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Novel rearrangements of fused zwitterionic heterocyclic systems

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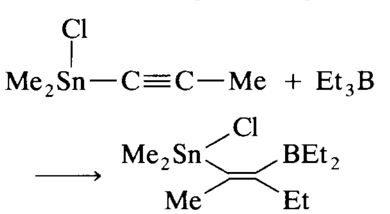
Abstract

(E)-2-Chlorodimethylstannyl-3-diethylboryl-2-pentene (1) reacts with the C-lithiated azoles 2 (derived from thiazole (**2a**), 4-methylthiazole (**2b**), 1,4-dimethylimidazole (**2c**), benzoxazole (**2d**) and benzthiazole (**2e**)) to eliminate LiCl, giving first mixtures containing compounds with either a coordinative N–B bond (**3**) or the zwitterionic isomer with an Sn–N bond (**4**), or both, and in some cases a rearranged product (**5**) with a 1,2,5-azastannaborole unit is also present. The zwitterionic compounds **4** tend to rearrange into the heterocycles **5** in which the heteroaromatic system is no longer present and two new C–C bonds, a new B–C and a new B–N bond are formed. The reactions were monitored by multinuclear NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N and ^{119}Sn NMR) which also served for the characterization of the final products. In the case of **5e**, the molecular structure was determined by single-crystal X-ray analysis (monoclinic; space group $P2_1/n$; $a = 11.691(2)$, $b = 12.396(2)$, $c = 13.149(2)$ Å; $\beta = 93.41(2)°$).

Keywords: Fused zwitterionic heterocycles; Tin; Boron; Nuclear magnetic resonance; X-ray diffraction

1. Introduction

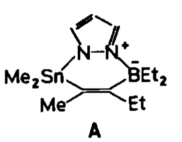
The synthesis of alkene derivatives with a stannyl and a boryl group in the *cis* position is readily achieved via 1,1-organoboration of 1-alkynyltin compounds [1]. Such systems are attractive starting materials in organometallic synthesis [2]. In **1** obtained via the reaction shown in Eq. (1) the presence of a reactive Sn–Cl



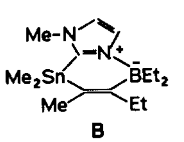
$$\overset{\text{Cl}}{\overset{|}{\text{Me}_2\text{Sn}}}\text{—C}\equiv\text{C—Me} + \text{Et}_3\text{B} \longrightarrow (\text{Cl})\text{Me}_2\text{Sn}(\text{Me})\text{C}{=}\text{C}(\text{Et})\text{BEt}_2 \qquad (1)$$

1

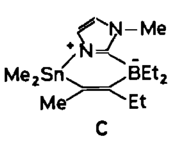
bond enhances further the synthetic potential as has been shown by numerous reactions between **1** and various nucleophiles [3–5]. One attractive property of **1** concerns the competition between the tin and the boron atom as electrophilic centers for nucleophilic attack. This aspect is of particular interest if two nucleophilic sites are offered at the same time. Previously, we have studied the reaction between **1** and some N- or C-lithiated azoles. The final products were fused heterocyclic systems, e.g. **A** and **B**; however, it was noted that, in the course of the formation of **B**, an isomer with the zwitterionic structure **C** was also present which slowly rearranged to **B** [6]:



A



B



C

Considering other canonical structures of **C** or **B**, it is conceivable that **B** and particularly **C** may become destabilized if the second heteroatom in the azole system is a sulfur or an oxygen atom. In this work we report the reaction between **1** and the C-lithiated azoles **2**.

The reaction mixtures were analysed by multinuclear NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N and ^{119}Sn NMR) and products of other potential rearrangement processes of the zwit-

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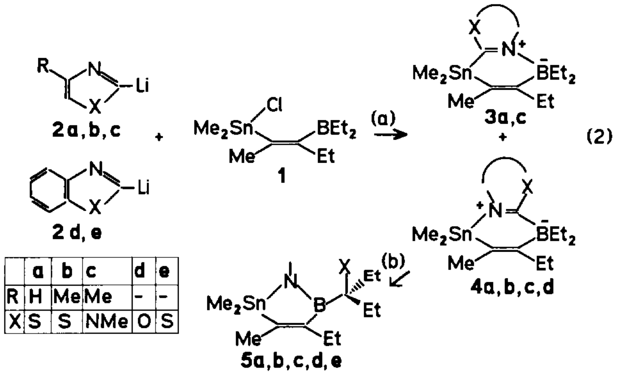
terionic systems of type **C** were identified, one (**5e**) by X-ray structure analysis.



