ELSEVIER

Journal of Organometallic Chemistry 545–546 (1997) 297–308

Journal of Organometallic Chemistry

Reactivity of bicyclic *N*-pyrrolylboranes [1]

Bernd Wrackmeyer *, Bernd Schwarze, Wolfgang Milius

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

Received 3 March 1997; received in revised form 11 April 1997

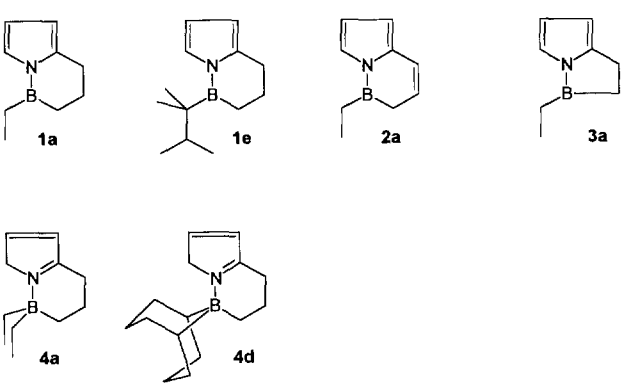
Abstract

Bicyclic B-alkyl-*N*-pyrrolylboranes (**1–3**) react with alkyl lithium or alkyl Grignard reagents to give the corresponding borates **5** which, in most cases can be protonated to the intramolecular 2*H*-pyrrole-borane adducts **4**. The molecular structure of **4d** was determined by X-Ray structural analysis. The adducts **4** can be deprotonated to the borates **5**. Cleavage of the B–N bond in **1a** by EtOH to give **7a** is reversible, and **1e** react with CF_3SO_3H by protonation of the pyrrole ring. The 2*H*-pyrrole-borane adducts **4a,d** react with CF_3SO_3H by cleavage of the B–N bond to give trialkylboranes as the 2*H*-pyrrolium salts **8a,d**. Cyclopentadiene reacts with the 2*H*-pyrrole borane adduct **4d** selectively by [4 + 2]cycloaddition to give **10** with *endo*-configuration. The boranes **1a** and **2a** react stereoselectively with mono-1-alkynyltin compounds in a 1:1 stoichiometry by an 1,1-organoboration to give the organometallic substituted alkenes **11–13**, in which the six-membered ring present in **1a** and **2a** is retained. In contrast, **3a** reacts under the same conditions exclusively by ring enlargement and in a 1:2 stoichiometry. The product from the reaction of **3a** with two equivalents of trimethyl(1-propynyl)tin is the 1,3-butadiene derivative **14** which rearranges selectively to its isomer **15** by changing the configuration at both double bonds. The reaction of **3a** with two equivalents of bis(trimethylstannyl)ethyne leads selectively to the organometallic substituted allene **16**, the result of an irreversible allylic rearrangement of a 1,3-butadiene derivative analogous to **14** or **15**. All products were characterized by ^{1}H, ^{11}B, ^{13}C, ^{14}N and ^{119}Sn NMR spectroscopy. © 1997 Elsevier Science S.A.

Keywords: Boron; Tin; Pyrrole; Borates; Borane adducts; Triorganoboranes; Diels–Alder reaction; Alkynes; Alkenes; 1,1-Organoboration; Allylic rearrangement

1. Introduction

The pyrrolyl group in *N*-pyrrolylboranes behaves more like an aryl substituent than an amino group as was shown by recent studies on the structure [1], NMR spectroscopy [1,2] and reactivity [3] of *N*-pyrrolylboranes. Even in the bicyclic *N*-pyrrolylboranes of the type **1** [2], **2** [4] and **3** [2], where the sterical situation for BN(pp)π interactions is most favourable, such interactions appear to be weak or negligible. Some aspects of the reactivity of simple *N*-pyrrolylboranes have been reported [5–8], but the properties of bicyclic *N*-pyrrolylboranes have not been studied so far. In this work, we report on the reactivity of **1–3** towards various Lewis bases, protic reagents, and mono-1-alkynyltin compounds, together with some reactions of the 2*H*-pyrrole-borane adduct **4a**, the precursor of **1a**, and its 9-borabicyclo[3.3.1]-nonane derivative **4d**. Furthermore, the molecular structure of **4d** was determined by X-ray structural analysis.



* Corresponding author.

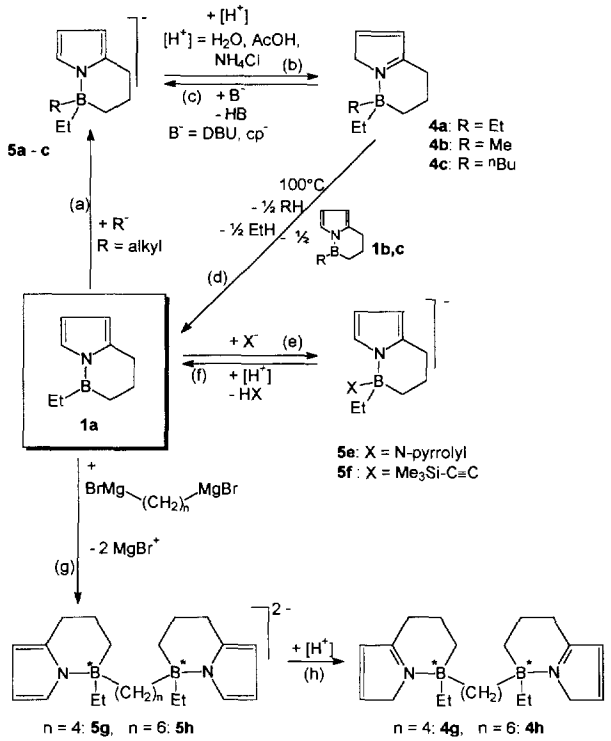
[1] Professor M. Weidenbruch on the occasion of his 60th birthday.

PII S0022-328X(97)00308-2

2. Results and discussion

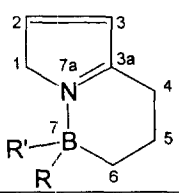
2.1. Reactions of 1–3 with anionic Lewis bases

Reactions of **1a** with anionic Lewis bases are summarized in Scheme 1. As shown in Scheme 1a, compound **1a** reacts with alkyllithium reagents to the *N*-pyrrolyl-borates **5a–c**, which can be protonated to give the 2*H*-pyrrole-borane adducts **4a–c** (Scheme 1b). Deprotonation (Scheme 1c) of **4a–c** leads back to the borates **5a–c**. Heating the adducts at ca. 100°C leads either to 1:1 mixtures of **1a** and **1b**, or of **1a** and **1c**, or to the pure compound **1a**, accompanied by elimination of ethane and methane, ethane and butane, or ethane (Scheme 1d). Compound **1a** reacts also with organolithium compounds or lithium amides with less nucleophilic anions e.g., *N*-pyrrolyl lithium or trimethylsilylethynyl lithium to give the borates **5e** and **5f** (Scheme 1e). However, protonation of these borates leads back to **1a** (Scheme 1f). The reaction of **1a** with 1,4-di(bromomagnesium)butane or 1,6-di(bromomagnesium)-hexane affords the coupled borates **5g** and **5h** as mixtures of diastereomers (Scheme 1g), and these can also be protonated to give the corresponding 2*H*-pyrrole-borane adducts (Scheme 1h).



Scheme 1.

