RING ENLARGEMENT BY 1,1-ORGANOBORATION. ROUTES TO NOVEL DIENES, TRIENES, AND ALLENES

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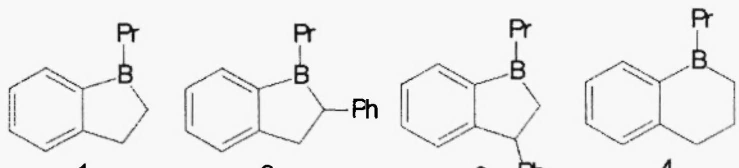
Abstract.
The reaction (1,1-organoboration) of the 1-propyl-1-boraindan derivatives **1** - **3** and of the 1-propyl-1-boratetralin **4** with an excess of various 1-alkynyltrimethyltin compounds $Me_3Sn-C{\equiv}CR^1$ **5** [R^1 = Me (**a**), ^{t}Bu (**b**), Ph (**c**), Me_3Si (**d**), Me_3Sn(**e**)] leads to kinetically controlled ring expansion by formation of a triene (**8a**), dienes (**9b**, **c**) or to allenes, again as a result of ring expansion (**11e**, **12e**, **14e**) or to an allene **23e** when the 1:1 reaction had first afforded the thermodynamically controlled 1,1-organoboration product **22e** in which the ring is not enlarged. The latter type of product was also identified from the reaction of 1-propyl-3-phenyl-1-boraindan **3** or 1-propyl-1-boratetralin **4** with one equivalent each of **5d**. In the case of **3** and **5d**, in the beginning all possible 1,1-organoboration products **15d** - **20d** were formed by insertion into endocyclic and exocyclic B-C bonds. This mixture equilibrates within 24 h, and mainly a single isomer **20d** was left, identified as the Z-isomer of the B-C_{propyl} insertion products. The borane **1** reacts with dimethyl-di(1-propynyl)silane to give a mixture of three silole derivatives **24** - **26**. The various structures are proposed on the basis of consistent sets of ^1H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR data.

INTRODUCTION

There are three different B-C bonds in the 1-boraindanes **1** - **3** and in the 1-boratetralin derivative **4**. It has been shown for **1** and **4** [1] that the different reactivities of these bonds can be demonstrated by 1,1-organoboration reactions [2] with 1-alkynylsilanes and -stannanes. With one exception, ring expansion, as the result of kinetic control, has been observed. Only in the case of the reaction of **1** with trimethyl(1-propynyl)silane, the transfer of the exocyclic n-propyl group, as the result of thermodynamic control, competes with ring expansion [1]. Ring expansion can take place either by insertion into the B-C_{aryl} or the endocyclic B-C_{alkyl} bond. The latter case is preferred if the 1-alkynyl-trimethyltin compound bears a bulky substitutent at the C≡C bond [1]. Previously it has been shown that the products formed by 1,1-organoboration of 1-alkynylstannanes can react with a second or even a third equivalent of 1-alkynylstannane to give either dienes [3] or allenes [4,5], or trienes [3]. Although one might expect that dienes or trienes should be favoured starting from cyclic boranes such as **1** - **4**, there is also a recent report [6] that allenes can be formed.