2. Results and discussion

Lithiation of the azoles as described [7-9] afforded the organolithium compounds **2**. The reaction between **1** and **2** had already started at −78°C and was complete in all cases at room temperature. ^{11}B NMR spectra of the reaction mixtures showed that one (**4b**–**5e**) or two (**3c**–**4c** and **4d**–**5d**) and in one case three different products (**3a**, **4a** and **5a**) were present. Compounds of type **3** were detected only in the cases of **3a** and **3c**, in contrast with the finding when C-lithiated imidazoles or triazoles were used, and the compounds **3** turned out to be the more stable isomers [6]. In the cases of **3c** and **4c** which are present in the beginning as a 1 : 1 mixture, the methyl group in the 4-position of the azole ring appears to hamper a fast rearrangement of **4c** into **3c**. The rearrangement to **3c** required several hours at 80°C, and it also led to a small amount (less than 10%) of **5c** according to the ^{11}B NMR spectrum ($\delta(^{11}B) = 42.0$ ppm). As can be seen from Eq. (2), the formation of the zwitterionic product **4** is preferred if C-lithiated thiazoles or oxazoles react with **1**. In the case of **4e**, the final rearrangement to **5e** had already taken place below room temperature. Compound **4d**, present as a minor component in the mixture with **5d**, rearranged completely to **5d** within 12 h at room temperature, whereas the partial rearrangement to **4a** required heating to 70°C for 24 h. Distillation of a mixture of **3a**, **4a** and **5a** gave pure **5a** as a colorless liquid as the final product. Prolonged heating of **4b** also led to **5b** ($\delta(^{11}B) = +40.5$) accompanied by unidentified decomposition products. The compound **4b** is a yellow, air- and moisture-sensitive solid. The products **5d** and **5e** were isolated as a light-orange solid (**5d**) and light-yellowish crystals (**5e**). The molecular structure of **5e** was determined by single crystal X-ray analysis (see below).

Starting from Et_3B in Eq. (1), the three B–Et bonds are finally converted into three C–Et bonds (Eq. (2b)). There are only few reactions in which all three organyl groups in triorganoboranes can be used to form new C–C bonds [10]. The conversion of **4** to **5** can be

Table 1
^{11}B, ^{119}Sn, ^{14}N and ^{13}C NMR data [a,b] of **3** and **4**

Compound	$\delta(^{11}B)$ (ppm)	$\delta(^{119}Sn)$ (ppm)	$\delta(^{14}N)$ (ppm)	$\delta(^{13}C)$ (ppm) [$J(^{119}Sn^{13}C)$ (± 1 Hz)]						
				Sn*C*=	B*C*=	Sn*Me*	B*Et*	=C*Me*	=C*Et*	Azole
3a	+2.5	−106.5	−92	125.1 [647.0]	172.3 (br) [b]	−8.0 [333.6]	19.1, 10.6 (br) [b]	21.3 [111.3]	26.2, 14.2 [104.4][16.2]	176.5 [d] [195.4]
3c	−0.3	−137.4	NM [c]	124.2 [685.7]	173.6 (br) [b]	−9.5 [333.2]	18.9, 11.0 (br) [b]	21.3 [110.6]	25.9, 14.7 [101.7][14.0]	153.5 [e] [310.3]
4a	−9.6	+15.2	−149	[f]	[f]	−4.0 [304.0]	24.5, 12.4 (br) [h]	20.5	25.3, 14.8	[f]
4b	−9.0	+7.6	−147	125.2 [685.6]	168.1 (br) [b]	−3.5 [306.4]	23.9, 12.4 (br) [b]	19.9 [140.2]	25.0, 14.8 [111.6][16.9]	176.9 [g] (br) [b]
4c	−11.3	−20.0	NM	123.5 [696.8]	177.0 (br) [b]	−4.7 [320.4]	15.5, 8.7 (br) [b]	20.6	25.7, 15.1 [111.9]	177.0 [h] (br) [b]
4d	−11.3	+29.4	NM	125.4	[f]	−4.7 [303.9]	[f], 13.0	20.4	25.4, 14.8	[f]

