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1,2-Dihydro[1,3,2]diazaborolo[1,5-*a*]pyridines: a novel class of heterocycles

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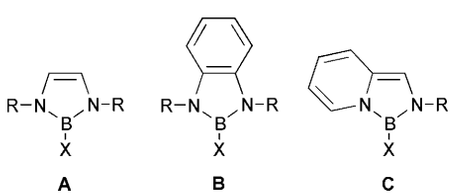
Reaction of a pyridine carbaldimine 2-^{t}BuN=CHC$_5$H$_4$N **1a** with a molar equivalent of boron tribromide afforded a bicyclic 1,3,2-diazaborolium bromide **2a** as an orange solid, whereas **1a** and the corresponding 2-(2,6-Me$_2$C$_6$H$_3$)N=CHC$_5$H$_4$N **1b** with two equivalents of boron trifluoride gave non-ionic yellow adducts **3a** and **3b**. The reduction of compounds **2a**, **3a** and **3b** with an excess of sodium amalgam in a hexane slurry led to the formation of 1-X-2-R-1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridines **4** (X = Br; R = ^{t}Bu), **5a** (F; ^{t}Bu) and **5b** (F; 2,6-Me$_2$C$_6$H$_3$) as yellow oils (**4a**, **5a**) or a yellow wax (**5b**), respectively. Treatment of **4** with an excess of chlorotrimethylsilane caused a Br/Cl exchange to afford chloro derivative **6**. The addition of a methyl group to the boron atom was effected by reaction of heterocycle **4** with methyllithium. The BCN derivative **8** resulted from treatment of **4** with silver cyanide. Reduction of **4** with lithium aluminium hydride gave the 1-hydro-derivative **9**, whereas the BS^{t}Bu compound was obtained from the reaction of **4** with KS^{t}Bu. Compound **8** was subjected to an X-ray diffraction analysis.

Introduction

The recent development of high-yield syntheses of boron-functionalized 2,3-dihydro-1*H*-1,3,2-diazaboroles (**A**)[1] has



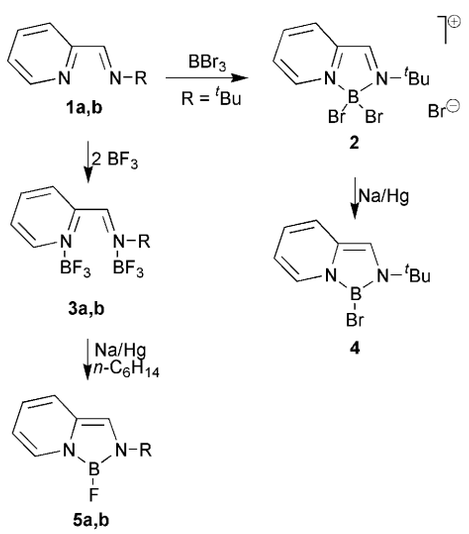
made a new impact upon the chemistry of such heterocycles.[2] Chemical reactions with 2-halogeno-2,3-dihydro-1*H*-1,3,2-diazaboroles either occur with retention of the ring skeleton or with a transformation thereof. Processes of the first type usually involve nucleophilic displacements at boron, where hydrogen,[3] carbon,[1–3] tin,[3] nitrogen,[4] oxygen,[1] sulfur[5] or halogen atoms[5] serve as donor functions. The conversion of 2,3-dihydro-1*H*-1,3,2-diazaboroles into 1,3,2-oxazaborolidines was achieved by treatment with ketenes.[6]

Searching for novel boron–nitrogen systems, our interest has been focused on molecules with fused 1,3,2-diazaborole rings. From a formal point of view molecules **A** are derived from pyrrole by replacement of a C=C double bond by the isoelectronic B=N group. Consistently, the bicyclic system **B** is a BN analogue of indole, and compounds such as **C** may be envisaged as BN derivatives of indolizine. In contrast to a series of benzo-1,3,2-diazaboroles **B**,[7] molecules of type **C** are unknown to date.

In this paper we give an account on the synthesis, structure and reactivity of the first 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]-pyridines **C**.

Results and discussion

The protocol which previously has been devised for the synthesis of 2-halogeno-1,3,2-diazaboroles[1] proved to be suitable for the preparation of the 2-bromo derivative **4** and the 2-fluoro derivatives **5a**,**5b** as well (Scheme 1). Thus combination of



Scheme 1

equimolar amounts of the pyridine carbaldimine **1a** and boron tribromide in *n*-hexane at ambient temperature afforded the borolium salt **2** as an orange precipitate in 85% yield. The solid usually was contaminated with small amounts (<10%) of the corresponding tetrabromoborate, which however has no influence on the designed reaction sequence. Reduction of a slurry of **2** in *n*-hexane with an excess of sodium amalgam to compound **4** was achieved in 79% yield. The product was isolated as an air- and moisture-sensitive yellow oil, which is thermally sufficiently stable to be distilled at 10^{-3} mbar by heating with a hot air gun (150–200 °C). In contrast to the formation of borolium salt **2**, the reaction of *n*-hexane solutions of the pyridine carbaldimine **1a** (R = ^{t}Bu) or **1b** (R = 2,6-Me$_2$C$_6$H$_3$)

