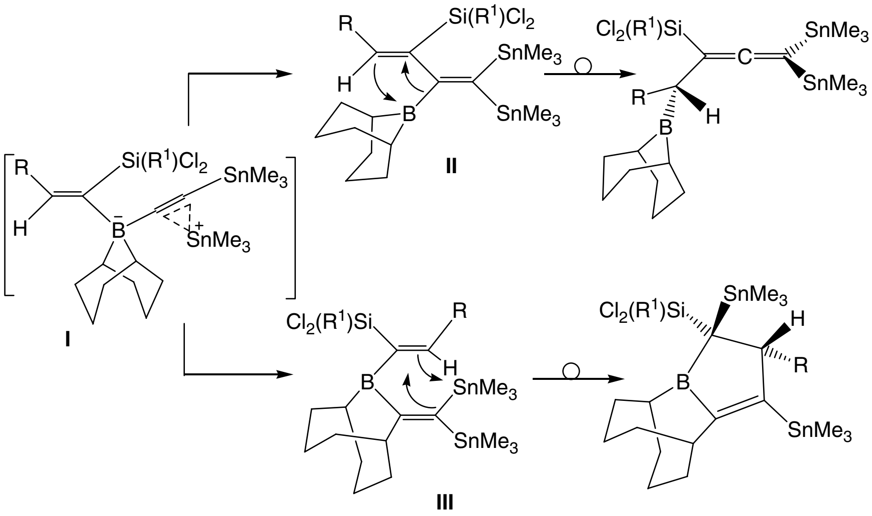
The ^{11}B chemical shifts of starting compounds and the final products cover the typical range δ^{11}B $\approx$ 85–70 ppm.[11,13,20] The low frequency shift by about 15 ppm relative to the starting materials is typical for the borol-2-enes and by about 7–10 ppm for the allenes containing the boryl group in an allylic position.[11]

X-ray Structure Analyses of 8b and 10b

The molecular structures of **8b** and **10b** are shown in Figs 5 and 6, respectively. Selected bond lengths and angles are listed in Table 4 and data pertinent to the X-ray structure determinations can be found in Table 5. In both cases, intermolecular interactions



Scheme 5. Mixture of products obtained as a result of the reaction of trimethyl-(propyn-1-yl)stannane **7** and the 1-silyl-1-borylalkenes **2a** and **3b**.



Scheme 6. Two possible reaction pathways leading to allenes or borol-2-enes.

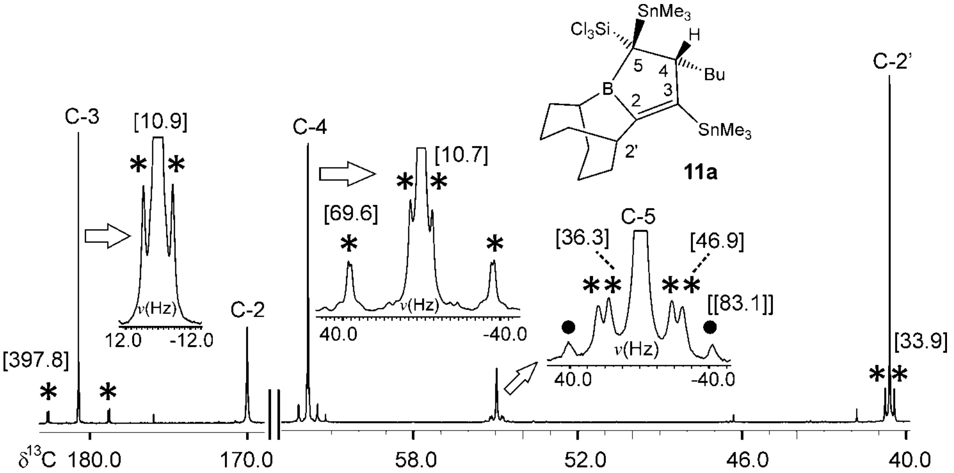


Figure 1. The 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum of **11a** (in C_6D_6, *ca* 15% solution v/v at 23 °C). Expansions are shown for the signals with $^{117/119}Sn$ satellites, marked by asterisks, corresponding to $^nJ(^{117/119}Sn, ^{13}C)$ where $n = 1, 2$ or 3. For C-5 ^{29}Si satellites corresponding to $^1J(^{29}Si, ^{13}C)$ are marked by solid circles.