Table 1
^{11}B, ^{13}C and ^{14}N NMR data[a] of **4a–4c**, **4g–4i**[b]

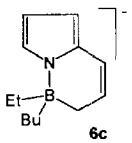


4

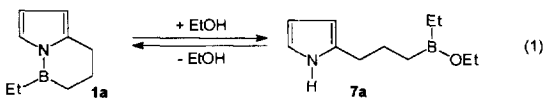
	No.					
	4a	**4b**	**4c**	**4g**[b]	**4h**[b]	**4i**
R	Et	Me	^{n}Bu	1,4-butanediyl	1,6-hexanediyl	$-OSO_2CF_3$[c]
R′	Et	Et	Et	Et	Et	thexyl
$\delta^{11}B$	−5.1	−6.0	−5.1	−5.4	−5.1	35.6
$\delta^{14}N$	−131.0	n.m.	n.m.	n.m.	n.m.	−164.5
$\delta^{13}C$						
C-1	62.9	62.8	62.9	63.1	62.8	65.7
C-2	148.1	148.2	148.0	148.1	147.8	159.2
C-3	129.8	129.8	129.6	129.7	129.5	130.9
C-3a	179.1	178.2	178.8	178.6	178.6	193.3
C-4	30.4	30.4	30.3	30.5	30.2	30.5
C-5	20.2	19.9	20.2	20.4	20.1	17.4
C-6	16.8 [br]	19.5 [br]	17.2 [br]	17.1 [br]	17.1 [br]	16.3 [br]
R	19.5 [br] (CH_2) 10.9 (CH_3)	10.8 [br]	28.0 [br] (C-1′) 14.8(CH_3)	29.2 [br] (B-CH_2) 30.0(C-2′)/27.9(C-3′)	28.5 [br] (B-CH_2) 32.8/32.6[b] 27.8/27.7[b]	120.1 (q), $^1J(^{19}F,^{13}C)$ = 318 Hz 35.5/35.4[b]
R′	see R	19.5 [br] (CH_2) 11.2 (CH_3)	19.4 [br] (CH_2) 11.0 (CH_3)	20.0 [br] (CH_2) 11.2 (CH_3)	19.5 [br] (CH_2) 11.0 (CH_3)	28.8 [br] (B–*C*) 34.4(CH)/20.7(CH-CH_3) 18.2 (C-CH_3)

[a] C_6D_6, 25°C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling; n.m. = not measured.
[b] **4g** and **4h** are diastereomers.
[c] The $[CF_3OSO_2]^-$ anion coordinates only weakly to boron.

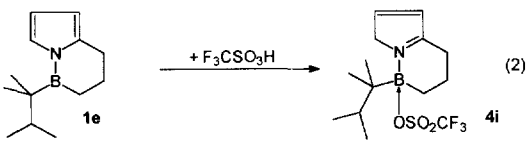
The reaction of **2a** with *n*-butyl lithium affords the borate **6c**, analogous to **5c**. However, **6c** cannot be protonated without decomposition. The bicyclic *N*-pyrrolylborane **3a**, containing a boron atom as a part of a five-membered ring, undergoes in principle the same reactions as **1a**. However, **3a** appears to be much more reactive, and the reactions are accompanied by numerous side reactions which give other non-identified products.



6c



(1)



(2)

All these reactions are more typical of triorganoboranes than of amino(diorgano)boranes. The protonation of the borates **5** to give the intramolecular adducts **4** is a particular feature of the pyrrolyl group, and this opens new synthetic aspects (vide infra) not accessible by starting from other borates.

2.2. Reactions of 1 with EtOH and CF_3SO_3H

Compound **1a** reacts with EtOH by cleavage of the B–N bond (Eq. 1). Surprisingly, this reaction is reversible by removing EtOH in vacuo. This unusual behaviour demonstrates the stability of the bicyclic ring system.

The reaction of **1e** with CF_3SO_3H does not cleave the B–N bond. Instead protonation of the pyrrole ring takes place (Eq. 2). The resulting structure **4i** looks similar to the other 2*H*-pyrrole adducts **4**, but the Lewis acid–base interaction between the anion and the boron atom is only weak (δ^{11}B of **4i**: 35.6, see Table 1).

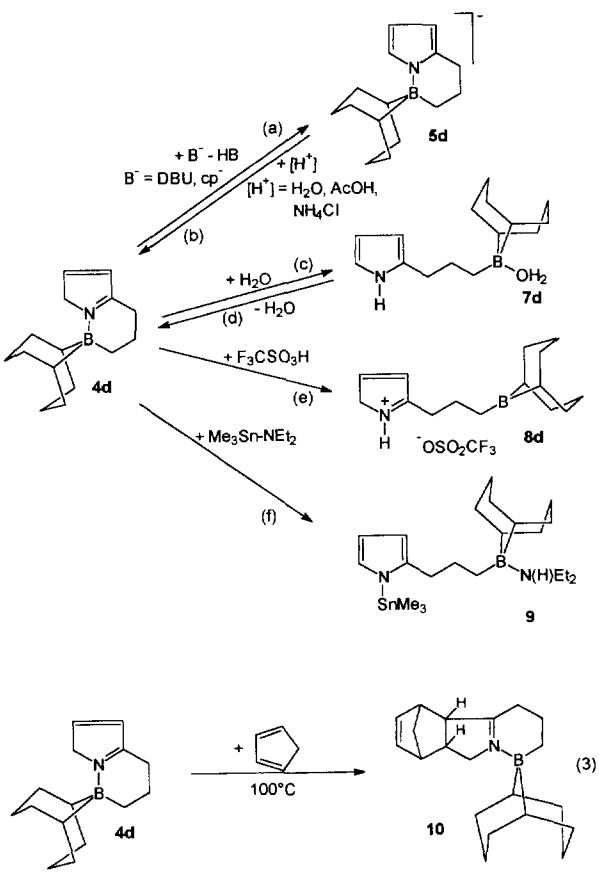
2.3. Reactivity of the 2H-pyrrole-borane adducts

The borate **5d** can be obtained by treatment of the adduct **4d** with a base (Scheme 2a), and protonation leads back to **4d** (Scheme 2b). Interestingly, mixtures of **5d**[H-DBU]$^+$ with benzene are possible only in the ratio 1:8. Less benzene leaves undissolved material, more benzene leads to a second phase which does not contain **5d**[H-DBU]$^+$. Investigations of such mixtures by dynamic light scattering indicate the presence of a microemulsion with ball-like micelles with a hydrodynamic diameter of 74 Å.

The addition of a weak Lewis base in excess like water to **4d** opens the six-membered ring in a slow equilibrium reaction by coordination to the boron atom to give **7d** (Scheme 2c,d).

The adducts **4a,d** react with CF_3SO_3H by cleavage of the B–N bond to give interesting ionic trialkylboranes **8a,d** (Scheme 2e). This might open a way to trialkylboranes which are soluble and stable in water. The properties of **8a,d** are currently under investigation.

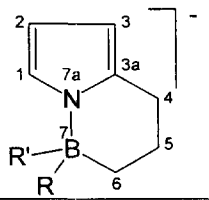
Since one of the NCH_2-protons in **4** appears to be fairly acidic, the reaction of **4d** with diethylamino(trimethyl)tin was studied with respect to cleavage of the Sn–N bond. The result is shown in Scheme 2f. As expected, a proton is abstracted and the Sn–N bond is cleaved, but at the same time cleavage of the B–N bond takes place similar to the reaction with water (Scheme 2c,d) and the final product is the *N*-stannylpyrrole derivative **9**.



(3)

Scheme 2.

Table 2
^{11}B, and ^{13}C NMR data[a] of **5b–5f**



5 [b]

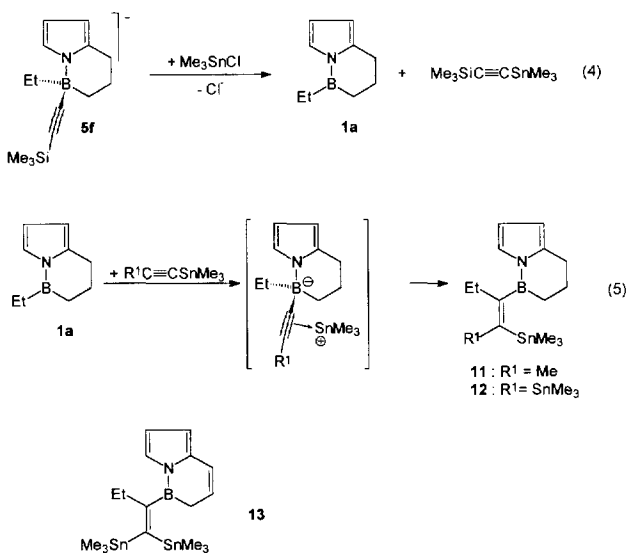
	No.				
	5b	**5c**	**5d**	**5e**	**5f**
R	Et	^{n}Bu	1,5-cyclooctane-diyl	*N*-pyrrolyl	C≡C–$SiMe_3$[b]
R′	Et	Et	1,5-cyclooctane-diyl	Et	Et
$\delta^{11}B$	−7.6	−8.1	−8.2	−2.5	−10.1
$\delta^{13}C$					
C-1	120.0	119.7	123.5	119.9	118.3
C-2	103.2	102.9	102.4	104.4	109.8
C-3	100.2	100.0	100.9	101.3	106.1
C-3a	135.2	134.6	135.6	134.6	136.6
C-4	29.9	29.8	30.0	28.8	28.3
C-5	25.0	24.8	23.4	23.1	23.8
C-6	[br], n.o.	[br], n.o.	23.9 [br]	19.0 [br]	16.6 [br]
R	[br], n.o. (CH_2) 12.1 (CH_3)	[br], n.o. (C-1′) 30.9 (C-2′) 28.6 (C-3′) 15.0 (CH_3)	27.0 [br] (C-1′/5′) 35.6/33.4 (C-2′/4′/6′/8′)	121.8(N-*C*H) 104.0	140.0 [br] (B–*C*) 137.3 (*C*–Si) 1.0 (Si*C*H_3)
R′	see R	[br], n.o.(CH_2) 11.8 (CH_3)	27.5/ 27.6 (C-3′/7′)	22.1 [br] (CH_2) 11.0 (CH_3)	20.2 [br] (CH_2) 10.9 (CH_3)