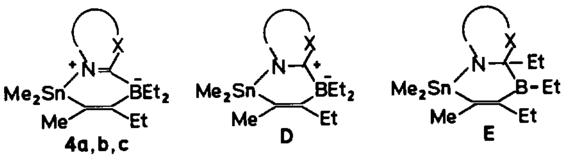
[a] In C_6D_6 (almost 10–20%; tubes 5 mm in outside diameter; 26 ± 1°C).
[b] (br), broadened ^{13}C NMR signal of a boron-bound carbon atom.
[c] NM, not measured.
[d] Other ^{13}C(azole) resonances: 142.6 [19.0] (C-4), 121.2 (C-5).
[e] Other ^{13}C(azole) resonances: 129.1 (C-4), 124.1 (C-5), 32.2 (Me-N^1), 13.0 (Me-C^4).
[f] Assignment in the mixture is uncertain.
[g] Other ^{13}C(azole) resonances: 146.6 (C-4), 115.3 (C-5), 15.3 (Me-C^4).
[h] Other ^{13}C(azole) resonances: 130.2 (C-4), 119.8 (C-5), 35.6 (Me-N^1), 11.6 (Me-C^4).

Table 2
^{11}B, ^{119}Sn, ^{14}N and ^{13}C NMR data [a,b] of **5**

Compound	$\delta(^{11}B)$ (ppm)	$\delta(^{119}Sn)$ (ppm)	$\delta(^{14}N)$ (ppm)	$\delta(^{13}C)$ (ppm) $[J(^{119}Sn^{13}C)\ (\pm 1\ Hz)]$						
				Sn*C*=	B*C*=	Sn*Me*	B*C*Et$_2$	=C*Me*	=C*Et*	C*Et*
5a [b]	+40.6	+77.3	−244	156.9 [597.9]	160.5 (br) [c]	−6.0 [331.4]	43.6 (br) [c]	19.4 [104.6]	23.9, 14.5 [99.6][11.0]	31.4, 11.4
5d [d]	+43.8	+70.8	−250	155.9 [596.3]	158.5 (br) [c]	−5.2 [335.7]	82.8 (br) [c]	19.1 [104.2]	23.4, 14.5 [81.5][12.8]	32.9, 10.5
5e [e]	+44.4	+75.8	−260	155.6 [585.0]	160.8 (br) [c]	−4.7 [337.0]	43.7 (br) [c]	19.1 [99.2]	23.7, 14.8 [81.4][12.8]	30.6, 11.0

[a] In C_6D_6 (about 10–20%; tubes 5 mm in outside diameter; 26 ± 1°C).
[b] Other ^{13}C resonances: 129.4 [16.2] (NC=), 102.3 [22.0] (SC=).
[c] (br), broadened ^{13}C NMR signal of a boron-bound carbon atom.
[d] Other ^{13}C resonances: 151.3, 133.9, 122.6, 119.6, 119.6, 116.5.
[e] Other ^{13}C resonances: 144.7, 128.7, 125.5, 121.3, 120.3.

understood if the canonical structure **D** is taken into account:



The 1,2 shift of one B-ethyl group (**D** → **E**) is reminiscent of the second step in the reaction between isonitriles and triorganoboranes [11]. Since **E** was not detected, the next step must be a fast $(1,2)^2$ shift [12] to give the new heterocyclic systems **5**.

