From Azole–Borane Adducts to Azaboles – Molecular Structure of an Imidazabole

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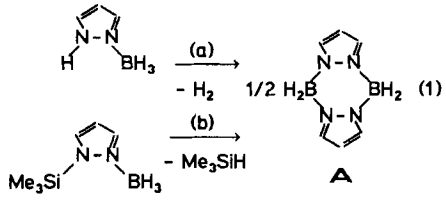
Elimination of H_2 from the imidazole–borane adduct **1** leads to a mixture of the imidazaboles **2** and **2'**. The symmetrical isomer **2** (two H_2BNC fragments) is isolated in pure state and characterized by an X-ray structure analysis (monoclinic, space group $P2_1$). 2-(Trimethylstannyl)thiazole (**3a**) and 1-methyl-5-(trimethylstannyl)-1,2,4-triazole (**3b**) react with triethylborane to form adducts **4** from which, in the presence of an excess of Et_3B, tetraalkyltin is elimated to give the thiazabole **5a** and the triazabole **5b**, respectively. Multinuclear ^1H-, ^{11}B-, ^{13}C-, ^{14}N-, and ^{119}Sn-NMR spectroscopy serve for following the reactions (compounds **3** to **5**) and to characterize all final products.

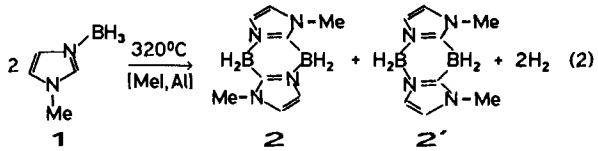
Pyrazabole (**A**)[1a] and its derivatives are recognized as an important class of boron compounds and, consequently, many routes have been developed for the synthesis of these compounds[1,2]. Other types of azaboles, in particular those with endocyclic N–B and C–B bonds, have received scant attention so far. Elimination reactions according to eqs. (1a)[1a] and (1b)[3] have been observed previously in the synthesis of pyrazaboles, but to the best of our knowledge this type of elimination has not yet found application to the synthesis of other azaboles.

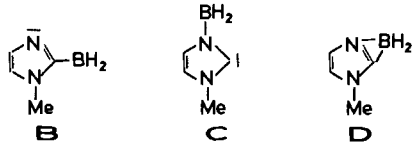


In this paper we show that elimination of H_2 from the *N*-methylimidazole–borane adduct **1**[4] affords a mixture of the imidazaboles **2** and **2'** [eq. (2)]. Another route to azaboles starts with 2-(trimethylstannyl)thiazole (**3a**) or 1-methyl-5-(trimethylstannyl)-1,2,4-triazole (**3b**), which are first converted to the triethylborane adducts **4** as intermediates. Elimination of tetraalkyltin leads to the azaboles **5** [eqs. (3) and (4)]. All compounds have been characterized by multinuclear NMR data (^1H-, ^{11}B-, ^{13}C-, ^{14}N-, and ^{119}Sn NMR), and crystals suitable for an X-ray structure analysis have been obtained from the imidazabole **2**.

Results and Discussion

The conversion of the borane adduct **1** into the imidazaboles **2** and **2'** requires harsh reaction conditions [eq. (2)] and a catalyst. The catalyst induces intermediate formation of BH_2I adducts which react with **1** to form the C(2)–B bond and HI thus closing the catalytic cycle. The compounds **2** and **2'** are formed as colorless, air-stable, high-melting solids in an approximate ratio of 2:1. The amount of **2** increases on heating the melt for several hours to 320°C. This is accompanied by some decomposition. Isomerization of pyrazaboles derived from 3-methylpyrazole has been observed previously, and a sigmatropic shift of the boryl group in the monomer has been assumed to explain the results[5a]. Fast isomerization of monomeric (3,5-di-*tert*-butylpyrazolyl)boranes has been firmly established[5b]. If monomeric boranes are also involved in the isomerization of **2** and **2'**, one has to consider the relative stability of the 2-substituted 1-methylimidazole **B** and the carbene derivative **C**[6a] or a zwitterionic type of structure **D**[5b,6b]. The reaction between **B** and **C** would afford **2'** whereas two molecules of either **B** or **C** would recombine to yield **2**. Pure samples of **2** are obtained by crystallization from CH_2Cl_2 (suitable for X-ray structure analysis) or from sublimation of the reaction mixture.





