Monomeric Aldimino-diorganoboranes and Aspects of Their Chemistry

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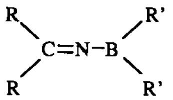
The hydroboration of benzo-, tolu-, *p*-methoxybenzo-, or pivalonitriles with bis(9-borabicyclo[3.3.1]nonane) **(9H-9-BBN)$_2$** affords the corresponding 9-aldimino-9-borabicyclo[3.3.1]-nonanes (**1a – d**) in about 80% yields. Compounds **1a** and **1d** readily react with an excess of **(9H-9-BBN)$_2$** to form the 1:1 adducts **2a** or **2d**, respectively, containing a NB$_2$H four-membered ring (X-ray structure of **2a**). The adducts **2** are thermally rather stable. Compound **2a** is converted to benzylbis(1,5-cyclooctanediylboryl)amine (**3a**) only after 48 h at reflux in mesitylene. Compounds **1a – d** are stable towards strong N-bases. Compound **1d** reacts with Et$_2$O · BF$_3$ to form 9-fluoro-9-borabicyclo[3.3.1]nonane (**4**) and the 1:1 cyclic adduct (**5d**) of (2,2-dimethylpropylideneamino)difluoroborane (**6d**) and **1d**.

The direct hydroboration of nitriles with hydrodiorganoboranes was studied some twenty years ago[1,2]. The aldimino-diorganoboranes **II** formed are, in contrast to the ketimino-diorganoboranes **I** which are often monomeric[3], generally reported to be unstable and to dimerize to compounds of the type **II** with tetracoordinated boron atoms[4]. Presumably this dimeric structure prevents the further hydroboration by an excess of $\rangle$B – H borane reagent. Similar dimers are formed when nitriles are heated with an excess of triethylborane at 200°C[5]. In this reaction the diethylhydroborane generated as an intermediate is thought to be the reactive species. We have in the past frequently observed that the 9-borabicyclo[3.3.1]non-9-yl group (**9-BBN**) displays special steric properties which alter the stabilities of certain labile intermediates and thus the course of the reactions[6]. Therefore, we have reinvestigated the hydroboration of nitriles by using **(9H-9-BBN)$_2$** in the hope of isolating monomeric aldiminoboranes which are stable enough to allow a chemistry other than simple dimerization. In this paper we report on our preliminary results.



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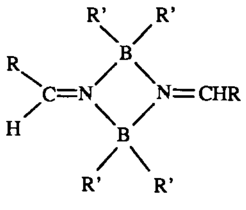

II

Results and Discussion

To avoid the complicating effects of the expected imino-enamino equilibria[7,8] only some derivatives of benzonitrile and pivalonitrile which have no α-hydrogen atoms, have been chosen for this study. The reaction of an excess of these nitriles with **(9H-9-BBN)$_2$** at 60 – 110°C furnishes the corresponding products in high yields, as revealed by their ^{11}B-NMR spectra exhibiting signals at about δ = 37. The colorless monomeric aldiminoboranes **1a – d** are generated from benzo-, tolu-, *p*-methoxybenzo-, and pivalonitrile, respectively. Compounds **1a – d** have proved to be extremely air-sensitive. Even the slow passage of dry and oxygen-free argon gas through a vessel containing them causes partial decomposition, as indicated by rapid yellow coloration[9]. The mass spectra of the products show molecular ions corresponding to the monomeric species. The strong absorption bands at 1800 for the aryl- and 1840 cm^{-1} for the *tert*-butyl-substituted products indicate considerable lone-pair overlap from the nitrogen to the boron atom resulting in a heterocumulene limiting structure. Another indication for the existence of such a structure is obtained from the low-temperature ^{13}C-NMR spectra of **1a**. Beginning at about −30°C the signals for the β and γ carbon atoms of the **9-BBN** carbon skeleton become broad, and at −80°C each resolve into two signals at δ = 33.5 and 32.3 for the β carbon atoms and at 23.7 and 23.3 for the γ carbon atoms. A similar low-temperature resolution is also observed for the β and γ carbon atoms of the **9-BBN** moiety of **1d**. This shows that the **9-BBN** group, in agreement with the structure indicated, no longer rotates freely.