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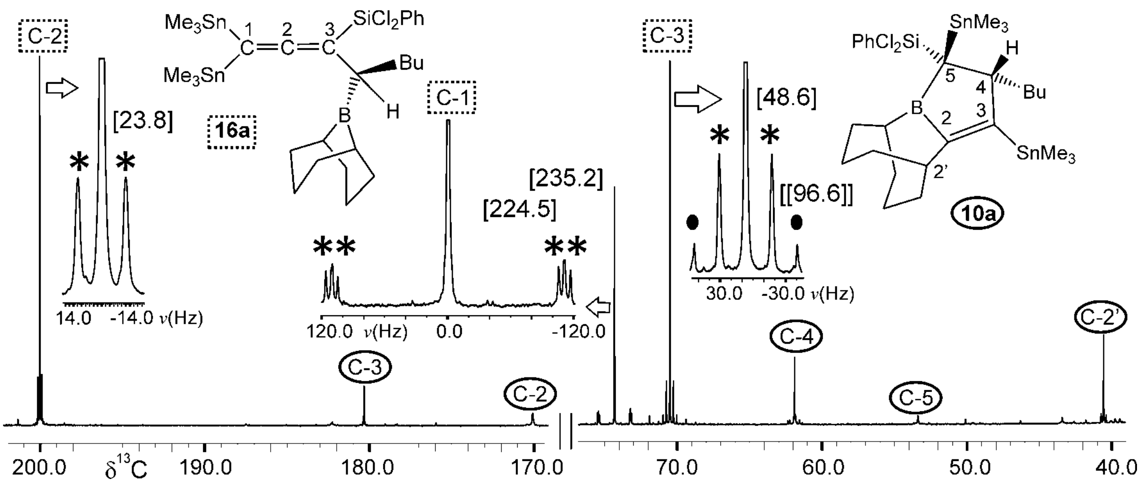

Figure 2. The 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum of the mixture containing **10a** and **16a** (in C_6D_6,15% solution v/v at 23 °C). Expansions are shown for the signals belonging to **16a** with $^{117/119}$Sn satellites, marked by asterisks, corresponding to $^nJ(^{117/119}Sn, ^{13}C)$ where $n = 1, 2$ or 3. The ^{29}Si satellites, marked by solid circles, correspond to $^1J(^{29}Si, ^{13}C)$.

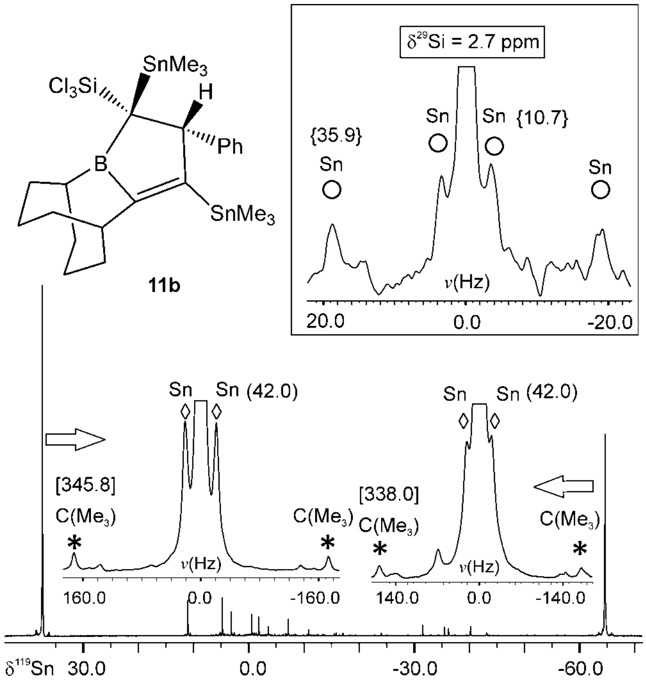

Figure 3. The 149.1 MHz $^{119}Sn\{^1H\}$ (lower) and 79.4 MHz $^{29}Si\{^1H\}$ (upper inserted) NMR spectra of the reaction mixture containing mainly **11b** (in C_6D_6, 15% solution v/v at 23 °C). Expansions are shown for the signals with ^{13}C satellites for $^1J(^{119}Sn, ^{13}C)$, $^{117/119}$Sn satellites for $^4J(^{117/119}Sn, ^{117/119}Sn)$ and ^{29}Si satellites for $^{2/4}J(^{117/119}Sn, ^{29}Si)$, marked by asterisks, diamonds and circles, respectively.