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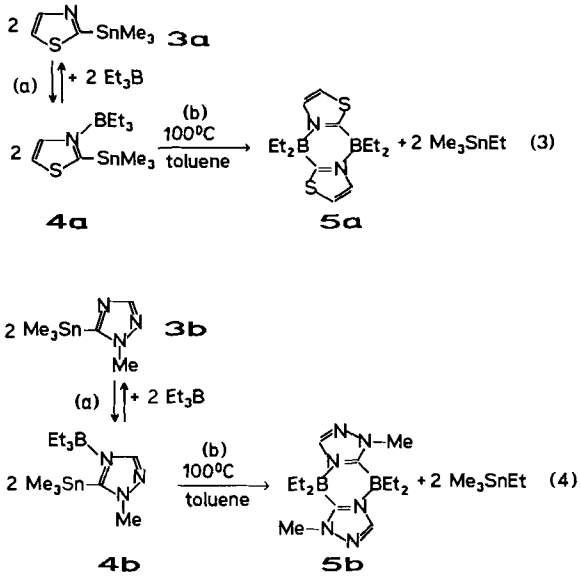
In the case of thiazole–borane adducts, procedures analogous to that in eq. (2) lead to extensive decomposition even under much less drastic conditions. However, the polar Sn–C(2) bond in the trimethylstannyl-substituted azoles **3a, b** invites for carrying out various exchange reactions. Treatment of toluene solutions of **3** with an excess of Et_3B shifts the equilibrium in eqs. (3a) and (4a) towards the Et_3B adducts **4**. Heating of these solutions in the presence of an excess of Et_3B leads to the formation of Me_3SnEt (monitored by ^{119}Sn NMR) and the azaboles **5** (monitored by ^{11}B NMR) [eqs. (3b) and (4b)]. The thiazabole **5a** is a malodorous, air-sensitive, yellow, crystalline solid, readily purified by sublimation. The triazabole **5b** is a colorless, crystalline solid which is stable in dry air for several minutes. ^1H-, ^{11}B-, ^{13}C-, and ^{14}N-NMR data of the azaboles **2**, **2′** and **5** are given in Table 1. Table 2 contains ^{11}B-, ^{13}C-, ^{14}N- and ^{119}Sn-NMR data of the trimethyltin-substituted azoles **3** and their Et_3B adducts **4**.



NMR Spectroscopic Results

All NMR data are in agreement with the proposed structures of the azaboles **2**, **2′**, and **5**. The $\delta^{11}B$ values are found in the typical range[7] of tetracoordinate boron atoms, depending in the usual way on the presence of $CCBH_2$, $NNBH_2$, $NCBH_2$, and $NCBEt_2$ moieties. The increased ^{11}B nuclear shielding in **5b** ($\delta^{11}B$ −6.1) as compared to **5a** ($\delta^{11}B$ −2.5) points towards better delocalization of the positive charge in the triazole system. The presence of coordinative N–B bonds is also supported by the increase in ^{14}N nuclear shielding of the pyridine-type nitrogen atoms as compared to the free azoles[8]. The linkage of the boron atom to C(2) (**2**, **2′**, **5a**) or C(5) (**5b**) is evident from the relevant extremely broad $^{13}C(2)$- or $^{13}C(5)$-NMR signals as a result of partially relaxed scalar ^{13}C-^{11}B spin-spin coupling[7b,c,9]. The deshielding of $^{13}C(2)$ in **5a** also points towards inefficient charge delocalization in the thiazole ring, reflecting the contribution of the canonical structure with a positive charge at C(2).