The structures of **3**, **4** and **5** follow from a consistent set of NMR data (see Fig. 1 for ^{11}B, ^{14}N and ^{119}Sn NMR spectra of a mixture containing **3a**, **4a** and **5a**). Relevant data are given in Table 1 (**3** and **4**), Table 2 (**5**) and in Experimental details. The $\delta(^{11}B)$ values of **3** and **4** are typical of tetracoordinate boron atoms [13]. The ^{11}B nuclear shielding in **4** is increased compared with **3** and the ^{11}B NMR signals of **4** are much sharper. This is expected considering the more symmetric charge distribution around the boron atom in **4** with four B–C bonds and a formal borate character. In compounds of type **3**, the $\delta(^{119}Sn)$ values are close to the range observed for 1-stanna-2,5-cyclohexadienes [14], whereas considerable deshielding of the ^{119}Sn nucleus indicates the influence of the Sn–N bond in **4**. The $\delta(^{11}B)$ values of **5** fall into the expected range for this particular structural fragment [13] and this is also true for the $\delta(^{119}Sn)$ values [15]. Finally, ^{14}N NMR spectra prove that the azole-type nitrogen atom [16] has been converted into an amine-type nitrogen in **5** with $\delta(^{14}N)$ values typical of amino(diorgano)boranes [17]. These data are very instructive, especially in the case of mixtures. ^{1}H and ^{13}C NMR spectra serve for the final structural assignment of **5** since they prove the absence

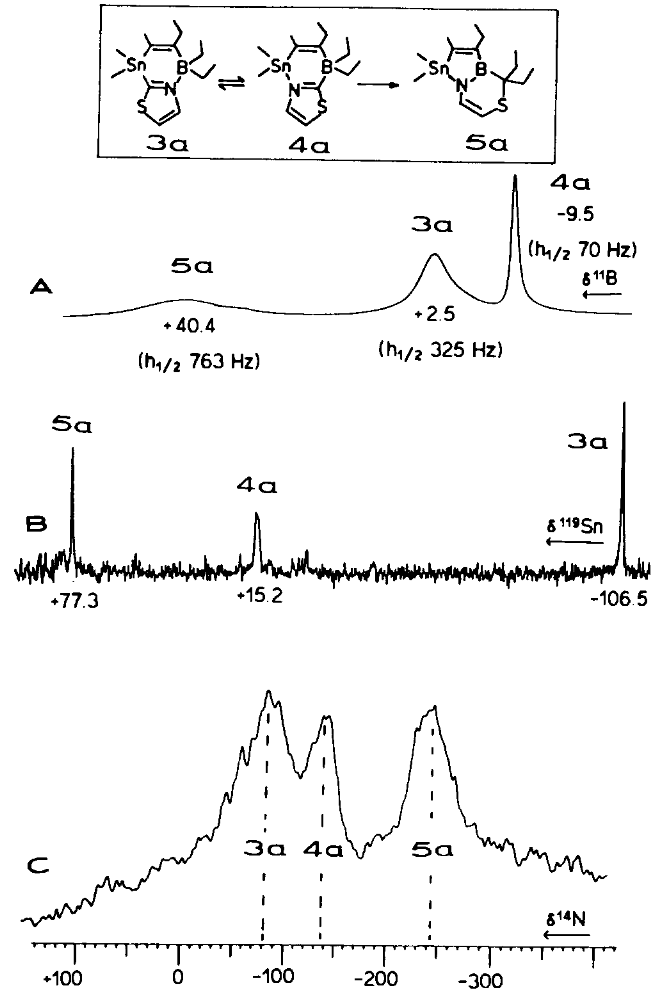


Fig. 1. NMR study of the reaction solution containing **3a**, **4a** and **5a**: curve A, 64.2 MHz ^{11}B NMR spectrum with $\delta(^{11}B)$ values and widths at half-height $h_{1/2}$ of the ^{11}B NMR signals (note the great difference in the $h_{1/2}$ values for the isomers **3a** and **4a**); curve B, 74.6 MHz ^{119}Sn NMR spectrum (^{1}H inverse gated decoupled for suppression of the negative NOE); curve C, 14.57 MHz ^{14}N NMR spectrum.