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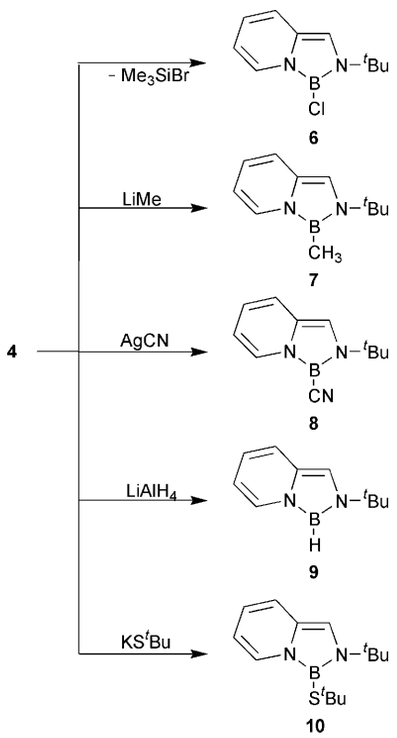
with two molar equivalents of $BF_3{\cdot}OEt_2$ dissolved in diethyl ether led to precipitation of the yellow adduct **3a** or **3b** (78–81% yield). Stirring slurries of the adduct **3a** or **3b** in *n*-hexane with an excess of sodium amalgam during 48 h at room temperature cleanly afforded the heterocycle **5a** as a yellow oil (67% yield) or **5b** as a yellow wax in 63% yield. Both compounds were purified by short path vacuum distillation.

Compound **4** turned out to be an excellent starting material for further chemical transformations (Scheme 2). Treatment



Scheme 2

of it with a slight excess of chlorotrimethylsilane at 20 °C in *n*-hexane solution led to a clean Br/Cl exchange. Chloro derivative **6** was isolated by vacuum distillation as a yellow oil in 95% yield. Generally this synthetic approach to 2-chloro-1,3,2-diazaboroles RNCH=CHN(R)BCl (R = ′Bu or 2,6-$Me_2C_6H_3$) is more convenient than the previously described route *via* 2-dichloroborolium chlorides, because it circumvents the use of free boron trichloride and guarantees a clean work-up (the only by-product is volatile Me_3SiBr!) with high yields. Methyllithium and **4** underwent reaction in an *n*-hexane–diethyl ether solution in the temperature range between 0 and 20 °C to generate the methylated heterocycle **7** as a yellow oil (58% yield). Cyano derivative **8** resulted from the metathesis reaction between **4** and silver cyanide in acetonitrile at ambient temperature in the absence of daylight. It was isolated by vacuum distillation as light yellow crystals in 73% yield. The synthesis of the light yellow oily borohydride **9** was achieved in 79% yield by combination of equimolar amounts of **4** and lithium aluminium hydride in a tetrahydrofuran–*n*-hexane mixture. The ligation of a sulfur-containing substituent onto the boron atom of the bicyclic skeleton was accomplished by reaction of **4** with solid KS′Bu in *n*-hexane. Compound **10** was isolated as a light yellow oil after distillation (10^{-3} mbar, 300 °C, hot air gun).

Inspection of the ^{11}B-{^1H} NMR spectra of the novel 1,2-dihydro[1,3,2]diazaborolo[1,5-*a*]pyridines **4**, **5a**, **6**–**9** showed an increased shielding as follows: **7** (δ 23.9) > **10** (19.9) > **5a** (18.0) ≈ **6** (17.9) ≈ **9** (17.9) > **4** (14.7) > **8** (8.9). A similar trend was observed for the monocyclic 1,2-dihydro-1,3,2-diazaboroles ′BuNCH=CHN(′Bu)BX: X = CH_3 (δ 26.2) > S′Bu (21.9) > F (20.3) ≈ Cl (20.2) > H (18.9) > Br (16.2) > CN (12.0). It is obvious, however, that the increased delocalization

Table 1 Selected bond lengths (Å) and angles (°) for compound **8**

N(1)–C(9)	1.386(2)	N(1)–C(5)	1.416(2)
N(1)–B(2)	1.429(2)	B(2)–N(3)	1.420(2)
B(2)–C(10)	1.538(3)	N(3)–C(4)	1.395(2)
N(3)–C(12)	1.4934(19)	C(4)–C(5)	1.362(2)
C(5)–C(6)	1.424(2)	C(6)–C(7)	1.353(2)
C(7)–C(8)	1.425(3)	C(8)–C(9)	1.339(2)
C(10)–C(11)	1.148(2)		
C(9)–N(1)–C(5)	120.26(14)	C(9)–N(1)–B(2)	132.16(15)
C(5)–N(1)–B(2)	107.58(13)	N(3)–B(2)–N(1)	106.53(15)
N(3)–B(2)–C(10)	128.95(15)	N(1)–B(2)–C(10)	124.51(15)
C(4)–N(3)–B(2)	107.63(14)	C(4)–N(3)–C(12)	124.34(14)
B(2)–N(3)–C(12)	128.03(14)	C(5)–C(4)–N(3)	110.14(14)
C(4)–C(5)–N(1)	108.11(13)	C(4)–C(5)–C(6)	133.62(15)
N(1)–C(5)–C(6)	118.27(14)	C(7)–C(6)–C(5)	119.82(16)
C(6)–C(7)–C(8)	120.58(16)	C(9)–C(8)–C(7)	120.30(16)
C(8)–C(9)–C(1)	120.77(16)	N(11)–C(10)–B(2)	178.86(17)

