Reaction of 1,3-Dialkyl-4,5-dimethylimidazol-2-ylidenes with 2-Bromo-2,3-dihydro-1*H*-1,3,2-diazaboroles (Alkyl = *i*Pr and *t*Bu)☆

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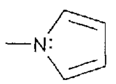
Received January 17, 1997

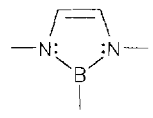
Keywords: Boron / Diazaboroles / Carbenes / Heterocycles / Imidazoles

2-Bromo-2,3-dihydro-1*H*-1,3,2-diazaboroles (**3a**–**c**) were synthesized by cyclocondensation of dilithiated 1,4-diazabutadienes (**5a**–**c**) with boron tribromide in hexane. **3a** was also obtained by sodium amalgam reduction of the corresponding borolium salt **1** in hexane. If this reaction was conducted in ether solvents, diboroxane (**2**) resulted as the main product. Compound **3a** and 1,3-dialkyl-4,5-dimethylimidazol-2-ylidenes (**6a**, **b**) underwent halide displacement to afford the borolylimidazolium salts **7a**, **b**. Compounds **2**, **3a**–**c**, and **7a**, **b** were characterized by elemental analyses and spectroscopic methods (^{1}H, ^{11}B, ^{13}C NMR; IR; MS). The molecular structures of **2** and **7a** were established by single-crystal X-ray diffraction analyses.

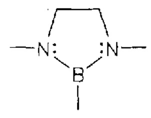
The formal replacement of a C=C fragment in pyrrole **I** by a B–N unit leads to 2,3-dihydro-1*H*-1,3,2-diazaboroles (**II**).



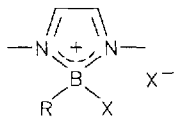
I



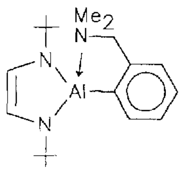
II



III



IV



V

Heterocycles of type **II** are accessible by the catalytic dehydrogenation of the corresponding saturated 2,3,4,5-tetrahydro-1,3,2-diazaboroles (1,3,2-diazaborolidines, **III**)[3], or by the dehalogenation of borolium salts **IV** (X = Br, Cl) using sodium metal[1–5]. 2,3-Dihydro-1*H*-1,3,2-diazaboroles have attracted interest for being 6π-Hückel heteroarenes[3] and for their potential as π ligands in transition-metal complexes[2,6]. Aluminium[7] and gallium[8] homologues of **II** have also been studied and found to be dimeric in structure featuring an M_2N_2 ring skeleton. Dimerization may be avoided by providing an additional donor function at the aryl substituent as shown in **V**[7]. Apart from the synthesis of $Cr(CO)_3$ complexes with η^5-1,3,2-diazaborole ligands[2,6] and the cleavage of the N–Si bond in *N*-silylated derivatives by metal amides or alcoholates to afford the corresponding alkali metal 1,3,2-diazaborolides[9], surprisingly little information regarding the chemical properties of such heterocycles is available. This is due to the lack of functional groups in the 2,3-dihydro-1*H*-1,3,2-diazaboroles examined to date. The availability of 2-halo-2,3-dihydro-1*H*-1,3,2-diazaboroles offers new synthetic potential but these compounds are found to be very unstable and can only be detected in the reaction mixture by ^{11}B-NMR spectroscopy[5].

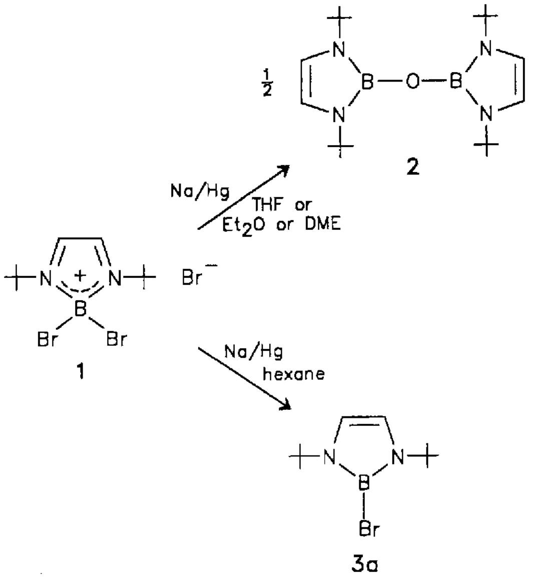
The intention of the investigations described in this paper, was to provide an efficient synthesis for 2-bromo-2,3-dihydro-1*H*-1,3,2-diazaboroles and to study their reactivity towards nucleophilic carbenes of the imidazol-2-ylidene type.

