ELSEVIER

Journal of Organometallic Chemistry 541 (1997) 97–107

Journal of Organometallic Chemistry

1,1-Organoboration of mono-1-alkynyltin compounds using dialkyl(*N*-azolyl)boranes-stepwise ring enlargement of boron heterocycles [1]

Bernd Wrackmeyer [a,*], Heidi E. Maisel [a], Bernd Schwarze [a], Wolfgang Milius [a], Roland Köster [b]

[a] *Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany*
[b] *Max-Planck-Institut für Kohlenforschung, D-45466 Mülheim a.d. Ruhr, Germany*

Received 12 December 1996; accepted 15 December 1996

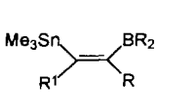
Abstract

Mono-1-alkynyltin compounds **1–4** ($Me_3Sn-C\equiv CR^1$; $R^1 = H$ (**1**), Me (**2**), Ph (**3**), $SnMe_3$ (**4**)) react with various dialkyl(*N*-azolyl)boranes **5–9** (azolyl = pyrrolyl (**a**), 2,5-dimethylpyrrolyl (**b**), indolyl (**c**), carbazolyl (**d**)) stereospecifically by 1,1-organoboration to give organometallic-substituted alkenes **10–20**, **22–25**, with the trimethylstannyl and the boryl group in cis-positions at the C=C bond. These reactions proceed via an alkynylborate-like zwitterionic intermediate ZI, and exchange of the azolyl against the 1-alkynyl group may compete (Eq. (1)(b)) with the 1,1-organoboration (Eq. (1)(a)), depending on the reactivity of the boron carbon bonds and the steric requirements. It is also shown that in addition to the products formed in the reactions with 1:1 stoichiometry other products result from the reaction of two equivalents of **1** with one equivalent of the borane. These products may be either 1,3-butadiene derivatives or allenes formed by allylic rearrangement. All products were characterized by ^1H, ^{11}B, ^{13}C and ^{119}Sn NMR. The molecular structure of the allene **24a** was determined by X-ray structural analysis. © 1997 Elsevier Science S.A.

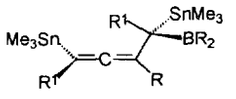
Keywords: Tin; 1,3-Butadienes; 1,1-Organoboration; Allylic rearrangement; Stepwise ring enlargement; X-ray analysis

1. Introduction

Acetylene chemistry is an active research area [1], and the presence of organometallic substituents enhances the synthetic potential of alkynes. Alkynyltin compounds are readily available [2] and serve as prominent examples for the influence of organometallic substituents on the reactivity of alkynes. Thus, the remarkably facile 1,1-organoboration of 1-alkynyltin compounds by triorganoboranes has opened numerous useful synthetic routes to organometallic-substituted alkenes (**A**), allenes (**B**), and various heterocyclic compounds (**C**, **D**, **E**), to name some examples [3].

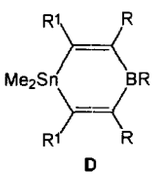


A

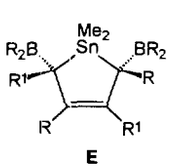


B

C



D



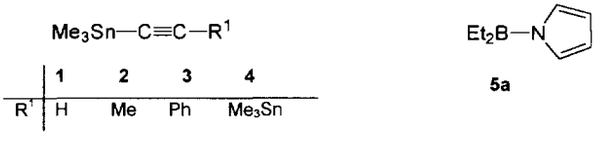
E

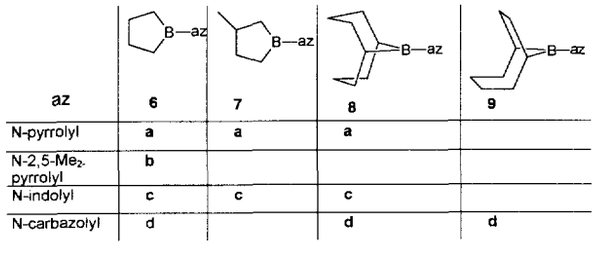
* Corresponding author.

[1] Dedicated to Professor G. Huttner on the occasion of his 60th birthday.

PII S0022-328X(97)00019-3

Many of these products are of considerable interest for further transformations either at the site of the tin or the boron atom. In the latter case, the synthetic potential would be much greater with a functional group attached to boron. However, all attempts to use alkoxy(dialkyl)boranes or dialkyl(amino)boranes instead of triorganoboranes in 1,1-organoboration reactions proved to be unsuccessful [4]. The exceptional reactivity of the *N*-pyrrolyl group in **5a** towards $Et_2C{=}O$ was demonstrated many years ago [5] forming a new type of boron heterocycle. In recent studies on *N*-azolylboranes [6–8] we have found that the *N*-azolyl group behaves more as an aryl than an amino substituent. Therefore, we have now studied the reactivity of the dialkyl(*N*-azolyl)boranes **5–9** towards the mono-1-alkynyltin compounds **1–4**.

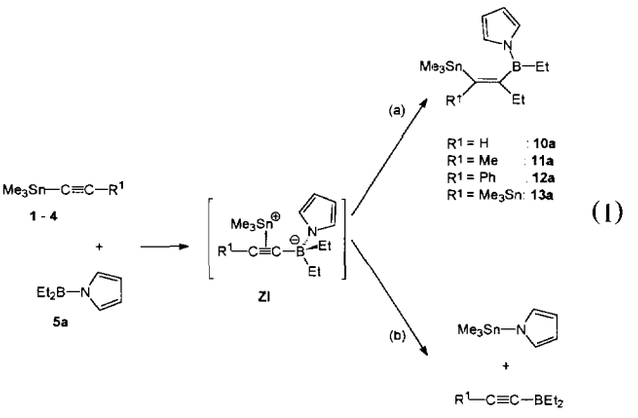




2. Results and discussion

2.1. Reactions of mono-1-alkynyltin compounds 1–4 with diethyl(N-pyrrolyl)borane 5a

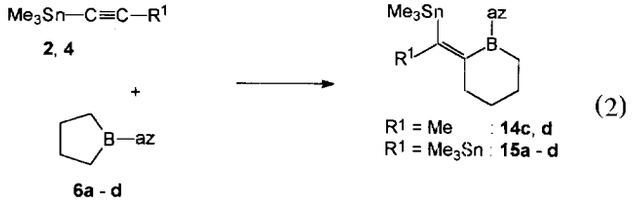
The mono-1-alkynyltin compounds **1–4** react stereoselectively with diethyl(*N*-pyrrolyl)borane **5a** by 1,1-organoboration to give the alkenes **10a–13a** in quantitative yield as extremely air-sensitive, colourless to yellowish, oily liquids or as a colourless solid (**13a**) (Eq. (1)(a)). There is no evidence for the transfer of the *N*-pyrrolyl group from boron to carbon and also not for (Eq. (1)(b)). The reaction is somewhat slower than the 1,1-organoboration with triethylborane [3]. The configuration at the C=C bond in **10a–13a** follows from the $^1H/^1H$ NOE difference spectra [9] and the consistent data set of all NMR data (vide infra).



(1)

2.2. Reactions of mono-1-alkynyltin compounds 2,4 with 1-(N-azolyl)-1-boracyclo-pentanes 6,7

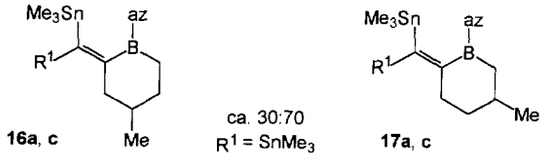
It is known that 1-organo-1-borolanes react with mono-1-alkynyltin compounds to give six-membered rings with an exocyclic C=C bond, and, in general, a mixture of *E/Z*-isomers is obtained [10]. Furthermore, the reaction is readily reversible (deorganoboration) [10]. In the reaction of the 1-*N*-azolylborolanes **6a,d**, with **2** the five-membered ring is also extended in each case and the *E*-isomers **14c** are formed stereospecifically, again in quantitative yield (Eq. (2)). The borinane ring in **14** appears to be reasonably stable with respect to deorganoboration. Similarly, the compounds **15** are formed in quantitative yield. However, distillation of **14** and **15** under reduced pressure leads to decomposition.