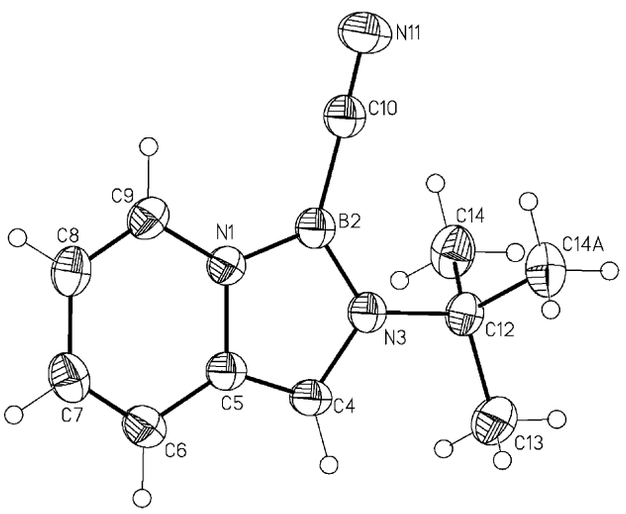


Fig. 1 Crystal structure of compound **8**.

of π electron density in the bicyclic systems is accompanied by a high-field shift of the ^{11}B NMR signals $\Delta\delta$ = 1.0–3.1 ppm, when compared with the corresponding monocyclic systems. In the monocyclic systems the ^1H NMR resonances for the ring protons of the HC=CH unit were observed in the narrow range of δ 5.99 (X = F) to 6.43 (X = S′Bu). In the BN-perturbed indolizines the remaining CH protons of the five-membered ring give rise to absorptions at nearly the same positions.

In the ^{13}C-{^1H} NMR spectra the ^{13}C nuclei of the CH=CH unit in ′BuNCH=CHN(′Bu)BX give rise to a singlet at δ 109.9 (X = F)–114.8 (X = S′Bu). In the fused systems generally a high-field shift of this resonance is obvious ranging from δ 99.74 for **5a** (X = F) to 106.1 for **8** (X = CN) and **10** (X = S′Bu). The adjacent quaternary carbon atom of the C=CH unit was observed in the range from δ 125.3 for **5a** to 128.0 for **8**.

In the ^1H NMR spectrum of compound **9** a quartet at δ 4.75 ($^1J_{BH}$ = 154 Hz) is attributed to the hydrogen atom ligated to the boron atom. Consistently the non-^1H-decoupled ^{11}B NMR spectrum displays a doublet with $J_{B,H}$ = 155 Hz. In ′BuNCH=CHN(′Bu)BH the BH unit gives rise to a quartet at δ 4.78 (J_{BH} = 150 Hz) in ^1H NMR spectrum.

X-Ray structural analysis of compound 8

For a full characterization of the novel ring systems an X-ray structural analysis of compound **8** was performed. Single crystals (light yellow blocks) were grown from *n*-hexane at −20 °C. Selected bonding parameters are compiled in Table 1. The structure (Fig. 1) features a planar molecule which may be considered as a 2,3-dihydro-1*H*-1,3,2-diazaborole connected to a 1,3-butadiene unit *via* the two adjacent carbon and nitrogen