When the reactions are carried out with stoichiometric amounts of the nitriles and **9H-9-BBN** the crude products containing **1a – d** are always contaminated by varying amounts of another product as seen by the formation of a suspension and the presence of a pair of signals in their ^{11}B-NMR spectra at either δ = 2.6 and −6.5 in the case of **1a**, or δ = 2.3 and −9.3 for the product mixture containing **1d**, always in a 1:1 ratio. After the separation of these colorless solids from the product mixture and recrystallization, they show the same ^{11}B-NMR signals and very broad

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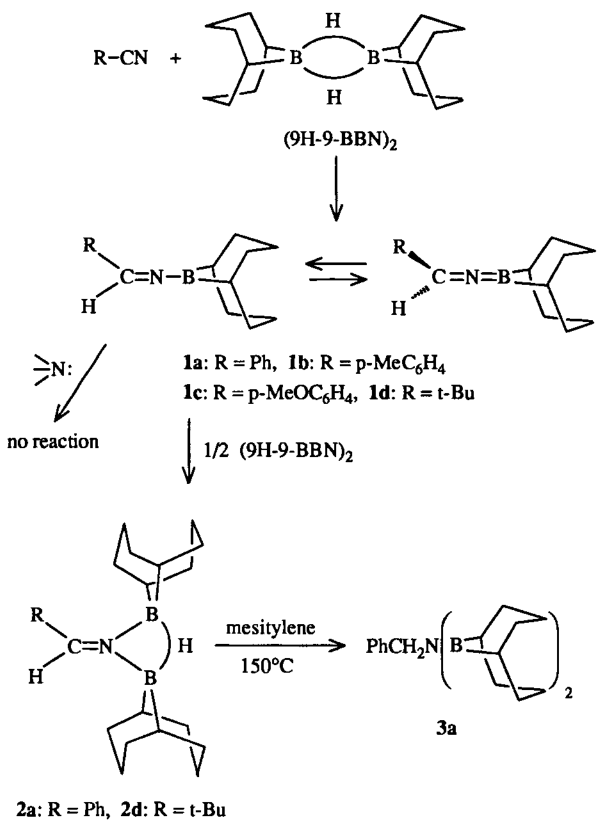


>BHB< absorption bands in their IR spectra centred at about 1900 as well as at 1650 cm^{-1} for the C=N bonds. Their elemental analyses, mass spectra, as well as their ^{1}H- and ^{13}C-NMR spectra are in good agreement with the addition complexes **2a** and **2d**. In these cases there are two sets of signals for the β and γ carbon atoms of each of the two chemically distinct **9-BBN** groups. A confirmation of this assignment has been obtained from the single crystal X-ray diffraction of **2a**. Figure 1 shows the structure of this molecule.

In the four-membered NB2H ring the B–N bonds are with about 1.54 Å unusally short[10]. Also the B1NB2 angle is at 80.8° very small, leading to the short non-bonding B1···B2 distance of 1.99 Å. The four-membered ring is nearly coplanar with respect to the benzene ring (torsion angle B1NCOC17 = 6.6°) allowing a maximum overlap of the π electron system of the molecule. This also results in a significant shortening of the CO–C17 bond, indicating some double bond character. There are also, as shown in Figure 1, a number of very short intramolecular non-bonding H···H distances. Presumably, it is these interactions which lead to the widening of the B1NCO and COC17C22 angles compared to the corresponding angles of B2NCO and COC17C18.