2-Bromo-2,3-dihydro-1*H*-1,3,2-diazaboroles

We recognized the two-electron reduction of borolium salts by sodium amalgam, previously outlined, as a satisfactory pathway to 2-bromo-2,3-dihydro-1*H*-1,3,2-diazaboroles[4,5]. The attempted reduction of **1a** in ether solvents such as diethyl ether, tetrahydrofuran, dioxane or 1,2-dimethoxyethane invariantly led to the formation of the diboroxane **2**, which was isolated as a colorless crystalline solid in 66% yield. Moisture cannot be considered a source of the oxygen atom in **2** because all of the solvents were freshly distilled from $LiAlH_4$, and Karl-Fischer determinations proved the absence of traces of water. Therefore, ether cleavage has most likely occurred in this reaction. Accordingly, the reduction of **1a** with sodium amalgam in hexane cleanly afforded **3a** in 85% yield (Scheme 1).

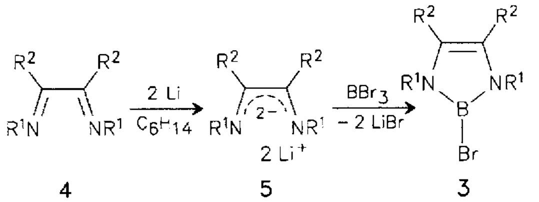
An alternative route to compounds **3a**–**c** made use of the reduction of the 1,4-diazabutadienes [**4a** (R = *t*Bu)[10], **4b** (R = 2,6-Me_2-C_6H_3)[11] and **4c** (R = *t*$BuCH_2$)][12] by two equiv. of lithium in hexane, and the subsequent cyclo-

Scheme 1



condensation of the dilithio salts **5a–c** with boron tribromide (Scheme 2).

Scheme 2

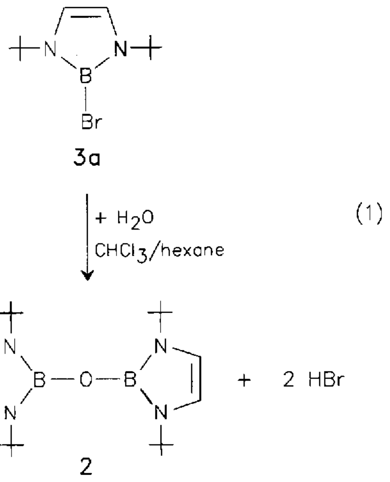


3–5	R^1	R^2	yield %
a	tBu	H	55
b	2,6-$Me_2C_6H_3$	H	54
c	tBuCH_2	Me	64

Compound **3a** was obtained as a colorless distillable oil which readily solidified at room temperature. The analogous heterocycles **3b** and **3c** are brown viscous oils. In contrast to **3a**, which can be stored at −30°C for at least 6 months without decomposition, **3b** and **3c** are heat- and lightsensitive.

The novel 2,3-dihydro-1*H*-1,3,2-diazaboroles were characterized by elemental analyses and spectroscopic data. The replacement of the methyl group in tBuNCH=CHN(tBu)BCH$_3$ ($\delta^{11}B$ = 26.2) by a bromine atom in **3a** (δ = 16.2) is accompanied by a highfield shift of the signal of **3a** by about 10 ppm. In general organoboron-substituted 2,3-dihydro-1,3,2-diazaboroles display ^{11}B-NMR absorptions at δ = 25–27[1–4]. The diazaboroles **3b**, **3c** and bis(1,3,2-diazaborolyl)oxane (**2**) give rise to ^{11}B-NMR resonances amidst these extremes ($\delta^{11}B$ = 19.2–21.1). Singlets in the ^{1}H-NMR spectra of **2**, **3a** and **3b** at δ = 5.90–6.34 are indicative of a *cis*-configured HC=CH unit in 1,3,2-diazaboroles. The respective carbon atoms in the $^{13}C\{^1H\}$-NMR spectra of **3a–c** (δ = 113–120) are markedly deshielded in comparison to tBuN–CH=CH–N(tBu)BCH$_3$ (δ = 111.5) and **2** (δ = 110.6). In the mass spectra of **3a–c** the molecular ions are registered as peaks with the highest *m/z* ratio. Correct isotopic patterns (^{11}B ^{81}Br, ^{10}B ^{81}Br, ^{11}B ^{79}Br, ^{10}B ^{79}Br) provide additional proof for the composition of the compounds.

Diboroxane (**2**) was also synthesized by controlled hydrolysis of **3a** dissolved in hexane/chloroform.