[a] C_6D_6/THF (1:1), 25°C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling; n.o. = not observed due to overlap with other signals.
[b] $\delta^{29}Si = -21.2$ ppm.
The chemical shifts are largely independent of the cation (in this case, Li^+).

The C=C bond in the adducts **4** can act as a dienophile in Diels–Alder cycloadditions. Since the adducts **4a–c** are thermally labile (Scheme 1d), the much more stable adduct **4d** is a potential candidate. The reaction of **4d** with cyclopentadiene takes place at 100°C and affords selectively the [4 + 2]cycloaddition product **10** (Eq. 3). The proposed *endo*-conformation of **10** is in agreement with the only other example of a Diels–Alder reaction of a 2*H*-pyrrole derivative [9], and should be energetically favoured [10,11].

2.4. 1,1-Organoboration of mono-1-alkynyl(trimethyl)tin compounds with 1–3

Recently, it was found that diorgano(*N*-pyrrolyl)boranes can be used for stereoselective 1,1-organoboration reactions of 1-alkynyltin compounds [3] in a way very similar to triorganoboranes [12–15]. While the reaction of **5f** with trimethyl tin chloride leads only back to **1a** and trimethylsilyl(trimethylstannyl)ethyne (Eq. 4), **1a** reacts directly with mono-1-alkynyl(trimethyl)tin compounds to give the organometallic-substituted alkenes **11** and **12** (Eq. 5). In contrast with many other cyclic boranes [3,16,17] ring enlargement is not observed. Only the exocyclic B-ethyl group is transferred. However, the usual stereochemistry [9] is observed, with the boryl and the stannyl group in *cis*-positions at the C=C bond.



Compound **2a** reacts with bis(trimethylstannyl)ethyne

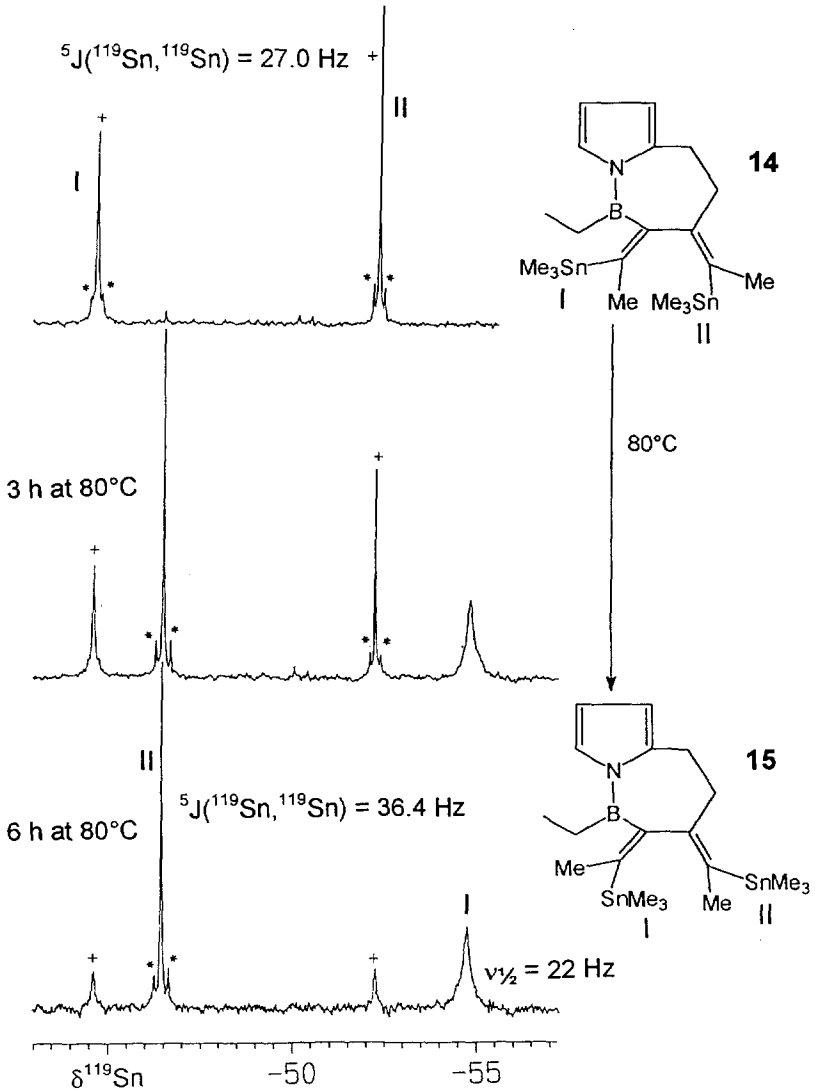
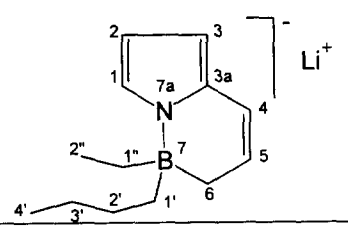


Fig. 1. 93.3 MHz $^{119}Sn\{^1H\}$ NMR spectra (^1H inverse gated decoupled; 25°C) of the thermal rearrangement of **14** (marked by +) to **15** at 80°C after different reaction times. $^{117/119}Sn$ satellites are indicated by *.

in the same way as **1a** to give the alkene **13**. There was no indication of a product with ring enlargement.

In all cases studied so far [3,16–18], ring enlargement can be considered as the result of kinetic control of the 1,1-organoboration reaction. In one case [18], it has been shown unambiguously that the transfer of the exocyclic alkyl group is the result of thermodynamic control. Therefore, in both **1a** and **2a** either the endo-

Table 3
^{11}B and ^{13}C NMR data[a] of **6c**

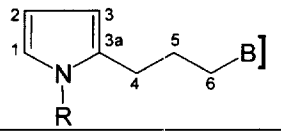


6c

$\delta^{11}B$	$\delta^{13}C$												
	C-1	C-2	C-3	C-3a	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-1′	C-2′
−7,9	120,6	103,4	102,8	134,3	121,3	126,5	24,4 [br]	28,0 [br]	30,6	28,5	15,0	19,9 [br]	11,6

[a] C_6D_6/THF (1:1), 25°C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling.