atoms. Alternatively, the compound may be derived from an indolizine in which the CC double bond of the five membered ring adjacent to the nitrogen atom is replaced by the isoelectronic and isosteric BN unit. In contrast to a series of symmetrically substituted 2,3-dihydro-1*H*-1,3,2-diazaboroles the bonding parameters within the borole part of **8** differ significantly. The B–N distances [1.420(2), 1.429(2) Å] indicate multiple bond character. In diazaboroles the B–N bond lengths range from 1.395(4) to 1.450(2) Å.[1–4] The bond length C(4)–C(5) in **8** [1.362(2) Å] compares well with the corresponding CC multiple bond in (2,6-$Me_2C_6H_3$)NCH=CHN(2,6-$Me_2C_6H_3$)BI [1.362(8) Å],[1b] and thus appears at the upper end of the range 1.315(11)–1.362(8) Å encountered for such bonds in diazaboroles. The endocyclic bonds N(3)–C(4) [1.395(2) Å] and N(1)–C(5) [1.416(2) Å] differ significantly in length. In ^{t}BuNCH=CHN(^{t}Bu)BCN→Cr(CO)$_5$ the CN separations are 1.373(6) and 1.389(7) Å and were regarded as having multiple bond character.[3] The calculated value for a C_{sp^2}–N_{sp^2} single bond is 1.45 Å.[8] In **8** this is only valid for N(3)–C(4). The CN bond which is common to both rings is elongated and compares with one of the exocyclic single bonds N_{sp^2}–C_{sp^2} measured in 2,6-$Me_2C_6H_3$NCH=CHN(2,6-$Me_2C_6H_3$)BH [1.421(3) Å].[3] The carbon–carbon distances in the six-membered ring of **8** alternate. Double bonds are C(8)–C(9) [1.339(2) Å] and C(6)–C(7) [1.353(2) Å], whereas the longer bonds C(5)–C(6) [1.424(2) Å] and C(7)–C(8) [1.425(3) Å] may be considered as single bonds. The boron atom is linked to a cyano group *via* a B–C_{sp} single bond of 1.538(3) Å. The C(10)–N(11) bond length of 1.148(2) Å resembles that in cyanogen (1.15 Å).[9] The endocyclic angles N(1)–B(2)–N(3) [106.53(15)], B(2)–N(3)–C(4) [107.63(14)], N(3)–C(4)–C(5) [110.14(14)], C(4)–C(5)–N(1) [108.11(13)], and B(2)–N(1)–C(5) [107.58(13)°] correspond to those in (2,6-$Me_2C_6H_3$)NCH=CHN(2,6-$Me_2C_6H_3$)BH.[3] Owing to the unsymmetrical substitution pattern, the exocyclic bonds at boron atom B(2) [124.51(15); 128.95(15)°] and at the nitrogen atoms N(1) [132.16(15)°] and N(3) [124.34(14); 128.03(14)°] are significantly different.

Experimental

General procedures

All manipulations were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques. All solvents were dried by common methods and freshly distilled prior to use. The compounds 2-^{t}BuN=CHC$_5$H$_4$N **1a**[10] and 2-(2,6-$Me_2C_6H_3$)N=CHC$_5$H$_4$N **1b**[11] were prepared according to literature methods. Boron tribromide, boron trifluoride–diethyl ether, chlorotrimethylsilane, methyllithium, silver cyanide, lithium aluminium hydride and ^{t}BuSH were purchased commercially. NMR spectra were recorded on a Bruker AM Avance DRX 500 spectrometer (^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si) using $SiMe_4$, BF_3·OEt_2 and $CFCl_3$ as external standards. The IR spectra were recorded on Bruker FT-IR Vector 22 instruments. Mass spectra: VG Autospec sector field mass spectrometer (Micromass).

Preparations

[^{t}BuN=CHCCH=CHCH=CHNBBr_2]Br 2a. A three-necked flask, equipped with two dropping funnels and a stirrer, was filled with 400 ml of *n*-hexane. Simultaneously, solutions of the pyridine carbaldimine **1a** (4.99 g, 30.7 mmol) in 100 ml of *n*-hexane and boron tribromide (7.70 g, 30.7 mmol) in 100 ml of *n*-hexane were added dropwise at 20 °C. After the addition stirring was continued for 2 h. The orange precipitate was filtered off and washed with *n*-hexane (3 × 50 ml). The filter cake was dried at 10^{-3} mbar to afford salt **2a** as an orange powder, yield 10.78 g (85%) (Found: C, 27.46; H, 3.32; N, 6.02. $C_{10}H_{14}BBr_3N_2$ requires C, 29.10; H, 3.42; N, 6.79%). The salt also contains about 10% of BBr_4^- as an anion. ^{1}H NMR ($CDCl_3$): δ 1.93 (s, 9H, ^{t}Bu), 8.21 (t, $^3J_{H,H}$ = 6.9, 1H, CH), 8.77 (t, $^3J_{H,H}$ = 7.5, 1H, CH), 8.95 (s, 1H, ^{t}BuNCH), 9.37 (d, $^3J_{H,H}$ = 8.2, CH) and 11.36 (d, $^3J_{H,H}$ = 8.2 Hz, NCH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 30.66 [s, C(CH_3)$_3$], 67.17 [s, C(CH$_3$)$_3$], 130.46 (s, CH), 130.52 (s, CH), 143.02 (s, ^{t}BuNCH), 143.56 (s, CH), 146.97 (s, CH) and 161.83 (s, CHN). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ −2.2 (s).

$C_5H_4N(BF_3)$[CH=N(^{t}Bu)BF_3]-2 3a. A solution of Et_2O·BF_3 (8.11 g, 57.2 mmol) in 40 ml of diethyl ether was added dropwise at 20 °C to a stirred solution of 6.01 g (28.6 mmol) of compound **1a** in 100 ml of *n*-hexane. After the addition was complete stirring was continued for 1 h. The precipitate was filtered off and washed with *n*-hexane (3 × 20 ml). Drying of the filter-cake at 10^{-3} mbar afforded adduct **3a**, yield 8.04 g (81%) as a yellow solid (Found: C, 41.41; H, 4.53; N, 9.32. $C_5H_7BF_3N$ requires C, 40.33; H, 4.74; N, 9.41%). ^{1}H NMR ($CDCl_3$): δ 1.69 (s, 9H, ^{t}Bu), 8.21 (m, 1H, CH), 8.69–8.73 (m, 2H, CH), 8.91 (d, $^3J_{H,H}$ = 8.2 Hz, N=CH) and 9.66 (s, 1H, ^{t}BuN=CH). ^{13}C-{^{1}H} NMR [$(CD_3)_2SO$]: δ 27.9 [s, C(CH_3)$_3$], 61.9 [s, C(CH$_3$)$_3$], 127.5 (s, CH), 131.2 (s, CH), 144.0 (s, CH), 148.2 (s, CH), 150.3 (s, CH=C) and 165.1 (s, HC=N^{t}Bu). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ −1.35 (s). ^{19}F-{^{1}H} NMR [$(CD_3)_2SO$]: δ −148.6.