appear to be negligible. In the structure of **8b**, the atoms of the five-membered borol-2-ene ring are almost exactly in one plane (mean deviation = 2.6 pm). The phenyl group is twisted by 75.9° against the principle plane of the borol-2-ene ring. The atom Sn2 and the phenyl group are in *trans*-positions. The surroundings of the boron atom are trigonal planar within the experimental error. When compared with other Sn–C bond lengths, the bond C18–Sn2 (223.3 pm) is markedly elongated. This elongation can be explained using the concept of hyperconjugation,[21] confirmed by the small magnitude of the coupling constant $^1J(^{117/119}Sn, ^{13}C)$.

Table 4. Selected bond lengths (pm) and bond angles (deg) of **8b** and **10b**. Numbers in parentheses represent the estimated standard deviation

$C_{24}H_{39}BCl_2SiSn_2$ (**8b**)		$C_{30}H_{43}BCl_2SiSn_2$ (**10b**)	
C18–C19	156.6(7)	C2–C8	157.4(10)
C7–C19	153.1(8)	C8–C9	151.8(10)
C7–C17	135.2(8)	C9–C10	136.0(11)
C17–B1	155.3(9)	C10–B1	156.0(11)
C18–B1	155.5(9)	C2–B1	155.8(11)
C18–Sn2	223.4(6)	C2–Sn1	224.2(7)
C7–Sn1	214.3(5)	C9–Sn2	214.8(7)
C18–Si1	183.3(6)	C2–Si1	183.4(8)
–	–	C25–Si1	185.7(8)
Si1–Cl1	206.5(2)	Si1–Cl1	206.7(3)
B1–C18–C19	105.1(5)	B1–C2–C8	103.8(6)
C7–C19–C18	105.6(5)	C9–C8–C2	105.5(6)
C17–C7–C19	112.5(5)	C10–C9–C8	112.3(7)
C7–C17–B1	110.3(5)	C9–C10–B1	109.6(7)
Si1–C18–Sn2	108.3(3)	Si1–C2–Sn1	107.2(3)
C17–B1–C13	121.3(5)	C10–B1–C15	119.8(7)
C17–B1–C18	106.2(5)	C10–B1–C2	106.2(7)
C13–B1–C18	132.5(5)	C15–B1–C2	134.0(7)
C19–C7–Sn1	121.7(4)	C8–C9–Sn2	120.6(5)

The structural features of **10b** are quite close to those of **8b**. All the bond lengths and bond angles are well comparable. The borol-2-ene ring in **10b** is slightly less planar (mean deviation = 6.4 pm) than in **8b**, and the surroundings of the boron atom are trigonal planar. The phenyl group forms an angle of 96.2° with the mean plane of the borol-2-ene ring. Again, the Sn–C2 bond (224.2(7) pm) is elongated, as was the comparable Sn–C18 bond in **8b**.

Conclusions

The present work has shown a new access to C-substituted borol-2-enes. In contrast to borol-3-enes, which are somewhat better known,[13,22,23] rather few borol-2-enes have been prepared

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Table 5. Crystal data and structure refinement details for compound **8b** and **10b**

Formula	$C_{24}H_{39}BCl_2SiSn_2$ (**8b**)	$C_{30}H_{43}BCl_2SiSn_2$ (**10b**)
Formula weight	674.73	750.82
Crystal	Prism	Prism
Dimensions (mm)	0.33 × 0.30 × 0.25	0.48 × 0.40 × 0.31
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/*n*	P − 1
Temperature (K)	133 (2)	143(2)
Z	4	2
Lattice parameters		
a (pm)	1021.35(9)	971.70(10)
b (pm)	2441.84(17)	1042.10(10)
c (pm)	1133.14 (9)	1640.3(2)
α (deg)	90.00	83.383(10)
β (deg)	95.883(6)	81.228(10)
γ (deg)	90.00	76.202(10)
Absorption coefficient (mm^{-1})	2.020	1.796
Measuring range (deg)	1.7–25.7	2.0–25.6
Volume (Å^3)	2811.1 (4)	1588.8 (3)
Density (mg m^{-3})	1.594	1.569
F(000)	1344	752
Goodness-of-fit on F^2	1.105	1.367
Completeness to θ	25.7°: 98.9%	25.6°: 99.4%
Reflections collected	10464	20547
Reflections with $I > 2\sigma(I)$	4295	5439
Refined parameters	275	325
Diffractometer	STOE IPDS II	STOE IPDS II
Wavelength (pm)	71.069	71.069
R_1/wR_2 [$I > 2\sigma(I)$]	0.0476/0.126	0.0607/0.1446
Maximum/minimum residual electron density [epm^{-3} × 10^{-6}]	2.027/−0.738	1.396/−1.257

so far. Some C-unsubstituted derivatives can be prepared by isomerization of the borol-3-enes.[24] Otherwise the access appears to be difficult.