Table 4
^{11}B, and ^{13}C NMR data[a] of **7a**, **7d** and **9**



7, 9

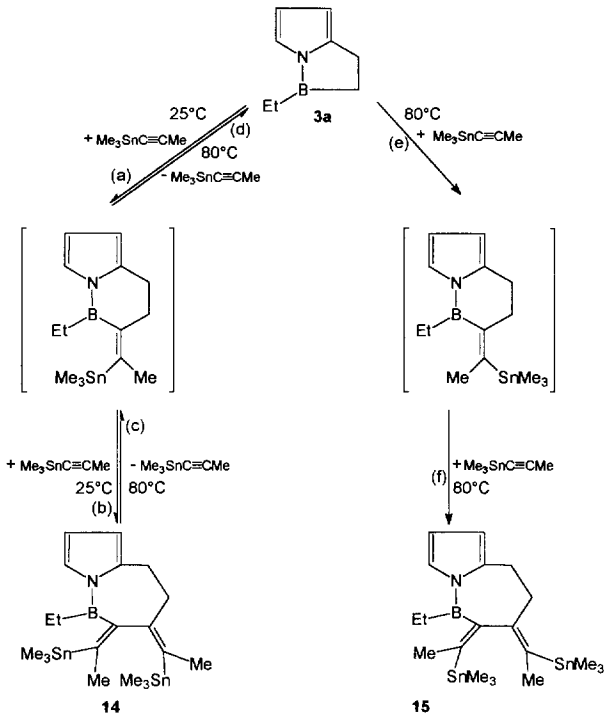
	No.		
	7a[b]	**7d**[c]	**9**[d]
B]	B(Et)OEt	9-BBN($\leftarrow OH_2$)	9-BBN($\leftarrow HNEt_2$)
R	H	H	$SnMe_3$
$\delta^{11}B$	54.8	12.9	−0.4
$\delta^{13}C$ [$J(^{119}Sn, ^{13}C)$]			
C-1	116.2	114.7	122.9 [16.4]
C-2	108.6	106.8	109.9 [22.4]
C-3	105.6	103.5	107.2 [15.3]
C-3a	132.6	133.9	140.8 [10.7]
C-4	31.0	32.4	36.2
C-5	25.0	26.1	29.1
C-6	20.1 [br]	24.6 [br]	20.5 [br]

[a] C_6D_6, 25°C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling.
[b] $\delta^{13}C$ (OEt) = 61.0 (CH_2); 17.5 (CH_3); $\delta^{13}C$ (Et) = 12.3 [br] (CH_2); 8.2 (CH_3).
[c] Measured in THF; $\delta^{13}C$ (9-BBN group) = 32.0 ($CHCH_2$); 24.7($CHCH_2CH_2$); (BCH) not observed due to overlap with other signals.
[d] $\delta^{119}Sn$ = 62.5, $\delta^{13}C(SnMe_3)$ = −4.8 $^1J(^{119}Sn,^{13}C)$ = 384 Hz, $\delta^{13}C$ (NEt_2) = 44.7 (CH_2); 15.7 (CH_3). $\delta^{13}C$ (9-BBN group) = 24.0 [br] (BCH); 32.6 (br) ($CHCH_2$); 25.3 ($CHCH_2CH_2$).

cyclic B–C bond is much less reactive than the exocyclic B–C bond or the ring extension to seven-membered rings is unfavourable for sterical reasons.

In the light of the results of the 1,1-organoboration reactions of **1a** and **2a**, **3a** behaves in a surprisingly different way towards mono-1-alkynyltin compounds. The products with 1:1 stoichiometry were not observed at all, only the products with 1:2 stoichiometry were detected and identified. Therefore these primary reaction products must be more reactive than **3a**.

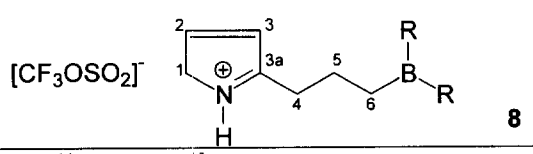
The reaction of **3a** with trimethyl(1-propynyl)tin proceeds selectively between −78°C to 25°C to give the



Scheme 3.

1,3-butadiene derivative **14** in which the five-membered ring in **3a** has been extended by two olefinic carbon atoms (Scheme 3a,b). It is well known that 1,1-organoboration reactions are reversible [12,13], however, the behaviour of **14** is without precedent. By heating in benzene at 80°C, **14** rearranges completely and selectively to **15**. This means that deorganoboration starting from **14** takes place twice (Scheme 3c,d), followed by twofold 1,1-organoboration (Scheme 3e,f) with the opposite stereochemistry, leading under these conditions irreversibly to **15**. If trimethyl(1-propynyl)tin is added to a benzene solution of **3a** at 80°C, mixtures of **14** and **15** (the ratio **14**/**15** depends on the reaction time) are observed. ^{119}Sn NMR spectroscopy proved to be the ideal tool for monitoring this rearrangement (Fig. 1).

Table 5
^{11}B and ^{13}C NMR data[a] of **8**

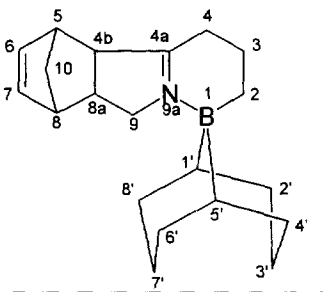


8

No.	R/R	$\delta^{11}B$	$\delta^{14}N$	$\delta^{13}C$						
				C-1	C-2	C-3	C-3a	C-4	C-5	C-6
8a[b]	Et/Et	86.4	n.m.	61.1	156.7	128.6	188.8	33.3	21.2	27.1 [br]
8d[c]	1,5-cyclo-octanediyl	92.0	−194.0	61.4	156.9	128.5	188.4	33.3	21.5	27.2 [br]

[a] C_6D_6, 25°C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling; n.m. = not measured.
[b] $\delta^{13}C$ (R) = 19.3 [br] (BCH_2); 7.9 (Me); $\delta^{13}C$ (CF_3) = 120.0 (q); $^1J(^{19}F, ^{13}C)$ = 318.0 Hz.
[c] $\delta^{13}C$ (R) = 31.2 [br] (BCH); 33.3 ($CHCH_2$); 23.4 ($CHCH_2CH_2$).

Table 6
^{11}B and ^{13}C NMR data[a] of **10**



10

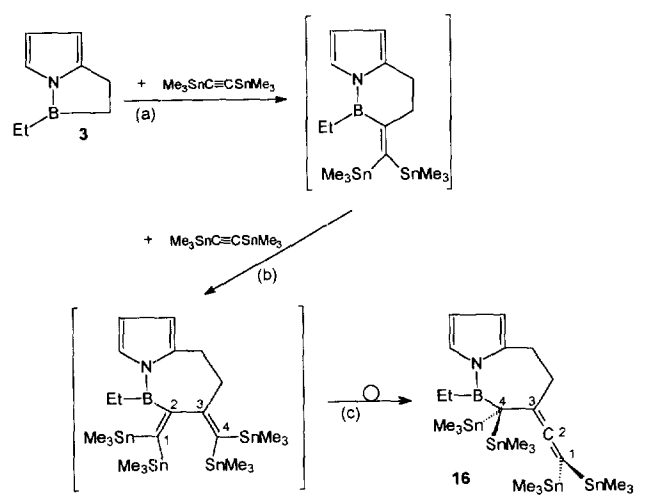
$\delta^{11}B$	$\delta^{13}C$											
	C-2	C-3	C-4	C-4a	C-4b	C-6/7	C-9	C-5/8/8a	C-10	C-1′/5′	C-2′/4′/6′/8′	C-3′/7′
−4.7	19 [br]	17.5	34.5	182.1	60.4	135.2/134.6	64.1	46.2/45.7/38.3	51.0	26 [br]	34.2/32.7/32.6/29.9	25.5/25.4

[a] C_6D_6, 25°C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling.

If two equivalents of bis(trimethylstannyl)ethyne react with a triorganoborane [15,19–22] or with diorgano-*N*-pyrrolylboranes [3] the final products are in general organometallic-substituted allenes. This is also true for **3a** which reacts quantitatively with two equivalents of bis(trimethylstannyl)ethyne to give the allene **16** (Scheme 4); the postulated intermediates are shown. The 1,3-butadiene derivative, analogous to **14** or **15** undergoes irreversible allylic rearrangement to the allene **16**.

