Nucleophilic Substitution Reactions with the 3-Borane-1,4,5-trimethylimidazol-2-ylidene Anion. – Unexpected Formation of an Imidazabole Isomer

Andreas Wacker,[a] Hans Pritzkow,[a] and Walter Siebert*[a]

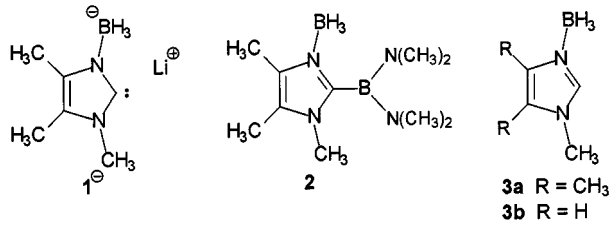
Dedicated to Prof. Bernt Krebs on the occasion of his 60th birthday

Keywords: Boranes / Carbenes / Heterocycles / Imidazoles / X-ray structures

The nucleophilic carbene 3-borane-1,4,5-trimethylimidazol-2-ylidene anion (**1**$^-$) reacts with the electrophiles CH_3I, $(CH_3)_3SiCl$, $(CH_3)_3SnCl$, and the bromodiazaboroline **7** to form the 2-substituted imidazoles **4**, **5**, **6**, and **8**. With triethylborane, the anionic carbene borane adduct **9**$^-$ is obtained. An unexpected result was achieved when chlorodimethoxyborane and $HBCl_2 \cdot S(CH_3)_2$ were used as electrophiles. In both cases only the imidazabole **14a** could be isolated. Imidazole **5**, the imidazole borane adduct **3a** and the imidazabole **14a** were characterized by X-ray structure analyses.

Introduction

Imidazol-2-ylidenes are stable carbenes which have attracted wide attention[1]. Recently, we described the synthesis and characterization of the first anionic imidazol-2-ylidene, the 3-borane-1,4,5-trimethylimidazol-2-ylidene anion (**1**$^-$),[2] and showed that it reacts with bis(dimethylamino)chloroborane to form **2**. We now report further details on the reactivity of **1**$^-$ towards various electrophiles.

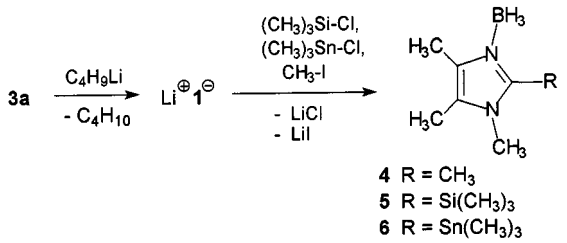


Results and Discussion

Formation of Substituted Imidazoles

The anion **1**$^-$ reacts with iodomethane, chlorotrimethylsilane and -stannane to give the expected 2-substituted imidazoles (Scheme 1). The products **4**, **5**, and **6** are obtained as air-stable compounds.

The reaction of **1**$^-$ with iodomethane results in the formation of 3-borane-1,2,4,5-tetramethylimidazole (**4**), which was first prepared[3] from 1,2,4,5-tetramethylimidazole and $BH_3 \cdot SMe_2$. The donor-acceptor compound is isoelectronic with the pentamethylimidazolium ion[3]. **4** is separated from LiI by sublimation which, however, lowers the yield com-



Scheme 1

pared with that of **5** and **6**. In the ^{1}H-NMR spectrum the signal for the methyl group in 2-position is found at δ = 2.45 which is 0.33 ppm at low-field compared with the shift for the CH_3 substituents in 4- and 5-position. The ^{13}C-NMR spectrum shows the expected high-field shift of the C2 carbon atom from δ = 191.3 in **1** to δ = 142.3. In the ^{11}B-NMR spectrum a 1:3:3:1 quartet is observed at δ = −22.4, [^1J(BH) = 82 Hz].

The analogous reaction of **1**$^-$ with chlorotrimethylsilane leads to 3-borane-1,4,5-trimethyl-2-(trimethylsilyl)imidazole (**5**) in quantitative yield. Its NMR data are similar to those of **4**. The trimethylsilyl group shows a resonance in the ^{1}H-NMR spectrum at δ = 0.52 and in the ^{13}C-NMR spectrum at δ = 1.7. As in **4**, the C2 carbon atom again experiences a high-field shift to δ = 146.9 and the ^{11}B-NMR signal is found as a quartet at δ = −19.7. **5** is an isomer of the 1-borane-2,4,5-trimethyl-3-trimethylsilylimidazole adduct (δ^{11}B = −21.8)[3].

