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Novel zwitterionic heterocycles containing hypervalent tin

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Abstract

The reactions of (*E*)-2-chloro(dimethyl)stannyl-3-diethylboryl-*N*,*N*-dimethyl-2-pentenylamine **2**, containing penta-coordinate tin, with lithium diethylamide, -diiso-propylamide, -bis(trimethylsilyl)amide, with N-lithiated azoles (pyrrole, 1,2,4-triazole), and C-lithiated azoles (*N*-methylimidazole, thiazole and 4-methylthiazole) were studied. Most of the products **3**–**11** correspond closely to those obtained previously from (*E*)-2-chloro(dimethyl)stannyl-3-diethylboryl-2-pentene **1**. However, there is a tendency for the increase in the coordination number of tin in the 1,2,5-azoniastannaboratole derivative **3**, the 1,3-stannaborole derivative **4**, the bis(trimethylsilyl)amide **5** and the *N*-pyrrolylborane **6**. In the products derived from 1,2,4-triazole (**7**), *N*-methylimidazole (**8**), thiazole (**9**, **10**) and 4-methyl-thiazole (**11**), the coordinative N–Sn bonding with the dimethylamino group is strong, as indicated by multinuclear magnetic resonance data in solution (^{1}H-, ^{11}B-, ^{13}C-, $^{14/15}$N-, ^{119}Sn-NMR), and by X-ray structural analysis of **11** in the solid state. In the cases of **10** and **11**, zwitterionic structures are formed, in which tin is linked to nitrogen, and boron to carbon of the thiazole. These compounds can be classified as carbene–borane adducts.
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1. Introduction

The presence of two electrophilic organometallic substituents in *cis*-positions at the C=C bond in alkenes is a challenge for studying reactions with nucleophiles. The behaviour of the alkene **1** [1], where the tin and the boron atom are the electrophilic centres, readily accessible by 1,1-organoboration [2], has been studied in detail [3,4]. It was shown that an analogous alkene **2**, in which the tin atom may increase its coordination number by N–Sn bonding, can be prepared by similar methods [5]. This type of hypervalent tin compounds is particularly well known for aryltin compounds in which one or two ancillary dimethylaminomethyl groups are in appropriate positions relative to the stannyl group [6,7]. In the present work, we have carried out some reactions of **2** with lithium amides and N- or C-lithiated azoles in order to compare the results with those for **1**. Clearly,

the influence of the amino group in **2** on the product distribution and the structure of the products was of particular interest.
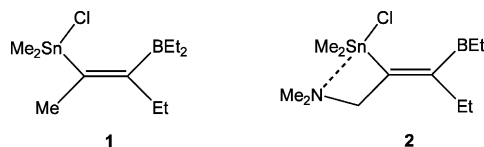

2. Results and discussion

2.1. Reactions of the alkene **2** with lithium amides

The reactions of **2** with lithium diethylamide, -diisopropylamide (LDA) and -bis(trimethyl-silyl)amide are summarised in Scheme 1. In principle, the analogous results are obtained as for **1**, except that the formation of a 1,4-distanna-2,5-cyclohexadiene derivative [8] was not observed. The 1,2,4-azoniastannaboratole derivative **3** with the bridging NEt₂ group is expected [9]. In

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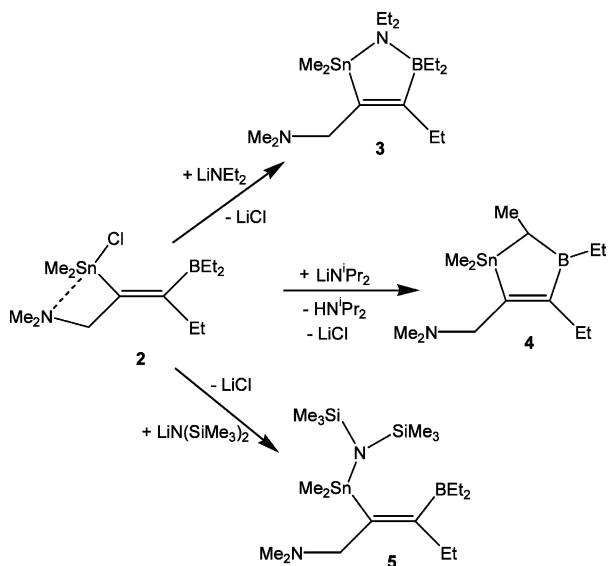
Scheme 1.

contrast, the N^iPr_2 group is too bulky for coordinative N–B bonding. Owing to its high basicity, the N^iPr_2 group abstracts a proton from one of the ethyl groups at boron [10], and leaves the molecule as HN^iPr_2 by forming the heterocycle **4**. The $N(SiMe_3)_2$ group is also too bulky for N–B coordinative interactions [11]; however, the basicity of the nitrogen atom is low, and therefore, the $N(SiMe_3)_2$ group in **5** is just a substituent at the tin atom. The compounds **3**–**5** are air- and moisture-sensitive, oily liquids which decompose during attempts of further purification (distillation or chromatography on alumina or silica). It should be noted that in all three compounds **3**, **4** and **5** coordinative N–Sn bonding with the NMe_2 group plays a minor role according to the NMR parameters (Table 1; vide infra) when compared with data for the analogous products obtained from **1**.