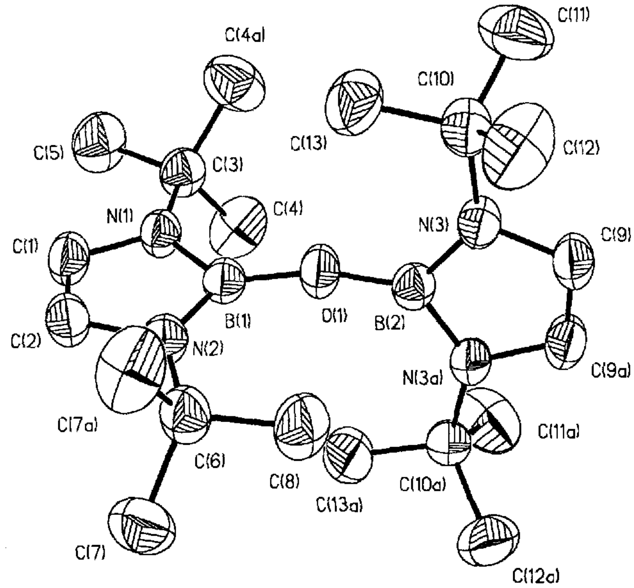


This reaction parallels the formation of the saturated diboroxanes, [MeN(CH$_2$)$_n$N(Me)B]$_2$O (n = 2, 3), by hydrolysis of the corresponding methylthiolates[13]. Compound **2** is the first bis(2,3-dihydro-1,3,2-diazaboryl)oxane to be synthesized on a preparative scale, and fully characterized. It is conceivable, however, that the compound previously obtained by the reduction of borolium salt **1a** in THF, and detected by its ^{11}B-NMR signal at δ = 21.7, was in fact **2** and not the bromo derivative **3a** as reported[5]. In the mass spectrum of thermolabile 2-pyrazolyl-1,3-dimethyl-1*H*-1,3,2-diazaborole, a peak corresponding to a contaminant was attributed to [(Me)NCH=CHN(Me)B]$_2$O. Unfortunately, no additional information concerning this molecule was given[14].

X-Ray Structural Analysis of 2

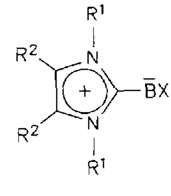
Diboroxanes[15] are of interest due to their isoelectronic relationship with allenes as well as with monomeric alkylidene iminoboranes[16], and one might expect corresponding structural similarities. An electron-diffraction study of gaseous (Me$_2$B)$_2$O revealed a bent molecule (B–O–B = 144.4(2.7)°[17]), whereas in the crystalline phase the compound was found to be dimeric[15]. The X-ray structure-analyses of tetramesityldiboroxane[18] and bis(4-benzoborepinyl)oxane[19] displayed B–O–B angles of 165.5(12)° and 159.4(10)°, respectively. The molecular structure of **2** (Figure 1) has an overall similarity to the bent, twisted structure of (Mes$_2$B)$_2$O[18], with an angle B(1)–O(1)–B(2) of 157.1(3)°. The atoms N(1), C(1), C(2), N(2), B(1), O(1) and B(2) are located on a crystallographic symmetry plane, and the angle ψ between the planes of the 1,3,2-diazaborole rings amounts to 90°. The corresponding parameters in

Figure 1. Molecular structure of **2** in the crystal[a]



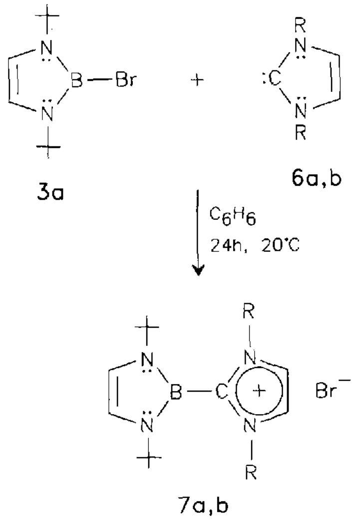
[a] Selected bond lengths [Å] and angles [°]: O(1)−B(1) 1.365(4), O(1)−B(2) 1.354(4), B(1)−N(1) 1.439(4), B(1)−N(2) 1.434(4), B(2)−N(3) 1.442(3), N(1)−C(1) 1.394(4), N(2)−C(2) 1.410(4), N(3)−C(9) 1.402(3), C(1)−C(2) 1.328(5), C(9)−C(9a) 1.338(5); B(1)−O(1)−B(2) 157.1(3), O(1)−B(1)−N(1) 122.6(3), O(1)−B(1)−N(2) 130.4(3), N(1)−B(1)−N(2) 107.0(3), O(1)−B(2)−N(3) 126.7(1), N(3)−B(2)−N(3a) 106.4(3), B(1)−N(1)−C(1) 106.4(3), B(1)−N(2)−C(2) 105.7(3), N(1)−C(1)−C(2) 110.4(3), N(2)−C(2)−C(1) 110.5(3), C(1)−N(1)−C(3) 124.4(3), C(2)−N(2)−C(6) 119.2(3), B(2)−N(3)−C(9) 106.5(2), B(2)−N(3)−C(10) 133.5(2), N(3)−C(9)−C(9a) 110.3(1), C(9)−N(3)−C(10) 120.0(2).