Analogously, 3-borane-1,4,5-trimethyl-2-(trimethylstannyl)imidazole (**6**) is quantitatively synthesized from **1**$^-$ and chlorotrimethylstannane. The NMR spectra of **6** are nearly identical with those of **5**: The trimethylstannyl group is found in the ^{1}H-NMR spectrum at δ = 0.49 and in the ^{13}C-NMR spectrum at δ = −5.1. The signal for the C2 carbon atom appears at δ = 151.5 which is five ppm low-field com-

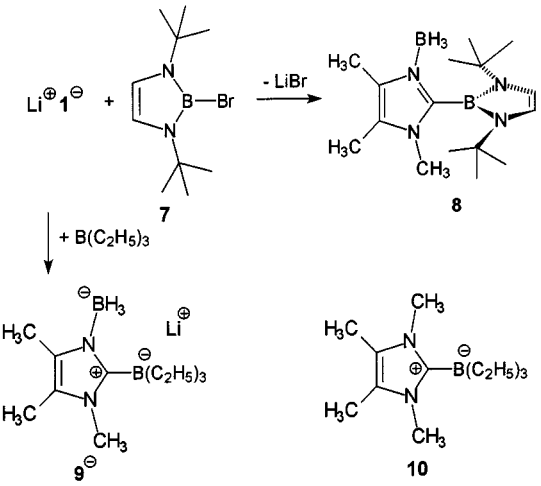
[a] Anorganisch-Chemisches Institut der Universität,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany
Fax: (internat.) + 49(0)6221/54-5609
E-mail: ci5@ix.urz.uni-heidelberg.de

  1434–1948/99/0505–0789 $ 17.50+.50/0

pared to that of **5**. In the ^{11}B-NMR spectrum the signal appears at $\delta = -19.9$.

2-Bromo-1,3-di(*tert*-butyl)-1,3,2-diazaboroline (**7**) reacts with the anion $\mathbf{1}^-$ to give **8** (Scheme 2) which is characterized by NMR and mass spectroscopy. The ^{1}H-NMR spectrum shows three singlets for the methyl groups of the imidazole ring at $\delta = 2.14$, 2.20, and 3.38. The signals for the diazaboroline substituent are found at $\delta = 1.18$ (*tert*-butyl) and 6.46 (C-H). The appearance of only two singlets indicates that the C_2N_2B-ring is orientated perpendicular to the imidazole plane, due to the steric hindrance of the *tert*-butyl substituents. As expected, all signals are shifted to higher field compared with those of a cationic carbene borane adduct, obtained from **7** and 1,3-dimethyl-imidazol-2-ylidene[4].

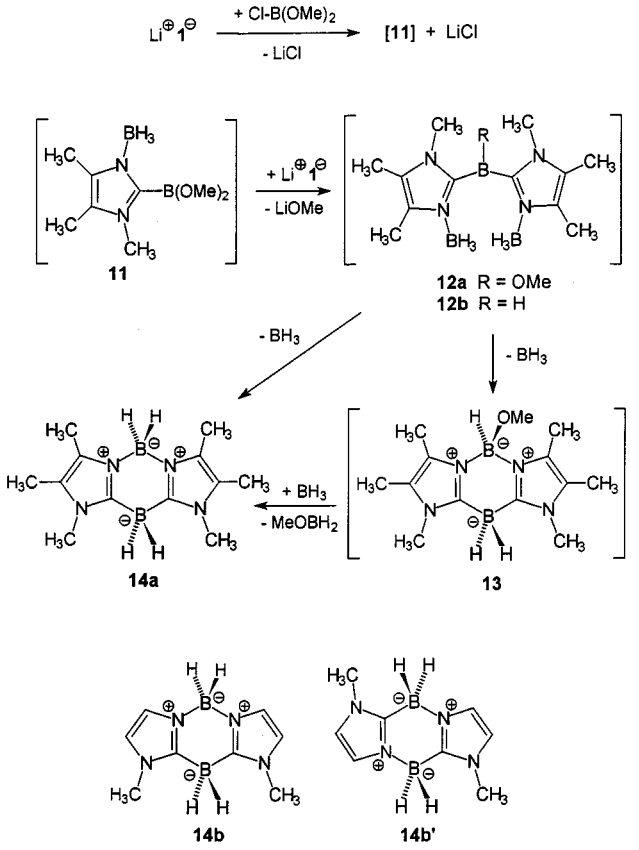
The ^{13}C-NMR spectrum shows the signals for the diazaboroline ring at $\delta = 31.0$, 53.1, and 114.7 and five more at $\delta = 8.6$, 10.1, 32.8, 123.9, and 132.0 belonging to the imidazole. The C2 atom is not observed. In the ^{11}B-NMR spectrum two signals at $\delta = 19.1$ (C-BN_2) and -20.1 (N-BH_3) are found.