The addition complexes **2a** and **2d** can be prepared in higher yields either by the reaction of the corresponding monomeric aldiminoborane with one equivalent of **9H-9-BBN**, or directly from the reagents in a 1:2 stoichiometry. The adduct **2d** is unstable in solution. As seen in its NMR spectra, it partially dissociates in solution into the components **1b** and **(9H-9-BBN)$_2$**. This is attributed to the severe steric interactions of the *tert*-butyl and the **9-BBN** groups. Surprisingly, these addition complexes are rather stable towards further hydroboration and are only very slowly converted to the corresponding bis(diorganylboryl)amine. For example **2a** is completely converted into **3a** only when refluxed in mesitylene for 48 h.

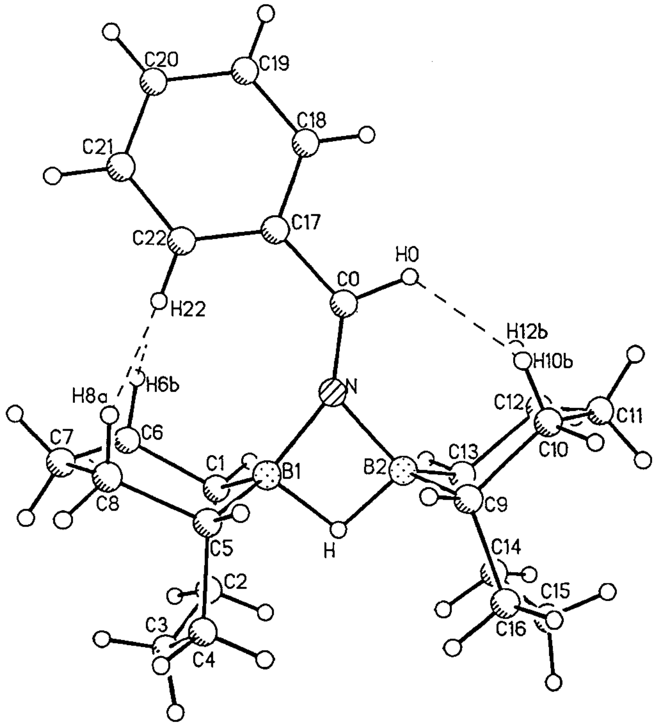
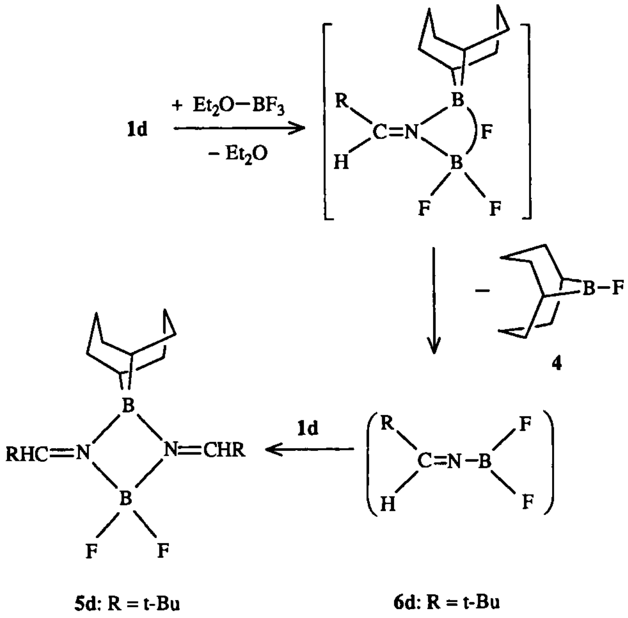


Figure 1. Molecular structure of **2a**. Dotted lines show very short intramolecular non-bonded distances. Bond lengths [Å]: B1H 1.305(16), B2H 1.277(17), B1N 1.540(3), B2N 1.537(3), B1C1 1.588(3), B1C5 1.597(2), B2C9 1.584(3), B2C13 1.601(2), NCO 1.278(3), COH 1.049(18), COC17 1.462(3). – Bond angles [°]: NB2H 89.6(7), NB1H 88.5(8), B1NB2 80.8(1), B1NCO 148.5(2), B2NCO 130.3(1), NCOC17 129.7(2), COC17C18 117.4(1), COC17C22 124.1(2)°