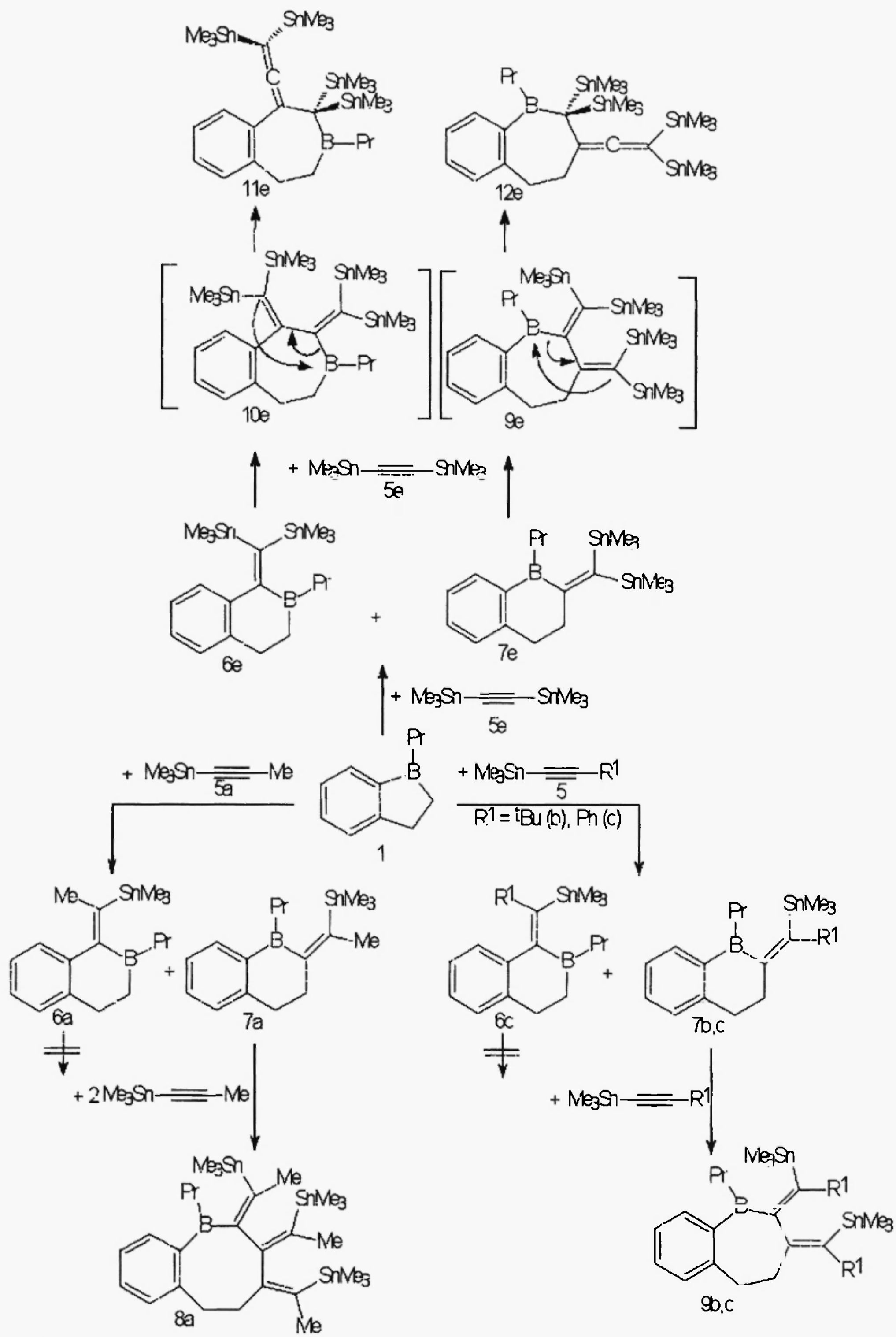


1 2 3 4

We have now studied the reactivity of **1** - **4** in the presence of an excess of 1-alkynyltin compounds $Me_3SnC{\equiv}CR^1$ **5** [R^1 = Me (a), ^{t}Bu (**b**), Ph (**c**), Me_3Si (**d**), Me_3Sn (**e**). The reaction of **1** with dimethyl-di(1-propynyl)silane, $Me_2Si(C{\equiv}CMe)_2$ **6**, was included in order to look for further synthetic potential.

RESULTS AND DISCUSSION

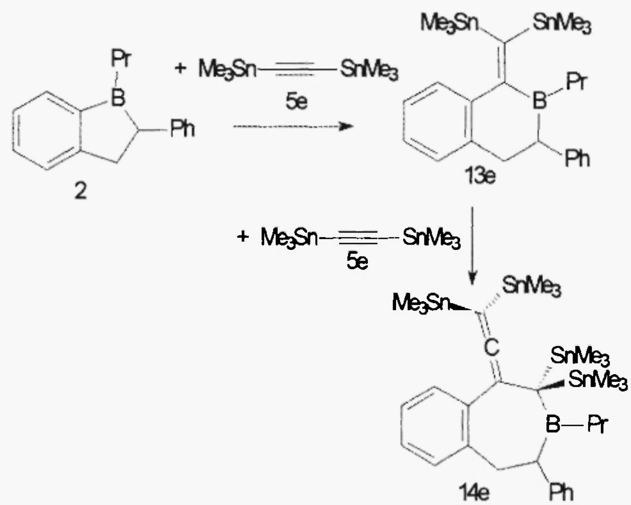
The reactions of **1** with **5** are summarized in Scheme 1. In each case it proved possible to obtain first the products of the 1:1 reaction which then react fast with **5a**, **c**, e or slow, in the case of **5b,** to give further products.



Scheme 1

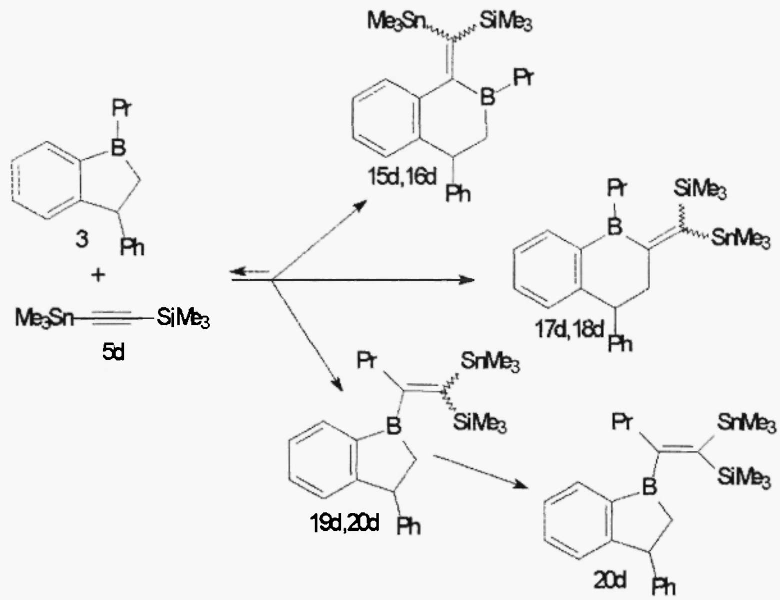
The isomers **6** and **7** are formed in the cases of R^1 = Me, Ph and $SnMe_3$, whereas **7b** is obtained selectively [1]. The isomers **6** do not react or react rather slowly with an excess of the respective 1-alkynyltin compound **5**. In contrast, the isomers **7** are almost as reactive as the 1-boraindan **1** itself. It is remarkable that the diene **9a** is not detected in an appreciable amount in the reaction mixture, but the triene **8a** is obtained instead (even in the presence of only two equivalents of **5a** as compared to **1**). If R^1 = ^{t}Bu or Ph, the dienes **9b**,**c** are the preferred products, starting from **7b**,**c** and **5b**,**c**. It has been reported [6] that a similar diene may completely change its configuration at the C=C bonds after heating at 80°C for some time. The samples of **8a** and **9b**,**c** were kept for prolonged time at room temperature and no changes were noted. Therefore, it is assumed that the same configuration at the C=C bonds is present as in **7a**-**c**. The diene **9b** rearranges slowly to an allene, presumably of type **12**. After several weeks, the typical ^{13}C NMR signals of the allene unit appear, and there is the characteristic absorption in the IR spectrum with ν_{as}(C=C) = 1875 cm^{-1}. An excess of **5e** leads to the allenes **11e** and **12e**. The intermediacy of the dienes **9e** and **10e** must be assumed, but monitoring of the reaction by ^{119}Sn NMR did not reveal the characteristic ^{119}Sn NMR signals of such dienes. The signals for **6e** and, faster, of **7e** lost intensity in favour of growing broad signals (conformational changes; vide infra) in the typical region for such allenes.