Scheme 2

Reaction of 1^- with Boranes

When $\mathbf{1}^-$ is treated with the Lewis acid triethylborane, the anionic borane adduct $\mathbf{9}^-$ is obtained (Scheme 2). Neutral carbene-borane adducts of 1,3-dialkyl-imidazol-2-ylidenes and BH_3 or BF_3 are already known[5] as well as 1,3,4,5-tetramethyl-2-(triethylborane)imidazoline (**10**), which was recently prepared by a different route[2]. $\mathbf{9}^-$ and **10** are isoelectronic, a formal substitution of CH_3 in **10** by BH_3^- leads to $\mathbf{9}^-$. In its ^{1}H-NMR spectrum the signals for the B-C_2H_5 substituents are found as a broad multiplet ($\delta = 1.1-1.3$) and for the methyl groups at $\delta = 1.68$, 2.24, and 3.55. In the ^{13}C-NMR spectrum the B-C_2H_5 substituents show resonance at $\delta = 12.6$ (CH_3) and 16 (CH_2) of which the latter signal is broadened. The C2 carbon atom in $\mathbf{9}^-$ ($\delta = 175$) exhibits a different chemical shift compared with those of **4**, **5**, and **6**. – As expected, $\mathbf{9}^-$ shows two signals



Scheme 3

in the ^{11}B-NMR spectrum at $\delta = -12.5$ (C-BEt_3) and -21.6 (N-BH_3).

An interesting observation was made, when $\mathbf{1}^-$ was treated with chlorodimethoxyborane. In analogy to the formation of **4**–**6**, and **8**, we expected to find the dimethoxyboryl-substituted imidazole **11** but to our surprise, the only product that could be isolated was the imidazabole **14a** (Scheme 3). It is likely that in the first step **11** is formed, however, it then reacts with additional $\mathbf{1}^-$ to give **12a**. Obviously, ring closure to **13a** occurs with elimination of BH_3 and migration of H^- to the B–R group The methoxy group in **13a** is exchanged for hydrogen to give **14a** and [$(CH_3O)BH_2$] of which the latter was not identified.

To study the influence of boranes on the formation of **14a** the anion $\mathbf{1}^-$ was treated with $BH_3 \cdot$ thf. In the reaction mixture **14a** could be identified in the ^{11}B-NMR spectrum besides other signals that were not assigned. When $\mathbf{1}^-$ was treated with $HBCl_2 \cdot S(CH_3)_3$ in a ratio of 2:1, **14a** was obtained in 48% yield (calculated for $\mathbf{1}^-$). With a 3:1 ratio, the yield increased to 66%. These findings indicate that BH_3, set free in the ring closure process, participates in the reaction with $\mathbf{1}^-$ to give **14a**.

The structure of **14a** follows from the NMR and MS data. The two triplets in the ^{11}B-NMR spectrum at $\delta = -10$ (C_2BH_2) and -32 (N_2BH_2) clearly show that **14a** has been formed. In the ^{1}H-NMR spectrum three signals appear at $\delta = 2.10$, 2.17, and 3.49 and in the ^{13}C-NMR spectrum at $\delta = 9.2$, 10.3, and 31.9. The signals for the ring

carbon atoms are observed at δ = 123.6 and 127.3, that of the C2 atom was not found.

14a is isomeric to the imidazabole **14b′** which was obtained by Contreras, Wrackmeyer et al. in the thermolysis reaction of **3b**[6]. During their investigations they could isolate both isomers **14b** and **14b′**. We did not observe the formation of **14a′**. Thus, a change of the substituents at the boron atom by choosing chlorodimethoxyborane instead of a chlorodiaminoborane leads to a completely different reaction pathway in which the substituted imidazoles **11** and **12b** are postulated intermediates. Different reaction conditions like changing the order in which the starting materials are added as well as carrying out the reaction at elevated temperature have no influence on product formation.