2.2. Reactions of the alkene 2 with N-lithiated azoles

The reactions of **2** with N-lithiopyrrole and N-lithio-1,2,4-triazole are shown in Scheme 2. Again the results are comparable to those found for **1**. In the case of the N-pyrrolyl derivative **6**, an ethyl group is transferred from boron to tin and the N-pyrrolyl group becomes linked to the boron atom [12] (see NMR data in Table 1). This suggests that the primary nucleophilic attack takes place at the boron atom to form a N-pyrrolylborate as an intermediate. The elimination of LiCl is then accompanied by transfer of the ethyl group. In the case of N-lithio-1,2,4-triazole, there are at least two nucleophilic sites where the lithium can be accommodated even after formation of an intermediate borate, and the elimination of LiCl is accompanied by formation of the six-membered ring in **7**. In contrast with the situation in the compounds **3**–**6**, NMR data of **7** (Table

Table 1
^{11}B-, ^{13}C- and ^{119}Sn-NMR data ^{a} of the compounds **1**–**6**

	δ^{13}C (Sn–C=)	δ^{13}C (B–C=)	δ^{13}C (SnMe$_2$)	δ^{13}C (BEt)	δ^{13}C (Et)	δ^{13}C (CH$_2$NMe$_2$)	δ^{13}C (other)	δ^{11}B	δ^{119}Sn
1	134.3 [611.0]	166.7 (br)	−1.0 [345.0]	21.7 (br), 8.7	23.3 [108.8], 13.1 [11.9]	—	18.8 [83.6]	82.3	81.1
2	143.0 [798.2]	163.3 (br)	0.3 [413.7]	20.3 (br), 9.4	24.8 [128.1], 12.9 [15.6]	61.9 [60.6], 45.3	—	80.1	−5.6
3 ^{b}	140.2 [738.0]	180.0 (br)	−1.6 [300.0]	14.0 (br), 12.1	27.6 [116.0], 14.8 [8.9]	60.8 [83.4], 45.4	45.6, 14.0	4.1	116.6
4 ^{c}	165.0 [481.9]	167.4 (br)	−8.9 [314.0], −6.4 [280.0]	13.5 (br), 8.8	25.0 [84.0], 15.3 [12.0]	62.0 [52.0], 45.9	31.2 (br), 12.1	78.8	−0.7
5 ^{d,e}	145.2 [650.9]	162.1 (br)	1.4 [362.8]	21.7 (br), 9.1	23.5 [106.8], 14.1 [12.6]	60.7 [40.0], 45.5	5.7 [8.7]	85.3	−22.6
6 ^{f}	149.8 [507.2]	155.6 (br)	−9.2 [312.8], −9.3 [313.0]	13.6 (br), 9.2	25.1 [73.7], 14.3 [10.0]	62.0 [36.8], 45.7	4.8 [380.4], 10.9 [22.9], 124.2, 127.3, 113.9, 115.1	55.9	−50.2

^{a} In C_6D_6 (ca. 5–10%); coupling constants $J(^{119}$Sn,^{13}C) are given in brackets [±0.5 Hz]; (br) denotes a broad ^{13}C-NMR signal for a carbon atom linked to boron.
^{b} Relevant NMR data for the analogous compound obtained from **1**: δ ^{13}C(Sn–C=) = 128.9 [653.9]; δ^{11}B = −2.1 [276.0]; δ^{13}C(SnMe$_2$) = 1.8; δ^{119}Sn = 124.1.
^{c} Relevant NMR data for the analogous compound obtained from **1**: δ ^{13}C(Sn–C=) = 158.9 [453.3]; δ^{13}C(SnMe$_2$) = −8.1 [274.7], −10.2 [301.4]; δ^{11}B = 75.2; δ^{119}Sn = 7.3.
^{d} $^1J(^{29}$Si, ^{13}C) = 55.5 Hz; δ^{29}Si = 2.7; $^2J(^{119}$Sn,^{29}Si) = 18.4 Hz.
^{e} Relevant NMR data for the analogous compound obtained from **1**: δ ^{13}C(Sn–C=) = 138.7 [625.6]; δ^{13}C(SnMe$_2$) = 0.1 [355.1]; δ^{11}B = 83.8; δ^{119}Sn = −13.0.
^{f} Relevant NMR data for the analogous compound obtained from **1**: δ ^{13}C(Sn–C=) = 141.1 [489.5]; δ^{13}C(SnMe$_2$) = −11.0 [309.0]; δ^{11}B = 53.5; δ^{119}Sn = −40.1.
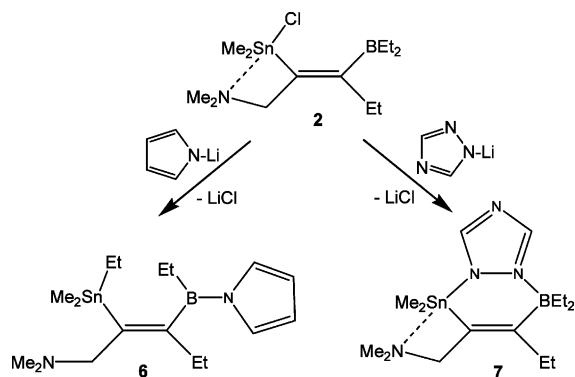
Scheme 2.