Table 1. ^1H-, ^{11}B-, ^{13}C-, and ^{14}N-NMR data[a] of the imidazaboles **2**, **2′**, the thiazabole **5a**, and the triazabole **5b**

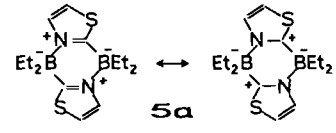
	2	**2′**	**5a**	**5b**
$\delta^{13}C$ (δ^1H) NMe	33.4 (3.56)	34.0 (3.66)	-	37.8 (3.52)
BEt_2	-	-	21.3 [br] (0.98) 10.6 (0.77)	16.6 [br] (0.96) 10.5 (0.75)
=C–B	161.0 [br]	161.0 [br]	195.0 [br]	169.0 [br] [C(5)]
C(4), C(3)	122.1 (7.01)	121.8 (7.01)	119.4 (6.40)	143.6 [C(3)] (7.70)
C(5)	121.7 (6.86)	120.2 (6.86)	136.6 (7.16)	169.0 [br]
$\delta^{11}B$ [$^1J(^{11}B^1H)$]	-19.2 [94][b]	-8.7 [102] -32.7 [87]	-2.5	-6.1
$\delta^{14}N$	-217 -188[c]	[d]	-105	-160 -50[e]

[a] In $CDCl_3$ (**2**) and in C_6D_6 (**5a, b**) at 26 ± 1°C in 5-mm tubes; [br] denotes the broad ^{13}C-NMR signal of a carbon bound to boron. – [b] δ^1H (BH_2) = 3.4. – [c] $\delta^{14}N$ ± 2; by comparison with $\delta^{14}N$ of **1**[6c], the signal at δ −217 is assigned to the N–Me and that at −188 to the N–B nitrogen atom. – [d] Not resolved owing to overlap with ^{14}N signals of **2**. – [e] $\delta^{14}N$ values ± 8; signal at δ −160 has twice the intensity of the signal at δ −50; therefore, it is assigned to the N–Me and to the N–B nitrogen atoms.

Table 2. ^{11}B-, ^{13}C-, and ^{14}N-NMR data[a] of the trimethylstannyl-substituted azoles **3** and their Et_3B adducts **4**

	3a	**4a**	**3b**	**4b**
$\delta^{13}C$ NMe	-	-	36.4 [≤6.0]	38.8 [≤6.0]
$SnMe_3$	-8.5 [373.8]	-4.2 [385.4]	-9.2 [380.0]	-4.3 [390.6]
=C–Sn	173.2 [461.5]	175.5 [310.1]	159.3 [450.8]	156.4 [298.4]
C(4), C(3)	145.9 [68.6]	145.3 [34.2]	152.6 [61.0]	148.3 [29.8]
C(5)	121.3 [≤ 4]	121.4 [8.6]	-	-
$\delta^{11}B$ [b]	-	+2.2	-	0.1
$\delta^{14}N$	-34	-68	-145[c]	n.m.
$\delta^{119}Sn$	-32.6	-15.1	-48.1	-39.5

[a] In C_6D_6 at 26 ± 1°C in 5-mm tubes; coupling constants $J(^{119}Sn^{13}C)$ [Hz] are given in square brackets (±1 Hz); n.m. = not measured. – [b] $\delta^{11}B$ values are markedly dependent on the presence of a slight excess of Et_3B. – [c] $\delta^{14}N$ of NMe; other $\delta^{14}N$ values: N(4) −115, N(2) −45; all $\delta^{14}N$ values ±5.



The comparison of the ^{13}C-NMR data of **3** with those of the Et_3B adducts **4** is of interest. The $\delta^{13}C$ data of the azole carbon atoms are hardly affected by the adduct formation

whereas there are dramatic changes in the magnitude of the coupling constants $|J(^{119}Sn^{13}C)|$. The magnitude of $|^1J(^{119}Sn^{13}C(2))|$ (**4a**) or $|^1J(^{119}Sn^{13}C(5))|$ (**4b**) is reduced by ≈150 Hz as compared to **3a** or **3b**. Similarly, the values $|^3J(^{119}Sn^{13}C(4))|$ (**4a**) or $|^3J(^{119}Sn^{13}C(3))|$ (**4b**) are halved with respect to **3a** or **4a**. This can be explained by the influence of the nitrogen lone pair[10] on these coupling constants.