The reaction of **2** with an excess of **5e** (Scheme 2) proceeds selectively (in contrast with the analogous reaction of **1** with **5e**) in the first step to give **13e** which reacts with **5e** (at a rate comparable with that for **2**) to the allene **14e**. Again, intermediates were not detected. The selectivity in the first step of the reaction is ascribed to the steric influence of the phenyl group which prevents insertion into the endocyclic B-C$_{alkyl}$ bond.



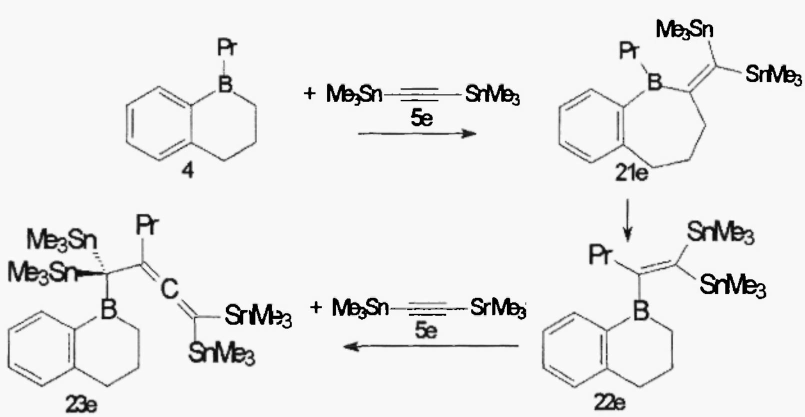
Scheme 2

The reaction of the 1-boraindan derivative **3** with an excess of **5d** was studied because it is known [4c] that **5d** behaves similarly to **5e**, however, it is somewhat less reactive and therefore, the reaction with a second equivalent of **5e** should not interfere with the formation of thermodynamically controlled products. The result of this reaction is shown Scheme 3. After warming the reaction mixture from -78°C to room temperature, a mixture of mainly six compounds was formed together with an excess of **5e**. After 24 h at 25 °C, mainly (> 85 %) a single product (which had been a minor species in the beginning) remains together with **5e**. On the basis of ^{1}H and ^{13}C NMR data, this product is the alkene derivative **20d**, as the result of insertion into the exocyclic B-C$_{propyl}$ bond. After several days at 25°C, allene formation becomes noticeable, and a complex mixture results which was not analysed. Apparently. the steric effect of the phenyl group in 3-position does not help to stabilise the product resulting from insertion into the endocyclic B-C$_{alkyl}$ bond. Insertion into the B-C$_{aryl}$ bond is not favourable either because of the bulky groups at the C=C bond and the neighbourhood to the rigid benzene ring. Further reactions e.g. towards allenes are slow (in contrast with the situation for **13e**). Therefore, the way out is insertion into the exocyclic B-C$_{propyl}$ bond which leads to the thermodynamically controlled products **19d** and **20d**, of which the Z-isomer **20d** seems to be favoured. In order to get this product from the mixture of **15d** - **19d**, sequences of 1,1-organoboration and deorganoboration are necessary. It is known [2] that such processes occur readily if these particular substituents are attached to the C=C bond.



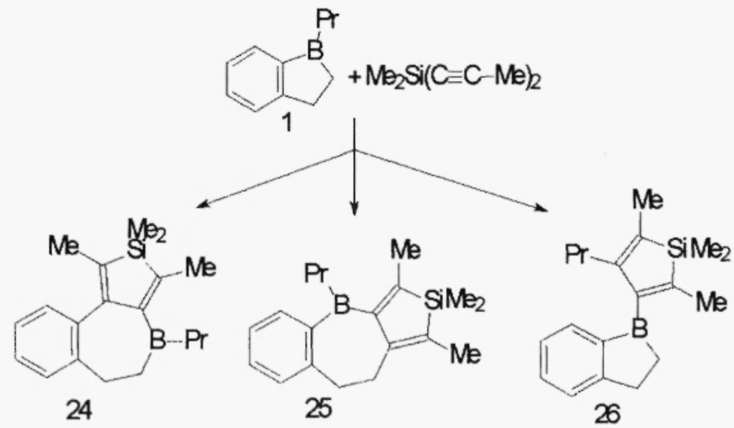
Scheme 3

The NMR data of **20d** prompted us to reinvestigate the reaction of **4** with **5d** and **5f**. It has been reported [1] that **4** reacts selectively with **5e** to the alkene derivative **21e**. Although this may be correct if the reactions are carried out at rather low temperature observing mild reaction conditions as in the case of **6e** and **7e**, the structural assignment based on the reported NMR data [1] turned out to be wrong. If the reaction solutions are allowed to reach room temperature, the thermodynamically controlled products E- **22d** and Z-**22d**, and **22e**, analogous to **19d** and **20d,** are formed by fast deorganoboration and organoboration reactions. In the case of **22e** a further reaction takes place with an excess of **5e** to give the allene **23e** as the sole product (Scheme 4). Intermediates were not detected.