The formation of addition complexes of the type **2** suggests that the monomeric aldiminoboranes are reactive dipolar species and can be expected to form adducts with both Lewis bases and acids. Disappointingly, the addition of either pyridine or quinuclidine does not result in any shift of the ^{11}B-NMR signal. This indicates that without the simultaneous complexation of the adjacent nitrogen atom, the Lewis acidity of the boron atom of **1a** or of **1d** is very low. On the other hand, the addition of stoichiometric amounts of diethyl ether–trifluoroborane to a toluene solution of **1d** at room temperature results in a slow reaction, as seen by the gradual disappearance of the ^{11}B-NMR signal at about $\delta = 36$ and the formation of new peaks at $\delta = 64.1$ d, 1.1 m, and 0.4 br (in a 1:1:1 ratio). Distillation of the volatile components in vacuo separated the two components present. The volatile fraction was identical with 9-fluoro-9-borabicyclo[3.3.1]nonane (**4**)[11]. The solid residue gives after purification the colorless microcrystalline solid **5d** (m.p. 135–136°C) with a molecular ion peak at $m/z = 338$ (B_2) in its mass spectrum corresponding to the molecular formula of $C_{18}H_{34}B_2F_2N_2$. The NMR spectra of **5d** are in agreement with the symmetrical structure indicated. Thus, there are only one set of signals for the β and γ carbon atoms of the **9-BBN** moiety and only one set of signals for the carbon atoms of the arene or *tert*-butyl groups. Concerning **5d**, the configuration of the *tert*-butyl groups relative to the **9-BBN** rings has not been determined. On purely steric grounds, the *anti* configuration should be more stable.

Scheme 1. Proposed reaction pathway for the conversion of **1d** to **4** and **5d**



The initial step in the formation of **5d** is thought to be the borane exchange reaction as shown in Scheme 1. This leads to the formation of **4** and (2,2-dimethylpropylideneamino)difluoroborane (**6d**) as a reactive species which immediately reacts with an excess of the aldiminoborane **1d** to give **5d**.

Experimental

Melting points: Büchi apparatus, sealed capillary tubes. – MS: Varian MAT CH 5. – ^{1}H, ^{11}B, ^{13}C NMR: Bruker AC 200 with Me_4Si as internal and $Et_2O \cdot BF_3$ as external standards. Unless mentioned otherwise $CDCl_3$ was used as solvent at room temperature. – All operations were carried out under dry oxygen-free argon. All solvents were freshly distilled under argon from the appropriate drying agents.

9-(Benzylideneamino)-9-borabicyclo[3.3.1]nonane (**1a**): A solution of 5.94 g (24.3 mmol) of **(9H-9-BBN)$_2$** in 10.0 g (97.1 mmol) of benzonitrile was heated for 10 h. Excess nitrile was removed in vacuo, and the slightly yellow and viscous liquid residue was distilled, b.p. 105–110°C/10^{-3} Torr, 9.5 g (79%) of **1a**, an extremely air-sensitive (even on prolonged exposure to a current of argon it turned yellow) colorless liquid which solidified on cooling with liquid nitrogen. – MS (70 eV), *m/z* (%): 225 (100) [M$^+$], 196 (40), 182 (30), 129 (35), 116 (50). – IR (film): ν(C=N) 1800 cm^{-1}. – ^{1}H NMR: δ = 8.24 (s, 1H), 7.67 (m, 2H), 7.52 (m, 3H), 2.05 (m, 10H), 1.70 (m, 2H), 1.55 (br, 2H). – ^{11}B NMR: δ = 37.5 ($h_{1/2}$ = 200 Hz); (toluene, –40°C): δ = 31.0 ($h_{1/2}$ = 1000 Hz). – ^{13}C NMR: δ = 140.1 d, 136.0 s, 130.4 d, 128.2 d, 127.0 d, 33.0 t, 24.0 br, 23.4 t, (CD_2Cl_2, –80°C): δ = 139.8 (d, 1C), 135.3 (s, 1C), 130.7 (br, d, 1C), 128.7 (br, d, 2C), 127.2 (br, d, 2C), 33.5 (t, 2C), 32.3 (t, 2C), 23.7 (t, 1C), 23.7 (br, d, 2C), 23.3 (t, 1C).