2) strongly support the coordinative N–Sn bonding with the NMe_2 group as indicated in the formula. Compound **6** is a colourless, air- and moisture-sensitive oil, and **7** is a colourless, moderately moisture-sensitive, high-melting solid which could be recrystallised; however, suitable single crystals for X-ray analysis were not isolated.

2.3. Reactions of the alkene 2 with C-lithiated azoles

C-lithiated azoles react readily with **2**, as shown in Scheme 3. In the case of 2-lithiated *N*-methylimidazole, the "expected" product **8** is isolated, in which a new Sn–C bond is present. In contrast, 2-lithiated thiazole reacts with **2** to give a mixture of isomers **9** and **10** which differ by Sn–C/B–N and Sn–N/B–C bonds, respectively. Finally, the 2-lithiated 4-methylthiazole reacts exclusively to give **11** by formation of the Sn–N/B–C bonds which might be called the "unexpected" product. These results are similar to those observed for **1** [13,14]. However, products from **1** corresponding to **10** or **11** tend to rearrange further [14] which was not observed here. The compound **8** was obtained as a colourless, moisture-sensitive oil, containing impurities (ca. 10–15%) which could not be identified or separated. It was also not possible to separate the mixture of **9** and **10**. The compound **11**, a colourless, high-melting, moisture-sensitive solid, could be recrystallised from benzene to yield single crystals, suitable for X-ray analysis (vide infra). The solution-state NMR data (Table 2) indicate that the coordinative N–Sn bonding with the NMe_2 group has to be taken into account for the compounds **8**–**11**.
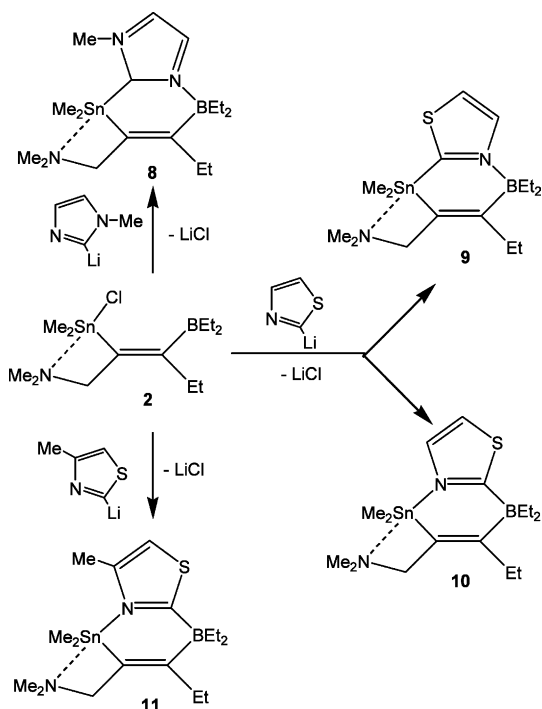
2.4. NMR spectroscopic results

NMR data of the compounds **1**–**11** are collected in Tables 1 and 2, together with data, given in the footnotes for comparison. The consistent set of NMR data (see Section 4 for ^{1}H-NMR data) is clearly in support of the proposed structures. As shown in Fig. 1, the ^{13}C-NMR spectra provide important information

Table 2
^{11}B-, ^{13}C- and ^{119}Sn-NMR data [a] of the fused heterocycles 7–11