X-ray Structure Analyses of 3a, 5, and 14a

Figure 1 shows the structure of planar **3a**. The B6−N1 distance of **3a** [1.584(3) Å] is similar to that of the trimethylsilyl derivative **5**. Single crystals of **5** were grown from a toluene/hexane solution and the structure is depicted in Figure 2. Comparism of **5** with the carbene anion **1**$^-$ and the imidazole borane adduct **3a** (Figure 1) shows that the structural parameters lie between those of **1**$^-$ and **3a**.

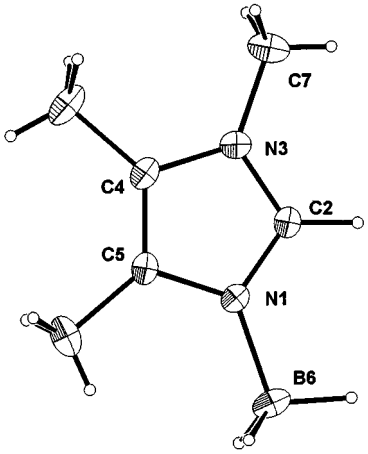


Figure 1. Structure of **3a** in the crystal; bond lenghts and angles are listed in Table 1

Imidazol-2-ylidenes characteristically have smaller N−C−N and larger C−N−C angles than imidazoles. Their C2−N1/2 bonds are equal in contrast to that of imidazole molecules which show single and double bond character[1−3]. In the case of **5**, the following observations are made: First, the C2−N1/2 distances with 1.348(3) and 1.367(3) Å exhibit bond length alternations as in imidazole molecules and they are shorter in comparison with those in **1**$^-$ but are still longer than in **3a** (Table 1). Second, the N−C−N angle of 106.6° has increased compared with that of **1**$^-$ but is still considerably smaller than that of **3a**. The third characteristic structural pattern, the C−N−C angles also show the same tendency: With 109.1° and 109.7° they lie between those found for **1**$^-$ and **3a**. A similar trend is observed in the ^{13}C-NMR shifts of the C2 atoms which

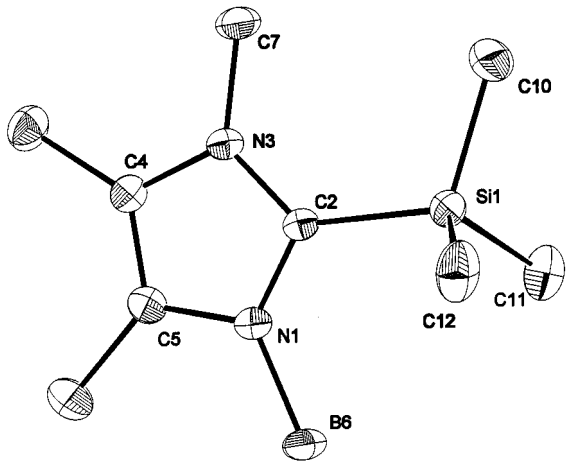


Figure 2. Structure of **5** in the crystal; bond lenghts and angles are listed in Table 1

Table 1. Selected bond lengths [Å] and angles [°] in Li$^+$ **1**$^-$, **3a**, and **5**

	Li$^+$ **1**$^-$ [2]	**5**	**3a**
N1−C2	1.373(3)	1.348(3)	1.320(2)
N3−C2	1.368(3)	1.367(3)	1.335(2)
N1−C5	1.398(3)	1.379(3)	1.386(2)
N3−C4	1.393(3)	1.385(3)	1.381(2)
C4−C5	1.355(3)	1.356(3)	1.358(3)
N1−B6	1.572(3)	1.588(3)	1.584(3)
N3−C7	1.463(3)	1.463(3)	1.461(3)
C2−Si1		1.913(2)	
N1−C2−N3	104.0(2)	106.6(2)	110.4(1)
C2−N1−C5	110.3(2)	109.1(2)	107.2(1)
C2−N3−C4	112.2(2)	109.7(2)	107.7(1)
N3−C4−C5	105.7(2)	106.2(2)	106.7(2)
N1−C5−C4	107.9(2)	108.4(2)	107.8(2)

move to higher field [δ = 191.3 (**1**$^-$), 146.9 (**5**), and 135.7 (**3a**)].

