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Reactivity of bicyclic N-pyrrolylboranes¹

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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 ¹H, ¹¹B, ¹³C, ¹⁴N and ¹¹⁹Sn 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 2H-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.



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

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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 2H-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 1,4di(brom om agnesium)butane o r 1.6di(bromomagnesium)-hexane affords the coupled borates 5g and 5h as mixtures of diastereomers (Scheme lg), and these can also be protonated to give the corresponding 2H-pyrrole-borane adducts (Scheme 1h).





4

	No.					
	4a	4b	4c	4g ^b	4h ^b	4i
R	Et	Me	"Bu	1,4-butanediyl	1,6-hexanediyl	-OSO ₂ CF ^c ₃
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
$\delta^{I3}C$						
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	$19.5 [br] (CH_2)$	10.8 [br]	28.0 [br] (C-1')	$29.2 [br] (B-CH_2)$	28.5 [br] (B-CH ₂)	$120.1 (q), {}^{1}J({}^{19}F, {}^{13}C) = 318 \text{ Hz}$
	10.9 (CH ₃)		14.8(CH ₃)	30.0(C-2')/27.9(C-3')	32.8/32.6 ^b	35.5/35.4 ^b
					27.8/27.7*	
R'	see R	19.5 [br] (CH ₂)	19.4 [br] (CH ₂)	$20.0 [br] (CH_2)$	$19.5 [br] (CH_2)$	28.8 [br] (B-C)
		11.2 (CH ₃)	11.0 (CH ₃)	11.2 (CH ₃)	11.0 (CH ₃)	34.4(CH)/20.7(CH-CH ₃) 18.2 (C-CH ₃)

 ${}^{a}C_{6}D_{6}$, 25°C; [br]: broad signal owing to partially relaxed ${}^{13}C-{}^{11}B$ scalar coupling; n.m. = not measured.

^b4g and 4h are diastereomers.

^c The [CF₃OSO₂]⁻ 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.



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 ($\delta^{11}B$ 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 NCH₂-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.







 ${}^{a}C_{6}D_{6}/THF$ (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.

 δ^{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 16 (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 1,1organoboration 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(trimethyl)stannyl)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.







Fig. 1. 93.3 MHz ¹¹⁹Sn^{{1}H} 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 alky group is the result of thermodynamic control. Therefore, in both 1a and 2a either the endo-

Table 3 ¹¹B and ¹³C NMR data^a of 6c



130

δВ	9.ºC													
	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	

^aC₆D₆/THF (1:1), 25°C; [br]: broad signal owing to partially relaxed ¹³C-¹¹B scalar coupling.



	1L	33 5 3	Ī
		N ¥ š R	7, 9
	No.		······································
	7a ^b	7d°	9 ^d
B]	B(Et)OEt	9-BBN(\leftarrow OH ₂)	9-BBN(\leftarrow HNE ₁₂)
R	н	н	SnMe,
δ ^{††} Β	54.8	12.9	- 0.4
δ 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]

 ${}^{a}C_{6}D_{6}$, 25°C; [br]: broad signal owing to partially relaxed ${}^{13}C-{}^{11}B$ scalar coupling.

^b δ^{13} C (OEt) = 61.0 (CH₂); 17.5 (CH₃); δ^{13} C (Et) = 12.3 [br] (CH₂); 8.2 (CH₃).

^cMeasured in THF: δ^{13} C (9-BBN group) = 32.0 (CHCH₂); 24.7(CHCH₂CH₂); (BCH) not observed due to overlap with other signals.

 ${}^{d}\delta^{119}$ Sn = 62.5, δ^{13} C(SnMe₃) = $-4.8 {}^{1}J({}^{119}$ Sn, 13 C) = 384 Hz, δ^{13} C (NEt₂) = 44.7 (CH₂); 15.7 (CH₃). δ^{13} C (9-BBN group) = 24.0 [br] (BCH); 32.6 (br) (CHCH₂); 25.3 (CHCH₂CH₂).

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





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 1,1organoboration 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. ¹¹⁹Sn NMR spectroscopy proved to be the ideal tool for monitoring this rearrangement (Fig. 1).

			[CF ₃ OSO ₂] ⁻	2 1 9 N H	3a 5 4	R B 6 R	8				
No.	R/R	δ''Β	$\delta^{14}N$	δ ¹³ C							
				C-1	C-2	C-3	C-3a	C-4	C-5	C-6	
8a ^b 8d ^c	Et/Et 1,5-cyclo-octanediyl	86.4 92.0	n.m. 194.0	61.1 61.4	156.7 156.9	128.6 128.5	188.8 188.4	33.3 33.3	21.2 21.5	27.1 [br] 27.2 [br]	-

 ${}^{a}C_{6}D_{6}$, 25°C; [br]: broad signal owing to partially relaxed ${}^{13}C_{-}{}^{11}B$ scalar coupling; n.m. = not measured.