	$\delta^{13}C$ (Sn-C=)	$\delta^{13}C$ (B-C=)	$\delta^{13}C$ (SnMe$_2$)	$\delta^{13}C$ (BEt)	$\delta^{13}C$ (Et)	$\delta^{13}C$ (CH$_2$NMe$_2$)	$\delta^{13}C$ (azole)	$\delta^{11}B$	$\delta^{119}Sn$
7 [b,c]	139.8 [832.9]	173.8 (br)	−4.0 [364.1]	19.5 (br), 12.0	28.4 [128.0], 13.7 [15.3]	63.5 [66.0], 45.4 [17.6]	149.3, 149.7	−0.8	−68.9
8 [d]	139.0 [765.0]	173.0 (br)	−7.4 [373.4]	19.8 (br), 11.0	28.4 [126.7], 14.6 [18.4]	62.6 [64.0], 45.7 [20.0]	34.8 [16.0], 159.6 [131.0] 128.1, 120.6	−1.1	−168.4
9 [e,f]	139.6 [n.m.]	171.4 (br)	−3.4 [376.2]	Not assigned	Not assigned	62.8 [62.5], 45.6	119.8, 135.6, 184	2.0	−149.2
10 [e,g]	140.6 [n.m.]	175.5 (br)	−5.9 [394.9]	Not assigned	Not assigned	63.4 [72.0], 45.6	120.6, 142.3 [7.9] 210 (br)	−9.5	−63.5
11 [h]	138.2 [857.4]	175.9 (br) [i]	−2.3 [380.4]	24.1 (br) [j] 12.8	27.7 [138.0], 14.8 [18.9]	63.1 [76.3], 45.3 [15.0]	15.7 [6.0], 146.8, 115.0 217.3 (br) [k]	−8.8	−61.6

[a] In C_6D_6 (ca. 5–10%), coupling constants $J(^{119}Sn, {}^{13}C)$ are given in brackets [±0.5 Hz]; (br) denotes a broad ^{13}C-NMR signal for a carbon atom linked to boron; n.m. means not measured.
[b] $\delta^{15}N = -124.2$ (Sn–N=), $^2J(^{15}N, {}^1H) = 12.5$ Hz; -137.6 (B–N=), $^2J(^{15}N, {}^1H) = 14.3$ Hz; -131.3 (=N–), $^2J(^{15}N, {}^1H) \approx 14.6$ Hz (for two hydrogen atoms); -337.1 (NMe$_2$).
[c] Relevant NMR data for the pyrazole derivative obtained from 1: $\delta^{13}C$(Sn-C=) = 125.7 [672.8]; $\delta^{119}Sn = -3.6$ [312.0]; $\delta^{11}B = 9.1$; $\delta^{15}N = 0.6$; $\delta^{15}N = -156.2$ [104.5], -119.0 [8.5].
[d] Relevant NMR data for the analogous compound obtained from 1: $\delta^{13}C$(Sn-C=) = 124.2 [685.7]; $\delta^{13}C$(SnMe$_2$) = -9.5 [333.2]; $\delta^{13}C$(2, azole) = 153.5 [310.3]; $\delta^{11}B = -0.3$; $\delta^{119}Sn = -137.4$.
[e] Mixture; only a few ^{13}C-NMR signals are assigned.
[f] Relevant NMR data for the analogous compound obtained from 1: $\delta^{13}C$(Sn-C=) = 125.1 [647.0]; $\delta^{13}C$(SnMe$_2$) = -8.0 [333.6]; $\delta^{11}B = 2.5$; $\delta^{119}Sn = -106.5$; $\delta^{14}N = -92.0$.
[g] Relevant NMR data for the analogous compound obtained from 1: $\delta^{13}C$(SnMe$_2$) = -4.0 [304.0]; $\delta^{11}B = -9.6$; $\delta^{119}Sn = 15.2$; $\delta^{14}N = -149.0$.
[h] $\delta^{14}N = -127.0$; relevant NMR data for the analogous compound obtained from 1: $\delta^{13}C$(Sn-C=) = 125.2 [625.6]; $\delta^{13}C$(SnMe$_2$) = -3.5 [306.4]; $\delta^{11}B = -9.0$; $\delta^{119}Sn = 7.6$; $\delta^{14}N = -143.5$.
[i] $^1J(^{13}C, {}^{11}B) = 65\pm5$ Hz.
[j] $^1J(^{13}C, {}^{11}B) = 48\pm5$ Hz.
[k] $^1J(^{13}C, {}^{11}B) = 65\pm5$ Hz.

Scheme 3.

and one nitrogen atom (e.g. fairly broad signals for **7**, **8** or **9**) or to four carbon atoms as in tetraorganoborates (e.g. rather sharp signals for **10**, **11**) [13,14,18]. The ^{119}Sn-NMR signals of the azole derivatives are broad as the result of unresolved three-bond [119]Sn–[11]B spin–spin coupling. Additional broadening comes from unresolved one-bond [119]Sn–[14]N coupling in the case of **7**, **10** and **11** (see Fig. 2). Furthermore, for the penta-coordinate tin atom unresolved one-bond Sn–[14]N(NMe$_2$) coupling will also contribute to the line-width of the ^{119}Sn-NMR signal.