$(Mes_2B)_2O$ are 165.5(12) and 85°. The B−O bond lengths in **2** [1.354(4) and 1.365(4) Å] are consistent with the mesityl derivative [av. 1.36(2) Å][18]. Bond distances and valence angles within the diazaborole rings resemble closely the respective data for $\overline{\mathrm{MeN{-}CH{=}CH{-}N(Me)B}}\mathrm{Me}$ and $\overline{\mathrm{EtN{-}CH{=}CH{-}N(Et)B}}\mathrm{Me}$[3]. In **2**, B−N atom distances range from 1.434(4) to 1.442(3) Å indicating multiple-bond character. The bond lengths of C(1)−C(2) and C(9)−C(9a) of 1.328(5) and 1.338(5) Å and the N−C(sp^2) atom-distances [1.394(4)−1.410(4) Å] are typical for 1,2-dihydro-1*H*-1,3,2-diazaboroles and are also reflected in the imidazolyl ring of compound **7a**. In contrast to 1,3,2-diazaboroles $\overline{\mathrm{RNCH{=}CHN(R)B}}\mathrm{Me}$ (R = Me, Et) where nearly identical exocyclic angles N−B−C ranging from 126.5(3) to 127.8(1)° were encountered, the corresponding angles N(1)−B(1)−O(1) [122.6(3)°] and N(2)−B(1)−O(1) [130.4(3)°] differ markedly due to steric interactions with second 1,3,2-diazaborole ring at atom O(1). These interactions also account for significant distortions of the angles B(1)−N(2)−C(6) [135.1(3)°] versus B(1)−N(1)−C(3) [129.2(3)°] and C(1)−N(1)−C(3) [124.4(3)°] versus C(2)−N(2)−C(6) [119.2(3)°]. Due to the presence of a crystallographic mirror plane bisecting the second 1,3,2-diazaborole ring, a symmetrical situation is observed with angles O(1)−B(2)−N(3) [126.70(13)°], B(2)−N(3)−C(10) [133.5(2)°] and C(9)−N(3)−C(10) [120.0(2)°].



R^1 = Me, Et, *i*Pr
R^2 = Me
X = F, H

VI



(2)

6,7	R
a	Me
b	*i*Pr

Reaction of 3a with 1,3-Dialkyl-4,5-dimethylimidazol-2-ylidenes

The fundamental investigations of Wanzlick[20] on nucleophilic carbenes have recently found an unexpected renaissance with the isolation of stable imidazol-2-ylidenes by Arduengo et al.[21]. Their work initiated an intense investigation of the chemical reactivity of heterocyclic nucleophilic carbenes[22]. These molecules not only form numerous stable transition-metal carbene[23] and lanthanoid carbene complexes[24], but also provide access to adducts with several electrophilic main-group compounds[25]. Boron compounds such as $Me_2S \cdot BH_3$ or $Et_2O \cdot BF_3$ and imidazol-2-ylidenes afforded stable carbene boranes[26].

In the course of reactivity studies on 1,3,2-diazaboroles we were interested in the chemical behavior of 2-bromo-1,3,2-diazaboroles **3** towards heterocyclic carbenes.

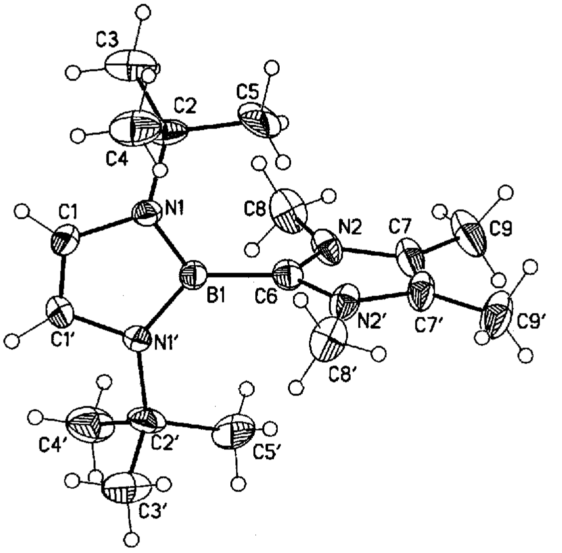
Upon mixing a benzene solution of **3a** with equimolar amounts of the imidazol-2-ylidenes **6a**, **b** (**a**: R = Me; **b**: R = *i*Pr)[27] the colorless salts **7a**, **b** precipitated in high yields. The cations of these thermally stable compounds can be regarded as 1,3,2-diazaborolyl-functionalized imidazolium ions. Such halide displacements have previously been observed in the reaction of the respective carbenes with Me_3SiI[25e], but not with haloboranes. As compared to **3a** the ^{11}B-NMR resonances of the salts **7a**, **b** appear slightly shielded ($\Delta\delta^{11}B \approx 1$). Due to the inductive effect of the imidazolium unit, the olefinic protons and the corresponding ^{13}C nuclei of **7a**, **b** experience downfield shifts of $\Delta\delta^1H = 0.2-0.3$ and $\Delta\delta^{13}C = 3.6-4.3$ as compared to precursor **3a**. The ^{13}C-NMR shifts for the carbon atoms of the