Experimental

Preparation of Starting Materials and General

All preparative work and handling of the samples were carried out observing precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glass ware were used throughout. 1-Silyl-1-borylalkenes **1-5**[8,25] and alkyn-1-ylstannanes **6**[26] and **7**[27] were prepared as described. Some of the starting materials (**1b, 3b** and **6**) were purified by recrystallization prior to use, and the others were used without further purification. Mass spectra (EI, 70 eV) were produced using a Finnigan MAT 8500 with direct inlet (data given for ^{1}H, ^{10}B, ^{12}C, ^{35}Cl, ^{28}Si, ^{118}Sn). Melting points (uncorrected) were determined using a Büchi 510 melting point apparatus. NMR measurements in C_6D_6 (concentration *ca* 5–10%) with samples in tubes (5 mm o.d.) at 23 ± 1 °C were carried out using a Varian Inova 300 and 400 MHz spectrometers for ^{1}H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR; chemical shifts are given relative to Me_4Si [δ^1H (C_6D_5H) = 7.15; δ^{13}C (C_6D_6) = 128.0; δ^{29}Si = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz]; Me_4Sn [δ^{119}Sn = 0 for $\Xi(^{119}Sn)$ = 37.290665 MHz] and external BF_3-OEt_2 [δ^{11}B = 0 for $\Xi(^{11}B)$ = 32.083971 MHz]. Chemical shifts are given to ±0.1 ppm for ^{13}C, ^{29}Si and ^{119}Sn, and ±0.4 ppm for ^{11}B; coupling constants are given ±0.4 Hz for $J(^{29}Si, ^{13}C)$ and $J(^{119}Sn, ^{13}C)$. ^{29}Si and ^{119}Sn NMR spectra were measured using the refocused INEPT pulse sequence,[28] based on $^3J(^{29}Si, ^1H)$ (25–35 Hz) and $^2J(^{119}Sn, ^1H_{Me})$ (50–60 Hz) after optimizing the delay times in the pulse sequence.

Reactions of 1-Silyl-1-borylalkenes 1–5 with bis(Trimethyl stannyl)ethyne, 6 and Trimethyl(propyn-1-yl)stannane, 7

The 1-silyl-1-borylalkene, **1b** (0.53 g, 1.62 mmol) was dissolved in hexane (10 ml) and an equimolar amount of a solution of bis(trimethylstannyl)ethyne, **6** (0.57 g; 1.62 mmol), in hexane (5 ml) was added slowly at room temperature. The stirring of the reaction mixture was continued for 30–40 min. Then, the solvent volume was reduced to *ca* 5 ml and the solution was kept undisturbed. After 3 h colorless crystals of **8b** were growing, which were separated from the mother liquor. A few crystals were dissolved in C_6D_6 to collect the NMR data, and a crystal of appropriate dimensions was used for X-ray structural analysis. In the case of the borolene, **10b**, hexane was completely evaporated under reduced pressure (10^{-2} Torr), and the residue was dissolved in pentane (3 ml). The process of crystallization was successful and a single crystal was studied by X-ray diffraction. All other borol-2-enes except **8b** and **10b,** were oily liquids and they were prepared exactly in the same way as described above. In the cases of **2a** and **3a**, the reactions afforded in high yield the allenes **15a** (*ca* 95%) and **16a** (*ca* 70%), respectively (according to NMR spectra). The reactions of trimethyl(propyn-1-yl)stannane **7** with the silanes **2a** and **3b** afforded complex mixtures containing borol-2-enes (**13a, 14b**), allenes (**17a, 18b**), butadiene derivatives (**19a, 20b**) and some unidentified products in small amounts. Purification and complete NMR assignments were not possible for such mixtures. However, the structures shown in Scheme 5 could be proposed based on characteristic NMR data.