The comparison of the NMR data for **1** and **2** show that the tin atom in **2** is tetra-coordinate, as to be expected, whereas there is penta-coordination of the tin atom in **2**. This follows from the marked increase in the magnitude of the coupling constants $|^1J(^{119}Sn,^{13}C)|$ in **2** for both the olefinic carbon and the methyl carbon

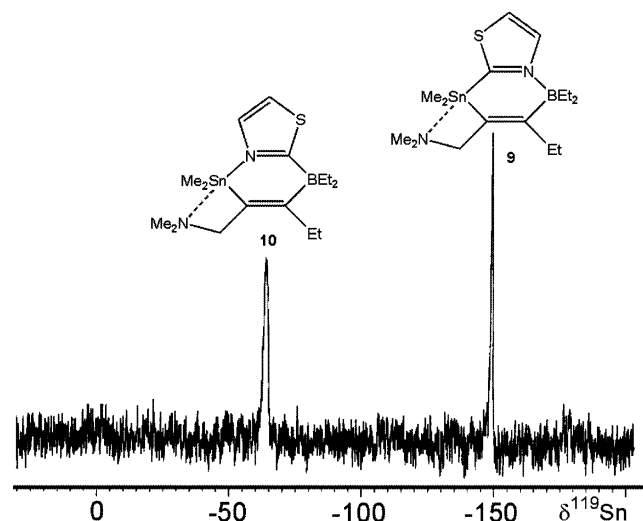because of the [117/119]Sn satellites and the sharp or broad NMR signals depending on the neighbourhood to the quadrupolar [11]B nucleus. The broadening of the ^{13}C resonance signals is the result of scalar relaxation of the second kind [15] owing to the usually fast quadrupolar relaxation rate of the [11]B nucleus [16]. If the quadrupolar relaxation mechanism becomes less efficient, the life time of the [11]B spin states increases, and the [13]C–[11]B spin–spin coupling is at least partially resolved (e.g. in **11**). The [11]B chemical shifts indicate the presence of three- or tetra-coordinate boron atoms in the usual way [17]. Furthermore, in the cases of tetra-coordinate boron atoms, the linewidths of the ^{11}B-NMR signals help to distinguish between boron atoms linked to three carbon

Fig. 2. 93.3 MHz ^{119}Sn{^{1}H}-NMR spectrum of **5b** (ca. 10% in C$_6$D$_6$, 23±1 °C; result of 3000 transients; acquisition time 0.3 s; repetition time 10 ms; pulse angle 30°), showing the signals (see text) for the isomers **9** and **10**.
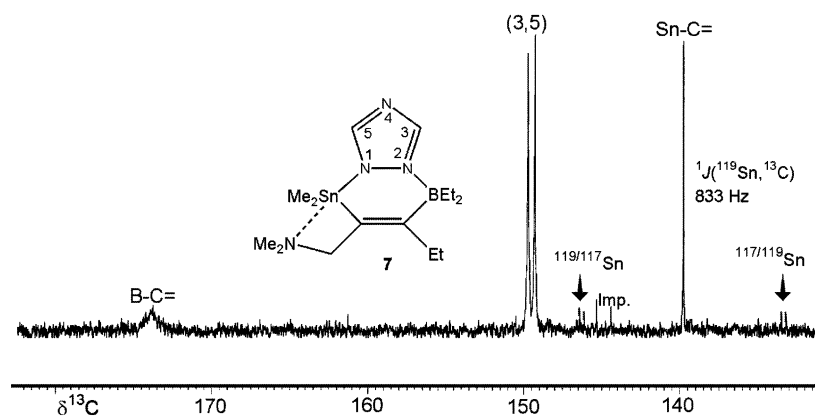
Fig. 1. 62.9 MHz ^{13}C{^{1}H}-NMR spectrum of the heterocycle **7** (5% in C$_6$D$_6$; 320 transients; acquisition time 1.5 s; repetition delay 10 ms; pulse angle 30°), showing the region of the olefinic ^{13}C-NMR signals (impurities are marked). Note the large coupling constant $^1J(^{119}Sn,^{13}C)$ which indicates pentacoordination of the tin atom, and also the typically [..] broad ^{13}C-NMR signal of the carbon atom linked to boron.