C_2Me_2 unit in the imidazolium ring of **7a**, **b** were observed at δ = 129.07 and 129.49 respectively, and thus agree with the data of $[EtNC(Me){-}C(Me){-}N(Et){-}C(SiMe_3)]^+I^-$ (δ^{13}C-4,5 = 129.07)[25e]. In carbene **6a** the corresponding carbon nuclei gave rise to resonances at δ = 122.55[27]. A signal for the ^{13}C atom directly bonded to the boron atom was not detected. From this data it was concluded that a 1,3,2-diazaborole moiety is directly connected to the carbon atom C-2 of the isoelectronic imidazolium system. Carbenium ions with boryl substituents are unprecedented, thus **7a**, **b** may be regarded as the first representatives of this class of compound.

X-Ray Structural Analysis of 7a

Single crystals of **7a** were grown from chloroform at 4 °C. The X-ray structural determination reveals the presence of a salt containing the novel 2-(1,3,2-diazaborolyl)-1,3,4,5-tetramethylimidazolium cation and four molecules of solvent in the asymmetric unit. There are no bonding contacts with the bromide ion, which is located above the B–C vector [Br···B(1) 5.68 Å, Br···C(6) 5.63 Å]. Both five-membered heterocycles are planar with an interplanar angle of 92.9°. The bond length B(1)–C(6) [1.580(11) Å] resembles that found in the carbene-borane adduct $EtNC(Me){-}C(Me){-}N(Et){-}C{-}BH_3$ [1.603(3) Å][26]. The metric parameters within the imidazolium part of this adduct and **7a** are not markedly different. Thus the C–N bond lengths in the adduct [1.352(2) and 1.392(2) Å] agree with the corresponding values in **7a** [1.345(6) and 1.397(7) Å]. The same is true for the C–C distance in both compounds [1.350(2) and 1.355(12) Å, respectively). The endocyclic angles N–C–N in **7a** are determined as 104.7(1)° and 106.5(6)°, respectively.

Figure 2. Structure of the cation of **7a** in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: B(1)–N(1) 1.434(6), N(1)–C(1) 1.414(7), C(1)–C(1') 1.315(11), N(1)–C(2) 1.492(7), B(1)–C(6) 1.580(11), N(2)–C(6) 1.345(6), N(2)–C(7) 1.397(7), N(2)–C(8) 1.466(7), C(7)–C(7') 1.355(12); N(1)–B(1)–N(1') 107.1(6), N(1)–B(1)–C(6) 126.5(3), B(1)–N(1)–C(1) 105.9(4), B(1)–N(1)–C(2) 133.9(5), N(1)–C(1)–C(1') 110.5(3), C(1)–N(1)–C(2) 120.1(4), B(1)–C(6)–N(2) 126.8(3), C(6)–N(2)–C(7) 110.1(5), N(2)–C(7)–C(7') 106.6(3), C(6)–N(2)–C(8) 124.9(5), C(7)–N(2)–C(8) 125.0(4).

Bond lengths and bond angles in the 1,3,2-diazaborolyl unit of the cation are in accordance with the structural parameters previously observed in $MeNCH{=}CHN(Me)BMe$[3] (vide supra).

This work was financially supported by the *Fonds der Chemischen Industrie*, Frankfurt/M., which is gratefully acknowledged. We are also grateful to Professor *N. Kuhn* (Univ. Tübingen) for valuable discussions.

Experimental Section

All manipulations were performed under dry argon. Solvents were rigorously dried with an appropriate drying agent and distilled before use. The following were prepared as described in the literature: Borolium salt ($tBuN{=}CH{-}CH{=}NtBuBBr_2$)Br (**1**)[5]; the 1,4-diazabutadienes, $tBuN{=}CH{-}CH{=}NtBu$ (**4a**), $2,6\text{-}Me_2C_6H_3N{=}CH{-}CH{=}NC_6H_3Me_2\text{-}2,6$ (**4b**)[9], $tBuCH_2N{=}C(Me){-}C(Me){=}NCH_2tBu$ (**4c**)[10]; the imidazol-2-ylidenes, $MeN{-}C(Me){=}C(Me){-}N(Me){-}C$ (**6a**)[27] and $iPrN{-}C(Me){=}C(Me){-}N(iPr){-}C$ (**6b**)[27]. – IR spectra: Bruker FTIR IFS66. – ^{1}H-, ^{11}B-, ^{13}C-NMR spectra: Bruker AC 250 (^{1}H, 250.13; ^{13}C, 62.90 MHz) and Bruker AM Advance DRX 500 (^{1}H, 500.13; ^{11}B, 160.46; ^{13}C, 125.75 MHz). Standards: $SiMe_4$ (^{1}H, ^{13}C), $BF_3 \cdot OEt_2$ (^{11}B). – Mass spectra: Varian MAT CH5-DF.