$C_{15}H_{20}BN$ (225.1)	Calcd. C 80.02	H 8.95	B 4.80
	Found C 79.76	H 8.68	B 5.05

9-(4-Methylbenzylideneamino)-9-borabicyclo[3.3.1]nonane (**1b**): A mixture of 7.2 g (61.5 mmol) of tolunitrile and 3.9 g (16.0 mmol) of **(9H-9-BBN)$_2$** was heated at 110°C for 16 h. The excess nitrile was removed in vacuo and the residue subjected to vacuum distillation (b.p. 115–120°C/10^{-3} Torr) to give 6.8 g (85%) of colorless **1b** which crystallized slowly. – MS (70 eV), *m/z* (%): 239 [B$_1$, M$^+$] (80). – ^{1}H NMR: δ = 7.79 (s, 1H), 7.18 (d, 2H), 6.82 (d, 2H), 2.03 (s, 3H), 1.8 (m, 10H), 1.42 (m, 4H). – ^{11}B NMR: δ = 37.5 ($h_{1/2}$ = 1000 Hz). – ^{13}C NMR: 140.9 d, 140.6 d, 134.0 s, 129.6 d, 127.4 d, 33.4 t, 24.8 br, d, 24.1 t, 21.1 q.

9-(4-Methoxybenzylideneamino)-9-borabicyclo[3.3.1]nonane (**1c**): As described above 8.1 g (6.1 mmol) of 4-methoxybenzonitrile and 4.3 g (17.6 mmol) of **(9H-9-BBN)$_2$** were heated at 110°C for 20 h; 7.9 g (81%) of colorless solid **1c**, b.p. 135–140°C/10^{-3} Torr. – MS (70 eV), *m/z* (%): 255 [B$_1$, M$^+$] (100), 226 (25), 212 (30), 159 (45), 146 (90). – ^{1}H NMR: δ = 7.82 (s, 1H), 6.24 (d, 2H), 6.58 (d, 2H), 3.27 (s, 3H), 1.9 (m, 10H), 1.55 (m, 4H). – ^{11}B NMR: δ = 36.8 ($h_{1/2}$ = 600 Hz). – ^{13}C NMR: δ = 162.2 d, 140.2 d, 129.3 s, 129.1 d, 114.4 d, 54.8 q, 34.0 t, 24.8 br, d, 24.2 t.

9-(2,2-Dimethylpropylideneamino)-9-borabicyclo[3.3.1]nonane (**1d**): A solution of 10.8 g (0.13 mol) of pivalonitrile and 15.5 g (64.0 mmol) of **(9H-9-BBN)$_2$** in 150 ml of toluene was initially stirred at 60°C for 2 h. The solution was then refluxed overnight. Upon cooling a suspension formed which was filtered from the colorless solid. From the filtrate the solvent was removed under atmospheric pressure and the viscous residue distilled at 10^{-3} bar to give the colorless liquid **1d**, b.p. 62–64°C (22.4 g, 86%). – MS (70 eV), *m/z* (%): 205 [B$_1$, M$^+$] (30), 148 (30), 121 (100). – IR (film): ν(C=N) 1840 cm^{-1}. – ^{1}H NMR: δ = 7.29 (s, 1H), 1.85 (m, 10H), 1.36 (m, 2H), 1.14 (br, s, 2H), 0.94 (s, 9H). – ^{11}B NMR: δ = 36.7 ($h_{1/1}$ = 50 Hz). – ^{13}C NMR: δ = 151.2 d, 36.5 s, 33.2 t, 25.9 q, 24.0 br, d, 23.2 t, (CD_2Cl_2, –80°C): δ = 151.2 d, 37.0 s, 33.1 t, 32.3 t, 24.0 q, 32.6 t, 22.9 t.