(2)

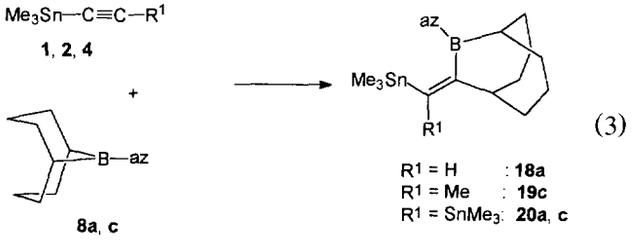
If one starts with the 1-*N*-azolyl-3-methylborolanes **7a,c**, a mixture of 1-*N*-azolyl-4-methylborinanes **16a,c** and 1-*N*-azolyl-5-methylborinanes **17a,c** (ratio ca. 30:70)

is obtained. The insertion takes place preferably at the site which is more distant from the methyl group.



2.3. Reactions of mono-1-alkynyltin compounds 1,2,4 with 9-(N-azolyl)-9-borabicyclo[3.3.1]nonanes 8 and 9-(N-carbazolyl)-9-borabicyclo[4.2.1]nonane 9d

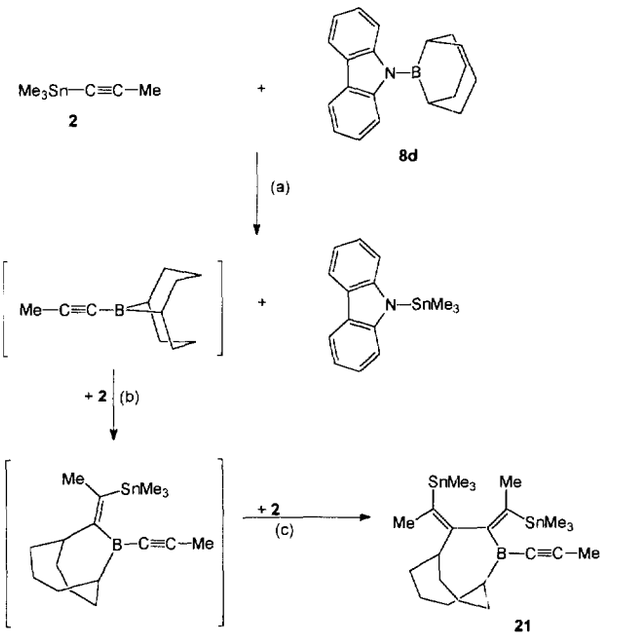
Products with the extension of the 9-borabicyclo[3.3.1]nonane system are formed as the result of the kinetical control of the reaction, as was shown for the reaction of 9-ethyl-9-borabicyclo[3.3.1]nonane with compounds of type **1–4** [11,12]. The analogous products **18–20** were formed in the reaction of **8a** or **8c** with **1,2,4** (Eq. (3)).



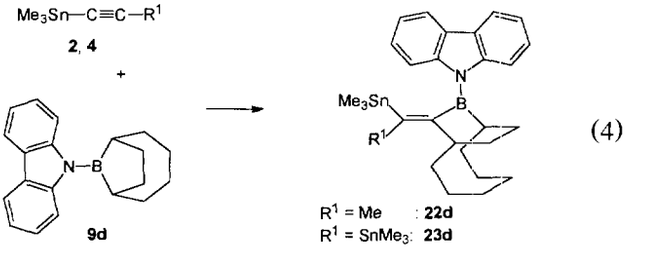
(3)

However, in the case of **8c** a side reaction takes place which becomes dominant in the reaction of **8d** with **2** and **4**: exchange of the *N*-azolyl group against the 1-alkynyl group (see Eq. (1)(b)), to give *N*-trimethylstannyl-carbazole and 9-alkynyl-9-borabicyclo-[3.3.1]nonane. This was studied in detail for the reaction of **8d** with **2** (Scheme 1). By using an excess of **2** the final products can be identified as *N*-trimethylstannyl-carbazole and the 9-borabicyclo[3.3.3]undecane derivative **21** which results from the stepwise reaction of 9-(1-propynyl)-9-borabicyclo[3.3.1]nonane with two equivalents of **2** (Scheme 1 (b)/(c)). The 9-borabicyclo[3.3.2]decane derivative of the 1:1 reaction could not be identified.

This competition between the reaction according Eq. (1)(a) and Eq. (1)(b) becomes effective in the case of steric crowding and if the extension of the bicyclic system is not a particularly strong driving force, as is evident for the 9-borabicyclo[3.3.1]nonane system [11]. The latter argument can be proved by studying the analogous reaction of **9d** [8] where we are dealing with a 9-borabicyclo[4.2.1]nonane system. The five-membered part of the bicycle should be the most reactive site for 1,1-organoboration, readily available for ring extension. Indeed, the reactions of **9d** with **2** and **4** lead mainly to the 1,1-organoboration products **22** and **23** with a 9-borabicyclo[4.2.2]decane group (Eq. (4)). The 1-alkynylazolyl exchange as in Scheme 1(a) is only a side reaction (10–30%).



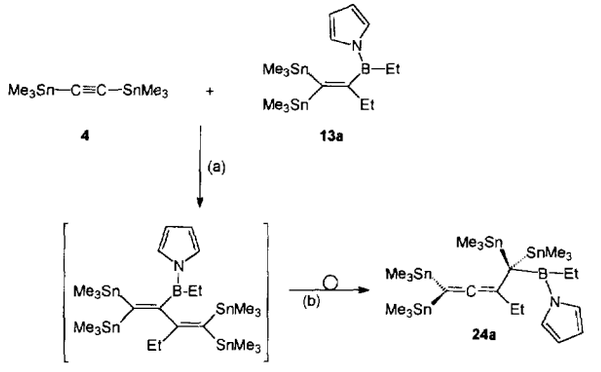
Scheme 1.



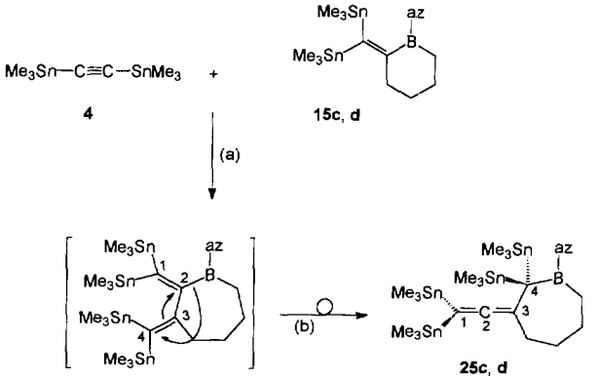
(4)

2.4. Reaction of the 1,1-organoboration products 13a and 15c,d with bis(trimethylstannyl)ethyne 4, a route to organometallic-substituted allenes

Organometallic-substituted allenes become available from the reaction of triorganoboranes with certain mono-1-alkynyltin compounds in a 1:2 ratio [13,14]. As shown in Scheme 2, the same route is open for diethyl(*N*-pyrrolyl)borane (**5a**). The reaction can be carried out either by starting with **13a** (as shown) or by starting with **5a** and two equivalents of **4**, without isolating the alkene **13a**. This is a quantitative reaction and the allene **24a** can be isolated as a colourless crystalline solid. Suitable crystals for X-ray analysis (vide infra) can be obtained from hexane at −78 °C.



Scheme 2.



Scheme 3.

The 1,3-butadiene derivative shown in Scheme 2 is the most likely intermediate on the way to the allene **24a**. The facile 1,3-allyl migration of the boryl group to **24a** requires a certain conformation of the butadiene system which is readily reached by non-cyclic systems but may be less favourable for cyclic systems. However, the reaction of the borinanes **15c,d** with **4** proceeds smoothly solely to the allenes **25c,d** with a borepane ring (Scheme 3). Therefore, repulsive forces between trimethylstannyl groups must be the driving force of the rearrangement to the allene. Again a borepane cycle is formed; however, the carbon atom C-4 is now part of the cycle and carbon atom C-2 has become part of the allene system (see Scheme 3).