[tBuN–CH=CH–N(tBu)B]₂O (**2**): *Path a:* A slurry of borolium salt **1** (3.80 g, 9.1 mmol) in 80 ml of 1,2-dimethoxyethane (DME) was stirred for 24 h with 150 g of sodium amalgam containing 1.20 g (52.2 mmol) of sodium metal at room temp., where upon an exothermic reaction commenced. The supernatant light yellow solution was decanted and concentrated to ca. 20 ml. After 120 h, 1.12 g (66.5%) of colorless crystalline **2** separated. Analogous reductions of **1** in THF or 1,4-dioxane yielded **2** in 45% and 38% yields, respectively.

Path b: A sample of **3a** (0.30 g, 1.2 mmol) was dissolved in 10 ml of a mixture of $CHCl_3$ and hexane (1:1). After the addition of 0.063 g (3.4 mmol) of water the solution was stirred overnight at ambient temp. The solvent was removed until crystallization occurred and was stored at 4 °C to afford 0.20 g (88.3%) of microcrystalline **2**. – IR (cm^{-1}, Nujol): $\tilde{\nu}$ = 1514 m, 1491 m, 1466 s, 1457 s, 1396 m, 1378 w, 1360 m, 1276 m, 1240 s, 1220 sh, 1129 m, 1031 w, 934 w, 922 w, 820 w, 723 w, 663 w, 627 s. – ^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 36 H, *t*Bu), 6.05 (s, 4 H, HC=). – $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 21.1. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.5 [s, $C(CH_3)_3$], 51.9 [s, $C(CH_3)_3$], 110.6 (s, =CH). – MS (CI), *m/z*: 375 [M^+ + H], 374 [M^+], 359 [M^+ + H – CH_4], 358 [M^+ – CH_4], 319 [M^+ + H – $Me_2C{=}CH_2$], 318 [M^+ – $Me_2C{=}CH_2$]. – $C_{20}H_{40}B_2N_4O$ (374.18): calcd. C 64.19, H 10.78, N 14.97; found C 63.98, H 11.31, N 14.89.

tBuN–CH=CH–N(tBu)BBr (**3a**): *Path a:* A sample of 3.80 g (9.00 mmol) of borolium salt **1** was stirred for 48 h with 207.0 g of 1% sodium amalgam (9.0 mmol sodium) in 100 ml of hexane. The colorless solution was decanted and the residual amalgam was washed with hexane (2 × 20 ml). Solvent was removed from the combined hexane solutions in vacuo to afford 1.98 g (85%) of colorless liquid **3a**. At room temp. the oil slowly solidified to give colorless crystals. In case of impurities the product was distilled at 80 °C (10^{-2} Torr) and the oil was crystallized from hexane at –0 °C to give colorless needles.

Path b: A solution of 2.00 g (12.0 mmol) of 1,4-diazabutadiene **4a** in 80 ml of hexane was stirred with 0.167 g (24.0 mmol) of lithium sand for 120 h at room temp. A solution of 3.00 g (12.0 mmol) of BBr_3 in 30 ml of hexane was dropped to the yellow slurry and stirring was continued overnight. Filtration and removal of solvent from the filtrate in vacuo gave 1.70 g (55%) of **3a**. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2975 s, 2933 sh, 2874 sh, 1669 w, 1629 w, 1465 m, 1398 s, 1368 s, 1329 m, 1316 s, 1281 m, 1234 s, 1224 m, 1135 m, 1028 w, 966 m, 934 w, 822 w, 805 w, 667 m, 617 s. – ^1H NMR (C_6D_6): δ = 1.40 (s, 18H, *t*Bu), 6.27 (s, 2H, =CH). – $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 16.2. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.1 [s, C(*C*H_3)$_3$], 53.6 [s, *C*(CH_3)$_3$], 113.6 (s, =*C*H). – MS (CI): *m/z* = 260 [M^+, ^{81}Br], 258 [M^+, ^{79}Br], 245 [M^+, ^{81}Br – CH_3], 243 [M^+, ^{79}Br – CH_3], 149 [M^+, ^{81}Br-CH_3, –$Me_2C=CH_2$], 147 [M^+, ^{79}Br-CH_3, –$Me_2C=CH_2$]. – $C_{10}H_{20}BBrN_2$ (259.03): calcd. C 46.36, H 7.79, N 10.81, Br 30.84; found C 46.43, H 7.75, N 10.61, Br 28.21.