2.5. NMR spectroscopic results

All products could be identified unambiguously by their characteristic set of ^{1}H (see Section 4), ^{11}B, ^{13}C, ^{14}N and ^{119}Sn NMR data as it is evident by inspection of Table 1 (2*H*-pyrrole-borane adducts **4**), Tables 2 and 3 (*N*-pyrrolylborates **5** and **6c**), Tables 4 and 5 (borane adducts **7** and **9**, and ionic triorganoboranes **8**), Table 6 ([2 + 4]cycloaddition product **10**) and Tables 7 and 8 (1,1-organoboration products). When the mutual assignment of relevant ^{1}H and ^{13}C resonance signals was not obvious, $^{13}C/^{1}H$ heteronuclear shift correlations were used. Chemical shifts $\delta^{11}B$ showed clearly the presence of tri- or tetra-coordinate boron atoms [23]. The typically broad ^{13}C resonances of boron-bonded ^{13}C nuclei [24] aided the assignment of ^{13}C NMR spectra, and, in the case of the organotin compounds, $^{117/119}Sn$ satellites owing to $^{n}J(^{117/119}Sn,^{13}C)$ ($n = 1–4$) provided additional support of the assignments [25]. The power of ^{119}Sn NMR in monitoring the 1,1-organoboration reactions has already been addressed in Fig. 1. The different



Scheme 4.

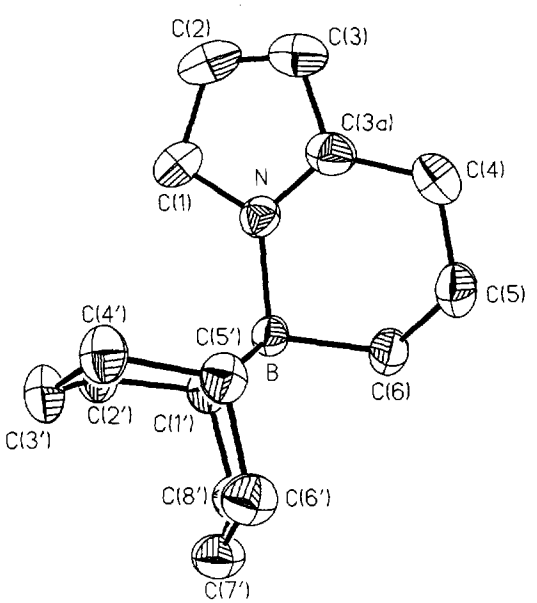
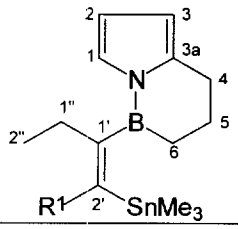
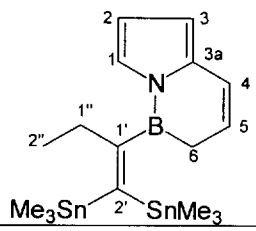


Fig. 2. ORTEP plot of the molecular structure of **4d** (hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (°): B–N 163.7(2), N–C(1) 146.0(3), C(1)–C(2) 148.3(2), C(2)–C(3) 131.2(4), C(3)–C(3a) 145.3(2), B–C(6) 162.3(3), B–C(1′) 163.1(2), B–C(5′) 163.6(2); B–N–C(1) 127.6(1), B–N–C(3a) 124.3(2), C(1)–N–C(3a) 108.0(1), N–C(1)–C(2) 104.4(2), C(1)–C(2)–C(3) 108.6(2), C(2)–C(3)–C(3a) 108.2(2), C(3)–C(3a)–N 110.6(2).

Table 7
^{11}B, and ^{13}C NMR data[a] of **11–13**



11 : R^1 = Me
12 : R^1 = $SnMe_3$



13

	No.		
	11	**12**	**13**
R^1	Me	$SnMe_3$	$SnMe_3$
$\delta^{11}B$	55.5	55.7	53.8
$\delta^{119}Sn$			
$SnMe_3$	−43.5	−40.3	−40.0
R^1	–	−55.8	−55.2
$\delta^{13}C$ [$J(^{119}Sn, ^{13}C)$]			
C-1	123.7	123.5	123.1
C-2	113.7	114.1	115.3
C-3	110.8	111.0	111.6
C-3a	137.2	137.2	135.9
C-4	26.4	26.4	121.4
C-5	21.9	22.0	123.4
C-6	19.3 [br]	19.5 [br]	23.5 [br]
C-1′	156.2 [br]	178.0 [br]	177.2 [br]
C-2′	141.9 [516]	141.9 [334][228]	149.5
C-1″	24.4 [n.o.]	38.9 [128][110]	38.8 [126][111]
C-2″	14.3	15.2 [8.9]	15.3
Me_3Sn	−8.8 [325]	−6.5 [324]	−6.5 [315]
R^1	20.3	−5.4 [303]	−5.4 [306][9.6]

[a] C_6D_6, 25°C; [br]: broad signal owing to partially relaxed ^{13}C–^{11}B scalar coupling; n.o. = not observed due to overlap with other signals.

line widths of the ^{119}Sn NMR signals, as the result of partially relaxed scalar ^{119}Sn–^{11}B spin–spin coupling [26] are related to the difference in the magnitude of the coupling constants $|^3J(^{119}Sn, ^{11}B)_{trans}| > |^3J(^{119}Sn,^{11}B)_{cis}| >> |^4J(^{119}Sn, ^{11}B)|$, and indicate the respective position of the tin atoms in **14** and **15**. Together with ^{13}C NMR data (Table 8), there can be no doubt about the structural assignment.

2.6. X-ray structural analysis of 4d

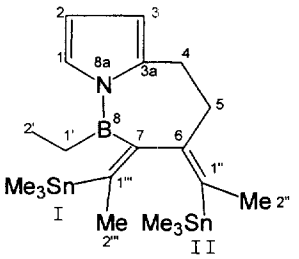
Data relevant to the structure are given in Section 4. [2] The molecular structure of **4d** is shown in Fig. 2. There are only a few molecular structures known containing the 2*H*-pyrrole structural element, and to the best of our knowledge none with two protons at the 2-position [9]. The bond lengths and angles in the 2*H*-pyrrole units differ in a wide range [27,28], depending on the various substituents, but the bond distances in the planar pyrrole ring of **4d** clearly indicate the 2*H*-pyrrole structural element. The B–N bond length [163.7(2) pm] lies well in the range of borane amine adducts or borane pyridine adducts [29,30]. Both six-membered rings of the 9-BBN fragment adopt a chair conformation as it has been found for several other 9-BBN derivatives [31–34]. The whole 9-BBN unit is slightly twisted against the plane of the pyrrole ring and the molecule shows no further symmetry.

3. Conclusions

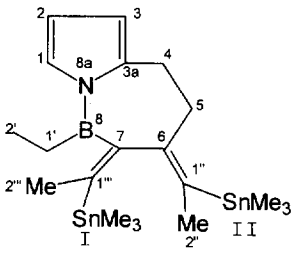
The result of the reactions of the bicyclic *N*-pyrrolylboranes with anionic nucleophiles reminds of the behaviour of triorganoboranes. However, a new aspect emerges since the protonation of the *N*-pyrrolylborates **5** leads to intramolecular 2*H*-pyrrole-borane adducts **4**, one of which was characterized by X-ray structural analysis. The adducts should become interesting reagents for further transformations, as was already shown here

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

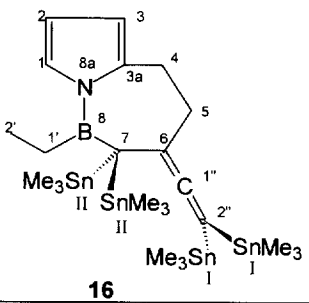
Table 8
^{11}B and ^{13}C NMR data[a] of **14–16**



14



15



16

	No.		
	14	**15**	**16**
$\delta^{119}Sn$			
Sn-I	−44.5[b]	−54.4[c]	−12.3[d]
Sn-II	−51.9[b]	−46.3[c]	8.8[d]
$\delta^{11}B$	53.5	52.4	56.5
$\delta^{13}C$ [$J(^{119}Sn, ^{13}C)$][b]			
C-1	124.2	124.0	123.7
C-2	113.7	113.2	111.8
C-3	112.0	112.2	111.7
C-3a	131.6	134.4	136.7
C-4	26.5 [11.7]	26.2	28.9 [23.6]
C-5	31.7 [56.9] [14.0]	37.9 [47.2] [6.0]	39.5 [28.5]
C-6	150.0 [81.6] [34.0]	150.8 [43.3] [25.6]	89.3 [71.9] [23.6]
C-7	161.0 [br]	158.9 [br]	39.2 [br]
C-1′	15.4 [br]	14.2 [br]	16.4 [br]
C-2′	10.6	9.9	11.1
C-1″	141.2 [696.3]	140.4 [345.0]	207.8 [39.4] [33.5]
C-2″	19.8 [55.7]	22.5 [53.4]	82.5 [280.6] [7.9]
C-1‴	146.3 [488.2]	147.8 [448.0] [12.8]	–
C-2‴	22.0 [62.2]	25.4 [68.6] [5.3]	–
$Sn(I)CH_3$	−8.0 [330.4]	−8.5 [328.0]	−6.9 [328.8]
$Sn(II)CH_3$	−7.9 [326.9]	−8.1 [323.1]	−3.2 [316.0]