The structure of **14a** is shown in Figure 3. Single crystals were obtained from a $CDCl_3$ solution. The molecule is disordered, the structure found is a superposition of two orientations, created by a rotation around the axis through C4 and C4′. Therefore all other positions in the ring are occupied partly by nitrogen and carbon. The distances found are mean values, and the chemically different boron atoms cannot be distinguished. The result of the structure analysis

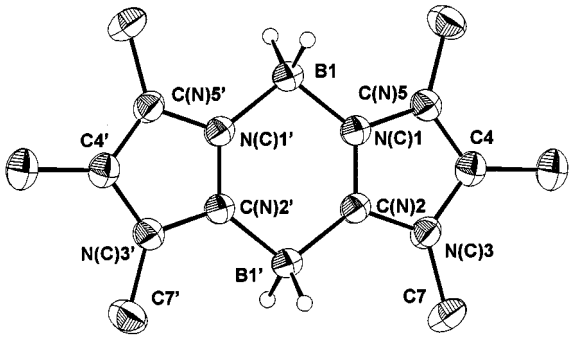


Figure 3. Structure of **14a** in the crystal

does not allow to distinguish **14a** from **14a′** (the analog of **14b′**) in contrast to the ^{11}B-NMR spectrum. A discussion of the angles and distances is therefore not meaningful.

Conclusion

The nucleophilic carbene union $\mathbf{1}^-$ obtained by deprotonation of the imidazole borane adduct **3a** reacts with electrophiles to form the 2-substituted imidazoles **4**, **5**, **6**, and **8**, which are confirmed by NMR and MS data and X-ray structure analyses for **3a** and **5**. With the Lewis acid BEt_3 the carbene addduct $\mathbf{9}^-$ is formed. Surprisingly, the reaction of $\mathbf{1}^-$ with $ClB(OMe)_2$, BH_3, or with $HBCl_2 \cdot SMe_2$ leads to the tricyclic imidazabole **14a**. In the crystal the molecule **14a** is disordered by superposition of two orientations. However, the ^{11}B-NMR spectrum of **14a** proves the presence of one C_2BH_2 and one N_2BH_2 group in the molecule.

Experimental Section

General: The reactions were carried out under dry argon, using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun in high-vacuum. − ^{1}H-, ^{13}C-, ^{11}B-NMR: Bruker AC 200 or AC 300 spectrometer, NMR references are $(CH_3)_4Si$ and $BF_3 \cdot Et_2O$. − Mass spectra were obtained with a Finnigan MAT 8200 plus spectrometer using EI technique. − Melting points (uncorrected) were obtained with a Büchi apparatus, using a capillary which was filled under argon and sealed. − 3-Borane-1,4,5-trimethylimidazole (**3a**)[2], chlorotrimethylstannane[7a] and 2-bromo-1,3-di(*tert*-butyl)-1,3,2-diazaboroline[7b] were prepared according to literature procedures.

General Procedure for the Preparation of the 2-Substituted Imidazoles 4, 5, and 6: To a suspension of **3a** [0.49 g (4.0 mmol) for **4**; 1.02 g (8.2 mmol) for **5** and 0.87 g (7.0 mmol) for **6**] in 30 mL of thf the equimolar amount of *n*-butyllithium (2.5 N in hexane) was added dropwise at −40°C. The mixture was allowed to warm to room temp. and was stirred for 1 h. Then the corresponding electrophiles [0.75 g (5.3 mmol) of iodomethane; 0.98 g (9.0 mmol) of chlorotrimethylsilane; 1.40 g (7.0 mmol) of chlorotrimethylstannane)] were added at −40°C, the solution again warmed to room temp. and stirred for 1 h. The solvent was removed in vacuo and the white precipitate (**4**) sublimed in vacuo (120−160°C, 10^{-2}−10^{-3} Torr). **5** and **6** were dissolved in toluene and LiCl was separated by filtration. The solution contained the pure product which was isolated by evaporating the solvent or by crystallization from a toluene/hexane solution.