atoms with respect to **1**, and from the increase in [119]Sn nuclear magnetic shielding in **2** by ca. 87 ppm. It has been reported that N–Sn coordination similar to that in **2** can lead to an increase in [119]Sn shielding of up to 100 ppm [6c]. The most likely surroundings of the tin atom in **2** should correspond to a distorted trigonal bipyramid, in which the three carbon atoms occupy the equatorial and nitrogen and chlorine atoms the axial positions. The differences in the NMR data pointed out for **2** and **1** are much less pronounced in the case of the compounds **3–6** derived from **2** and their counterparts derived from **1** (see footnotes in Table 1). However, there are small but systematic changes in the NMR parameters of the compounds **3–6**: in all cases the magnitude of $|^1J(^{119}\text{Sn},^{13}\text{C})|$ is slightly increased, and also the [119]Sn shielding is increased in **3–6** by a few ppm when compared with the derivatives without the NMe$_2$ group. These consistent changes can be interpreted to arise from weak coordinative N–Sn interactions. This picture changes dramatically in the case of the azole derivatives **7–11**. In all cases **7–11**, the penta-coordination of the tin atom is mirrored by larger values of $|^1J(^{119}\text{Sn},^{13}\text{C})|$ and shifts of the [119]Sn resonances to low frequencies. In some cases, the ^{13}C-NMR spectra reveal [119]Sn–[13]C(NMe$_2$) coupling which is observed only if all other evidence indicates penta-coordination of the tin atom. This type of bonding has important consequences for other NMR parameters. Thus, there is a rather small value of $|^1J(^{119}\text{Sn},^{13}\text{C}_{\text{azole}})|$ (131.0 Hz) in **8** which can be explained by considering the structure, where this particular azole carbon atom occupies an axial position in the distorted trigonal bipyramid. Since there is a crude relationship between the magnitude of $|^1J(^{119}\text{Sn},^{13}\text{C})|$ and the s-character of the Sn–C hybrid orbital [19], the increase in the magnitude of the values $|^1J(^{119}\text{Sn},^{13}\text{C})|$ for carbon atoms in equatorial positions and the smaller magnitude of $|^1J(^{119}\text{Sn},^{13}\text{C})|$ for carbon atoms in axial positions is in line with expectations [20,21]. The structural model assumed for the solutions is confirmed for the solid state by the X-ray structural analysis of **11** (vide infra).

The extreme deshielding of the boron-bonded azole carbon atom in **10** and **11** deserves a brief comment. These compounds can be understood to contain a heterocarbene fragment [22] which is stabilised by a coordinative C–B bond. In contrast to the parent 2,3-dihydrothiazol-2-ylidene [23], similar substituted heterocarbenes are fairly stable [22,24] or can be stabilised as ligands in transition metal complexes [25], and there are also a few examples for adducts with boranes [18,26]. Alternatively, the zwitterionic structure in **10** or **11** with a positive charge on nitrogen and a negative charge on boron can be written with a positive charge at the azole carbon atom next to boron, as in carbocations, which would also be in agreement with the observed ^{13}C nuclear magnetic deshielding.
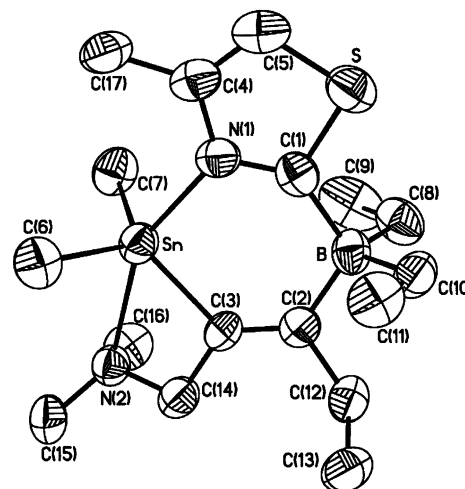

Fig. 3. ORTEP plot (40% probability level; hydrogen atoms are omitted for clarity) of the molecular structure of **11**; selected bond lengths (pm) and angles (°): SnC(3) 211.2(7), SnC(6) 214.2(6), SnC(7) 214.5(8), Sn–N(1) 123.0(7), SnN(2) 263.1(6), BC(1) 163.8(11), BC(2) 163.1(12), BC(8) 166.6(11), BC(10) 162.8(12), C(2)C(3) 133.4(10), C(1)N(1) 133.0(9), C(4)C(5) 134.7(11), C(4)N(1) 139.5(9), C(1)S 173.1(8), C(5)S 170.5(7); C(6)SnC(7) 114.5(3), C(3)SnC(6) 117.0(3), C(3)SnC(7) 122.9(3), C(3)SnN(1) 94.5, N(1)SnN(2) 154.2(2), C(1)BC(2) 115.5(6), C(8)BC(10) 109.9(6)C(1)SC(5) 92.9(4), N(1)C(1)S 108.8(6).

2.5. X-ray structural analysis of the heterocycle **11**

The molecular structure of **11** is shown in Fig. 3. The five-membered ring is planar within the experimental error. With the exception of the tin atom which is shifted by 28 pm out of the plane, the five- and the six-membered rings form one plane. This plane would also accommodate the four-membered ring. However, repulsion between the SnMe$_2$ and the NMe$_2$ groups (torsional angles C(6)SnN(2)C(15) = 6.3° and C7SnN(2)C(16) = 29.1°) forces the nitrogen atom out of a common plane. The distortion of the trigonal bipyramid is clearly seen along the N(2)SnN(1) axis (angle 154.2(2)°), and is also evident from the slight shift of the tin atom out of the C(3)C(6)C(7) plane towards N(1) by 21 pm. Both SnN(1) and in particular SnN(2) bond distances are long (223.0(7) and 263.1(6) pm), when compared with tin nitrogen compounds containing tetra-coordinate tin [27]. This is to be expected for axial ligands in penta-coordinate tin compounds [28]. The shortest Sn–C distance in **11** is measured for SnC(3) (211.2(7) pm) which fits to the observation of the rather large magnitude of the coupling constant $|^1J(^{119}\text{Sn},^{13}\text{C}(3))| = 857.4$ Hz. The distance BC(2) (165.8(11) pm) is similar or even longer than that for BC(8) and BC(10) (166.6 (11) and 162.8(12) pm), indicating that the formal hybridisation of the carbon atoms does not play a dominant role. Otherwise the