2.5. X-ray structural analysis of the allene *24a*

Data relevant to the structure are given in Section 4.2. [2] The molecular structure of **24a** is shown in Fig. 1. The structure is closely related to that of the corresponding allene obtained by 1,1-organoboration of two equivalents of **4** with triethylborane [14]. The allene unit is almost linear (angle C(1)–C(2)–C(3) = 174.0(5)°), and the angle between the planes Sn(1)C(1)Sn(2) and C(4)C3)C(5) is 90.50°, as expected for an allene. The bond lengths Sn–C are in the normal range except of Sn(3)–C(4) and Sn(4)–C(4) (219.8(4) and 220.7(4) pm) which are elongated as a result of Sn–C hyperconjugation. This has been observed for similar structures [14] and also for other organotin compounds containing an electron deficient boron atom [15,16]. The B–N bond (146.2(7) pm) in **24a** must be regarded as a single bond between sp^2 hybridized boron and nitrogen atoms. Since the plane of the pyrrole ring is only slightly twisted (20.3°) against the plane BC(4)C(19)N, this would in principle allow for significant BN(pp)π interactions. However, the long B–N bond, which is markedly longer than in typical aminoboranes (range of ca. 138–144 pm [17]), and even longer than in tris(2,5-dimethylpyrrolyl)borane where the pyrrolyl rings are severely twisted against the BN_3 plane [6], indicates that such π interactions must be rather weak.

2.6. NMR spectroscopic results

All NMR spectroscopic data support the proposed structures. ^{11}B, ^{13}C, ^{119}Sn NMR data of the alkenes are given in Table 1 (**10–13**), Table 2 (**14,15**) and Table 3(**18–20**, **22**, **23**). Table 4 contains NMR data of the bicyclic 1,3-diene **23**, and Table 5 lists the ^{11}B, ^{13}C and ^{119}Sn NMR data of the allenes **24** and **25**. ^{1}H NMR data and additional ^{13}C of the azolyl groups are given in Section 4. The ^{1}H and ^{13}C NMR signals were assigned by the usual 1D and 2D techniques. In the case of the ^{13}C NMR signals, $^{117/119}Sn$ satellites according to the coupling constants $J(^{117/119}Sn,^{13}C)$, and the broadening owing to partially relaxed scalar one-bond $^{13}C–^{11}B$ coupling serve as additional criteria.

Straightforward information on the progress of the reactions and the product distribution is provided by ^{119}Sn NMR spectra of reaction solutions (see Fig. 2).

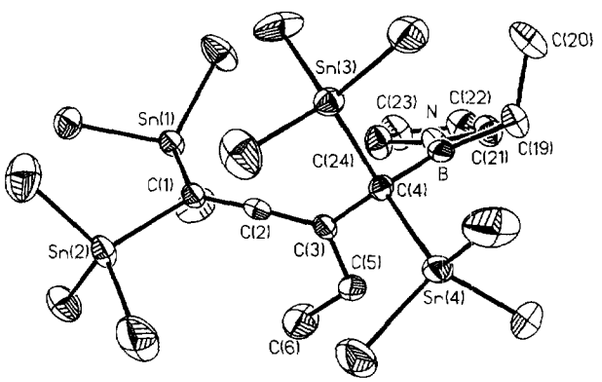
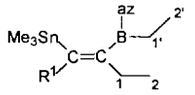


Fig. 1. Molecular structure of **24a**.

[2] Further details of the crystal structure are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-406408, the names of the authors and the journal citation.

Table 1
^{11}B, ^{13}C and ^{119}Sn NMR data [a] of the alkenes **10–13**



No.		**10a**	**11a**	**12a** [b]	**13a** [c]
R^1		H	Me	Ph	$SNMe_3$
az		pyrrolyl	pyrrolyl	pyrrolyl	pyrrolyl
$\delta^{11}B$		53.9	53.7	53.3	53.5
$\delta^{119}Sn$		−53.0	−45.3	−45.8	−44.8
$\delta^{13}C$ [$J(^{119}Sn,^{13}C$]	=CSn	132.0 [482]	140.3 [513]	148.9 [465]	147.8
	=CB	165.9 [br]	155.6 [br]	157.1 [br]	178.1 [br]
	C-1	34.0 [87.5]	23.6 [74.6]	26.8 [65.4]	38.5 [129] [112]
	C-2	14.2 [6.0]	13.0 [9.4]	14.5 [8.6]	14.8 [8.5]
	C-1′	13.8 [br]	12.9 [br]	14.0 [br]	13.1 [br]
	C-2′	9.8	8.9	9.6	9.7
	MeSn	−9.3 [343]	−10.0 [324]	−8.7 [333]	−7.8 [316]
	R^1	−	19.2 [63.8]	— [b]	−5.5 [306]

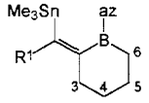
[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling.
[b] $\delta^{13}C(Ph) = 146.1$ [40.4] (C-1′); 128.6 (C-2′/6′); 126.9 (C-3′/5′); 125.3 (C-4′).
[c] $\delta^{119}Sn(R^1) = -55.8$ [br].

Differential broadening of the ^{119}Sn NMR signals as the result of partially relaxed scalar $^{119}Sn-^{11}B$ coupling across three bonds with $|^3J(^{119}Sn,^{11}B)_{trans}| > |^3J(^{119}Sn,^{11}B)_{cis}|$ is always observed for alkenes prepared from the organoboration of **4**. Another example is the ^{119}Sn NMR spectrum of the reaction solution resulting from the organoboration of **2** with **8d** which gave first evidence for the products (*N*-trimethylstannylcarbazole and the bicyclic 1,3-diene **21** (see Scheme 1) with one broad and one sharp ^{119}Sn NMR signal and $^5J(^{119}Sn,^{119}Sn) = 27.9$ Hz) of this fairly complex reaction.

^{11}B NMR spectra are less informative since $\delta^{11}B$ values of starting materials and products are rather similar, with few exceptions, although the larger linewidths of the ^{11}B NMR signals for the products indicate that a reaction has taken place.

There is a complete NMR data set available for alkenes [18,19], analogous to **10–13** in which the pyrrolyl group is replaced by an ethyl group. With

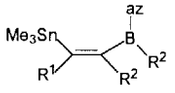
Table 2
^{11}B, ^{13}C and ^{119}Sn NMR data [a] of the alkenes **14**, **15**



No.		**14c**	**14d**	**15a** [b]	**15b** [c]	**15c** [d]	**15d** [e]
R^1		Me	Me	$SnMe_3$	$SnMe_3$	$SnMe_3$	$SnMe_3$
az		indolyl	carbazolyl	pyrrolyl	2,5-$(Me)_2$-pyrrolyl	indolyl	carbazolyl
$\delta^{11}B$		53.5	53.0	52.5	53.5	53.4	52.3
$\delta^{119}Sn$		−42.9	−44.8	−38.2	−44.5	−39.2/−40.0	−43.3
$\delta^{13}C$ [$J(^{119}Sn,^{13}C$]	=CSn	156.2	145.3	152.7 [338][286]	149.6 [342][293]	148.1 [337][289]/155.3 [335][282]	151.7 [603]
	=CB	n.o.	157.0 [br]	177.7 [br]	186.4 [br]	178.8 [br]/179.8 [br]	179.6 [br]
	C-3	33.4 [70.4]	33.2 [71.0]	49.6 [124][110]	48.8 [125][111]	48.2 [123][108]/49.5 [127][109]	48.3 [123][111]
	C-4	28.9	28.9	31.1 [6.7]	30.8	30.3/31.6	30.4 [26.0]
	C-5	26.3	26.7	27.7	27.6	26.7/28.5	27.4 [7.9]
	C-6	22.9 [br]	24.8 [br]	21.7 [br]	25.3 [br]	22.6 [br]/24.4 [br]	25.1 [br]
	MeSn	−8.4 [328]	−8.7 [325.9]	−6.8 [318]	−6.9 [312][10.8]	−6.4 [317][9.0]/−7.0 [313][8.9]	−6.8 [316][10.8]
	R^1	20.1	21.4	−6.0 [307]	−5.8 [303][9.8]	−5.7 [306][9.5]/−6.0 [305][9.8]	−5.9 [305][9.8]

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling.
[b] $\delta^{119}Sn(R^1) = -57.5$.
[c] $\delta^{119}Sn(R^1) = -55.6$.
[d] Rotational barrier at room temperature; $\delta^{119}Sn(R^1) = -56.0/-56.8$.
[e] $\delta^{119}Sn(R^1) = -53.9$.