3-Borane-1,2,4,5-tetramethylimidazole (4): Yield: 0.32 g (58%) white powder, m.p.: 140−160°C (decomp.). − ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 2.08, 2.14 (2s, 6 H, C-CH_3), 2.45 (s, 3 H, C-CH_3), 3.42 (s, 3 H, N-CH_3). − ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = δ = 8.6 (C-*C*H$_3$), 10.5 (C-*C*H$_3$), 11.2 (C-*C*H$_3$), 30.7 (N-CH$_3$), 122.4, 129.5 (C=*C*-N), 142.3 (N=C-N). − ^{11}B NMR (64.2 MHz, C_6D_6): δ = −22.4 (q, $^1J_{B\text{-}H}$ = 82 Hz). − $C_7H_{15}BN_2$ (138.0): calcd. C 60.91, H 10.95, N 20.29; found. C 60.46, H 10.82, N 20.24.

3-Borane-1,4,5-trimethyl-2-trimethylsilylimidazole (5): Yield: 1.48 g (92%) white powder, m.p.: 115−120°C. − ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.52 [s, 9 H, $Si(CH_3)_3$], 2.12, 2.20 (2s, 6 H, C-CH_3), 3.58 (s, 3 H, N-CH_3). − ^{13}C NMR (50.3 MHz, C_6D_6): δ = 1.7 (Si-CH_3), 8.4, 10.7 (C-*C*H$_3$), 32.3 (N-CH$_3$), 126.1, 133.4 (C=*C*-N), 146.9 (N=C-N). − ^{11}B NMR (64.2 MHz, C_6D_6): δ = −19.7 (q, $^1J_{B\text{-}H}$ = 93 Hz). − $C_9H_{21}BN_2Si$ (196.2): calcd. C 55.10, H 10.78, N 14.27; found. C 55.18, H 10.86, N 14.02.

3-Borane-1,4,5-trimethyl-2-trimethylstannylimidazole (6): Yield: 1.91 g (95%) colorless crystals, m.p. 110−115°C. − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.49 [s, 9 H, $Sn(CH_3)_3$, $^2J_{Sn\text{-}H}$ = 29 Hz],

Table 2. Crystal data and structure refinement for **3a**, **5**, and **14a**

	3a	**5**	**14a**
Empirical formula	$C_6H_{13}BN_2$	$C_9H_{21}BN_2Si$	$C_{12}H_{22}B_2N_4$
Formula weight	124.0	196.2	244.0
Crystal system	orthorhombic	monoclinic	triclinic
Space group	*Pmnb*	$P2_1/c$	$P\bar{1}$
Unit cell			
a [Å]	7.053(4)	8.510(4)	6.491(5)
b [Å]	8.537(4)	24.530(12)	7.465(7)
c [Å]	13.273(7)	12.351(6)	8.448(6)
α [deg]	90	90	101.41(7)
β [deg]	90	102.7(1)	111.45(6)
γ [deg]	90	90	107.12(9)
Volume [Å^3]	799.2(7)	2515(2)	342.0(5)
Z	4	8	1
Calc. density [g/cm^3]	1.03	1.034	1.19
Adsorp.coeff. [mm^{-1}]	0.06	0.15	0.07
F(000)	272	864	132
Crystal size [mm]	0.30 × 0.34 × 0.80	0.45 × 0.80 × 0.80	0.10 × 0.35 × 0.50
Θ-range [deg]	30	25	25
Index-ranges	0/+9, 0/+12, 0/+18	−10/+9, 0/+29, 0/14	−7/+6, −8/+8, 0/+10
No. of reflections			
unique	1255	4426	1175
observed [I>2σ(I)]	865	3459	1061
Transmission	0.92 − 1.00	0.94 − 1.00	0.91 − 1.00
Parameters	68	273	99
Final R indices			
*R*1 [$I > 2\sigma(I)$]	0.050	0.045	0.041
*wR*2	0.181	0.127	0.111
Largest diff.peak / hole[e/Å^3]	0.20 / −0.18	0.37 / −0.24	0.28 / −0.15

2.10, 2.16 (2s, 6 H, C-CH_3), 3.53 (s, 3 H, N-CH_3). – ^{13}C NMR (50.3 MHz, C_6D_6): δ = −5.1 (s, Sn-CH_3, $^1J_{Sn-C}$ = 380 Hz), 8.8, 10.4 (C-*C*H_3), 33.2 (N-CH_3), 126.3, 132.5 (C=*C*-N), 151.5 (N=C-N). – ^{11}B NMR (64.2 MHz, C_6D_6): δ = −19.9 (q, $^1J_{B-H}$ = 87 Hz). – $C_9H_{21}BN_2Sn$ (286.8): calcd. C 37.69, H 7.38, N 9.76; found. C 37.77, H 7.21, N 9.88.