8b: m.p. = 133–135 °C; recovered yield after recrystallization = 72%; ^{1}H NMR (400 MHz): $\delta = -0.1$ [s, 9H, $^2J(^{119}Sn, ^1H) = 54.0$ Hz, $SnMe_3$], 0.2 [s, 9H, $^2J(^{119}Sn, ^1H) = 52.6$ Hz, $SnMe_3$], 1.2–1.9, 2.2, 2.9 (m, m, m, 14H, 9-BBN), 4.2 [s, 1H, $^3J(^{119}Sn, ^1H) = 28.6$, 6.9 Hz, C^4H], 5.2 [s, 1H, $^1J(^{29}Si, ^1H) = 286.1$ Hz, $^3J(^{119}Sn, ^1H) = 7.8$ Hz, Si–H], 6.9–7.1 (m, 5H, Ph); elemental analysis: calcd (%): C 42.72, H 5.83; found (%): C 43.34, H 5.461.

9a: *ca* 5%, ^{1}H NMR signals were not assigned in the mixture ecause of overlap with other signals.

9b: ^{1}H NMR (400 MHz): $\delta = 0.01$ [s, 9H, $^2J(^{119}Sn, ^1H) = 54.5$ Hz, $SnMe_3$], 0.3 [s, 9H, $^2J(^{119}Sn, ^1H) = 52.6$ Hz, $SnMe_3$], 0.2 [s, 3H, $^2J(^{29}Si, ^1H) = 7.8$ Hz, Si–Me], 4.3 [s, 1H, $^3J(^{119}Sn, ^1H) = 30.2$, 7.1 Hz, C^4H], 3.0, 2.5, 1.3–2.1, 2.5, 3.0 (m, m, m, 14H, 9-BBN), 6.9–7.3 (m, 5H, Ph); EI-MS: *m/z* (%) = 688 (5) [M^+], 673 (100) [$M^+ - CH_3$], 674 (81) [$M^+ - CH_4$], 653 (4) [$M^+ - Cl$], 510 (51) [$M^+ - SnMe_3$], 489 (5), 289 (28), 165 (79).

10a: ^{1}H NMR (400 MHz): $\delta = 0.1$ [s, 9H, $^2J(^{119}Sn, ^1H) = 54.2$ Hz, $SnMe_3$], 0.1 [s, 9H $^2J(^{119}Sn, ^1H) = 55.0$ Hz, $SnMe_3$], 0.9, 1.2–1.3, 2.5 (t, m, m, 9H, Bu), 1.6–1.9, 2.4, 2.8 (m, m, m, 14H, 9-BBN), 3.4 [t, 1H, $^3J(^{119}Sn, ^1H) = 27.7$ Hz, $^3J(^1H, ^1H) = 4.6$ Hz, C^4H], 7.0–7.8 (m, 5H, Si– Ph).

10b: m.p. = 144–145 °C; yield after recrystalization = 83.8%; ^{1}H NMR (400 MHz): $\delta = -0.1$ [s, 9H, $^2J(^{119}Sn, ^1H) = 54.6$ Hz,