surroundings of the boron atom is analogous to that in other heterocycles containing the =C(Et)−BEt$_2$−L fragment [29].

3. Conclusions

Both weak and strong coordinative N−Sn interactions can be traced by ^{13}C- and ^{119}Sn-NMR data in solution. The magnitude of the coupling constants $|^1J(^{119}Sn,^{13}C)|$ is particularly sensitive to structural changes when the carbon atoms are forced either into the equatorial or the axial position of a trigonal bipyramid. The increase in ^{119}Sn nuclear magnetic shielding as a result of a coordination number > 4 is useful in assessing weak interactions. The structural characterisation of the fused zwitterionic heterocycle containing a penta-coordinate tin has revealed structural features which are in good agreement with the interpretation of the NMR data.

4. Experimental

4.1. General

Preparation and handling of all compounds were carried out in an atmosphere of dry Ar, observing all necessary precautions to exclude air and moisture. Starting materials were commercially available (amines, azoles, butyl lithium (1.6 M in hexane), and **2** was prepared as described [5]. Lithiated azoles were prepared by standard methods [30] and used in situ. NMR measurements were carried out for solutions in C$_6$D$_6$, if not mentioned otherwise, with samples in 5 mm tubes at 23 ± 1 °C: Bruker ARX 250 and Bruker DRX 500: ^{1}H-, ^{11}B-, ^{13}C-NMR, and ^{29}Si-NMR (refocused INEPT [31] based on $^2J(^{29}Si,^1H(Me))$ ca. 7 Hz), and ^{119}Sn-NMR (either by refocused INEPT [31], based on $^2J(^{119}Sn,^1H_{Me})$ ca. 55 Hz, or by straightforward ^{1}H decoupling, since negative NOE effects [19a,19b] were found to be unimportant); chemical shifts are given with respect to Me$_4$Si [δ^1H (C$_6$D$_5$H) = 7.15; δ^{13}C (C$_6$D$_6$) = 128.0; δ^{29}Si = 0 for $\Xi(^{29}Si) = 19.867184$ MHz]]; external BF$_3$−OEt$_2$ [δ^{11}B = 0 for $\Xi(^{11}B) = 32.083971$ MHz], external neat MeNO$_2$ [δ^{15}N = 0 for $\Xi(^{15}N) = 10.136767$ MHz, and δ^{14}N = 0 for $\Xi(^{14}N) = 7.226324$ MHz] and external Me$_4$Sn [δ^{119}Sn = 0 for $\Xi(^{119}Sn) = 37.290665$ MHz]. Melting or decomposition points: Büchi 510 melting point apparatus.

4.2. Reaction of the organotin chloride **2** with lithium diethylamide, -diisopropylamide, bis(trimethylsilyl)amide, and N-lithio-pyrrole to give the compounds **3**−**6**

All reactions were carried out as described for **1** [9−12], using the same work-up procedures. Purification by distillation under reduced pressure was not successful owing to decomposition.

3: ^{1}H-NMR (250 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.45 [49.7] (s, 6H, SnMe$_2$), 1.1−0.80 (m, 13H, BEt$_2$ and CH$_3$ of =C-Et group), 2.20 (s, 6H, NMe$_2$), 3.2 [83.0] (s, 2H, NCH$_2$), 2.55 (q, 2H, =C-CH$_2$), 2.80, 1.1 (q, t, 4H, 6H, NEt$_2$). **4**: ^{1}H-NMR (250 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.17 [54.0] (s, 3H, SnMe), 0.25 [54.0] (s, 3H, SnMe), 1.52, 0.98 (m, m, 5H, BEt), 1.54 (d, 3H, C-Me), 1.62 (q, 1H, C-H), 2.40, 0.98 (q, t, 5H, =C-Et), 2.13 (s, 6H, NMe$_2$), 3.20 [66.0] (s, 2H, NCH$_2$)..**5**: ^{1}H-NMR (250 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.34 (s, 18H, SiMe$_3$), 0.44 [52.2] (s, 6H, SnMe$_2$), 1.44−0.94 (m, 13H, BEt$_2$ and CH$_3$ of =C-Et group), 2.21 (q, 2H, =C-CH$_2$), 2.21 (s, 6H, NMe$_2$), 3.21 [72.2] (s, 2H, NCH$_2$). **6**: ^{1}H-NMR (250 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.01 [49.4] (s, 6H, SnMe$_2$), 0.47, 0.82 (m, m, 5H, SnEt), 1.34, 1.13 (m, m, 5H, BEt), 2.04, 0.94 (q, t, 5H, =C-Et), 2.16 (s, 6H, NMe$_2$), 3.14 [63.0] (s, 2H, NCH$_2$).