Table 3
Data of the X-ray structure determination of the tricyclic compound **5e**

Formula	$C_{18}H_{28}BNSSn$
Molecular mass	419.99
Crystal size (mm)	Platelet: 0.40–0.30 × 0.16
Lattice parameters	
a (pm)	11.691(2)
b (pm)	12.396(2)
c (pm)	13.149(2)
β (°)	93.41(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	4
Volume (Å^3)	1902.1(5)
ρ_{calc} (g cm^{-3})	1.467
Diffractometer	Siemens P4; graphite monochromator
Radiation	Mo Kα, $\lambda = 0.71073$ Å
Temperature (K)	173
2Θ range (°); scan type	$3.0 \leqslant 2\Theta \leqslant 60$; ω
Measured sections of reciprocal space	hkl, $hk\bar{l}$
Number of reflections collected	4465
Number of unique reflections	3352 (no reflections omitted, $f > 0\sigma(F)$)
System used	SHELXTL-PLUS
Solution	Direct methods
Weighting scheme	$w^{-1} = \sigma^2(F)$
R; *w*R	0.027; 0.020
Number of parameters refined	200
Maximum; minimum residual electron density (e A^3)	0.46; −0.39

of B-ethyl groups and the formation of a new B–C bond. The quaternary carbon atom in the S(B)CEt$_2$ or O(B)CEt$_2$ group gives rise to a characteristic broad ^{13}C NMR signal because of partially relaxed scalar ^{13}C–^{11}B coupling [13b,c].

2.1. X-Ray analysis of 5e

Experimental data of the X-ray analysis of **5e** are given in Table 3 [1] and the molecular structure of **5e** is shown in Fig. 2 with selected bond distances and bond angles in the caption for Fig. 2. The five-membered ring is planar within the experimental error, and all bond lengths and bond angles are in the normal range. It is fused via the N–B bond with the six-membered ring which has a distorted half-chair conformation with C(8) shifted by 92.8 pm out of the best plane formed by B–N–C(18)–C(13)–S. This causes a torsion angle between the five-membered and the benzene ring of 32.5°. The linear relationship proposed for the C–Sn–C bond angles of Me$_2$Sn groups and $^1J(^{119}Sn^{13}C_{Me})$ (predicted [18], 448 Hz; found, 337 Hz) is not well fulfilled. Although this relationship refers to values $^1J(^{119}Sn^{13}C_{Me})$ measured in the solid state, it is unlikely that marked changes in the rigid structure of **5e** occur in solution. It appears that the correlation between $^1J(^{119}Sn^{13}C)$ and the C–Sn–C bond angle [18] is of questionable value, as was found for other examples [19].

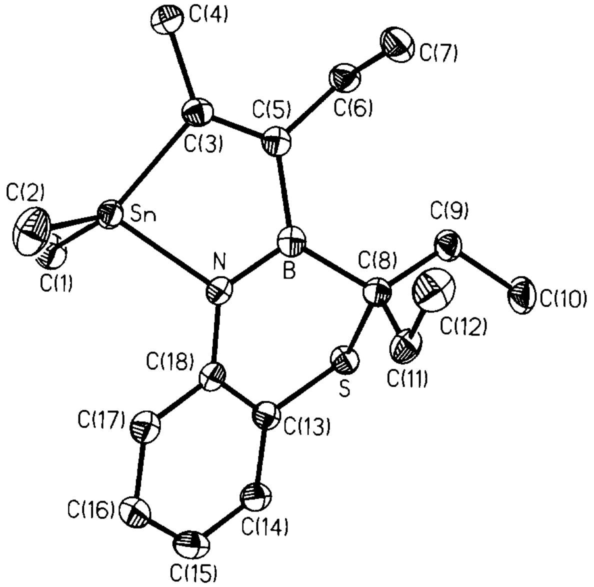


Fig. 2. Molecular structure of the tricyclic compound **5e**. Selected bond lengths and bond angles are as follows: Sn–N, 209.4(2) pm; Sn–C(1), 213.4(3) pm; Sn–C(2), 213.6(3) pm; Sn–C(3), 212.4(3) pm; B–N, 142.0(4) pm; B–C(5), 160.3(4) pm; B–C(8), 161.9(4) pm; C(3)–C(5), 135.2(3) pm; N–C(18), 139.7(3) pm; S–C(8), 185.7(3) pm; S–C(13), 176.0(3) pm; C(1)–Sn–C(2), 114.6(1)°; Sn–N–B, 111.3(2)°; N–B–C(8), 116.1(1)°; N–B–C(5), 115.2(2)°; C(5)–B–C(8), 128.7(2)°; N–Sn–C(3), 84.3(1)°; C(8)–S–C(13)°, 100.2(1)°.