2,6-Me₂C₆H₃N–CH=CH–N(2,6-Me₂C₆H₃)BBr (**3b**): Lithium sand (0.15 g, 22.0 mmol) was added to a slurry of 3.00 g (11.0 mmol) of 1,4-diazabutadiene **4b** in 150 ml of hexane, and the yellow slurry was stirred for 96 h at room temp. Then a solution of 2.80 g (11.0 mmol) of BBr_3 in 30 ml of hexane was added during 3 h. Stirring was continued for another hour. After filtration the solvent was removed at 10^{-3} Torr to afford analytically pure **3b** as a brown viscous oil (yield 2.10 g, 54%). – ^1H NMR (C_6D_6): δ = 2.17 (s, 12H, CH_3), 5.90 (s, 2H, =CHN), 6.99 (s, 6H, H-aryl). – $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 19.2. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 18.2 (s, CH_3), 118.6 (s, =*C*HN), 127.3 (*p*C-aryl), 135.7 (*o*C-aryl), 140.1 (*i*C-aryl). – MS (EI, 70 eV): *m/z* = 356 [M^+, ^{81}Br, ^{11}B], 355 [M^+, ^{81}Br, ^{10}B], 354 [M^+, ^{79}Br, ^{11}B], 353 [M^+, ^{79}Br, ^{10}B], 275 [M^+, ^{11}B-Br], 274 [M^+, ^{10}B-Br]. – $C_{18}H_{20}BBrN_2$ (355.11): calcd. C 60.87, H 5.68, N 7.89; found C 60.42, H 5.62, 7.68.

tBuCH₂N–C(Me)=C(Me)–N(CH₂tBu)BBr (**3c**): Lithium sand (0.22 g, 32.0 mmol) was added to a solution of 3.50 g (15.0 mmol) of 1,4-diazabutadiene (**4c**) in 100 ml of hexane. After stirring the mixture for 96 h at room temp. the resulting green slurry was chilled to –10°C, whereupon a solution of 3.75 g (15.0 mmol) of BBr_3 in 50 ml of hexane was added dropwise (10 min). After another hour of stirring at 0°C the red brown slurry was filtered and the solvent removed in vacuo to afford **3c** as a dark red viscous oil (yield 3.00 g, 64%). The pure compound could not be stored at room temp. for longer than 1 h without decomposition. Solutions of **3c** in *n*-alkanes decomposed completely within 3 h at 20°C. – ^1H NMR (C_6D_6): δ = 0.91 (s, 18H, *t*Bu), 1.76 (s, 6H, CH_3), 3.27 (s, 4H, CH_2). – $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 21.0. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 11.2 (s, =C–*C*H_3), 28.6 [s, C(*C*H_3)$_3$], 34.3 (s, N*C*H_2), 54.1 [*C*(CH_3)$_3$], 120.1 (s, C=C). – MS (EI, 70 eV): *m/z* = 316 [M^+, ^{11}B, ^{81}Br], 315 [M^+, ^{10}B, ^{81}Br], 314 [M^+, ^{11}B, ^{79}Br], 313 [M^+, ^{10}B, ^{79}Br], 259 [M^+ – *t*Bu]. – $C_{14}H_{28}BBrN_2$ (315.15): calcd. C 53.35, H 8.97, N 8.89; found C 53.43, H 8.55, N 8.94.

tBu–N–CH=CH–N(tBu)B–C–N(Me)–C(Me)–C(Me)–N(Me)]⁺Br⁻ (**7a**): A solution of 0.54 g (4.40 mmol) of 1,3,4,5-tetramethylimidazol-2-ylidene (**6a**) in 20 ml of benzene was added dropwise to a well stirred solution of 1.13 g (4.4 mmol) of **3a** in 20 ml of benzene at 20°C. Stirring was continued for 24 h and the colorless precipitate was filtered. The filter cake was washed (*n*-pentane, 5 × 20 ml) and dried to afford 1.00 g of crude **7a** which was crystallized twice from chloroform. The crystals contained inclusions of solvent and turned powderous upon drying at 10^{-3} Torr at 20°C (yield 0.90 g (52%). – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2978 s, 2939 sh, 1642 w, 1576 w, 1505 m, 1476 m, 1456 m, 1411 m, 1394 s, 1370 m, 1365 m, 1342 w, 1237 s, 1196 w, 1130 m, 943 w, 865 w, 820 w, 719 w, 702 m, 677 w, 666 m, 567 w. – ^1H NMR ($CDCl_3$): δ = 1.18 (s, 18H, *t*Bu), 2.35 (s, 6H, =C–CH_3), 3.66 (s, 6H, NCH_3), 6.63 (s, 2H, =CH). – $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 15.3. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 9.92 (s, =C–*C*H_3), 31.48 [s, C(*C*H_3)$_3$], 35.33 (s, NCH_3), 53.89 [s, *C*(CH_3)$_3$], 116.63 (s, =CH), 129.07 (s, =*C*–CH_3). – MS (LSI-MS, *p*-nitrobenzyl alcohol matrix): *m/z* = 303 [M – Br^-]. – $C_{17}H_{32}BBrN_4$ (383.17): calcd. C 53.28, H 8.41, N 14.62; found C 53.35, H 7.97, N 14.35.