Table 3
^{11}B, ^{13}C and ^{119}Sn NMR data [a] of the alkenes **18–20**, **22**, **23**



No.		**18a** [b]	**19c** [c]	**20a** [d]	**20c** [e]	**22d** [f]	**23d** [g]
R^1		H	Me	$SnMe_3$	$SnMe_3$	Me	$SnMe_3$
R^2–R^2		1,5-cyclooctanediyl	1,5-cyclooctanediyl	1,5-cyclooctanediyl	1,5-cyclooctanediyl	1,4-cyclooctanediyl	1,4-cyclooctanediyl
az		pyrrolyl	indolyl	pyrrolyl	indolyl	carbazolyl	carbazolyl
$\delta^{11}B$		54.2	56.7	53.0	58.1	58.7	60.8
$\delta^{119}Sn$		−53.0	−43.4	−39.9	−40.1/−42.6	−45.6	−47.7
$\delta^{13}C$ [$J(^{119}Sn,^{13}C)$]	=CSn	144.8 [474]	142.0	161.5	147.8 [587]/158.3 [570]	146.9	160.3
	=CB	169.4 [br]	162.0 [br]	182.6 [br]	182.6 [br]/184.8 [br]	165.7 [br]	181.3 [br]
	$C(R^2)$–C=	49.2 [78.5]	—	−49.8	48.9 [120][112]	37.8 [66.6]	54.9 [113]
	MeSn	−8.2 [348]	−8.0	−5.2 [324]	−5.3 [304][9.8]/−5.5 [305][9.8]	−8.1 [324]	−6.5 [315][9.8]
	R^1	—	21.1	−6.2 [317]	−6.0 [317][9.8]/−6.2 [315][9.8]	26.0	−5.7 [315][9.8]

[a] C_6D_6, 25 °C; [br] broad signal owing to partially relaxed ^{13}C–^{11}B scalar coupling.
[b] $\delta^{13}C$(1,5-cyclooctanediyl) = 34.0 (br, due to slow rotation around the BN bond); 29.6; 25.8 [br]; 23.1.
[c] Coalescence temperature at 25 °C. $\delta^{13}C$(1,5-cyclooctanediyl): not resolved.
[d] $\delta^{13}C$(1,5-cyclooctanediyl = 33.9; 31.6; 31.3; 29.8; 26.2 [br]; 23.5; 22.4; $\delta^{119}Sn(R^1) = -59.7$.
[e] Rotational barrier at room temperature. $\delta^{13}C$(1,5-cyclooctanediyl) = 48.7 [118][110]; 34.9; 33.7; 31.2; 30.9; 30.8; 30.3; 29.9; 29.6; 27.5 [br]; 25.9 [br]; 24.1; 23.8; 23.1; 22.8; $\delta^{119}Sn(R^1) = -46.1/-58.4$.
[f] $\delta^{13}C$(1,4-cyclooctanediyl) = 36.2; 35.3; 32.1; 29.5 [br]; 26.3; 25.3; 21.7.
[g] $\delta^{13}C$(1,5-cyclooctanediyl): = 35.7; 35.2; 24.5; 30.5 [br]; 26.1; 25.5; $\delta^{119}Sn(R^1) = -57.3$; $^2J(^{119}Sn,^{119}Sn) = 897$ Hz.

respect to these compounds one observes in **10–13** a fairly constant shift of the $^{13}C(Sn-C=)$ resonances to higher frequencies (ca. 7–8 ppm) and of the $^{13}C(B-C=)$ resonances to lower frequencies (ca. 6–8 ppm). The latter effect is in the same direction and in a similar range as for the $^{13}C(BCH_2)$ resonance and, therefore, it is related mainly to σ-bonding, whereas the change in the $^{13}C(Sn-C=)$ signal is related to the effect of the boryl group on the σ and π interactions of the C=C bond. The temperature dependence of the ^{1}H and ^{13}C NMR spectra of the alkenes **10–20** is analogous to that studied for similar alkenes [20]. The plane of the boryl group is preferably oriented orthogonal to the C=CB plane [21], and at the same time there is restricted rotation about the B–N bond for steric reasons. In any case, the difference in the influence on the bonding situation in the alkene exerted by an *N*-azolyl(alkyl)boryl or the dialkylboryl group appears to be small since the changes in the $\delta^{119}Sn$ values are small. In general, ^{119}Sn nuclear magnetic shielding is very sensitive to small changes in the bonding situation [22]. However, in the case of the alkenes **10–13**, ^{119}Sn nuclear shielding is reduced only by 2–3 ppm when compared with the analogous diethylboryl compounds [18,19].

The solid-state structures of the allene **24a** and its Et_2B analogue [14] are similar, and this is also true for relevant NMR data. In the case of the cyclic derivatives **25c** and **25d**, one notes the influence of the steric requirements of the carbazolyl group in particular for the $\delta^{11}B$ and the $\delta^{119}Sn$ values (Table 5). In contrast to **24a** and **25c** the ^{119}Sn NMR signals of **25d** are close together (see Fig. 3) and the ^{119}Sn satellites show the typical pattern of an AB spin system. Since the molecular structure of **24a** (Fig. 1) shows four different surroundings for the Me_3Sn groups, ^{1}H, ^{13}C and ^{119}Sn NMR spectra were measured at low temperature. At −50 °C, one observes four different ^{1}H, ^{13}C and ^{119}Sn NMR signals for the Me_3Sn groups. As a result of quadrupolar decoupling at low temperature. the ^{13}C NMR signals for boron-bonded carbon atoms become sharp and $^{117/119}Sn$ satellites according to coupling constants $J(^{117/119}Sn,^{13}C)$ become resolved. The fairly small magnitude of $|^{1}J(^{119}Sn,^{13}C)| = 160.0$ and 128.0 Hz for the quaternary aliphatic carbon atom (δ 38.1) supports the concept of Sn–C hyperconjugation. The ^{119}Sn

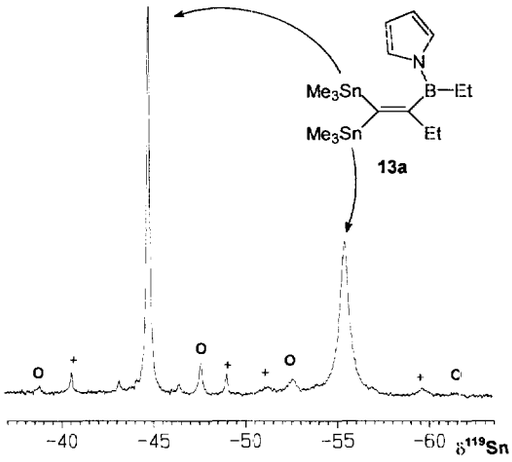
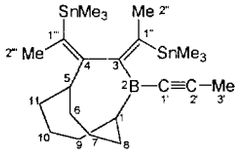


Fig. 2. 93.3 MHz $^{119}Sn\{^{1}H\}$ NMR spectrum (inverse gated) of **13a** in the reaction mixture at room temperature. The ^{119}Sn atom in trans-position to the boron atom shows a broad signal owing to partially relaxed scalar coupling $^{2}J(^{119}Sn,^{11}B)$. The ^{119}Sn satellites represent an AB spin system (indicated with O, $^{2}J(^{119}Sn,^{119}Sn) = 830$ Hz). The ^{117}Sn satellites are indicated with +.