Scheme 4

Finally, the reaction of **1** with dimethyl-di(1-propynyl)silane, $Me_2Si(C{\equiv}CMe)_2$ was studied. This reaction was complete after heating in boiling toluene for 72 h. A mixture of three silole derivatives **24** - **26** (ratio 1 : 0.8 : 0.6) was formed (Scheme 5). This corresponds to the finding that $Me_2Si(C{\equiv}CMe)_2$ reacts with thermally stable trialkylboranes such as Et_3B to give siloles [7].



Scheme 5

NMR spectroscopic results

The proposed structures are in agreement with the NMR data sets. ^{11}B NMR spectra showed broad signals all in the region of δ^{11}B 75 ± 2 which was not helpful for analysis. ^{1}H NMR spectra were rather complex in most cases, except for the typical regions of Me_3Sn, Me_3Si or ^{t}Bu groups (these data are not listed). ^{13}C and ^{119}Sn NMR data (see Tables 1 - 5) were particularly useful for structural assignments. The $^{117/119}$Sn satellites in ^{13}C and ^{119}Sn NMR spectra reveal the presence of two or more different tin atoms in the molecules [8]. Further typical features concern broadening of ^{13}C [9] (if a boron atom is linked directly to carbon) and ^{119}Sn resonance signals (if the tin and the boron atoms are linked in vicinal positions to the C=C bond [8,10]). ^{119}Sn NMR is an excellent tool for the analysis of mixtures [11], and this is shown in Figure 1 for the triene **8a** (see Table 1for NMR data) and in Figure 2 for the diene **9c**.

Table 1. ^{13}C and ^{119}Sn NMR data [a] of the triene **8a**

δ^{13}C	**8a**
Me$_3$Sn	-9.0 [319.3] -8.4 [328.1 -7.8 [327.5]
Me-C=	22.9 [48.8, 7.2] 19.2 [72.0, < 4] 18.6 [69.8,6.0]
=C-Sn [b]	132.2 [475.2] 137.6 [514.0] 141.4 [504.0]
=C	146.4 [89.1, 59.2, 30.5] 150.9 [33.0, 25.6]
=C-B	163.2 (broad)
CH$_2$-CH$_2$-C=	36.0 [18.3] 43.7 [46.4]
aryl	141.1 (broad), 148.5, 131.3, 132.5, 125.7, 135.6
CH$_3$-CH$_2$-CH$_2$-B	17.8, 19.4, 24.9 (broad)
δ^{119}Sn	-54.0 [79.0], -46.3 [56.0. 22.0]. -43.3 [22.0]

[a] In $CDCl_3$ at 25°C; coupling constants J(^{119}Sn,^{13}C) [± 1 Hz] and J(^{119}Sn,^{117}Sn) [± 2 Hz] are given in brackets; (broad) denotes a ^{13}C NMR signal of a boron bonded carbon atom (scalar relaxation of the second kind).

The changes in the ^{119}Sn NMR spectra in Figure 1 clearly indicate that the diene **6a** does not react with an excess of **5a**, whereas **7a** reacts rather fast. ^{13}C NMR data support the suggested triene structure (e.g. the signal at δ 146.4 shows three sets of $^{117/119}$Sn satellites).

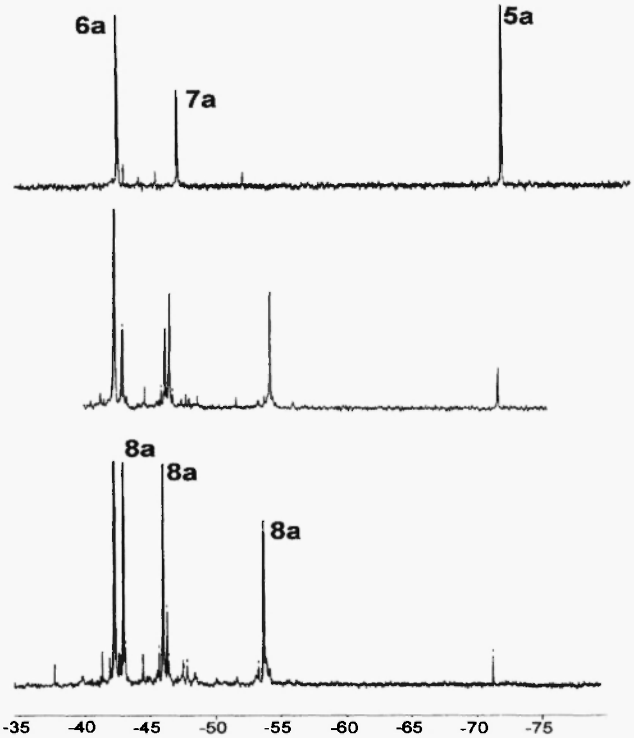


Figure 1. 93.3 MHz ^{119}Sn{^{1}H-inverse gated} NMR spectra of the reaction mixture containing the alkenes **6a** and **7a**, together with Me_3Sn-C≡CMe (**5a**) at -30°C (upper trace), -10°C (middle trace) and +25°C (lower trace). While the signal of **6a** remains unaffected, the signals of **7a** and **5a** loose intensity and the three new signals of the triene **8a** are growing.