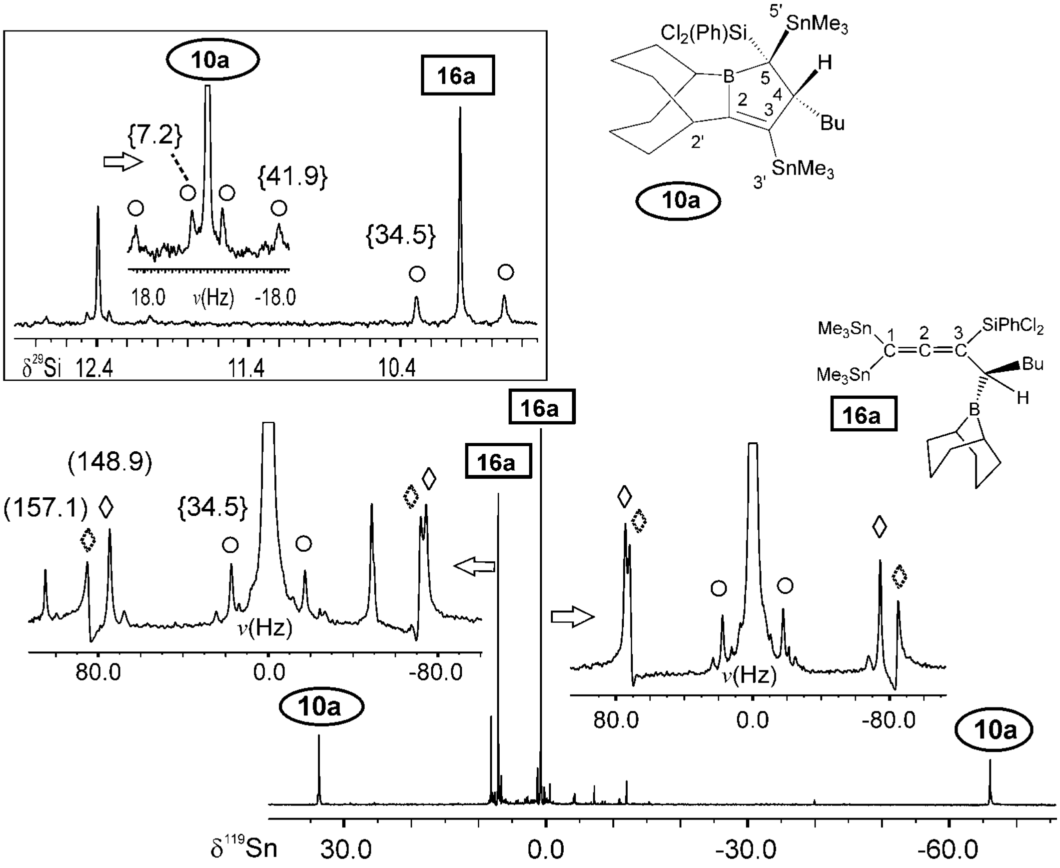

Figure 4. 149.1 MHz ^{119}Sn{^{1}H} (lower trace) and 79.4 MHz ^{29}Si{^{1}H} (upper insert) NMR spectra of the mixture containing borol-2-ene **10a** and allene **16a.** Expansions are given for the signals showing the respective $^{117/119}$Sn satellites for $J(^{117/119}Sn, ^{117/119}Sn)$ and $J(^{117/119}Sn, ^{29}Si)$. Note the distorted phase for ^{119}Sn satellites, typical of INEPT experiments with homonuclear spin–spin coupling.

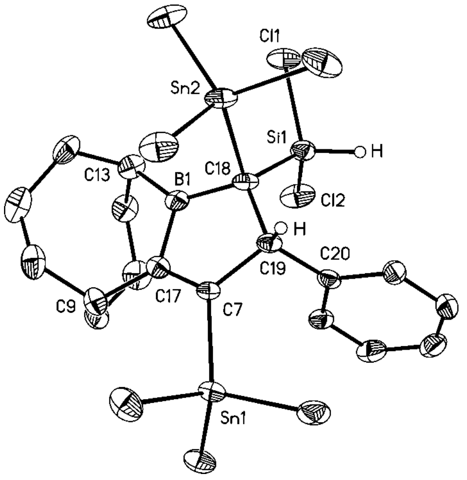

Figure 5. Molecular structure of **8b**; ORTEP plot (40% probability level; hydrogen atoms except H19 and H1Si, are omitted for clarity). For structural parameters see Table 4.

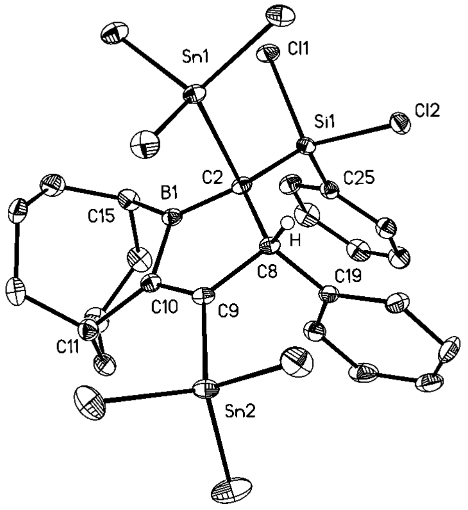

Figure 6. Molecular structure of **10b**; ORTEP plot (40% probability level; hydrogen atoms except H8 are omitted for clarity). For structural parameters see Table 4.

SnMe$_3$], 0.3 [s, 9H, $^{2}J(^{119}Sn, ^{1}H) = 52.3$ Hz, SnMe$_3$], 1.3–1.9, 2.6, 2.9 (m, m, m, 14H, 9-BBN), 4.3 [s, 1H, $^{3}J(^{119}Sn, ^{1}H) = 28.4, 7.2$ Hz, C^{4}H], 6.6–7.3 (m, 10H, Si–Ph, Ph); elemental analysis: calcd (%): C 47.99, H 5.77; found: C 48.32, H 5.77.