2-(1-Borane-3,4,5-trimethylimidazolyl)-1,3-di(*tert*-butyl)-1,3,2-diazaboroline (8): To a suspension of 310 mg (2.5 mmol) of **3a** in 25 mL of thf 1.0 mL of *n*-butyllithium (2.5 N in hexane) were added dropwise at −40°C. The mixture was allowed to warm to room temp. and stirred for 1 h. Then a solution of 650 mg (2.5 mmol) of 2-bromo-1,3-(*tert*-butyl)-1,3,2-diazaboroline in 5 mL of thf was added at −78°C. During warming to room temp. the solution became orange colored and was then stirred for 1 h. The solvent was removed in vacuo, the white precipitate dissolved in toluene and LiBr was separated by filtration. After adding hexane to the solution at −30°C the product precipitates. Yield: 170 mg (32%) white powder, sensitive to air and moisture. – ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.18 [s, 18 H, C(CH_3)$_3$], 2.14, 2.20 (2s, 6 H, C-CH_3), 3.38 (s, 3 H, N-CH_3), 6.46 (s, 2 H, C-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 8.6, 10.1 (C-*C*H_3), 31.0 [N-C(*C*H_3)$_3$], 32.8 (N-CH_3), 53.1[N-*C*(CH_3)$_3$], 114.7 (C-H), 123.9, 132.0 (C=*C*-N), C2 (imidazole) not observed. – ^{11}B NMR (64.2 MHz, C_6D_6): δ = 19.1 (N-B-N), −20.1 (BH_3). – EI-MS; *m/z* (%) = 302 [M^+] (25), 245 [M^+ − C(CH_3)$_3$] (26), 123 [$C_6H_{12}BN_2^+$] (100).

Lithium 3-Borane-1,4,5-trimethyl-2-(triethylborane)imidazoline (Li^+ 9^-): To a suspension of 500 mg (4.0 mmol) of **3a** in 25 mL of thf 1.65 mL of *n*-butyllithium (2.5 N in hexane) were added dropwise at −40°C. The mixture was allowed to warm to room temp. and stirred for 1 h. Then 390 mg (4.0 mmol) of triethylborane were added at 0°C, then warmed to room temp. and stirred for 1 h. The solvent was removed in vacuo, leaving the product as a yellow oil. Yield: 1.58 g [96% for Li(thf)$_3^+$ 9^-], sensitive to air and moisture. – ^{1}H NMR (200.1 MHz, C_6D_6): δ = 1.1−1.3 (m, 15 H, C_2H_5), 1.4−1.5 (m, 12 H, thf), 1.68, 2.24 (2s, 6 H, C-CH_3), 3.5−3.6 (m, 15 H, N-CH_3 + thf). – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 9.2, 12.6 (C-*C*H_3), 12.6 (CH_2-*C*H_3), 16 (br., *C*$H_2$$CH_3$), 25.5 (thf), 33.1 (N-$CH_3$), 68.4 (thf), 121.8, 128.1 (C=*C*-N), 175 (br., N-C=N). – ^{11}B NMR (64.2 MHz, C_6D_6): δ = −12.5 (C-BEt_3), −21.6 (br., N-BH_3).

Imidazabole 14a: To a suspension of 500 mg (4.0 mmol) of **3a** in 20 mL of thf 1.7 mL of *n*-butyllithium (2.5 N in hexane) were added dropwise at −40°C. The mixture was allowed to warm to room temp. and stirred for 1 h. Then 450 mg (4.2 mmol) of chlorodi(methoxy)borane were added at −70°C, the solution was warmed to room temp. and stirred for 1 h. The solvent was removed in vacuo. The white precipitate was dissolved in toluene and LiCl was separated by filtration. **14a** was allowed to crystallize from a toluene/hexane solution at −30°C. Yield: 200 mg (54%) white, air-stable solid, m.p. > 270°C. – ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.10 (s, 6 H, C-CH_3), 2.17 (s, 6 H, C-CH_3), 3.49 (s, 6 H, N-CH_3). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 9.2, 10.3 (C-*C*H_3), 31.9 (N-CH_3), 123.6, 127.3 (C=*C*-N), 163 (br., N=C-N). – ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = −10.0 (t, C_2-BH_2, $^1J_{B-H}$ = 100 Hz), −31.4 (t, N_2-BH_2, $^1J_{B-H}$ = 87 Hz). – EI-MS: *m/z* (%) 243 (100) [M^+ − H].