Table 2. ^{13}C and ^{119}Sn NMR data[a] of the dienes **9b**, **c**

δ^{13}C	**9b**	**9c**
Me$_3$Sn	-2.6 [313.5][b] -2.3 [318.5]	-7.8 [336.9] -6.3 [329.5]
R^1-C=	40.8 [59.6] 41.6 [42.8, 2.0]; 31.8 [5.7] 32.3 [<4]	142.8 [48.8] 147.7 [43.6][b]
=**C**-Sn[b]	160.6 [497.3] 151.5 [517.0, 12.7]	
=**C**	138.6 [56.4, 21.5]	150.9 [37.2, 23.8]
=**C**-B	162.7 [60] (broad)	169.2 (broad)
CH$_2$-CH$_2$-C=	33.9 [11.7] 38.7 [66.0, 8.5]	33.9, 41.4 [41.3]
aryl	139.7 (broad), 150.5, 129.7, 130.9, 126.0, 134.8	not assigned
CH$_3$-CH$_2$-CH$_2$-B	18.5, 23.5, 29.2 (broad)	18.0, 18.9, 28.7 (broad)
δ^{119}Sn	-61.2 [38.7] -67.1 [broad]	-43.3 [30] -51.3 [30] [broad]

[a] In $CDCl_3$; **9b** at 25°C; **9d** at -40°C (^{13}C NMR) and 25°C (^{119}Sn NMR); coupling constants J(^{119}Sn,^{13}C) [± 1 Hz] and J(^{119}Sn,^{117}Sn) [± 2 Hz] are given in brackets; (broad) denotes a ^{13}C NMR signal of a boron bonded carbon atom (scalar relaxation of the second kind); [broad] denotes broadening as a result of dynamic processes.

Figure 2 also shows that the isomer **6c** does not react with an excess of **5c**, whereas **7c** reacts, and the diene **9c** (Table 2) is formed. The expansions show the $^{117/119}$Sn satellites with a splitting typical of ^{5}J(Sn,Sn) across a butadiene system. Together with ^{13}C NMR data (Table 2), this supports the diene structure of **9c**.

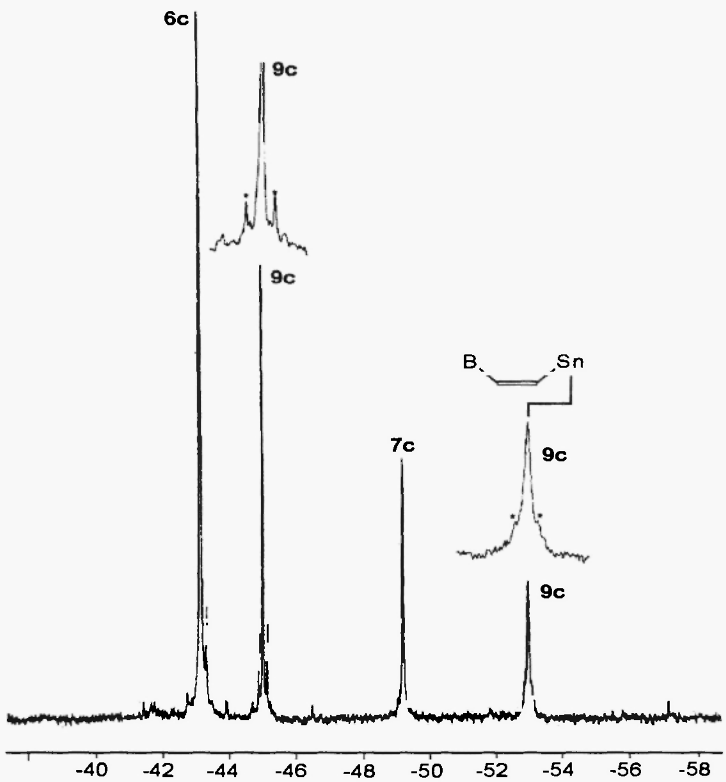


Figure 2. 111.9 MHz $^{119}Sn\{^1H$-inverse gated$\}$ NMR spectrum of the reaction mixture containing **6c**, **7c** and an excess of **5c**, recorded after slowly warming from -78°C to room temperature. $^{117/119}Sn$ satellites are marked with asterisks. The broader ^{119}Sn NMR signal is assigned to the Sn nucleus in *cis*--position to the boron atom (partially relaxed scalar ^{119}Sn-^{11}B coupling).

The allenes **11e**, **12e**, **14e** possess fluxional structures with respect to the conformation of the seven-membered rings which cause broad signals in both ^{13}C and ^{119}Sn NMR spectra. The NMR signals of **23**e are also broad, but in this case there is restricted rotation about CC and BC bonds, as has been observed previously [12]. The data given in the Tables 3 - 5 represent the best resolution obtained at various temperatures. The best ^{119}Sn NMR spectrum at low temperature was recorded for the allene **14e** (Figure 3), showing four different tin sites both for the abundant and less abundant isomer. It is assumed that these isomers differ with respect to equatorial and axial positions of the phenyl substituent. The pattern of the $^{117/119}Sn$ satellites (see Table 4) indicates that the magnitude of $^5J(Sn,Sn)$ depends on the dihedral angles formed by the respective Sn-C bonds. This is in agreement with previous results for an allene with a rigid structure, where a small value $^5J(Sn,Sn)$ has been measured [5] corresponding to a dihedral angle of close to 90°. In the meantime, X-ray structural data of such allenes have been obtained [6,12] which are also in support of these arguments. The large values $^5J(Sn,Sn)$ can then be assigned to dihedral angles either close to zero or 180°.