Table 4
^{11}B, ^{13}C and ^{119}Sn NMR data [a] of the butadiene derivative **21** [b]



21

$\delta^{11}B$	$\delta^{119}Sn$		$\delta^{13}C\ [J(^{119}Sn,^{13}C)]$		
	Sn–C-1''	Sn–C-1'''	C-1	C-3	C-4
67.0	−40.0 [b]	−53.1 [b]	35.5 [br]	165.9 [br]	147.2[86.3][26.6]
$\delta^{13}C\ [J(^{119}Sn,^{13}C)]$					
C-5	C-6/7/8/9/10/11		C-1'	C-2'	C-3'
37.1[109][55.1]	21.1/25.1/27.2/28.5/30.0/30.5		91.0 [br]	120.4	5.9
$\delta^{13}C\ [J(^{119}Sn,^{13}C)]$					
C-1''	C-2''	CH_3Sn(C-1'')	C-1'''	C-2'''	CH_3Sn(C-1''')
140.6 [548][9.8]	22.0 [54.1]	−7.1 [331.4]	135.0 [520][11.8]	20.8 [48.3]	−8.3 [320]

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed scalar coupling $^{1}J(^{13}C,^{11}B)$.
[b] $^{5}J[^{118}Sn,^{119}Sn] = 27.9$ Hz.

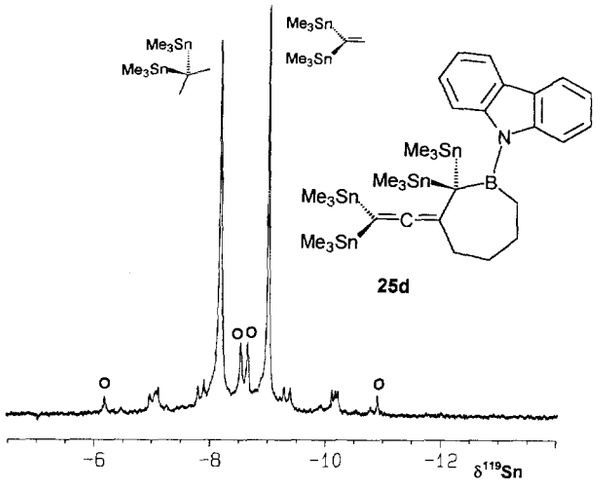


Fig. 3. 93.3 MHz $^{119}Sn\{^1H\}$ NMR spectrum (inverse gated) of **25d** at room temperature. The ^{119}Sn satellites represent an AB spin system (indicated with O, $^5J(^{119}Sn,^{119}Sn) = 219$ Hz). The ^{117}Sn satellites show eight AX spin systems which were not clearly resolved. Two for the respective $^2J(^{119}Sn,^{117}Sn)$ (ca. 224 Hz for $=CSn_2$ and ca. 216 Hz for $B-CSn_2$) and the $^5J(^{119}Sn,^{117}Sn)$ couplings due to the diastereotomers containing ^{117}Sn, and ^{119}Sn isotopomers (see also Ref. [14]).

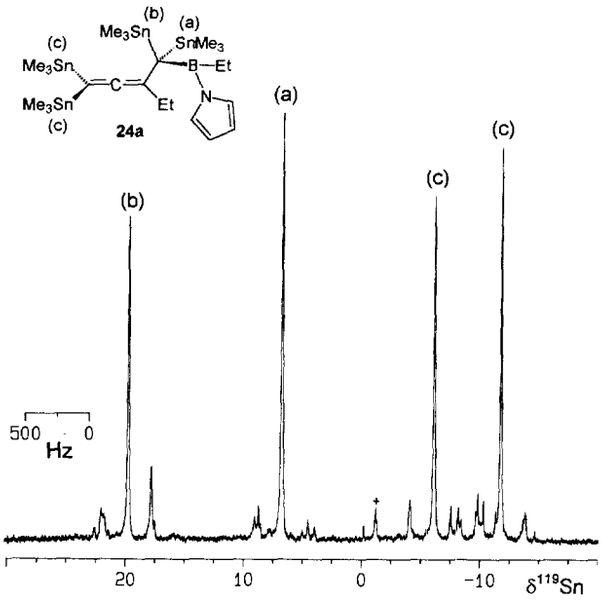
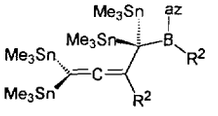


Fig. 4. 93.3 MHz $^{119}Sn\{^1H\}$ NMR spectrum (inverse gated) of **24a** at -50 °C. The splitting of the signals is due to the rotational barrier about the $=C-C$ bond. + indicates an impurity. The $^{117/119}Sn$ satellites are clearly visable: $^2J(^{119}Sn(c),^{119}Sn(c)) = 400$ Hz, $^2J(^{119}Sn(a),^{119}Sn(b)) = 441$ Hz, $^5J(^{119}Sn(a),^{119}Sn(c)) = 387$ Hz and $^2J(^{119}Sn(b),^{119}Sn(c)) = 20$ Hz (not resolved in Fig. 1).

NMR spectrum of **24a** at -50 °C (see Fig. 4) shows that the parent signals are accompanied by all kinds of $^{117/119}Sn$ satellites. In comparison with the averaged room temperature ^{119}Sn NMR spectrum it is evident that there is now one set each of small and large coupling constants $^5J(^{119}Sn,^{119}Sn)$ (ca. 20 and ca. 387 Hz). By comparison with $^5J(^{119}Sn,^{119}Sn)$ for a cyclic derivative where the mutual positions of the tin atoms are fixed [13], it can be assumed that the large value for $|^5J(^{119}Sn,^{119}Sn)|$ belongs to Sn(1)–Sn(3) and Sn(2)–Sn(3) coupling (torsion angle Sn(3)–C(4)–C(3)–C(2) = 11.8°), and the small value for $|^5J(^{119}Sn,^{119}Sn)|$ to Sn(1)–Sn(4) and Sn(2)–Sn(4) coupling (torsion angle Sn(4)–C(4)–C(3)–C(2) = 127.0°).

Table 5
^{11}B, ^{13}C and ^{119}Sn NMR data [a] of the allenes **24**, **25**



No.		**24a** [b]	**25c** [c]	**25d** [d]
R^2		Et	1,4-butanediyl	1,4-butanediyl
az		pyrrolyl	indolyl	carbazolyl
$\delta^{11}B$		—	54.0	70.3
$\delta^{119}Sn$	SnC=	−10.3	−13.7	−9.0
	SnCB	11.6	8.9	−8.2
$\delta^{13}C$ [$J(^{119}Sn,^{13}C)$]	=CSn	86.0 [286][8.3]	82.2	81.7 [279][7.9]
	=C=	208.1 [40.4][33.1]	209.4	207.9 [41.0][27.8]
	$=C-R^2$	92.9 [75.4][25.7]	90.9	89.3 [79.0][27.4]
	CSn_2	40.1 [br]	n.o.	n.o.
	*Me*SnC=	−5.6 [324][5.5]	−5.8	−6.8 [327]
	*Me*BCSn	−3.2 [329][8.3]	−3.5 [315]	−2.3 [320]

[a] C_6D_6, 25 °C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling.
[b] $\delta^{13}C(Et) = 29.5$ [31.5][25.7] ($=CCH_2$); 16.3 [br] (BCH_2); 13.2 ($=CCH_2CH_3$); 11.1 (BCH_2CH_3). At −50 °C: $\delta^{119}Sn(BCSn_2) = 19.7$; 6.8: $\delta^{119}Sn(=CSn_2) = -6.1$; −11.6. $\delta^{13}C(SnMe_3) = -3.9$; −4.3; −6.2; −6.4.
[c] $\delta^{13}C(1,4\text{-butanediyl}) = 32.9$; 27.0; 23.6; 22.0 [br]; $^5J(^{119}Sn,^{119}Sn) = 205$ Hz.
[d] $\delta^{13}C(1,4\text{-butanediyl}) = 43.1$; 32.0; 26.7 [br]; 22.4; $^5J(^{119}Sn,^{119}Sn) = 216$ Hz.