 ${}^{b}\delta^{13}C(R) = 19.3 [br] (BCH_2); 7.9 (Me); \delta^{13}C (CF_3) = 120.0 (q); {}^{1}J({}^{19}F, {}^{13}C) = 318.0 \text{ Hz}.$

 $^{\circ}\delta^{13}C(R) = 31.2 \text{ [br] (BCH)}; 33.3 (CHCH_2); 23.4 (CHCH_2CH_2).$





^aC₆D₆, 25°C; [br]: broad signal owing to partially relaxed ¹³C-¹¹B 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 ¹H (see Section 4), ¹¹B, ¹³C, ¹⁴N and ¹¹⁹Sn 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



Scheme 4.

(1,1-organoboration products). When the mutual assignment of relevant ¹H and ¹³C resonance signals was not obvious, ¹³C/¹H heteronuclear shift correlations were used. Chemical shifts δ^{11} B showed clearly the presence of tri- or tetra-coordinate boron atoms [23]. The typically broad ¹³C resonances of boron-bonded ¹³C nuclei [24] aided the assignment of ¹³C NMR spectra, and, in the case of the organotin compounds, ^{117/119}Sn satellites owing to ⁿJ(^{117/119}Sn, ¹³C) (n = i-4) provided additional support of the assignments [25]. The power of ¹¹⁹Sn NMR in monitoring the 1,1-organoboration reactions has already been addressed in Fig. 1. The different



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).

	2^{-1} 3^{-3} 3	11 : R ¹ = Me 2" 12 : R ¹ = SnMe ₃ Me	2 1 1 1 1 1 1 1 1	
	No.			
	11	12	13	
R ¹ δ ¹¹ B	Me 55.5	SnMe ₃ 55.7	SnMe ₃ 53.8	
δ ¹¹⁹ Sn				
SnMe ₂	- 43.5	- 40.3	-40,0	
R ¹	_	- 55.8	-55.2	
$\delta^{13}C[J(1)^{9}Sn, 13]$	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	
Ae ₃ Sn	- 8.8 [325]	-6.5 [324]	-6.5 [315]	
^ر آ	20.3	-5.4 [303]	- 5.4 [306][9.6]	

Table 7 ¹¹B, and ¹³C NMR data³ of 11-13

 ${}^{a}C_{6}D_{6}$, 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 ¹¹⁹Sn NMR signals, as the result of partially relaxed scalar ¹¹⁹Sn-¹¹B spin-spin coupling [26] are related to the difference in the magnitude of the coupling constants $|{}^{3}J({}^{119}Sn, {}^{11}B)_{trans}| > |{}^{3}J({}^{119}Sn, {}^{11}B)_{cis}| > |{}^{4}J({}^{119}Sn, {}^{11}B)|$, 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 2H-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 sixmembered 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 2H-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.



	2 1 5 1 8 7 6 1 8 7 6 1 1 Me ₃ Sn 2''' I I I I	$ \begin{array}{c} 2 \\ 1 \\ 1 \\ 8 \\ 2' \\ 1'' \\ 8 \\ 7'' \\ 8 \\ 7'' \\ 8 \\ 7'' \\ 8 \\ 7'' \\ 8 \\ 7'' \\ 1''' \\ 5 \\ 1''' \\ 1''' \\ 5 \\ 1''' \\ 1''' \\ 5 \\ 1''' \\ 1''' \\ 5 \\ 1'''' \\ 1''' \\ 1''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1'''' \\ 1''''' \\ 1''''' \\ 1''''''''''$	$ \begin{array}{c} 2 \\ 3 \\ 1 \\ 8 \\ 8 \\ 3 \\ 4 \\ 5 \\ 5 \\ Me_3 Sn \\ 11 \\ Me_3 Sn \\ He_3 Sn$	
<u> </u>	<u>14</u>	15	16	
	14	15	16	
δ119Sh	· · · · · · · · · · · · · · · · · · ·			
Sn-I	-44.5 ^b	54.4°	- 12.3 ^d	
Sn-11	-51.9 ^b	-46.3°	8.8 ^d	
δ ¹¹ Β	53.5	52.4	56.5	
$\delta^{13}C[J(1)^{y}Sn]$	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]	

 ${}^{3}C_{6}D_{6}$, 25°C; [br]: broad signal owing to partially relaxed ${}^{13}C_{-11}B$ scalar coupling. ${}^{55}J_{119}^{(119}Sn, {}^{119}Sn) = 27.0$ Hz. ${}^{55}J_{119}^{(119}Sn, {}^{119}Sn) = 36.4$ Hz.