In the case of the allene **23e** (see Table 5), it proved possible to measure $^1J(^{119}Sn,^{13}C)$ = 155 Hz for the carbon atom linked to the two tin and one boron atom. This small value has been interpreted as the result of hyperconjugative effects [12,14].

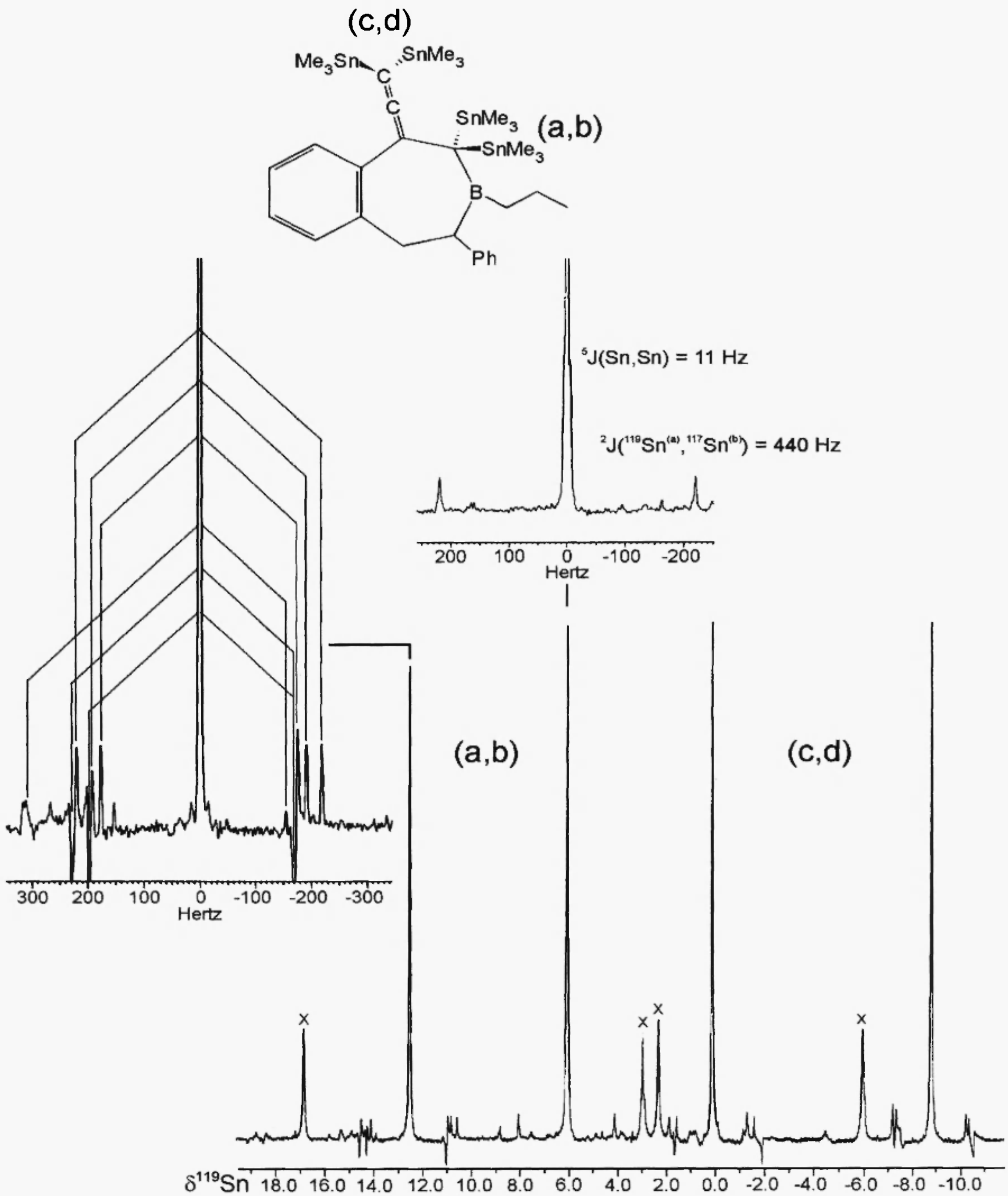


Figure 3. 111.9 MHz $^{119}Sn\{^1H\}$ NMR spectrum of **14e**, recorded at -50°C in $CDCl_3$ by using the refocused INEPT pulse sequence [13], based on $^2J(^{119}Sn,^1H)$ = 50 Hz. The signals of the minor isomer (see text) are marked. The expansions show the pattern of $^{117/119}Sn$ satellites for the $(Me_3Sn)_2C(B)$-group. The satellites which are out of phase belong to the $^{119}Sn/^{119}Sn$ isotopomer, for which the magnetisation due to homonuclear ^{119}Sn-^{119}Sn coupling is not correctly refocused in the INEPT experiment.