[tBu–N–CH=CH–N(tBu)B–C–N(iPr)–C(Me)–C(Me)–N(iPr)]⁺Br⁻ (**7b**): Analogously 2.20 g of crude **7b** were obtained from 1.52 g (6.0 mmol) of **3a** and 1.08 g (6.0 mmol) of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**6b**) in 150 ml of benzene. The crude product was crystallized from THF at –30°C to afford 1.94 g (73.6%) of pure colorless **7b**. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 3081 w, 2977 s, 2962 s, 2939 s, 2879 w, 1629 w, 1563 w, 1483 sh, 1464 m, 1403 s, 1371 s, 1326 w, 1298 m, 1246 s, 1221 m, 1195 m, 1138 m, 1112 m, 939 w, 905 w, 823 w, 760 w, 735 w, 717 m, 682 w, 630 m. – ^1H NMR ($CDCl_3$): δ = 1.17 (s, 18H, *t*Bu), 1.57 [d, $^3J_{HH}$ = 6.9 Hz, 12H, (C*H*$_3$)$_2$CH], 2.44 (s, 6H, =C–CH_3), 4.41 [sept, $^3J_{HH}$ = 6.9 Hz, 2H, (CH_3)$_2$C*H*], 6.55 (s, 2H, =CH). – $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 15.0. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 10.96 (s, =C–*C*H_3), 21.48 [s, CH(*C*H_3)$_2$], 31.39 [s, C(*C*H_3)$_3$], 51.00 [s, *C*H(CH_3)$_2$], 53.71 [s, *C*(CH_3)$_3$], 117.33 (s, =CH), 129.49 (s, CH_3*C*=). – MS (EI, 70 eV): *m/z* = 359 [M – Br^-], 316 [M – Br^-, –$CHMe_2$], 301 [M – Br^-, –$CHMe_2$, –CH_3]. – $C_{21}H_{40}BBrN_4$ (439.27): calcd. C 57.41, H 9.17, N 12.76; found C 55.91, H 8.92, N 12.37.

X-Ray Structural Analysis of **2**: Single crystal from dimethoxyethane; 0.8 × 0.3 × 0.3 mm; T = 293 K, Siemens $P2_1$ diffractometer; Mo-K_α (graphite monochromator, λ = 0.71073 Å), empirical formula $C_{20}H_{40}B_2N_4O$, orthorhombic space group *Cmca*; unit cell dimensions: a = 13.655(4), b = 27.882(5), c = 12.090(3) Å; $\alpha = \beta = \gamma = 90°$; d_{calcd} = 1.080 g cm^{-3}, V = 4603(2) $Å^3$, Z = 8; μ(Mo-K_α) = 0.066 mm^{-1}; range for data collection: $4.5 \leqslant 2\Theta \leqslant 55°$; ω scan; index ranges: $0 \leqslant h \leqslant 17$, $0 \leqslant k \leqslant 36$, $0 \leqslant l \leqslant 15$; reflections collected 2772; independent reflections 2772; parameters 139; no absorptions correction. Program used: Siemens SHELXLTL-Plus and SHELXL-93. Structure solution: direct methods; structure refinement: Full matrix least-squares on F^2, $R1$ = 0.069, $wR2$ = 0.144 based on 1381 reflections with $I < 2\sigma(I)$, with $w = 1/[\sigma^2(F_o^2) + (0.0717P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

X-Ray Structural Analysis of **7a**: Single crystal from chloroform; 0.41 × 0.29 × 0.23 mm; T = 150 K, Siemens P4 four circle diffractometer; Mo-K_α (graphite monochromator, λ = 0.71069 Å), empirical formula $C_{19}H_{32}BBrN_4$ × 4 $CHCl_3$, monoclinic space group C2/c; unit cell dimensions: a = 11.188(2), b = 18.898(4), c = 18.260(4) Å; β = 97.12(3)°; d_{calcd} = 1.492 g cm^{-3}, V = 3830.7(13) $Å^3$, Z = 4; μ(Mo-K_α) = 1.930 mm^{-1}; range for data collection: $4.3 \leqslant 2\Theta \leqslant 45.2°$; ω scan; index ranges: $-12 \leqslant h \leqslant 10$, $-18 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 19$; reflections collected 4414; independent reflections 2408; parameters 178; absorptions correction: empirical, ψ-scans, min/max transmission 0.537/1.000 (R_{merg} before/after 0.0987/0.0327). Program used: Siemens SHELXTL-Plus Ver. 5.03. Structure solution: direct methods; structure refinement: Full matrix least-squares on F^2, $R1$ = 0.054, $wR2$ = 0.138 based on 1997 reflections with $I < 2\sigma(I)$, with $w = 1/[\sigma^2(F_o^2) + (0.0824P)^2 + 11.41P]$, where $P = (F_o^2 + 2F_c^2)/3$.

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* Dedicated to Professor *Adolf Zschunke* on the occasion of his 60th birthday.

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