3. Conclusions

Dialkyl(*N*-azolyl)boranes are attractive reagents for stereoselective 1,1-organoboration reactions. Their advantage compared to trialkylboranes lies in the presence of a functional group at the boron atom which can be exploited for further reactions as will be shown in future studies. There is now much more evidence for the application of 1,1-organoboration to ring expansion of boron heterocycles. The products of the 1,1-organoboration reactions are of considerable interest for multinuclear NMR spectroscopic studies. In the case of the allene **24a**, the NMR data at low temperature, in particular the ^{119}Sn NMR parameters, correspond closely to prominent structural features determined by X-ray structural analysis.

4. Experimental details

All reactions and handling of compounds were carried out observing necessary precautions to exclude oxygen and moisture. The mono-1-alkynyltin compounds **1**–**4** were prepared by closely following literature procedures [23]. Diethyl(*N*-pyrrolyl)borane **5a** [24] was available and the other *N*-azolylboranes including **9d** were prepared as described recently [8]. Elemental analysis were carried out by Pascher, Remagen. Mass spectra (EI-MS; 70 eV) were recorded with a Varian-MAT CH 7 instrument with direct inlet. NMR spectra were measured for solutions in $CDCl_3$ or C_6D_6 at 25 °C by using Jeol EX270 (^{1}H,^{13}C) and Bruker ARX 250 and DRX 500 spectrometers equipped for multinuclear measurements (chemical shifts are referred to Me_4Si (δ^1H($CHCl_3$/$CDCl_3$) = 7.24, (C_6D_6) = 7.15; δ^{13}C($CDCl_3$) = 77.0, (C_6D_6) = 128.0), Et_2O–BF_3 (δ^{11}B with Ξ(^{11}B) = 32.083971 MHz), and Me_4Sn (δ^{119}Sn with Ξ(^{119}Sn) = 37.290665 MHz)).

4.1. Preparative work

General procedure for all 1,1-organoboration reactions: the respective 1-alkynyltin compound (5 mmol in general but 10 mmol of **4** in the case of the synthesis of the allenes **24** and **25**) was dissolved in 25 ml of hexane, cooled to −78 °C and 5 mmol of the *N*-azolylborane were added in one portion. The mixture was warmed to room temperature and heated for 5 min at 60 °C. Then the solvent was removed in vacuo and the pure compounds were left as colourless to yellowish, oily liquids or solids.

If reactions were carried out for NMR measurements, the respective *N*-azolylborane (1 mmol) was dissolved in 0.5 ml of C_6D_6 in an NMR tube and 1 mmol of the mono-1-alkynyltin compound was added. The compounds were mixed and the progress of the reactions was monitored by ^{11}B and ^{119}Sn NMR. The samples were stored at room temperature. After 2 days the reactions were complete. All 1,1-organoborations proceeded quantitatively.

10a: yellow liquid; yield 67% after distillation (b.p.: 69 °C/0.05 Torr) ^{13}C NMR (C_6D_6, 62.9 MHz): δ^{13}C(pyrrolyl group) = 127.6/124.2 (C-2/5); 115.2/114.2 (C-3/4). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [J(^{1}H,^{1}H)][J(^{119}Sn,^{1}H)] = 7.15 (m)(H-2/5, pyrrolyl group); 6.52 (s)(89.0 Hz)(=C*H*); 6.42 (m)(H-3/5, pyrrolyl group); 2.37 (qd)[7.3 Hz][1.5 Hz](=CCH_2); 1.42 (q)[7.9 Hz](BCH_2); 1.16 (t)[7.3 Hz](=CCH_2CH_3); 1.08 (t)[7.9 Hz](BCH_2CH_3); 0.07 (s)(54.2 Hz)($SnMe_3$).

11a: yellow liquid; yield 65% after distillation (b.p.: 55 °C/10^{-3} Torr). ^{13}C NMR (C_6D_6, 62.9 MHz): δ^{13}C(pyrrolyl group) = 126.9/123.4 (C-2/5); 114.8/113.2 (C-3/4). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [J(^{1}H,^{1}H)][J(^{119}Sn,^{1}H)] = 7.01 (m)(H-2/5, pyrrolyl group); 6.33 (m)(H-3/4, pyrrolyl group); 2.40 (m)(=CCH_2); 2.04 (s)(51.2 Hz)(=C*Me*); 1.30 (q)(BCH_2); 1.03 (t)[7.1 Hz](=CCH_2CH_3); 0.86 (t)[8.0 Hz](BCH_2CH_3); −0.07 (s)(52.2 Hz)($SnMe_3$). EI-MS ($C_{14}H_{26}BNSn$): m/z(%) = 324 (15) [M^+]; 296 (10) [M^+ − 2Me]; 147 (100) [M^+ − C($SnMe_3$)$_2$].

12a: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): δ^{13}C(pyrrolyl group) = 127.5/124.3 (C-2/5); 115.3/114.3 (C-3/4). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [J(^{1}H,^{1}H)][J(^{119}Sn,^{1}H)] = 7.28/7.07 (m)(H-2/5, pyrrolyl group); 7.20 (m); 7.00 (m) 6.33 (m)(H-3/4, pyrrolyl group); 2.50/2.20 (m)(=CCH_2); 1.57/1.48 (m)(BCH_2); 1.27 (t)[7.1 Hz](=CH_2CH_3); 0.89 (t)[7.5 Hz](BCH_2CH_3); 0.00 (s)($SnMe_3$).

13a: colourless solid; yield 93% (m.p.: 55 °C). C_{calc} = 39.5%, H_{calc} = 6.6%, C_{found} = 39.4%, H_{found} = 6.6%. ^{13}C NMR (C_6D_6, 62.9 MHz): δ^{13}C(pyrrolyl group) = 127.2/124.7 (C-2/5), 115.1/114.2 (C-3/4. ^{1}H NMR (C_6D_6, 250 MHz): δ^1H [J(^{1}H,^{1}H)][J(^{119}Sn,^{1}H)] = 7.00 (m)(H-2/5, pyrrolyl group), 6.31/6.24 (m)(H-3/4, pyrrolyl group), 2.40/2.22 (m)(=CCH_2); 1.35/1.19 (m)(BCH_2), 1.02 (t)[7.0 Hz](=CCH_2CH_3). 0.86 (t)[7.8 Hz](BCH_2CH_3); 0.28 (s)($SnMe_3$); −0.03 (s)($SnMe_3$, R^1). EI-MS ($C_{16}H_{32}BNSn_2$): m/z(%) = 489 (5) [M^+]; 474 (8) [M^+ − Me]; 323 (25) [M^+ − $SnMe_3$]; 165 (100) [$SnMe_3^+$].

14c: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): δ^{13}C(indolyl group) = 140.9 (C-7a); 134.2 (C-3a); 133.5 (C-2); 123.4 (C-5); 122.9 (C-4); 121.1 (C-6); 116.6 (C-7). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H [J(^{1}H,^{1}H)][J(^{119}Sn,^{1}H)] = 7.60 (m); 7.44 (d)[3.3 Hz]; 7.33 (m); 7.14 (m); 6.61 (d); 2.13 (s)(=C*Me*)(49.7 Hz); overlapping multiplets at 1.87–1.62; −0.07 (s)(51.2 Hz)($SnMe_3$).

14d: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): δ^{13}C(carbazolyl group) = 144.2 (C-4a/5a); 128.8 (C-1a/8a); 126.3 (C-3/6); 123.1 (C-7); 120.1 (C-1/8); 117.6 (C-5/5). ^{1}H NMR (C_6D_6; 250 MHz): δ^1H =

overlapping multiplets at 7.90–7.65 and 7.25–6.95 (carbazolyl group); overlapping multiplets at 2.70–1.40; 1.97 (s)(=C*Me*); −0.33 (s)($SnMe_3$).

15a: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(pyrrolyl group) = 126.7/124.5 (C-2/5); 115.6/114.8 (C-3/4). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 7.20 (m)/7.03 (m)(pyrrolyl group); 2.48 (m); 1.99 (m); overlapping multiplets at 1.80–1.00; 0.31 (s)(50.3 Hz)($SnMe_3$); −0.01 (s)(50.3 Hz)($SnMe_3$, R^1).