X-Ray Analysis of the Imidazabole 2

Table 3 contains experimental data[11] for the X-ray structure analysis of **2**. Its molecular structure is shown in Figure 1, and selected bond lengths and bond angles are given in the legend to Figure 1. The molecular structures of pyrazabole **A**[12] or derivatives of **A**[13] show either a boat or a chair for the N_4B_2 ring, and there are also examples of a planar arrangement of all three rings. In the case of **2**, the deviation from a planar structure is small (mean deviation 1.2 pm). As for most of the pyrazaboles, this deviation is likely to be due to packing effects. The mean bond length d_{BN} = 155.8 pm is close to d_{BN} in the pyrazabole A (155.3 pm[12]).

Table 3. Data for the X-ray analysis of the imidazabole **2**

Formula $C_8H_{14}B_2N_4$, molecular mass 187.95, crystal size 0.50 × 0.50 × 0.20 mm³, space group $P2_1$ (monoclinic), Z = 2, a = 867.3(1), b = 632.5(1), c = 978.0(1) pm, β = 100.71(7)°, V = 536.5(1) Å³, ρ(calc) = 1.18 g/cm³, diffractometer CAD 4 F, radiation Mo-K_α, λ = 71.069 pm (graphite monochromator), temperature 297 K, 2Θ range: 2.8–50°, reflections collected 1081, unique reflections 1081, reflections with $I > 2\sigma I$ = 767, system used: MOLEN (Enraf Nonius), solution: direct methods, hydrogen atoms: located and refined isotropically, non-hydrogen atoms: refined anisotropically; abs. coeff. corr.: 0.713 < coeff. < 0.997, weighting scheme $[(\sigma F)^2 + (0.2 \cdot F)^2]^{-1}$, R = 0.077, R_w = 0.062, number of variables 179; residual electron density (min.) −0.01 eÅ^{-3}, (max) 0.33 eÅ^{-3}

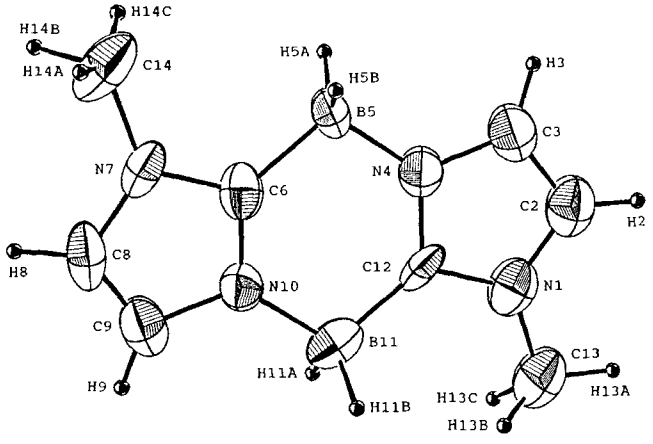


Figure 1. Molecular structure of the imidazabole **2**. Selected bond lengths [pm] and bond angles [°]: N(10)–B(11) 153.0(7), N(4)–B(5) 158.6(7), C(12)–B(11) 159.0(7), C(6)–B(5) 157.9(7), N(10)–C(6) 134.6(6), N(4)–C(12) 133.4(6), N(7)–C(6) 135.2(6), N(7)–C(8) 138.2(7), N(7)–C(14) 143.2(7), N(10)–C(9) 136.8(6), C(8)–C(9) 137.4(8), N(1)–C(12) 135.9(5), N(1)–C(2) 136.4(7), N(1)–C(13) 147.4(7), N(4)–C(3) 140.3(6), C(2)–C(3) 129.3(7); N(10)B(11)C(12) 106.6(4), N(4)B(5)C(6) 107.0(4), N(10)C(6)B(5) 127.3(4), N(4)C(12)-B(11) 128.6(4), C(6)N(10)B(11) 126.5(4), C(12)N(4)B(5) 123.9(4)