[a] C_6D_6, 25°C; [br]: broad signal owing to partially relaxed $^{13}C-^{11}B$ scalar coupling.
[b5] $J(^{119}Sn, ^{119}Sn) = 27.0$ Hz.
[c5] $J(^{119}Sn, ^{119}Sn) = 36.4$ Hz.
[d2] $J(^{119}Sn(Sn\text{-}I), ^{117}Sn(Sn\text{-}I)) = 362.5$ Hz; $^2J(^{119}Sn(Sn\text{-}II), ^{117}Sn(Sn\text{-}II)) = 430.3$ Hz; $^5J(^{119}Sn, ^{119}Sn) = 212.7$ Hz.

by the synthesis of novel ionic triorganoboranes **8** and by selective formation of a [4 + 2]cyclo addition product **10**. The bicyclic *N*-pyrrolylboranes behave in 1,1-organoboration of 1-alkynyltin compounds in a way very similar to triorganoboranes. Surprisingly, the enlargement of the six-membered ring of **1a** or **2a** was not observed, whereas even twofold enlargement of the five-membered ring containing the boron atom in **3a** occurred, accompanied by partly unprecedented (**14** → **15**) selective and irreversible rearrangements.

4. Experimental

All reactions and handling of compounds were carried out observing necessary precautions to exclude oxygen and moisture. The bicyclic *N*-pyrrolylboranes were prepared as described [2,4]. The mono-1-alkynyltin compounds [35] and diethylamino-trimethylstannane [36] were prepared following literature procedures. Cyclopentadiene was generated by thermal cracking of commercial dicyclopentadiene. ^{n}BuLi in hexane (1.6 M) ^{t}BuLi in pentane (1.7 M), MeLi in Et_2O (1.6 M), DBU and trifluoromethylsulfonic acid were commercial products and used without further purification. Dynamic light scattering (He/Ne LASER, wavelength 632.8 nm) was measured with a BI 9 instrument (Brookhaven Instruments). 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 (^1H, ^{13}C), and Bruker ARX 250 or DRX 500 spectrometers equipped for multinuclear measurements [chemical shifts are referred to Me_4Si [$\delta^1H(CHCl_3/CDCl_3) = 7.24$, $(C_6D_5H) = 7.15$; $\delta^{13}C(CDCl_3) = 77.0$, $(C_6D_6) = 128.0$; $\delta^{29}Si$: $\Xi(^{29}Si) = 19.867184$ MHz], Et_2O-BF_3

[δ^{11}B: $\Xi(^{11}B)$ = 32.083971 MHz], neat $MeNO_2$ [δ^{14}N: $\Xi(^{14}N)$ = 7.226455 MHz] and Me_4Sn [δ^{119}Sn: $\Xi(^{119}Sn)$ = 37.290665 MHz].

4.1. 7a-aza-7-borata-4,5,6,7-tetrahydro-7aH-indenes 5 and 7a-aza-7-borata-7-butyl-7-ethyl-6,7-dihydro-7aH-indene 6c

4.1.1. General procedure

A solution of 2 mmol of the respective *N*-pyrrolylborane in 2 ml of hexane was cooled to −78°C and 2 mmol of the respective alkyl-lithium or alkyl-Grignard compound in Et_2O or hexane were added. The products precipitated as colourless wax-like solids. The solvent was removed and the residue was washed with pentane. Removal of all volatile material in vacuo left the pure products. The *N*-pyrrolylborates are insoluble in aliphatic, slightly soluble in aromatic solvents, and give yellow solutions with THF. The dianion **5g** is insoluble in THF. The characterization of most of the products was carried out by protonation (see Section 4.2).

5c, R = ^{n}Bu/R′ = Et, 0.4 g (95%): ^{1}H NMR (C_6D_6/THF (1:1), 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 6.55 (m) (H-1); 5.70 (m) (H-2); 5.44 (m) (H-3); 2.60 (t) [6.0] (H-4); 1.76 (m); 1.25 (m); 0.85 (m); 0.38 (m).

5e, R = *N*-Pyrrolyl/R′ = Et, 0.3 g (70%): ^{1}H NMR (C_6D_6/THF (1:1), 25°C): δ^1H = 6.60 (m) (H-2); 6.48 (m) (*N*-C*H*/pyrrolyl group); 5.83 (H-3); 5.79 (m) (NCHC*H*/pyrrolyl group); 5.61 (m) (H-3); 2.72 (m); 2.62 (m); 1.66 (m); 1.35 (m); 0.82 (m).

5f, R = 2′-trimethylsilylethynyl/R′ = Et, 0.28 g (60%): ^{1}H NMR (C_6D_6/THF (1:1), 25°C): δ^1H = 6.73 (m) (H-1); 6.07 (H-2); 5.76 (m) (H-3); 2.55 (m); 1.80 (m); 1.28 (m); 0.59 (m); −0.02 (s) (SiCH_3).

6c, R = ^{n}Bu/R′ = Et 0.4 g (95%): ^{1}H NMR (C_6D_6/THF (1:1), 25°C): δ^1H [($^nJ^1H, ^1H$)] = 6.61 (m) (H-1); 5.97 (d) [9.5] (H-4); 5.71 (t) [2.6 Hz] (H-2); 5.69 (m) (H-5); 5.57 (m) (H-3); 1.57 (m) (H-2′); 1.24 (m) (H-3′); 0.83 (t)/0.78 (t) (H-4′/H-2″); 0.44 (m) (H-6); 0.34 (m) (H-1′/H-1″).

4.2. Protonation of N-pyrrolylborates: 7a-azonia-7-borata-4,5,6,7-tetrahydro-1H-indenes 4

4.2.1. General procedure

To a solution or suspension of 2 mmol of the respective *N*-pyrrolylborate in THF at room temperature 34 μl (2 mmol) of H_2O or 0.12 ml (2 mmol) of acetic acid or 0.1 g (2 mmol) of NH_4Cl were added in one portion. For the preparation of the products **4g** and **4h** 1 mmol of the dianions were used. The mixtures were stirred at room temperature for one day. Then the solvent was removed in vacuo, the residue was suspended in hexane and stirred for one more day; the mixture was filtered, the solvent was removed from the filtrate, and the residue was distilled (**4g** and **4h** could not be distilled without decomposition). All products are colourless oily liquids.

4a, R = Me/R′ = Et, 0.2 g (63%) (b.p.: 95°C/0.1 Torr): ^{1}H NMR (C_6D_6, 25°C): δ^1H [$nJ(^1H, ^1H)$] = 6.53 (m) (H-2); 5.73 (m) (H-3); 3.92 (m) (H-1); 2.20 (m) (H-5); 1.74 (m) (H-4); 0.95 (t) [7.6] (CH_2CH_3); 0.66 (m) (H-6); 0.53 (m) (CH_2CH_3); −0.03 (s) (BCH_3).

4c, R = ^{n}Bu/R′ = Et 0.34 g (82%) (b.p.: 120°C/0.1 Torr): ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ^1H, ^1H$)] = 6.36 (m) (H-2); 5.60 (m) (H-3); 3.85 (H-1); 2.11 (m) (H-2′); 1.75 (m) (H-5); 1.50 (m) (H-1′/H-3′/H-4); 1.06 (t) [6.8 Hz] (H-4′); 0.10 (t) [8.1] (CH_2CH_3); 0.75 (m) (H-6); 0.57 (m) (CH_2CH_3).