Formation of 14a from 1^- and $HBCl_2 \cdot S(CH_3)_2$: To a suspension of 1.00 g (8.1 mmol) [1.05 g (8.5 mmol)] of **3a** in 30 mL of thf 3.5 mL [3.4 mL] of *n*-butyllithium (2.5 N in hexane) were added dropwise at −40°C. The mixture was allowed to warm to room temp. and stirred for 1 h. Then 600 mg (4.2 mmol) [390 mg (2.7 mmol)] of $HBCl_2 \cdot S(CH_3)_2$ were added at −78°C and the solution was allowed to warm to room temp. After stirring for 1 h, the solvent was removed in vacuo and the white precipitate dissolved in toluene. LiCl was separated by filtration. The solvent was evaporated, the residue dissolved in chloroform and allowed to crystallize at −30°C. Yield: 470 mg (48%) [680 mg (66%)] white, air-stable **14a** (analytical data see above).

Crystal Structure Determinations of 3a, 5, and 14a: Crystal data and details of the structure determinations are listed in Table 2. Unique sets of intensity data were collected at −70°C (**5**, **14a**) and at 23°C (**3a**) with a 4-circle diffractometer (Mo-*K*α-radiation λ = 0.71073 Å, graphite monochromator, ω-scan). Empirical absorption corrections (ψ-scans) were applied. The structures were solved by direct methods [SHELXS86][8] and refined by least-squares methods based on F^2 with all measured reflections [SHELXL97][9]. All non-hydrogen atoms were refined anisotropically. The structure of **14a** is disordered. A refinement in $P\bar{1}$ did not converge and gave no reasonable result.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallograhpic Data Center as supplementary publication no. CCDC 102759 (**3a**), 102760 (**5**), 102761 (**14a**). Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +44(1223) 336-001; e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This work was supported by Deutsche Forschungsgemeinschaft (SFB 247) and Fonds der Chemischen Industrie.

[1] [1a] A.J. Arduengo, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361−363. – [1b] A.J. Arduengo, H.V. Rasika Dias, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530−5534. – [1c] N. Kuhn, T. Kratz, D. Bläser, R. Boese, *Chem. Ber.* **1995**, *128*, 245−250. – [1d] M. Regitz, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 725−728, *Angew. Chem.* **1996**, *108*, 791−794. – [1e] W.A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256−2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162−2187.
[2] A. Wacker, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1998**, 843−849.
[3] N. Kuhn, G. Henkel, J. Kreutzberg, *Z. Naturforsch.* **1991**, *46b*, 1706−1712.
[4] L. Weber, E. Dobbert, H.-G. Stammler, B. Neumann, R. Boese, D. Bläser, *Chem. Ber./Recueil* **1997**, *130*, 705−710.
[5] N. Kuhn, G. Henkel, T. Kratz, J. Kreutzberg, R. Boese, A.H. Maulitz, *Chem. Ber.* **1993**, *126*, 2041−2045.
[6] I. I. Padilla-Martinez, F. J. Martinez-Mastinez, A. López-Sandoval, K. I. Girón-Castillo, A. Brito, and R. Contreras *Eur.. J. Inorg. Chem.* **1998**, 1547−1553.
Note added in proof (February 17, 1999): New imidazabole derivatives are reported by: I. I. Padilla-Martinez, F. J. Martinez-Martinez, A. López-Sandoral, K. I. Girón-Castillo, A. Brito, R. Contreras, *Eur. J. Inorg. Chem.* **1988**, 1547−1553.
[7] [7a] Gmelin, *Handbuch der Anorg. Chemie, Sn-organische Verbindungen*, Teil 5, S. 63 (**1978**). – [7b] G. Schmid, J. Schulze, *Chem. Ber.* **1977**, *116*, 2744−2749.
[8] G. M. Sheldrick, *SHELXS86*, Univ. Göttingen, **1986**.
[9] G. M. Sheldrick, *SHELXS97*, Univ. Göttingen, **1997**.

Received August 28, 1998
[I98295]