 $d^{2}J(^{119}Sn(Sn-I)) = 362.5 Hz; ^{2}J(^{119}Sn(Sn-II)) = 430.3 Hz; ^{5}J(^{119}Sn, ^{117}Sn) = 212.7 Hz.$

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 1,1organoboration 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 $(14 \rightarrow$ 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-alkynyl-

tin compounds [35] and diethylamino-trimethylstannane [36] were prepared following literature procedures. Cyclopentadiene was generated by thermal cracking of commercial dicyclopentadiene. "BuLi in hexane (1.6 M) 'BuLi in pentane (1.7 M), MeLi in Et₂O (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 CDCl₃ or C₆D₆ at 25°C by using Jeol EX270 (¹H, ¹³C), and Bruker ARX 250 or DRX 500 spectrometers equipped for multinuclear measurements [chemical shifts are referred to Me₄Si [δ^{+} H(CHCl₃/CDCl₃) = 7.24, $(C_6 D_5 H) = 7.15; \quad \delta^{13} C(CDCl_3) = 77.0, \quad (C_6 D_6) =$ 128.0; δ^{29} Si: $\Xi(^{29}$ Si) = 19.867184 MHz], Et₂O-BF₃

 $[\delta^{11}B: \Xi(^{11}B) = 32.083971 \text{ MHz}]$, neat MeNO₂ $[\delta^{14}N: \Xi(^{14}N) = 7.226455 \text{ MHz}]$ and Me₄Sn $[\delta^{119}Sn: \Xi(^{119}Sn) = 37.290665 \text{ MHz}]$.

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-7aHindene 6c

4.1.1. General procedure

A solution of 2 mmol of the respective *N*-pyrrolyborane in 2 ml of hexane was cooled to -78° C and 2 mmol of the respective alkyl-lithium or alkyl-Grignard compound in Et₂O 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%): ¹H NMR (C_6D_6/THF (1:1), 25°C): $\delta^{1}H[{}^{n}J({}^{1}H, {}^{1}H)] = 6.55$ (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%): ¹H NMR (C_6D_6 /THF (1:1), 25°C): $\delta^1H = 6.60$ (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%): ¹H NMR (C₆D₆/THF (1:1), 25°C): δ^{1} H = 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) (SiCH₃).

6c, $R = "Bu/R' = Et 0.4 g (95\%): ^1H NMR (C₆D₆/THF (1:1), 25°C): <math>\delta^1H [("J^1H, ^1H)] = 6.61 (m)$ (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-7borata-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 μ l (2 mmol) of H₂O or 0.12 ml (2 mmol) of acetic acid or 0.1 g (2 mmol) of NH₄Cl 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): ¹H NMR (C₆D₆, 25°C): δ^{1} H [*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] (CH₂CH₃); 0.66 (m) (H-6); 0.53 (m) (CH₂CH₃); -0.03 (s) (BCH₃).

4c, $R = {}^{n}Bu/R' = Et \ 0.34 g (82\%) (b.p.: 120°C/0.1 Torr): {}^{1}H NMR (C_{6}D_{6}, 25°C): \delta^{1}H [{}^{n}J^{1}H, {}^{1}H)] = 6.36 (m) (H-2); 5.60 (m) (H-3); 3.85 (H-1); 2.11 (m) (H-2'); 1.75 (m) (H-5); 1.50 (m) (H-1'/H-3'/H-4); 1.06 (t) [6.8 Hz] (H-4'); 0.10 (t) [8.1] (CH₂CH₃); 0.75 (m) (H-6); 0.57 (m) (CH₂CH₃).$

4g, R = 1,4-butanediyl/R' = Et, 0.1 g (30%): ¹H NMR (C_6D_6 , 25°C): δ^1 H [" $J(^1$ H, 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] (CH₂CH₃); 0.63 (m) (H-6); 0.48 (m) (H-1'/CH₂CH₃).

4h, R = 1,6-hexanediyl/R' = Et, 0.12 g (33%): ¹H NMR (C₆D₆, 25°C): δ^{1} H ["J(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] (CH₂CH₃); 0.68 (m) (H-6); 0.50 (m) (H-1'/CH₂CH₃).

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 '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); ¹H NMR (C_6D_6 /THF (1:1), 25°C): $\delta^1H = 6.95$ (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.