15b: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(2,5-dimethylpyrrolyl group) = 136.1 (C-2/5); 114.9 (C-3/4); 18.4 (Me). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^1H,^1H)$] = 5.91 (s)(pyrrolyl group); 2.57 (t)[5.9 Hz](H-3); 2.23 (s)(pyrrolyl-Me); overlapping multiplets at 1.58–1.52; 1.14 (t)[7.6 Hz](H-6); 0.28 (s)($SnMe_3$); 0.02 (s)($SnMe_3$, R^1).

15c: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(indolyl group) = 141.1/140.7 (C-7a); 134.4/133.8 (C-3a); 133.5/131.2 (C-2); 125.1/123.2(2 signals)/123.1/121.3/121.0/117.2/116.4 (C-4/C-5/C-6/C-7); 110.6/109.8 (C-3). ^1H NMR (C_6D_6; 250 MHz): δ^1H = overlapping multiplets at 7.5–6.5 (indolyl group), overlapping multiplets at 2.2–1.0; 0.35 (s)/0.34 (s)($SnMe_3$); −0.06 (s)/−0.20 (s)($SnMe_3$, R^1).

15d: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(carbazolyl group) = 144.0 (C-4a/5a), 128.8 (C-1a/8a), 126.3 (C-3/6), 123.1 (C-2/7), 120.1 (C 1/8), 117.6 (C-4/5). ^1H NMR (C_6D_6; 250 MHz). δ^1H = overlapping multiplets at 7.92–7.23 (carbazolyl group), overlapping multiplets at 2.87–1.40, 0.46 (s)($SnMe_3$), −0.10 (s)($SnMe_3$, R^1).

16a/17a (30:70): yellow oil. ^{119}Sn NMR (C_6D_6, 93.3 MHz): $\delta^{119}Sn$(**16a**) = −37.9; −57.1 (R^1). $\delta^{119}Sn$(**17a**) = −38.2; −57.7 (R^1). ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(**16a**)[$J(^{119}Sn,^{13}C)$] = 124.6 (C-2/5, pyrrolyl group); 114.8 (C-3/4, pyrrolyl group); 177.5 [br](B*C*=); 152.2 (=*C*Sn); 58.1 (122 Hz); 37.9; 36.1; 22.2 (C-*Me*); 20.8 [br](B*C*H_2); −5.9 (306 Hz)($SnMe_3$, R^1); −6.8 (319 Hz)($SnMe_3$). $\delta^{13}C$(**17a**)[$J(^{119}Sn,^{13}C)$] = 126.7 (C-2/5, pyrrolyl group); 115.5 (C-3/4, pyrrolyl group); 177.5 [br](B*C*=); 152.9 (=*C*Sn); 48.7 (124 Hz)(108 Hz); 39.4; 35.8; 31.2 [br](B*C*H_2); 25.9 (C*Me*); −5.9 (317 Hz)($SnMe_3$, R^1); −6.8 (325 Hz)($SnMe_3$). ^{11}B NMR (C_6D_6, 80.3 MHz): $\delta^{11}B$(**16a/17a**) = 52.0. ^1H NMR (C_6D_6; 250 MHz): δ^1H(**16a/17a**) = 7.15 (m); 7.02 (m); 6.31 (m); 6.27 (m); 2.43 (m); overlapping multiplets at 1.81–0.77; 0.28 (s)($SnMe_3$); −0.05 (s)($SnMe_3$, R^1).

16c/17c (30:70): yellow oil. ^{119}Sn NMR (C_6D_6, 93.3 MHz): $\delta^{119}Sn$(**16c**) = −42.0; −55.5/−56.8 (R^1). $\delta^{119}Sn$(**17c**) = −39.2; −56.3/−56.9 (R^1). ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(**16c/17c**, indolyl groups)[$J(^{119}Sn,^{13}C)$] = 141.1; 141.0; 140.6; 140.5; 134.4; 134.2; 133.8;133.5; 133.4; 132.9; 131.2; 130.6; signals between 115 and 125 are not resolved due to slow rotation about the B–N bond; 111.2; 109.8 (2 signals); 107.7. $\delta^{13}C$(**16c/17c**, boryl groups) = 179.1 [br]; 178.9 [br]; 178.8 [br]; 178.5 [br]; 154.6; 154.3; 148.5; 148.1; 57.8; 48.6; 48.3; 39.9; 39.3; 38.6; 37.7; 36.8; 36.5; 35.7; 35.5; 26.0; 22.4; −5.6; −5.9 (2 signals); −6.2; −6.7; −6.9. ^{11}B NMR (C_6D_6, 80.3 MHz): $\delta^{11}B$(**16c/17c**) = 51.0. ^1H NMR (C_6D_6; 250 MHz): δ^1H = 7.41 (m); 7.09 (m); 6.48 (m); overlapping multiplets at 2.51–0.83; 0.29 (s)($SnMe_3$); −0.13 (s)($SnMe_3$, R^1).

18a: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz). $\delta^{13}C$(pyrrolyl group) = 122.0 (broad due to intramolecular rotation)(C-2/5); 114.8 (C-3/4). ^1H NMR (C_6D_6; 250 MHz): δ^1H [J()]) = 7.10 (m)(H-2/5, pyrrolyl group); 6.68 (s)(85.2 Hz)(=H); 6.35 (m)(H-3/4, pyrrolyl group); 2.83 (m); 2.08 (m); 1.64 (m); 1.23 (m); 0.87 (m); −0.04 (s)(54.3 Hz)($SnMe_3$).

19c: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(indolyl group) = 147.0 (C-7a), 139.1 (C-3a); 134.0 (C-2), 123.0 (C-5); 122.1 (C-4); 121.2 (C-6); 116.9 (C-7); 110.0 (C-3). ^1H NMR (C_6D_6; 250 MHz): δ^1H = overlapping multiplets at 7.5–6.5 (indolyl group), 2.90 (m); overlapping multiplets at 2.10–1.20; 1.95 (s)(=C*Me*); 0.23 (s)($SnMe_3$).

20a: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(pyrrolyl group) = 127.6/123.9 (C-2/5); 115.6/114.0 (C-3/4). ^1H NMR (C_6D_6, 250 MHz). δ^1H = 7.17/6.97 (m)(H-2/5, pyrrolyl group), 6.37/6.27 (m)(H-3/4, pyrrol group), 2.82 (m), overlapping multiplets at 2.04–1.20, 0.30 (s)(50.6 Hz)($SnMe_3$), −0.02 (s)(51.3 Hz)($SnMe_3$, R_1).

20c: yellow oil: ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(indolyl group) = 141.0/140.4 (C-7a); 135.1/133.9 (C-3a); 130.8 (C-2); 123.5/122.6/121.4 (2 signals)(C-4/C-5/C-6); 117.3/116.4 (C-7); 110.2/109.6 (C-3). ^1H NMR (C_6D_6; 250 MHz): δ^1H = overlapping multiplets at 7.80–7.15 (indolyl group); 6.71 (m); 3.05 (m); overlapping multiplets at 2.10–1.37; 0.49 (2 signals)($SnMe_3$); 0.14/−0.08 (s)($SnMe_3$, R^1).

22d: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(carbazolyl group) = 145.0/144.0 (C-4a/5a); 128.8/128.2 (C-1a/8a); 126.8/125.9 (C-3/6); 122.8/122.6 (C-2/7); 120.2/119.9 (C-1/8); 117.6/116.7 (C-4/5). ^1H NMR (C_6D_6; 250 MHz): δ^1H = 8.20 (m); 7.53 (m); overlapping multiplets at 7.25–7.08; 3.67 (m); overlapping multiplets at 2.52–1.35; 1.99 (s) (=C*Me*); 0.80 (m); −0.41 (s)(51.0 Hz)($SnMe_3$).

23d: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(carbazolyl group) = 144.4/144.0 (C-4a/5a); 128.7/128.6 (C-1a/8a); 126.9/125.3 (C-3/6); 123.1/122.8 (C-2/7); 120.1/119.8 (C-1/8); 118.4/116.9 (C-4/5). ^1H NMR (C_6D_6; 250 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 8.35 (m); 7.96 (m); 7.78 (m); overlapping multiplets at 7.40–7.0; 3.14 (m); overlapping mul-

tiplets at 2.57–0.90; 0.36 (s)(50.2 Hz)($SnMe_3$); −0.32 (s)(51.0 Hz)($SnMe_3$, R^1).