$C_5H_4N(BF_3)$[CH=N(2,6-$Me_2C_6H_3$)(BF_3)]-2 3b. Analogously 6.54 g (31.1 mmol) of compound **1b** and 8.81 g (62.2 mmol) of BF_3·OEt_2 were combined to yield 8.4 g (78%) of adduct **3b** as a light yellow powder (Found: C, 48.57; H, 4.18; N, 8.09. $C_7H_7BF_3N$ requires C, 48.61; H, 4.08; N, 8.10%). ^{1}H NMR [$(CD_3)_2SO$]: δ 2.08 (s, 6H, *o*-CH_3), 6.96 (t, $^3J_{H,H}$ = 7.5, 1H, *p*-H of aryl), 7.08 (d, $^3J_{H,H}$ = 7.5, 2H, *m*-H of aryl), 7.63–7.65 (m, 1H, CH), 8.08 (dt, $^3J_{H,H}$ = 7.5, $^5J_{H,F}$ = 1.3, 1H, CH), 8.25 (d, $^3J_{H,H}$ = 8.2, CH), 8.34 (s, 1H, aryl N=CH) and 8.75 (d, $^3J_{H,H}$ = 4.4 Hz, CH). ^{13}C-{^{1}H} NMR [$(CD_3)_2SO$]: δ 17.91 (s, *o*-CH_3), 121.92 (s, CH), 124.12 (s, CH aryl), 126.31 (s, CH), 128.07 (s, CH aryl), 129.03 (s, *o*-C aryl), 138.61 (s, *i*-C aryl), 148.82 (s, CH), 149.76 (s, CH), 152.44 (s, NCCHN) and 162.7 (s, CH=N aryl). ^{11}B-{^{1}H} NMR [$(CD_3)_2SO$]: δ −1.1 (s). ^{19}F-{^{1}H} NMR [$(CD_3)_2SO$]: δ −146.58 (s).

^{t}BuNCH=CCH=CHCH=CHNBBr_2 4. A sample of 6.4 g (15.5 mmol) of salt **2** and 180 ml of *n*-hexane were added at 20 °C to an alloy made of 2.0 g (87.0 mmol) of sodium metal and 200 g of mercury. The slurry was vigorously stirred for 48 h. Storing overnight led to clean separation of two liquid phases. The yellow hexane phase was carefully decanted and liberated from solvent and volatile components at *ca.* 10^{-2} mbar (20 °C) to afford spectroscopically pure product **4** as a yellow viscous oil. Purification was achieved by short path distillation (column: 5 × 1 cm) with a hot air gun (10^{-3} mbar, 150–200 °C), yield 3.1 g (79%) (Found: C, 47.30; H, 5.44; N, 11.17. $C_{10}H_{14}BBrN_2$ requires C, 47.48; H, 5.58; N, 11.07%). ^{1}H NMR (C_6D_6): δ 1.34 (s, 9H, ^{t}Bu), 5.61 (t, $^3J_{H,H}$ = 6.1, 1H, CH), 5.99–6.05 (m, 1H, CH), 6.31 (s, 1H, ^{t}BuNCH=), 6.60 (d, $^3J_{H,H}$ = 9.5, 1H, CH) and 7.35 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, CNCH). ^{1}H NMR ($CDCl_3$): δ 1.64 (s, 9H, ^{t}Bu), 5.91 (t, $^3J_{H,H}$ = 6.3, 1H, CH), 6.24–6.28 (m, 1H, CH), 6.65 (s, 1H, ^{t}BuNCH=), 6.82 (d, $^3J_{H,H}$ = 9.4, 1H, CH) and 7.40 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CNCH). ^{13}C-{^{1}H} NMR (C_6D_6): δ 31.31 [s, C(CH_3)$_3$], 54.29 [s, C(CH$_3$)$_3$], 104.85 (s, ^{t}BuNCH), 107.83 (s, CH), 118.52 (s, CH) and 118.63 (s, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 31.41 [s, C(CH_3)$_3$], 54.41 [s, C(CH$_3$)$_3$], 104.47 (s, ^{t}BuNCH), 107.35 (s, CH), 118.10 (s, CH), 126.66 (s, CH) and 127.66 (s, CH). ^{11}B-{^{1}H} NMR (C_6D_6): δ 14.8. ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 14.7. MS/EI (70 eV): m/z = 252 (M^+, 22) and 196 [$M^+ - (CH_3)_2C{=}CH_2$, 100%].