Table 3. ^{13}C and ^{119}Sn NMR data of the allenes **11e** and **12e**

δ^{13}C	**11e**	**12e**
(Me_3Sn)$_2$C=	-3.5 [316][b]	-7.1 [326.5]
(**Me_3**Sn)$_2$C(B)	-3.5 [316][b]	-6.3 [327.8]
=**C**(Sn)$_2$	81.7 [279.6, 8.5]	81.0 [288.3, 7.3]
=**C**=	206.5 [39.7, 30.5]	208.3 [39.7, 33.6]
=**C**	92.7 [72.0, 18.3]	87.7 [73.2, 19.5]
C(B)(Sn)$_2$	46.8 (broad)	45.0 (broad)
-CH_2-CH_2-	30.7, 32.4 (broad)	41.6 [18.3] 34.0 [73.2, 19.5] ?????
aryl	143.3 [16.5] 144.1, 125.4, 128.3, 125.5, 126.5	147.0 (broad) 142.7, 125.5, 128.4, 127.1, 129.2
CH_3-CH_2-CH_2-B	18.0, 19.9, 31.7 (broad)	18.2, 20.2, 26.9 (broad)
δ^{119}Sn	-9.8 [broad] (Sn)$_2$C= -0.4 [broad] (Sn)$_2$C(B)	-13.3 [199.1, 369.3] [broad] (Sn)$_2$C= -1.4 [broad] (Sn)$_2$C(B)

[a] In $CDCl_3$; at -30°C (^{13}C NMR) and 25°C (^{119}Sn NMR); coupling constants J(^{119}Sn,^{13}C) [± 1 Hz] and J(^{119}Sn,^{117}Sn) [± 2 Hz] are given in brackets; (broad) denotes a ^{13}C NMR signal of a boron bonded carbon atom (scalar relaxation of the second kind); [broad] denotes broadening as a result of dynamic processes. - [b] Signals and satellites overlap

Table 4. ^{119}Sn NMR data of the allene **14e** (-50°C in $CDCl_3$)

	(Me_3Sn)$_2$C=	(**Me_3Sn**)$_2$C(B)
δ^{119}Sn	0.1, -8.8	12.5, 6.1
$^2J(^{119}Sn,^{117}Sn)$	320.0	440.0
$^5J(^{119}Sn,^{117}Sn)$	384.5 352.6	352.6, 11.0
$^5J(^{119}Sn,^{117}Sn)$	384.5	11.0
minor isomer		
δ^{119}Sn	2.4, -6.0	16.8, 2.8
$^2J(^{119}Sn,^{117}Sn)$	332.0	432.0
$^5J(^{119}Sn,^{117}Sn)$	16.0	340.0, 354.0, 16.0

Table 5. ^{13}C and ^{119}Sn NMR data of the allene **23e**

δ^{13}C	**23e**
(**Me_3**Sn)$_2$C=	-5.6 [319.8]
(**Me_3**Sn)$_2$C(B)	-3.4 [312.5]
=**C**(Sn)$_2$	84.6 [288.3, 7.3]
=**C**=	208.1 [40.9, 34.8]
=**C**	92.7 [75.7, 25.0]
C(B)(Sn)$_2$	47.5 [155.0, 25.0] (broad)
CH_3-CH_2-CH_2-C=	14.4, 21.6, 39.8 [25.6, 19.5]
aryl	(broad), 149.0, 128.3, 130.9,124.9, 135.5
-CH_2-CH_2-CH_2-B	34.4, 23.8, 28.1 (broad)
δ^{119}Sn	3.2 [broad] (Sn)$_2$C(B), -14.9 [broad] [270.0, 427.0] (Sn)$_2$C=
δ^{119}Sn (-40°C)	16.9, -3.6 (Sn)$_2$C(B), -10.2, -17.8 (Sn)$_2$C=

[a] In $CDCl_3$; at 25°C; coupling constants J(^{119}Sn,^{13}C) [± 1 Hz] and J(^{119}Sn,^{117}Sn) [± 2 Hz] are given in brackets; (broad) denotes a ^{13}C NMR signal of a boron bonded carbon atom (scalar relaxation of the second kind); [broad] denotes broadening as a result of dynamic processes. - [b] Signals and satellites overlap

The mixture containing the alkene derivatives **15d** - **20d** was studied by ^{29}Si and ^{119}Sn NMR spectroscopy. After warming to room temperature, both the ^{29}Si and ^{119}Sn NMR spectra showed mainly six signals ($\delta^{29}Si$ -5.3 [89.0], -5.5 [88.5], -5.7 [90.0], -8.7 [88.0], -8.8 [87.5], -9.1 [89.0}; $\delta^{119}Sn$ -62.4, -64.4, -56.4, -46.1, -42.7, -51.0). The structure of the main product **20d** (which is a minor product in the beginning, and is left as the main product after 48h at room temperature) could be deduced from ^{29}Si, ^{119}Sn and in particular from the ^{13}C NMR spectra (Table 6), which shows the signals of a propyl group with $^{117/119}Sn$ satellites linked to the C=C bond. This propyl group is also identified in ^{1}H NMR spectra where the connectivity of CH_3-CH_2-CH_2 follows from 500 MHz 2D $^{1}H/^{1}H$ COSY as well as from 1D homonuclear selective $^{1}H\{^{1}H\}$ experiments. Together with the appropriate 2D $^{13}C/^{1}H$ HETCOR experiment, the assignment of this propyl group is complete.