¹H NMR (C_6D_6 , 25°C): $\delta^1H = 8.84$ [br] (NH); 6.44 (m) (H-1); 5.99 (m) (H-2); 5.82 (m) (H-3); 4.46 (m) (OCH₂); 2.42 (m) (H-4); 1.56 (m) (BCH₂); 0.98 (m) (CH₃); 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: ¹H NMR (C_6D_6 , 25°C): δ^1 H [" $J(^1H, ^1H)$] = 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-CH₃); 0.71 (d) (CH-CH₃).

8a: ¹H NMR (C_6D_6 , 25°C): δ^1 H [$^nJ(^1H, ^1H)$] = 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: ¹H NMR (C_6D_6 , 25°C): δ^1 H ["J(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 μ l (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.

¹H NMR ($C_6 D_6$, 25°C): $\delta^1 H = 9.10$ [br] (NH); 6.02 (m) (H-1); 5.42 (m) (H-3); 5.26 (m) (H-2); 4.43 [br] (H₂O); 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. ¹H NMR (C_6D_6 , 25°C): $\delta^1H[^nJ(^1H, ^1H)] = 6.59$ (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] (CH₃); 0.30 (s) (SnCH₃).

4.8. Addition of cyclopentadiene: spiro-[9a-azonia-1borata-1,2,3,4,4b,5,8,8a octa-hydro-5,8-methano-9Hfluorene-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.

¹H NMR (C_6D_6 , 25°C): $\delta^1H = 5.81$ (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 ¹¹⁹Sn NMR spectroscopy. After 2 days the reactions were complete. The 1,1organoboration products **11–16** were yellowish liquids. In the case of **11** it was necessary to heat at 80°C for 24 h.

11: ¹H NMR (C_6D_6 , 25°C): $\delta^1H[^nJ(^1H, ^1H)] = 6.84$ (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: ¹H NMR (C_6D_6 , 25°C): δ^1 H [${}^nJ({}^1$ H, 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/CH₂CH₃); 0.29 (s) (trans-SnCH₃); -0.01 (s) (*cis*-SnCH₃).

13: ¹H NMR (C_6D_6 , 25°C): δ^1 H [${}^nJ({}^1$ H, 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] (CH₂CH₃); 10.26 (s) (*trans*-SnCH₃); -0.10 (s) (*cis*-SnCH₃).

14: ¹H NMR (C₆D₆, 25°C): δ^{1} H = 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^m) ³J(¹¹⁹Sn, ¹H) = 49.6 Hz; 1.71 (s) (H-2^m) ³J(¹¹⁹Sn, ¹H) = 49.9 Hz; 1.39 (m) (H-1'); 1.02 (t) (H-2'); 0.21 (s) (Sn(I)C H₃) ²J(¹¹⁹Sn, ¹H) = 50.2 Hz; 0.11 (s) (Sn(II)C H₃) ²J(¹¹⁹Sn, ¹H) = 52.0 Hz.

15, by heating of 14 to 80°C in C₆D₆ for 4 h: ¹H NMR (C₆D₆, 25°C): δ^{1} H ["J(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)C H₃); 0.10 (s) (Sn(I)C H₃).

16: ¹H NMR (C_6D_6 , 25°C): $\delta^1H[^nJ(^1H, ^1H)] = 6.76$ (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)CH₃); 0.14 (s) (Sn(II)CH₃). EI-MS ($C_{24}H_{48}BNSn_4$): m/z (%) = 841 (7) [M⁺]; 676 (17) [M⁺-SnMe₃]; 496 (68) [M⁺-2 SnMe₃-Me]; 165 (100) [SnMe₃⁺].

4.10. Crystal structure analysis of 4d¹

 $C_{15}H_{24}BN$ (M = 229.2); F(000) = 252, yellowish, irregularly 0.50 × 0.35 × 0.20 mm³ (m.p. 85°C); triclinic, P $\tilde{1}$; a = 8.387(2), b = 9.201(2), c = 10.424(2)Å, $\alpha = 66.25(2)^{\circ}$, $\beta = 85.49(2)^{\circ}$, $\gamma = 64.37(2)^{\circ}$, volume

659.3(2) $Å^3$; Z = 2; density (calc.) = 1.154 Mg/m³; absorption coefficient 2.982 mm⁻¹: data were collected with a Siemens P4 diffractometer (Mo K α ; graphite monochromator; $\lambda = 0.71073$ Å; $2.0 < 2\Theta < 60.0^{\circ}$); 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 $0.36 / - 0.17 \text{ e } \text{\AA}^{-3}$.

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