^{t}BuNCH=CCH=CHCH=CHNBF 5a. A 303 g quantity of 1% sodium amalgam (130.5 mmol Na) was combined at room

temperature with 5.1 g (17.1 mmol) of adduct **3a** and 180 ml of *n*-hexane. It was stirred for 48 h and worked up analogously to the preparation of **4**. Solvent was removed at 20 °C and 40 mbar, and the brown viscous residue subjected to distillation (10^{-3} Torr, 150 °C, hot air gun) to give 2.2 g (67% yield) of product **5a** as a yellow oil (Found: C, 62.41; H, 7.44; N, 14.52. $C_{10}H_{14}BFN_2$ requires C, 62.54; H, 7.35; N, 14.59%). ^{1}H NMR ($CDCl_3$): δ 1.43 (d, $^5J_{H,F}$ = 1.2, 9H, ^{t}Bu), 5.63 (t, $^3J_{H,H}$ = 6.3, 1H, CH), 6.01–6.04 (m, 1H, CH), 6.14 (s, 1H, ^{t}BuNC*H*), 6.58 (dd, $^3J_{H,H}$ = 9.4, $^5J_{H,F}$ = 1.3, 1H, CH) and 7.04 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 30.93 [s, C(*C*H$_3$)$_3$], 52.45 [s, *C*(CH$_3$)$_3$], 99.74 (s, ^{t}BuN*C*H), 105.75 (s, CH), 117.76 (s, CH), 118.14 (s, CH), 125.32 (s, ^{t}BuNCH=*C*) and 126.66 (s, CH); ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 18.0 (s). ^{19}F-{^{1}H} NMR ($CDCl_3$): δ −162.86 (s). MS/EI: *m*/*z* = 192 (M^+, 42) and 136 [M^+ − $(CH_3)_2C{=}CH_2$, 100%].

2,6-Me$_2$C$_6$H$_3$NCH=CCH=CHCH=CHNBF 5b. Analogously, 4.4 g (12.7 mmol) of adduct **3b** were reduced with 303 g of 1% sodium amalgam (130.5 mmol Na) to afford 1.92 g (63%) of yellow waxy compound **5b** after short path distillation (10^{-3} mbar, 250 °C, hot air gun) (Found: C, 70.42; H, 6.67; N, 11.34. $C_{14}H_{14}BFN_2$ requires C, 70.04; H, 5.88; N, 11.67%). ^{1}H NMR ($CDCl_3$): δ 2.12 (s, 6H, *o*-CH$_3$), 5.75 (t, $^3J_{H,H}$ = 6.3, 1H, CH), 5.96 (s, 1H, aryl NCH), 6.13–6.16 (m, 1H, CH), 6.67 (d, $^3J_{H,H}$ = 9.4, CH), 7.10–7.12 (m, 3H, CH aryl) and 7.17 (d, $^3J_{H,H}$ = 7.5 Hz, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 18.13 (s, *o*-CH$_3$), 103.09 (s, aryl N*C*H), 106.24 (s, CH), 118.34 (s, CH), 118.50 (s, CH), 124.75 (s, NCH=*C*), 126.79 (s, C aryl), 127.00 (s, C aryl), 128.08 (s, C aryl) and 135.16 (s, *i*-C aryl). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 17.9 (s). ^{19}F-{^{1}H} NMR ($CDCl_3$): δ −168.15 (s). MS/EI: *m*/*z* = 240 (M^+).

^{t}BuNCH=CCH=CHCH=CHNBCl 6. A solution of 1.0 g (9.2 mmol) of chlorotrimethylsilane in 20 ml of *n*-hexane was added dropwise at 20 °C to a solution of compound **4** (1.8 g, 7.1 mmol) in 30 ml of *n*-hexane, and stirring continued for 2 h. All volatile components were removed *in vacuo* (10^{-3} mbar) at 40 °C to afford product **6** as a yellow oil, yield 1.36 g (95%) (Found: C, 57.62; H, 7.03; N, 13.40. $C_{10}H_{14}BClN_2$ requires C, 57.61, H, 6.77; N, 13.44%). ^{1}H NMR (C_6D_6): δ 1.30 (s, 9H, ^{t}Bu), 5.59 (t, $^3J_{H,H}$ = 5.7, 1H, CH), 6.00–6.03 (m, 1H, CH), 6.21 (s, 1H, ^{t}BuNC*H*), 6.59 (d, $^3J_{H,H}$ = 9.4, 1H, CH) and 7.23 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CH). ^{1}H NMR ($CDCl_3$): δ 1.52 (s, 9H, ^{t}Bu), 5.79 (t, $^3J_{H,H}$ = 6.3, 1H, CH), 6.14–6.17 (m, 1H, CH), 6.46 (s, 1H, ^{t}BuNC*H*), 6.71 (d, $^3J_{H,H}$ = 9.4, 1H, CH) and 7.24 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CH). ^{13}C-{^{1}H} NMR (C_6D_6): δ 31.06 [s, C(*C*H$_3$)$_3$], 53.92 [s, *C*(CH$_3$)$_3$], 103.65 (s, ^{t}BuN*C*H), 107.44 (s, CH), 118.45 (s, CH), 118.51 (s, CH), 125.25 (s, ^{t}BuNCH=*C*) and 127.31 (s, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 31.11 [s, C(*C*H$_3$)$_3$], 53.98 [s, *C*(CH$_3$)$_3$], 103.19 (s, ^{t}BuN*C*H), 106.88 (s, CH), 118.03 (s, CH), 118.10 (s, CH), 125.26 (s, ^{t}BuNCH=*C*) and 127.05 (s, CH). ^{11}B-{^{1}H} NMR (C_6D_6): δ 18.0 (s). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 17.9 (s). MS/EI: *m*/*z* = 208 (M^+, 22) and 152 [M^+ − $(CH_3)_2C{=}CH_2$, 100%].