4g, R = 1,4-butanediyl/R′ = Et, 0.1 g (30%): ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 6.63 (m) (H-2); 5.85 (m) (H-3); 4.01 (m) (H-1); 2.24 (m) (H-5); 1.73 (m) (H-4); 1.53 (m) (H-2′); 0.88 (t) [6.6] (CH_2CH_3); 0.63 (m) (H-6); 0.48 (m) (H-1′/CH_2CH_3).

4h, R = 1,6-hexanediyl/R′ = Et, 0.12 g (33%): ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H$)] = 6.53 (m) (H-2); 5.75 (m) (H-3); 3.95 (m) (H-1); 2.18 (m) (H-5); 1.73 (m) (H-4); 1.55 (m) (H-3′); 1.50 (m) (H-2′); 0.90 (t) [8.2] (CH_2CH_3); 0.68 (m) (H-6); 0.50 (m) (H-1′/CH_2CH_3).

4.3. Deprotonation of 7a-azonia-7-borata-4,5,6,7-tetrahydro-1H-indenes 4

4.3.1. General procedure

To a solution of 1 mmol of **4a–4d** in 5 ml of hexane at −78°C 1 mmol of ^{t}BuLi in hexane or LiCp in THF or DBU (diazabicyclo[5.4.0]undec-7-ene) respectively were added. The mixtures were stirred at room temperature for 2 h. After that the solvent was removed in vacuo and the residue was washed with hexane. Removing of all volatile material in vacuo left the pure products.

5d, R/R′ = 1,5-cyclooctanediyl, 0.2 g (90%) (m.p.: 120°C under decomposition); ^{1}H NMR (C_6D_6/THF (1:1), 25°C): δ^1H = 6.95 (m) (H-1); 5.63 (m) (H-2); 5.42 (m) (H-3); 2.61 (m) (H-5); overlapping signals at 2.37, 2.12–1.17 (H-4/H-2′/H-3′/H-4′/H-6′/H-7′/H-8′); 0.79 (m) (H-6); 0.59 (m)/0.48 (m) (H-1′/H-5′).

4.4. 2-[3′-(Ethyl-ethoxyboryl)propyl]pyrrol 7a

To a solution of 0.15 g (1 mmol) of **1a** in 5 ml of hexane at room temperature 0.04 g (1 mmol) of EtOH were added. The reaction proceeds immediately. After removing of the solvent in vacuo 0.19 g (100%) of **7a** were left as a colourless oil. When **7a** is kept for a long time in vacuo it reacts back to **1a** by elimination of EtOH.

^{1}H NMR (C_6D_6, 25°C): δ^1H = 8.84 [br] (NH); 6.44 (m) (H-1); 5.99 (m) (H-2); 5.82 (m) (H-3); 4.46 (m) (OCH_2); 2.42 (m) (H-4); 1.56 (m) (BCH_2); 0.98 (m) (CH_3); 0.78 (m) (H-5/H-6).

4.5. Addition of trifluoromethylsulfonic acid

A solution of 1 mmol of **1e**, **4a** or **4d**, respectively, in 1 ml of CH_2Cl_2 was cooled to 0°C and 0.15 g (1 mmol) of trifluoromethylsulfonic acid were added. The solvent was immediately removed in vacuo. **4i** and **8a** were left as colourless viscous oils, **8d** as a colourless wax.

4i, R = trifluoromethylsulfonate/R′ = thexyl: ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 7.25 (m) (H-2); 6.16 (m) (H-3); 4.40 (m) (H-1); 2.35 (m) (H-4); 1.59 (septet) [6.5] (CH/Thexyl-Rest); 1.47 (quintet) [6.5] (H-5); 1.00 (m) (H-6); 0.72 (s) (C-CH_3); 0.71 (d) (CH-CH_3).

8a: ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 11.53 [br] (NH); 7.13 (m) (H-2); 6.19 (m) (H-3); 4.08 (m) (H-1); 2.43 (t) [7.5] (H-4); 1.49 (m) (H-5); overlapping signals at 1.05–0.83 (H-6/Et).

8d: ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 12.10 [br] (NH); 7.24 (d) [5.1] (H-2); 6.23 (d) [5.1] (H-3); 4.27 (m) (H-1); 2.54 (m) (H-4); 1.65 (m) (BC(C_2)H); 1.59 (m) (H-5); 1.23 (m) (H-6); 1.8–1.6 (m), 1.77 (m), 1.17 (m) (9-BBN group).

4.6. Addition of water

To a solution of 0.1 g (0.43 mmol) of **4d** in 1 ml of THF 40 μl (2.2 mmol) of water were added. The reaction proceeds immediately and gives a mixture of 90% of **7d** and 10% of **4d** in the equilibrium. An isolation of **7d** was not possible.

^{1}H NMR (C_6D_6, 25°C): δ^1H = 9.10 [br] (NH); 6.02 (m) (H-1); 5.42 (m) (H-3); 5.26 (m) (H-2); 4.43 [br] (H_2O); 2.07 (m) (H-4); 1.7–1.0 (m), 0.2 (m), 0.1 (m) (H-6/H-6/9-BBN group).

4.7. Addition of (diethylamino)trimethylstannane

To a solution of 0.23 g (1 mmol) of **4d** in 2 ml of pentane were added 0.24 g (1 mmol) of (diethylamino)trimethylstannane. The solvent was removed immediately and **9** was left as a colourless liquid. ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 6.59 (m) (H-1); 6.43 (t) [2.9 Hz] (H-2); 6.30 (m) (H-3); overlapping signals at 2.69–1.50; 0.82 (t) [7.3 Hz] (CH_3); 0.30 (s) (SnCH_3).

4.8. Addition of cyclopentadiene: spiro-[9a-azonia-1-borata-1,2,3,4,4b,5,8,8a-octa-hydro-5,8-methano-9H-fluorene-1,9′-9′-boratabicyclo[3.3.1]nonane ***10***

A mixture of 0.23 g (1 mmol) of **4d** in 10 ml of toluene and 0.26 g (4 mmol) of cyclopentadiene was stirred at 100°C for 20 h. After that, the solvent and the excess of cyclopentadiene were removed in vacuo and 0.3 g (100%) of **10** were left as a colourless liquid.

^{1}H NMR (C_6D_6, 25°C): δ^1H = 5.81 (m)/5.61 (m) (H-6/H-7); 3.60 (m) (H-9); overlapping multiplets at 3.25–0.50.

4.9. 1,1-organoboration reactions

4.9.1. General procedure (the reactions were carried out in NMR tubes)

To a solution of 1 mmol of the respective *N*-pyrrolylborane in 0.5 ml of C_6D_6 1 mmol of the mono-1-alkynyltin compound was added. For the preparation of the butadiene and allene derivatives 2 mmol of the mono-1-alkynyltin compound were used. The sample was stored at room temperature. The progress of the reaction can be followed by ^{119}Sn NMR spectroscopy. After 2 days the reactions were complete. The 1,1-organoboration products **11–16** were yellowish liquids. In the case of **11** it was necessary to heat at 80°C for 24 h.

11: ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 6.84 (m) (H-1); 6.19 (m) (H-2); 6.00 (m) (H-3); 2.62 (m) (H-4); 2.29 (s) (=CCH_3); 1.52 (m) (H-5); 1.25 (m) (H-6); 1.06 (m) (CH_2CH$_3$); 0.90 (t) [7.6] (CH_2CH_3); −0.05 (s) (SnCH_3).

12: ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 6.86 (m) (H-1); 6.23 (t) [3.0] (H-2); 5.99 (m) (H-3); 2.55 (m) (H-4); 1.53 (m) (H-5); 1.07/0.97 (m) (H-6/CH_2CH_3); 0.29 (s) (trans-SnCH_3); −0.01 (s) (*cis*-SnCH_3).

13: ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 6.90 (d) [2.9] (H-1); 6.50 (d) [9.7 Hz] (H-4); 6.27 (t) (H-2); 6.15 (m) (H-3); 5.76 (m) (H-5); 2.41 (m)/2.26 (m) (H-6); overlapping multiplets at 1.50; 0.85 (t) [7.5] (CH_2CH_3); 10.26 (s) (*trans*-SnCH_3); −0.10 (s) (*cis*-SnCH_3).