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Experimental

All compounds were handled under N_2 or Ar, using carefully dried glassware and dry solvents. Starting materials such as 1-methylimidazole, thiazole, 1,2,4-triazole, butyllithium (1.6 M) in hexane were commercial products. Borane–THF solutions (2 M)[14], triethylborane[15], 1-methyl-1,2,4-triazole[16], and the trimethylstannyl-substituted azoles **3**[17] were prepared according to methods described in the literature. – IR (KBr): Nicolet MX-1 FT spectrometer. – MS: EI-MS (70 eV), HP 5989 spectrometer, direct inlet. – $^1H/^{13}C$ NMR: Jeol GX 270 (270.67/67.94 MHz), Bruker WP 200 (200.13/50.32 MHz), Bruker AC 300 (300.13/75.7 MHz). – ^{11}B NMR: Jeol GX 270 (86.84 MHz), Bruker WP 200 (64.21 MHz), $Et_2O–BF_3$ as external standard [Ξ(^{11}B) = 32.083971 MHz]. – ^{14}N NMR: Bruker AC 300 (21.7 MHz), neat $MeNO_2$ as external standard [Ξ(^{14}N) = 7.226455 MHz]. – ^{119}Sn NMR: Bruker AC 300 (111.9 MHz), Me_4Sn as external standard [Ξ(^{119}Sn) = 37.290665 MHz].

N,N'-Dimethylimidazaboles **2**, **2'**: An open glass ampoule, containing 500 mg (5.2 mmol) of 1-methylimidazole–borane adduct **1** and 10 mg of MeI, was placed inside of an aluminium capsule which was closed after flushing with N_2. This capsule was heated in a sand bath to 320°C for 2 h to afford a 2:1 mixture of **2** and **2'** (^1H and ^{11}B NMR). The isomer **2** crystallized from CH_2Cl_2 at −17°C, and **2'** remained in solution which then contained a 1:1 mixture of **2** and **2'**. Sublimation of the mixture at 250°C/0.25 Torr gave 0.42 g (85%) of the pure imidazabole **2** (m.p. 204–206°C). Crystals of **2** suitable for an X-ray structure analysis were obtained from solutions in CH_2Cl_2. – **2**: IR: ν(BH) = 2304 cm^{-1}. – MS, *m/z* (%): 187 [M$^+$] (100). – $C_8H_{14}B_2N_4$ (187.8): calcd. C 51.15, H 7.51, N 29.83; found C 51.20, H 7.52, N 29.72.

B,B,B',B'-Tetraethylthiazabole **5a**, *B,B,B',B'-Tetraethyltriazabole* **5b** *General Procedure:* A solution of 5 mmol of the trimethylstannyl-substituted azole **3** in 10 ml of toluene was cooled to −78°C. After addition of ca. 2 g (20 mmol) of Et_3B in one portion, the mixture was warmed to room temp. and heated to reflux for 8 h. It was shown by ^{119}Sn-NMR spectra (formation of Me_3SnEt) that the reaction was complete. The residue which was left after all volatile materials had been removed in vacuo was sublimed twice (**5a**: 120°C/10^{-2} Torr; **5b**: 105°/10^{-2} Torr) to give the pure compounds **5** (for NMR data see Table 1).

5a: Light-yellow crystals (61% yield), m.p. 170–172°C. – $C_{14}H_{24}B_2N_2S_2$ (306.1): calcd. C 54.93, H 7.90, N 9.15; found C 54.65, H 7.93, N 8.76.

5b: Colorless crystals (69% yield), m.p. 135–138°C. – $C_{14}H_{28}B_2N_6$ (302.05): calcd. C 55.67, H 9.34, N 27.83; found C 55.53, H 9.42, N 27.24.

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