^{t}BuNCH=CCH=CHCH=CHNBCH$_3$ 7. A 1.6 M solution of methyllithium (2.7 ml, 4.3 mmol) in diethyl ether was added dropwise at 0 °C to a solution of compound **4** (1.10 g, 4.3 mmol) in 50 ml of *n*-hexane. After warming to ambient temperature the mixture was stirred for 2 h. Volatile components were removed *in vacuo*. The residue was extracted with 50 ml of *n*-hexane, and LiBr removed by filtration. The filtrate was freed from solvent to afford pure product **7** as a yellow oil, yield 0.47 g (58%) (Found: C, 70.26; H, 9.14; N, 15.03. $C_{11}H_{17}BN_2$ requires C, 70.25; H, 9.11; N, 14.89%). ^{1}H NMR ($CDCl_3$): δ 0.78 (s, 3H, CH$_3$), 1.47 (s, 9H, ^{t}Bu), 5.68 (t, $^3J_{H,H}$ = 6.3, 1H, CH), 6.06–6.09 (m, 1H, CH), 6.45 (s, 1H, ^{t}BuNC*H*), 6.70 (d, $^3J_{H,H}$ = 9.4, 1H, CH) and 7.20 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, CH). ^{13}C-{^{1}H} NMR: δ 31.83 [s, C(*C*H$_3$)$_3$], 53.41 [s, *C*(CH$_3$)$_3$], 103.50 (s, ^{t}BuN*C*H), 105.57 (s, CH), 117.37 (s, CH), 118.21 (s, CH) and 126.05 (s, ^{t}BuNCH=*C*). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 23.9 (s). MS/EI: *m*/*z* = 188 (M^+, 40) and 132 [M^+ − $(CH_3)_2C{=}CH_2$, 100%].

^{t}BuNCH=CCH=CHCH=CHNBCN 8. Silver cyanide (0.32 g, 2.4 mmol) and compound **4** (0.56 g, 2.2 mmol) were mixed in acetonitrile (50 ml) at ambient temperature and in the absence of light. After 30 min of stirring volatiles were removed *in vacuo* to afford a brown oil, which was subjected to short path distillation (10^{-3} mbar, 300 °C, hot air gun), yield 0.32 g (73%) of light yellow crystalline **8** (Found: C, 66.30; H, 7.05; N, 20.91. $C_{11}H_{14}BN_3$ requires C, 66.37; H, 7.09; N, 21.11%). ^{1}H NMR (C_6D_6): δ 1.20 (s, 9H, ^{t}Bu), 5.59 (t, $^3J_{H,H}$ = 6.1, CH), 5.99–6.05 (m, 1H, CH), 6.12 (s, 1H, ^{t}BuNC*H*), 6.58 (d, $^3J_{H,H}$ = 9.5) and 7.37 (d, $^3J_{H,H}$ = 7.0 Hz, CH). ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 9H, ^{t}Bu), 6.05 (t, $^3J_{H,H}$ = 6.9, 1H, CH), 6.35–6.38 (m, 1H, CH), 6.63 (s, 1H, ^{t}BuNC*H*), 6.90 (d, $^3J_{H,H}$ = 9.4, 1H, CH) and 7.60 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 31.85 [s, C(*C*H$_3$)$_3$], 54.67 [s, *C*(CH$_3$)$_3$], 106.10 (s, ^{t}BuN*C*H), 109.14 (s, CH), 118.34 (s, CH), 119.61 (s, CH), 128.02 (s, ^{t}BuNCH=*C*) and 128.39 (s, CH). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 8.9 (s). IR (KBr, cm^{-1}): $\tilde{\nu}$ (C≡N) 2200w. MS/EI: *m*/*z* = 199 (M^+, 20) and 143 [M^+ − $(CH_3)_2C{=}CH_2$, 100%].