4.3. Reaction of the organotin chloride **2** with 1-lithio-1-2,4-triazole, 2-lithio-1-methyl-imidazole, 2-lithio-thiazole, and 2-lithio-4-methyl-thiazole to give the fused heterocycles **7**−**11**

All reactions were carried out as described for **1** [13,14]. The work-up procedures were also similar. The compounds **7** and **8** were obtained first as yellow oils which slowly became solids which could be recrystallised from pentane to give colourless crystalline solids (yields 70−80%). The mixture of **9** and **10** (ca. 1:1 molar ratio) was obtained as an oily liquid which contained about 15% of non-identified impurities. It could not be purified or separated by crystallisation, and decomposed by the attempt of chromatography on silica or alumina. Compound **11** crystallised readily from benzene solutions to give the yellowish product in high purity (yield 72%). These crystals were also suitable for X-ray structural analysis. **7** (m.p. > 180 °C; decomposition): ^{1}H-NMR (250 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.37 [55.0] (s, 6H, SnMe$_2$), 1.00−0.80 (m, 10 H, BEt$_2$), 2.30, 1.05 (q, t, 5H, =C-Et), 2.10 (s, 6H, NMe$_2$), 3.20 [80.0] (s, 2H, NCH$_2$), 7.95, 8.46 (s, s, H^{3,5}-triazole). **8** (m.p. > 150 °C; decomposition): ^{1}H-NMR (250 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.37 [58.0] (s, 6H, SnMe$_2$), 1.40, 0.94 (m, m, 10H, BEt$_2$), 2.58, 1.11 (q, t, 5H, =C-Et), 2.86 (s, 3H, N-Me), 2.16 (s, 6H, NMe$_2$), 3.27 [70.0] (s, 2H, NCH$_2$) 6.26, 7.28 (d, d, $^3J(^1H,^1H) = 1.7$ Hz, 1H, 1H, H^{4,5}-azole). **9/10**: ^{1}H-NMR (250 MHz): δ^1H (no assign-

ment) $[J(^{119}Sn,^{1}H)] = 0.36$ [56.0] (s, 6H, SnMe$_2$), 0.44 [58.0] (s, 6H, SnMe$_2$), 0.82–1.35 (m, 20H, BEt$_2$), strong overlap of most other signals except in the azole region, 8.02, 6.91, 6.78, 6.69 (d, d, d, d, $^{3}J(^{1}H,^{1}H) = 3.5$ Hz, 1H, 1H, 1H, 1H, H^{4,5}-azole). **11**(m.p. $> 210\ ^\circ$C; decomposition): ^{1}H-NMR (250 MHz): δ^{1}H $[J(^{119}Sn,^{1}H)] = 0.41$ [54.0] (s, 6H, SnMe$_2$), 1.20–0.80 (m, 10H, BEt$_2$), 2.65, 1.32 (q, t, 5H, =C-Et), 1.99 (s, 3H, C-Me), 1.96 (s, 6H, NMe$_2$), 3.21 [79.0] (s, 2H, NCH$_2$), 6.35 (s, 1H, H^2-azole).

4.4. Crystal structure determination of the fused zwitterionic heterocycle 11

A single crystal of **11**, recrystallised from benzene at room temperature by slow evaporation of the solvent, was sealed under Ar in a Lindemann capillary. Intensity data were collected on a STOE image plate diffraction system IPDS I with Mo–K$_\alpha$-radiation ($\lambda = 71.073$ pm, graphite monochromator) at room temperature. The hydrogens are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

11: C$_{17}$H$_{33}$BN$_2$SSn, colourless prism of dimensions $0.15 \times 0.12 \times 0.08$ mm, crystallizes monoclinically, space group $P2_1/n$; $a = 794.00(16)$, $b = 3065.6(6)$, $c = 954.54(19)$ pm, $\beta = 113.00(3)^\circ$, $Z = 4$, $\mu = 1.291$ mm^{-1}; 13 760 reflections collected in the range 3°–26° in ϑ, 3966 reflections independent, 1791 reflections assigned to be observed ($I > 2\sigma(I)$); full-matrix least-squares refinement against F^2 with 196 parameters, R_1/wR_2-values 0.0494/0.0998, numerical absorption correction; max./min. residual electron density $1.40/-0.32$ e·10^{-6} pm^{-3}.

5. Supplementary information

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 206335 (**11**). Copies of this information may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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