3. Experimental details

All preparations were carried out in an atmosphere of dry nitrogen, using carefully dried glassware and dry solvents. The azoles and BuLi (1.6 M in hexane) were commercial products and the alkene derivative **1** was prepared according to the literature procedure [6]. The C-lithiated azoles **2a**, **2b** and **2c** were prepared as described [7–9] by adding one equivalent of BuLi in hexane to solutions of 5 mmol of the respective azole in 20 ml of Et$_2$O at −78°C. The same procedure works for **2d** and **2e** except that tetrahydrofuran (THF) serves as the solvent for the azoles. These solutions are ready to use after 12 h at −78°C. It is advisable to maintain a temperature below −50°C also during reactions between **2** and **1**.

NMR measurement data were as follows: ^{1}H/^{13}C (200.13/50.3 MHz, Bruker WP 200; 300.13/75.5 MHz,

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[1] Further details of the crystal structure analysis 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 401255, the names of the authors and the journal citation.

Bruker AC 300; 500.13/125.7 MHz, Bruker AM 500); ^{11}B (64.2 MHz, Bruker WP 200; 96.3 MHz, Bruker AC 300; external standard, BF_3–OEt_2, $\Xi(^{11}B) = 32.083\,971$ MHz); ^{14}N (14.5 MHz, Bruker WP 200; 21.7 MHz, Bruker AC 300; external standard, neat $MeNO_2$, $\Xi(^{14}N) = 7.226\,455$ MHz); ^{119}Sn (74.6 MHz, Bruker WP 200; 111.9 MHz, Bruker AC 300; external standard, Me_4Sn; $\Xi(^{119}Sn) = 37.290\,665$ MHz).

3.1. *Mixture of* ***3a**, **4a** and **5a***

The reaction between **1** and **2a** was carried out as described for **4b**. The resulting mixture contains at first **3a** and **4a** in a ratio of about 4 : 1 and only traces of **5a**. After heating the mixture to 70°C for 1 h, **3a**, **4a** and **5a** are present in approximates ratio 2 : 1 : 2. It was not possible to achieve complete conversion into **5a** without partial decomposition. Distillation gave 1.24 g (67%) pure **5a**; boiling point, 119°C at 10^{-2} Torr. Anal. Found: C, 46.3; H, 7.3. $C_{14}H_{26}BNSSn$ (370.3) Calc.: C, 45.4; H, 7.1%.

^{1}H NMR (200 MHz, C_6D_6): $\delta(^1H)$ [$J(^{119}Sn^1H)$] **3a** 0.22 [55.4] (s, 6H, $SnMe_2$), 0.62–1.32 (m, 10H, BEt_2); 2.07 [7.03] (s, 3H, =CMe), 2.60 (q, 2H, 1.26 t, 3H, =CEt), 7.90 [3.2], 6.57 [5.4] (=CH); **4a** 0.20 [52.5] (s, 6H, $SnMe_2$), 0.61–1.43 (m, 10H, BEt_2), 1.96 [84.8] (s, 3H, =CMe), 2.45 (q, 2H, 1.16 t, 3H, =CEt), 6.62 (s, 2H, =CH); **5a** 0.12 [56.5] (s, 6H, $SnMe_2$), 1.91 [64.8] (s, 3H, =CMe), 2.57 (q, 2H, 0.61 t, 3H, =CEt), 1.47–1.81 (m, 4H, 1.15 t, 6H, CEt_2); 5.44 (d, 1H, 6.13 d, 1H, =CH).

3.2. *6,7,7-Triethyl-3,4,4,5-tetramethyl-4H,7H-4a-azonia-4-stanna-7-borata-benzo[b]thiophene* (***4b***)

1.61 g (5 mmol) of the chloride **1** in 5 ml of hexane was added to the stirred solution of the 2-lithiated 4-methyl-thiazole (**2b**) in Et_2O at −78°C. The reaction starts immediately and a colorless precipitate is formed. After warming the mixture to room temperature, the insoluble material is filtered off, followed by ^{11}B NMR spectroscopic control of the reaction solution and removal of the solvents in vacuum. A yellow solid is left which is recrystallized from hexane to give 1.46 g (76%) of yellow crystals (melting point (m.p.), 108–110°C).