^{t}BuNCH=CCH=CHCH=CHNBH 9. A solution of compound **4** (1.77 g, 7.0 mmol) in 60 ml of *n*-hexane was added to a slurry of 0.27 g (7.0 mmol) of $LiAlH_4$ in 10 ml of THF and stirred for 30 min at room temperature. It was filtered and the filtrate evaporated to dryness. The residue was extracted with 50 ml of *n*-hexane. It was filtered and the filtrate liberated from volatile components to afford a yellow oil. Distillation with a short path at 10^{-3} mbar and a hot air gun (100 °C) afforded 0.96 g (79%) of pure **9** as a light yellow oil (Found: C, 68.39; H, 8.74; N, 15.92. $C_{10}H_{15}BN_2$ requires C, 69.01; H, 8.69; N, 16.10%). ^{1}H NMR (C_6D_6): δ 1.27 (s, 9H, ^{t}Bu), 5.60 (t, $^3J_{H,H}$ = 6.3, 1H, CH), 6.07–6.10 (m, 1H, CH), 6.34 (s, 1H, ^{t}BuNCH), 6.73 (d, $^3J_{H,H}$ = 9.4, 1H, CH) and 7.25 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, CH). ^{1}H NMR ($CDCl_3$): δ 1.44 (s, 9H, ^{t}Bu), 4.75 (q, $^1J_{B,H}$ = 154, 1H, BH), 5.73 (t, $^3J_{H,H}$ = 6.9, 1H, CH), 6.13–6.16 (m, 1H, CH), 6.51 (s, 1H, ^{t}BuNCH), 6.76 (d, $^3J_{H,H}$ = 9.4, 1H, CH) and 7.37 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CH). ^{13}C-{^{1}H} NMR (C_6D_6): δ 31.81 [s, C(*C*H$_3$)$_3$], 52.23 [s, *C*(CH$_3$)$_3$], 104.51 (s, ^{t}BuN*C*H), 106.80 (s, CH), 118.35 (s, CH), 118.72 (s, CH), 128.87 (s, ^{t}BuNCH=*C*) and 130.74 (s, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 31.88 [s, C(*C*H$_3$)$_3$], 52.37 [s, *C*(CH$_3$)$_3$], 104.02 (s, ^{t}BuN*C*H), 106.30 (s, CH), 118.07 (s, CH), 118.13 (s, CH), 127.90 (s, ^{t}BuNCH=*C*) and 130.52 (s, CH). ^{11}B NMR (C_6D_6): δ 18.0 (d, $^1J_{B,H}$ = 155). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 17.9 (s). MS/EI: *m*/*z* = 174 (M^+, 32) and 118 [M^+ − $(CH_3)_2C{=}CH_2$, 100%].

^{t}BuNCH=CCH=CHCH=CHNBS^{t}Bu 10. A quantity of K^{t}Bu (0.77 g, 6.0 mmol) was added to a solution of compound **4** (1.48 g, 5.8 mmol) in 80 ml of *n*-hexane and vigorously stirred at room temperature for 24 h. It was filtered and the filtrate freed from volatiles. The yellow oily residue was distilled at 10^{-3} mbar with a hot air gun (300 °C) to afford 0.96 g (63%) of product **10** as a light yellow oil (Found: C, 62.47; H, 8.94; N, 10.85. $C_{14}H_{23}BN_2S$ requires C, 64.13; H, 8.84; N, 10.68%). ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 9H, S^{t}Bu), 1.63 (s, 9H, N^{t}Bu), 5.86 (t, $^3J_{H,H}$ = 6.9, 1H, CH), 6.22–6.25 (m, 1H, CH), 6.67 (s, 1H, ^{t}BuNC*H*), 6.79 (d, $^3J_{H,H}$ = 9.4, 1H, CH) and 7.76 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 32.71 [s, NC(*C*H$_3$)$_3$], 34.93 [s, SC(*C*H$_3$)$_3$], 47.39 [s, S*C*(CH$_3$)$_3$], 55.13 [s, N*C*(CH$_3$)$_3$], 106.07 (s, ^{t}BuN*C*H), 106.83 (s, CH), 118.13 (s, CH), 118.54 (s, CH), 127.41 (s, ^{t}BuNCH=*C*) and 129.60 (s, CH). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 19.9 (s). MS/EI: *m*/*z* 262 (M^+, 32) and 206 [M^+ − $(CH_3)_2C{=}CH_2$, 100%].

Table 2 Crystallographic data for compound **8**

Empirical formula	$C_{11}H_{14}BN_3$
M_r	199.06
T/K	203
Space group	*Pnma*
Crystal system	Orthorhombic
a/Å	13.1155(5)
b/Å	6.8622(3)
c/Å	11.8952(4)
V/Å^3	1070.58(7)
Z	4
μ(Mo-Kα)/mm^{-1}	0.075
Reflections collected	13046
Independent reflections	1441 (R(int) = 0.034)
Reflections with $I > 2\sigma(I)$/parameters	1039/88
Final $R1$, $wR2$ ($I > 2\sigma(I)$)	0.0565, 0.1315
(all data)	0.0750, 0.1429

Crystal structure determination of compound 8

The data were collected with a Siemens SMART100 Detector System on a three axis platform using graphite-monochromatized Mo-Kα radiation. Software for structure solution/refinement: Bruker AXS SHELXTL Version 5.10 DOS/WIN95/NT. Hydrogen atoms treated as riding groups in idealized positions. All other data are summarized in Table 2.

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