14: ^{1}H NMR (C_6D_6, 25°C): δ^1H = 6.96 (m) (H-1); 6.26 (m) (H-2); 6.02 (m) (H-3); 2.70 (m) (H-5); 2.32 (m) (H-4); 1.93 (s) (H-2‴) $^3J(^{119}Sn, ^1H)$ = 49.6 Hz; 1.71 (s) (H-2″) $^3J(^{119}Sn, ^1H)$ = 49.9 Hz; 1.39 (m) (H-1′); 1.02 (t) (H-2′); 0.21 (s) (Sn(I)CH_3) $^2J(^{119}Sn, ^1H)$ = 50.2 Hz; 0.11 (s) (Sn(II)CH_3) $^2J(^{119}Sn, ^1H)$ = 52.0 Hz.

15, by heating of **14** to 80°C in C_6D_6 for 4 h: ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 6.95 (m) (H-1); 6.22 (m) (H-2); 6.01 (m) (H-3); 2.91 (m) (H-5); 82.61 (m) (H-4); 2.32 (m) (H-5); 1.97 (s) (H-2″/H-2‴); 1.47 (m) (H-1′); 1.11 (t) [7.7] (H-2′); 0.15 (s) (Sn(II)CH_3); 0.10 (s) (Sn(I)CH_3).

16: ^{1}H NMR (C_6D_6, 25°C): δ^1H [$^nJ(^1H, ^1H)$] = 6.76 (m) (H-1); 6.24 (m) (H-2); 5.97 (m) (H-3); 2.90 (t) [6.4] (H-5); 2.30 (t) (H-4); 1.12 (m) (H-1′); 0.94 (t) [7.4] (H-2′); 0.24 (s) (Sn(I)CH_3); 0.14 (s) (Sn(II)CH_3). EI-MS ($C_{24}H_{48}BNSn_4$): m/z (%) = 841 (7) [M^+]; 676 (17) [M^+-$SnMe_3$]; 496 (68) [M^+-2 $SnMe_3$-Me]; 165 (100) [$SnMe_3^+$].

4.10. Crystal structure analysis of ***4d***[1]

$C_{15}H_{24}BN$ (M = 229.2); $F(000)$ = 252, yellowish, irregularly 0.50 × 0.35 × 0.20 mm^3 (m.p. 85°C); triclinic, $P\bar{1}$; a = 8.387(2), b = 9.201(2), c = 10.424(2) Å, α = 66.25(2)°, β = 85.49(2)°, γ = 64.37(2)°, volume

659.3(2) Å^3; $Z = 2$; density (calc.) = 1.154 Mg/m^3; absorption coefficient 2.982 mm^{-1}; data were collected with a Siemens P4 diffractometer (Mo Kα; graphite monochromator; $\lambda = 0.71073$ Å; $2.0 < 2\Theta < 60.0°$); $T = 296$ K; 7108 reflections, 3710 independent reflections ($R_{int.} = 3.28\%$), 2858 observed reflections [$F > 12.0\ \sigma(F)$]; Lorentz and polarisation correction; structure solution by Patterson methods followed by difference Fourier synthesis using the SHELXTL-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 155 parameters, converged at $R/wR = 3.02/2.19\%$. The max/min residual electron density was $0.36/-0.17$ e Å^{-3}.

Acknowledgements

The support of this work by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and Volkswagen-Stiftung is gratefully acknowledged. We thank G. Sühler (Universität Bayreuth) for carrying out the light scattering measurements.

References

[1] B. Wrackmeyer, B. Schwarze, W. Milius, Inorg. Chim. Acta 241 (1996) 87.
[2] B. Wrackmeyer, B. Schwarze, J. Organomet. Chem., 1997, in press.
[3] B. Wrackmeyer, H.E. Maisel, B. Schwarze, W. Milius, R. Köster, J. Organomet. Chem., 1997, in press.
[4] B. Wrackmeyer, B. Schwarze, I. Ordung, J. Organomet. Chem., 1997, in press.
[5] P. Szarvos, J. Emri, B. Györi, Magy. Kem. Foly. 74 (1968) 142.
[6] R. Köster, H. Bellut, S. Hattori, Liebigs Ann. Chem. 720 (1968) 1.
[7] H. Bellut, R. Köster, Liebigs Ann. Chem. 738 (1970) 86.
[8] H. Bellut, C.D. Miller, R. Köster, Synth. React. Inorg. Metal-Org. Chem. 1 (1971) 83.
[9] M.P. Sammes, in: R.A. Jones (Ed.,) Pyrroles, Part 1, The Chemistry of Heterocyclic Compounds, A Series of Monographs, Interscience Publication, New York, 1990, 549–728.
[10] R. Hoffmann, R.B. Woodward, Angew. Chem. 82 (1969) 797.
[11] R. Hoffmann, R.B. Woodward, Angew. Chem. Int. Ed. Engl. 8 (1969) 781.
[12] B. Wrackmeyer, in: S. Hermanek (Ed.), Boron Chemistry, Proceedings of the 6th International Meeting on Boron Chemistry (IMEBORON VI), World Scientific, Singapore, 1987, pp. 387–415.
[13] B. Wrackmeyer, Coord. Chem. Rev. 145 (1995) 125.
[14] B. Wrackmeyer, Organometallics 3 (1984) 4.
[15] B. Wrackmeyer, U. Dörfler, G. Kehr, H.E. Maisel, W. Milius, J. Organomet. Chem. 524 (1996) 169.
[16] B. Wrackmeyer, H. Vollrath, Main Group Metal Chem. 19 (1996) 215.
[17] C. Bihlmayer, S.T. Abu-Orabi, B. Wrackmeyer, J. Organomet. Chem. 322 (1987) 25.
[18] C. Bihlmayer, B. Wrackmeyer, Z. Naturforsch. 36B (1981) 1265.
[19] B. Wrackmeyer, C. Bihlmayer, M. Schilling, Chem. Ber. 116 (1983) 3182.
[20] B. Wrackmeyer, R. Zentgraf, J. Chem. Soc., Chem. Commun., 1978, 402.
[21] B. Wrackmeyer, Z. Naturforsch. 33B (1978) 385.
[22] B. Wrackmeyer, J. Organomet. Chem. 205 (1981) 1.
[23] H. Nöth, B. Wrackmeyer, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), NMR—Basic Principles and Progress, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, Vol. 14, Springer, Berlin, 1978.
[24] B. Wrackmeyer, Prog. NMR Spectrosc. 12 (1979) 227.
[25] B. Wrackmeyer, in: M. Gielen, R. Willem, B. Wrackmeyer (Eds.), Physical Organometallic Chemistry—Advanced Applications of NMR to Organometallic Chemistry, Wiley, London, 1996, pp. 87–122.
[26] B. Wrackmeyer, Polyhedron 5 (1986) 1709.
[27] A. Gambocorta, R. Nicoletti, S. Cerrini, W. Fedeli, G. Gavuzzo, Tetrahedron 36 (1980) 1367.
[28] T.F. Lai, M.W.L. Chung, M.P. Sammes, J. Chem. Res., 1980, 408 and 1367.
[29] B. Wrackmeyer, H.E. Maisel, W. Milius, Z. Naturforsch. 50B (1995) 809.
[30] T. Murafuji, T. Mouri, Y. Sugihara, K. Takakura, Y. Mikata, S. Yano, Tetrahedron 52 (1996) 13933.
[31] P. Idelmann, G. Müller, W.R. Scheidt, W. Schüßler, K. Seevogel, R. Köster, Angew. Chem. 96 (1984) 145.
[32] P. Idelmann, G. Müller, W.R. Scheidt, W. Schüßler, K. Seevogel, R. Köster, Angew. Chem. Int. Ed. Engl. 23 (1984) 153.
[33] M. Yalpani, R. Köster, R. Boese, Chem. Ber. 122 (1989) 19.
[34] M. Yalpani, R. Köster, R. Boese, Chem. Ber. 123 (1990) 1285.
[35] W.E. Davidsohn, M.C. Henry, Chem. Rev. 67 (1967) 73.
[36] C.M. Wright, R.L. Muetterties, Inorg. Synth. 10 (1967) 137.