24a: colourless crystals from hexane at −78 °C (m.p.: 42 °C). ^{13}C NMR (C_6D_6, 125.8 MHz): $\delta^{13}C$(pyrrolyl group) = 124.9 (C-2/5); 111.7 (C-3/4). ^1H NMR (C_6D_6; 500 MHz): δ^1H [$J(^1H,^1H)$][$J(^{119}Sn,^1H)$] = 7.25 (m)(H-2/5, pyrrolyl group); 6.25 (m)(H-3/4, pyrrolyl group); 1.67 (q)[7.4 Hz](41.0 Hz)(6.1 Hz)(=CCH_2); 1.25 (q)[8.0 Hz](BCH_2); 0.98 (t)[8.0 Hz](BCH_2CH_3); 0.88 (t)[7.4 Hz](=CCH_2CH_3); 0.30 (s)(53.3 Hz)(BCSnMe_3); 0.27 (s)(51.5 Hz)(=CSnMe_3).

25c: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(indolyl group) = 140.9/140.6 (C-7a); 134.1 (C-3a); 132.9/130.5 (C-2); 123.3/123.2/121.2 (C-4/C-5/C-6); 116.9/115.8 (C-7); 109.8/107.6 (C-3). ^1H NMR (C_6D_6; 250 MHz): δ^1H = overlapping multiplets at 7.68–6.70 (indolyl group); 2.35 (m); 1.92–1.65 (m); 0.31 (s)($BCSnMe_3$); 0.13 (s) (=$CSnMe_3$).

25d: yellow oil. ^{13}C NMR (C_6D_6, 62.9 MHz): $\delta^{13}C$(carbazolyl group) = 143.4 (C-4a/5a); 125.8 (C-1a/8a); 125.2 (C-3/6), 120.8 (C-2/7), 119.7 (C-1/8),112.9 (C-4/5). ^1H NMR (C_6D_6; 250 MHz): δ^1H = 8.04 (m)(H-4/5, carbazolyl group), 7.57 (m)(H-1/8, carbazolyl group); 7.38 (m)(H-3/6, carbazolyl group), 7.24 (m)(H-2/7, carbazolyl group), 2.41 (m); 1.88 (m); 1.72 (m); 0.36 (s)($BCSnMe_3$); 0.17 (s)(=$CSnMe_3$).

21: in mixture with *N*-trimethylstannylcarbazole, left as a colourless solid. ^1H NMR (C_6D_6; 250 MHz): δ^1H = 3.33 (m)(H-1); overlapping multiplets at 2.40–1.20; 1.94 (s)(H-2″); 1.92 (s)(H-2‴); 1.75 (s)(H-3′); −0.28 (s)(Sn(C-1″)Me_3); 0.27 (s)(Sn)C-1‴)Me_3).

4.2. Crystal structure analysis of **24a**

$C_{24}H_{30}BNSn_4$ (M = 838.2); $F(000)$ = 812, colourless, isometrically 0.40 × 0.35 × 0.30 mm^3 (m.p. 42 °C); triclinic, $P\bar{1}$; a = 9.133(2), b = 12.105(2), c = 16.515(2) Å, α = 76.32(2), β = 82.63(2), γ = 69.71(2)°, volume 1661.7(5) $Å^3$; Z = 2; density (calc.) = 1.675 $Mg\,m^{-3}$; absorption coefficient 2.982 mm^{-1}; data were collected with a Siemens P4 diffractometer (Mo Kα; graphite monochromator; λ = 0.71073 Å; 3.0 < 2Θ < 55°); T = 173 K; 6923 reflections, 5725 independent reflections ($R_{int.}$ = 0.93%), 5725 observed reflections [$F > 0.0\sigma(F)$]; Lorentz and polarization correction; structure solution by Patterson methods followed by difference Fourier synthesis using the SHELTX-PLUS program and refined against F (non-hydrogen atoms anisotropic; all hydrogen positions were calculated and refined using the 'riding model' with fixed isotropic temperature factors). The refinement (full matrix least squares), using 272 parameters, converged at R/wR = 3.02/2.19%. The max./min. residual electron density was 1.68/−0.63 e^- $Å^{-3}$.

Acknowledgements

The support of this work by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and Volkswagenstiftung is gratefully acknowledged (B.W., H.E.M., B.S., W.M.). We thank J. Lichtenwald and M. Jandke for their help with experimental work.

References

[1] P.J. Stang, F. Diederich (Eds.), Modern Acetylene Chemistry, VCH, Weinheim, 1995.
[2] (a) W.E. Davidsohn, M.C. Henry, Chem. Rev. 67 (1967) 73. (b) C. Cauletti, C. Furlani, A. Sebald, Gazz. Chim. Ital. 118 (1988) 1. (c) V.S. Zavgorodnii, A.A. Petrov, Chem. Rev. 18 (1993) 1.
[3] B. Wrackmeyer, Coord. Chem. Rev. 145 (1995) 125.
[4] B. Wrackmeyer, B. Schwarze, unpublished results.
[5] H. Bellut, C.D. Miller, R. Köster, Synth. Inorg. Met. Org. Chem. 1 (1971) 83.
[6] B. Wrackmeyer, B. Schwarze, W. Milius, Inorg. Chim. Acta 241 (1996) 87.
[7] (a) B. Wrackmeyer, I. Ordung, B. Schwarze, J. Organomet. Chem. in press. (b) M. Yalpani, R. Boese, R. Köster, Chem. Ber. 121 (1988) 287.
[8] B. Wrackmeyer, B. Schwarze, J. Organomet. Chem. in press.
[9] J.K.M. Saunders, M.D. Mersh, Progr. NMR Spectrosc. 15 (1982) 353.
[10] A. Schmidt, B. Wrackmeyer, Z. Naturforsch. Teil B: 33 (1978) 835.
[11] C. Bihlmayer, B. Wrackmeyer, J. Organomet. Chem. 321 (1987) 25.
[12] C. Bihlmayer, S.T. Abu-Orabi, B. Wrackmeyer, J. Organomet. Chem. 321 (1987) 25.
[13] B. Wrackmeyer, J. Organomet. Chem. 205 (1981) 1.
[14] B. Wrackmeyer, G. Kehr, H.E. Maisel, U. Dörfler, W. Milius, J. Organomet. Chem. in press.
[15] (a) A. Berndt, Angew. Chem. 105 (1993) 1034; Angew. Chem Int. Ed. Engl. 32 (1993) 985. (b) D. Steiner H.-J. Winkler, S. Wocadlo, S. Fau, W. Massa, G. Frenking, A. Berndt, Angew. Chem. 106 (1994) 2172; Angew. Chem. Int. Ed. Engl. 33 (1994) 2964.
[16] J. Rosenplänter, B. Schmidt, A. Schmotz, G.E. Herberich, Int. Meet. on Boron Chemistry IMEBORON IX, Heidelberg, 1996, Poster P23.
[17] E. Fluck, E.H.E. Pietsch, A. Kotowski, M. Becke-Goehring (Eds.), Gmelin Handbook of Inorganic Organometallic Chemistry, vol. 3a, 4th Supplement, Springer, Berlin, 8th edition, 1991, pp. 219–239.
[18] G. Menz, B. Wrackmeyer, Z. Naturforsch. Teil B: 32 (1977) 1400.
[19] B. Wrackmeyer, C. Bihlmayer, M. Schilling, Chem. Ber. 116 (1983) 3182.
[20] S. Kerschl, B. Wrackmeyer, J. Chem. Soc. Chem. Commun. (1986) 403.
[21] R. Köster, G. Seidel, B. Wrackmeyer, Chem. Ber. 126 (1993) 319.
[22] B. Wrackmeyer, Annu. Rep. NMR Spectrosc. 16 (1985) 73.
[23] B. Wrackmeyer, in: R.B. King, J.J. Eisch (Eds.), Organometallic Synthesis, vol. 3, Elsevier, New York, 1986, p. 572.
[24] H. Bellut, R. Köster, Justus Liebigs Ann. Chem. 738 (1970) 86.