^{1}H NMR (200 MHz, C_6D_6): $\delta(^1H)$ [$J(^{119}Sn^1H)$] 0.20 [52.0] (s, 6H, $SnMe_2$), 0.66, 0.78 (m, 10H, BEt_2), 1.96 [70.5] (s, 3H, =CMe), 2.54 (q, 2H, 1.17 t, 3H, =CEt), 1.90 [3.0] (s, 3H, Me), 6.43 (s, 1H, =CH). Anal. Found: C, 47.32; H, 7.66; N, 3.66. $C_{15}H_{28}BNSSn$ (383.96) Calc.: C, 46.92; H, 7.35; N, 3.65%.

3.3. *Mixture of* ***3c** and **4c***

The mixture of **3c** and **4c** (approximately 1 : 1) is obtained under the same conditions as described for **4b**.

^{1}H NMR (200 MHz, C_6D_6): $\delta(^1H)$ [$J(^{119}Sn^1H)$] **3c** 0.23 [54.9] (s, 6H, $SnMe_2$), 0.6–1.09 (m, 10H, BEt_2); 2.12 (69.6] (s, 3H, =CMe), 2.60 (q, 2H, 1.23 t, 3H, =CEt), 1.59 (s, 3H, Me), 2.72 (s, 3H, NMe), 6.94 (s, 1H, =CH); **4c** 0.30 [52.5] (s, 6H, $SnMe_2$), 0.6–1.09 (m, 10H, BEt_2), 2.02 [81.2] (s, 3H, =CMe), 2.56 (q, 2H, 1.22 t, 3H, =CEt (assignment to **4c** and **3c** may be reversed)) 1.80 (s, 3H, Me), 3.39 (s, 3H, NMe), 5.98 (s, 1H, =CH).

3.4. *1,8,8-Triethyl-2,3,3-trimethyl-3H,8H-benzo(d)-7-oxa-3-stanna-8a-boraindolizine* (***5d***)

A solution of 1.61 g (5 mmol) of the chloride **1** in 10 ml of hexane is added at −78°C to a THF solution containing 5 mmol of the C-lithiated benzoxazole (**2d**). The mixture is kept for 3 h at −78°C before it is allowed to reach room temperature. ^{11}B NMR showed the presence of **4d** and **5d** (about 1 : 4). After 12 h at room temperature, **4d** can no longer be detected by ^{11}B NMR and the solvents are removed in vacuo. The residue is extracted with a small amount of hexane and 1.13 g (56%) of an orange solid (m.p., 78–82°C) precipitates upon cooling to −78°C.

^{1}H NMR (200 MHz, C_6D_6): $\delta(^1H)$ [$J(^{119}Sn^1H)$] 0.25 [57.1] (s, 6H, $SnMe_2$), 1.88 [66.2] (s, 3H, =CMe), 2.33 (q, 2H, 0.99 t, 3H, =CEt), 1.67–2.06 (m, 4H, 1.10 t, 6H, CEt_2), 6.40 (m, 1H, 6.70 m, 1H), 6.80 (m, 1H), 7.10 (m, 1H aryl-H). Anal. Found: C, 53.94; H, 7.21; N, 3.25. $C_{18}H_{28}BNOSn$ (403.92) Calc.: C, 53.52; H, 6.99; N, 3.47%.

Compound **5e** is prepared in the same way as **5d** but was isolated as a light-yellowish crystalline material (m.p., 93–95°C).

^{1}H NMR (300 MHz, C_6D_6): $\delta(^1H)$ [$J(^{119}Sn^1H)$] 0.29 [55.4] (s, 6H, $SnMe_2$) 1.97 [67.5] (s, 3H, =CMe), 2.57 (q, 2H), 0.97 (t, 3H, =CEt), 1.61–1.83 (m, 4H, 1.07 t, 6H, CEt_2), 6.60 (m, 1H, 6.70 m, 1H), 6.90 (m, 1H, 7.40 m, 1H, aryl-H).

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