11a: ^{1}H NMR (400 MHz): $\delta = 0.2$ [s, 9H, $^{2}J(^{119}Sn, ^{1}H) = 53.5$ Hz, SnMe$_3$], 0.2 [s, 9H, $^{2}J(^{119}Sn, ^{1}H) = 52.8$ Hz, SnMe$_3$], 0.8, 1.1–1.9, 2.1 (t, m, m, 9H, Bu), 3.3 [t, 1H, $^{3}J(^{119}Sn, ^{1}H) = 26.8$ Hz, $^{3}J(^{1}H, ^{1}H) = 4.9$ Hz, C^{4}H], 1.1–1.9, 2.4, 2.8 (m, m, m, 14H, 9-BBN).

11b: ^{1}H NMR (400 MHz): $\delta = -0.3$ [s, 9H, $^{3}J(^{119}Sn, ^{1}H) = 53.5$ Hz, SnMe$_3$], 0.1 [s, 9H, $^{2}J(^{119}Sn, ^{1}H) = 51.8$ Hz, SnMe$_3$], 1.0–1.7,

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2.2, 2.7 (m, m, m, 14H, 9-BBN), 4.2 [s, 1H, $^{3}J(^{119}\text{Sn}, {}^{1}\text{H}) = 28.6$, 6.9 Hz, C^{4}H], 6.7–6.9 (m, 5H, Ph); EI-MS: m/z (%) = 690 (28) [M^{+}], 655 (10) [$M^{+} - Cl$], 526 (13), 497 (10), 165 (100).

12b: ^{1}H NMR (400 MHz): $\delta = -0.1$ [s, 9H, $^{2}J(^{119}\text{Sn}, {}^{1}\text{H}) = 54.3$ Hz, $SnMe_3$), 0.3 [s, 9H, $^{2}J(^{119}\text{Sn}, {}^{1}\text{H}) = 52.2$ Hz, $SnMe_3$], 1.0, 1.2, 1.6, 1.9, 2.4, 2.5 (t, t, m, m, m, m, 10H, Et, BEt), 4.3 [s, 1H, $^{3}J(^{119}\text{Sn}, {}^{1}\text{H}) = 30.3$, 8.2 Hz, C^{4}H], 6.7–7.8 (m, 10H, Ph, Si– Ph).

13a: ^{1}H NMR (400 MHz): $\delta = 5.8$ [t, 1H, $^{3}J(^{119}\text{Sn}, {}^{1}\text{H}) = 21.3$ Hz, $^{1}J(^{1}\text{H}, {}^{1}\text{H}) = 7.8$ Hz, C^{4}H] other protons are without assignments.

14b: ^{1}H NMR (400 MHz): $\delta = 4.5$ [s, 1H, $^{3}J(^{119}\text{Sn}, {}^{1}\text{H}) = 21.9$ Hz, C^{4}H] other protons are without assignments.

NMR Data Belonging to Allene Derivatives

15a: ^{1}H NMR (400 MHz): $\delta = 0.2$, 0.2 (s, s, 18H, 2 × $SnMe_3$), 0.7 (s, 3H, Si–Me), 0.9, 1.1, 1.4, 1.8–2.1 (t, m, m, m, 9-BBN, Bu, -CH).

16a: ^{1}H NMR (400 MHz): $\delta = 0.2$, 0.2 [s, s, 18H, $^{2}J(^{119}\text{Sn}, {}^{1}\text{H}) = 52.8$ Hz, 2 × $SnMe_3$], other ^{1}H signals were obtained as overlapping multiplets with signals belonging to the compound **10a** in the mixtures.

17a, 18b, 19a, 20b were obtained in complex mixtures with other compounds, preventing the precise assignments of ^{1}H NMR signals.

X-ray Structural Analyses of the Borol-2-enes 8b and 10b

The X-ray crystal structural analyses (Table 5) of **8b** and **10b** were carried out for single crystals (selected in perfluorinated oil[29] at room temperature) at 133 (2) K using a STOE IPDS II system (Mo-K_{α}, 71.069 pm), equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[30] SHELXL-97,[31] and WinGX.[32] The data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications nos CCDC 719366 (**8b**) and 719365 (**10b**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, via www.ccdc.cam.ac.uk/data_request/cif).

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