Table 6. ^{13}C, ^{29}Si and ^{119}Sn NMR data of the alkene derivative **20d**

$\delta^{13}C$	**20d**
Me$_3$Sn	-4.7 [304.0]
Me$_3$Si	1.8
=**C**(Si)Sn	145.6 [306.0]
=**C**-B	145.0 (broad)
=**C**	92.7 [75.7, 25.0]
-**CH**-**CH$_2$**-B	51.6, 38.9 (broad)
aryl	not assigned
CH$_3$-**CH$_2$**-**CH$_2$**-C=	14.7, 23.9 [9.2], 46.0 [110.0]
$\delta^{119}Sn$ / $\delta^{29}Si$	-64.4 / -5.5 [88.5]

[a] In $CDCl_3$; at 25°C; coupling constants $J(^{119}Sn,^{13}C)$ [± 1 Hz] and $J(^{119}Sn,^{117}Sn)$ [± 2 Hz] are given in brackets; (broad) denotes a ^{13}C NMR signal of a boron bonded carbon atom (scalar relaxation of the second kind).

The siloles **23** - **25** were identified mainly from the three signals ($\delta^{29}Si$ 7.4, 6.9 and 6.5) in ^{29}Si NMR spectra in the region typical of siloles [7], and also from the pattern of ^{13}C NMR signals: 13 sharp signals for quaternary aromatic and olefinic carbon atoms; 5 broad signals for quaternary aromatic and olefinic carbon atoms linked to boron; 12 sharp signals for tertiary aromatic carbon atoms; 4 broad signals for **CH$_2$-B** groups; 9 sharp signals for methyl groups, and 8 sharp signals for **CH$_2$** groups.

EXPERIMENTAL

All necessary precautions were observed to exclude oxygen and moisture during the synthesis and handling of the compounds. The boranes **1** - **4** [15], the 1-alkynyltin compounds **5** and dimethyl-di(1-propynyl)silane [16] were obtained following the literature procedures. All NMR spectra were recorded either on Bruker ARX 250, Bruker AC 300 or Bruker DRX 500 spectrometers. Chemical shifts are given with respect to Me_4Si [$\delta^{1}H$ ($CHCl_3/CDCl_3$) = 7.24, ($C_6D_5CD_2H$) = 2.03, $\delta^{13}C$ ($CDCl_3$) = 77.0, ($C_6D_5CD_3$) = 20.4; $\delta^{29}Si$ = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz], BF_3-OEt_2 [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz], and M_4Sn [$\delta^{119}Sn$ = 0 for $\Xi(^{119}Sn)$ = 37.290665 MHz]. The assignment of ^{1}H and ^{13}C NMR signals was based on routinely performed 2D $^{1}H/^{1}H$ COSY and 2D $^{13}C/^{1}H$ HETCOR experiments. IR spectra: Perkin Elmer 983 G; for all allenes: ν_{as}(C=C) 1870 -1880 cm^{-1}.

NMR spectroscopic characterisation of **2** *and* **3** (see ref [1] for **1** and **4**); **2**: ^{11}B NMR (80.3 MHz, 25°C, $CDCl_3$); δ = +83.0; ^{13}C NMR (62.9 MHz, 25°C, $CDCl_3$): δ = 46.2 (broad) (2), 43.0 (3), 164.0 (3a), 125.3 (4), 133.5 (5), 125.9 (6), 133.5 (7), 143.2 (broad) (7a); 24.9 (broad), 18.6, 17.7 (B-$CH_2CH_2CH_3$); 144.4, 127.8, 128.4, 124.7 (2-Ph); **3**: ^{11}B NMR (80.3 MHz, 25°C, $CDCl_3$); δ = +83.0; ^{13}C NMR (62.9 MHz, 25°C, $CDCl_3$): δ = 37.2 (broad) (2), 50.9 (3), 166.9 (3a), 126.5 (4), 133.4 (5), 125.9 (6), 131.7 (7), 144.3 (broad) (7a); 25.3 (broad), 19.2, 17.7 (B-$CH_2CH_2CH_3$); 147.6, 127.5, 128.4, 125.6 (3-Ph).

1,1-Organoboration reactions. General procedure. Up to 3 mmol of the 1-alkynyltin compound **5** were dissolved in 15 ml of hexane. The stirred solution was cooled to -78°C and the borane 1mmol or less was added in one portion. The solution were slowly warmed to room temperature while stirring was continued. The progress of the reactions was monitored by taking samples at -30°C, -10°C and 25°C for ^{119}Sn NMR measurements. The measurements were repeated after 24h and 48h at room temperature. In the case of the reaction of **1** with dimethyl-di(1-propynyl)silane (1 : 1), the compounds were dissolved in toluene and the solution was heated at 110 - 115°C for 72h. The completeness of the reaction was indicated by ^{29}Si NMR. The mixtures of alkenes and dienes or the triene, all allenes, and the siloles were obtained as colourless to yellowish, oily liquids, sensitive to air and moisture. Attempts at crystallisation were not successful.

In the case of **7b**, an improved and correct ^{13}C NMR data set was recorded: ^{13}C NMR (125.8 MHz, 20°C, $CDCl_3$): $\delta^{13}C$ [$J(^{119}Sn,^{13}C)$] = -2.2 [316.8] Me_3Sn; 30.5 broad, 20.0, 18.4 B-$CH_2CH_2CH_3$; 40.0 [55.6], 32.8 [26.0] $C(CH_3)_3$; 37.6 [97.0], 35.8 [10.6] CH_2CH_2-aryl; 139.4 broad, 150.5, 128.1, 132.3, 125.9, 134.7 aryl; 165.9 [535.2] Sn-C=; 161.3 [66.0] broad, B-C=.

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