$C_{13}H_{24}BN$ (205.1)	Calcd. C 76.11	H 11.79	B 5.27
	Found C 76.25	H 11.90	B 4.98

9-(Benzylideneamino)-9-borabicyclo[3.3.1]nonane–**9H-9-BBN** *Addition Complex* **2a**: A solution of 4.1 g (16.8 mmol) of **(9H-9-BBN)$_2$** and 1.74 g (16.9 mmol) of benzonitrile in 80 ml of toluene was refluxed for 18 h. Colorless crystals of **2a** were obtained when the reaction mixture was cooled to –80°C, 4.9 g (84.0%), m.p. 149–150°C. – IR (nujol, film): ν(BHB) ca. 1900 v, br; ν(C=N) 1650 cm^{-1}. – MS (70 eV), *m/z* (%): 347 (20) [B$_2$, M$^+$], 237 (40), 236 (40), 225 (50), 196 (60), 125 (60), 116 (100). – ^{1}H NMR: δ = 8.85 (s, 1H), 7.75 (m, 2H), 7.45 (m, 3H), 1.9 (m, 25H), 0.92 (s, 2H), 0.84 (s, 2H). – ^{11}B NMR: δ = 2.6 ($h_{1/2}$ = 100 Hz); –6.5 ($h_{1/2}$ = 50 Hz). – ^{13}C NMR: δ = 159.4 d, 134.2 s, 131.2 d, 128.4 d, 128.1 d, 36.4 t, 34.5 t, 30.4 t, 30.1 t, 24.6 t, 24.4 t, 23.7 t, 23.4 t, 22.0 br, d, 21.0 br, d.

$C_{23}H_{35}B_2N$ (347.2)	Calcd. C 79.58	H 10.16	B 6.22
	Found C 79.81	H 10.30	B 6.01

X-Ray Single Crystal Structure Determination of **2a**: Data collection and calculations were carried out on a Nicolet R 3 m/v four-cycle diffractometer with Microvax II and SHELXTL-PLUS software[12]. The structural solution was performed by direct methods, and all hydrogen atoms except for H and H_0 were included as rigid groups (C–H bond lengths 0.96 Å, C–C–H and H–C–H

Table 1. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement factors ($Å^2 \cdot 10^4$)

	x	y	z	U_{eq}
B(1)	2688(2)	10851(2)	7492(2)	172(8)*
B(2)	1498(2)	8616(2)	7483(2)	168(8)*
N	2314(2)	9535(2)	6586(1)	154(6)*
C(0)	2336(2)	9094(2)	5576(2)	183(8)*
C(1)	1802(2)	11826(2)	7155(2)	188(7)*
C(2)	1543(2)	12278(2)	8299(2)	212(8)*
C(3)	3050(2)	13053(2)	9361(2)	237(8)*
C(4)	4069(2)	12259(2)	9574(1)	210(8)*
C(5)	4390(2)	11853(2)	8448(2)	181(7)*
C(6)	2810(2)	13187(2)	6600(2)	208(8)*
C(7)	4582(2)	14138(2)	7314(2)	241(8)*
C(8)	5416(2)	13278(2)	7958(2)	213(8)*
C(9)	2276(2)	7729(2)	8274(2)	176(7)*
C(10)	1814(2)	6273(2)	7492(2)	220(8)*
C(11)	22(2)	5270(2)	6901(2)	244(8)*
C(12)	-873(2)	6119(2)	6343(2)	233(8)*
C(13)	-399(2)	7613(2)	7090(2)	187(8)*
C(14)	-909(2)	7384(2)	8231(2)	216(8)*
C(15)	-85(2)	6718(2)	9171(2)	237(8)*
C(16)	1715(2)	7449(2)	9392(2)	210(8)*
C(17)	3044(2)	9987(2)	4703(1)	180(8)*
C(18)	2557(2)	9249(2)	3557(2)	254(8)*
C(19)	3124(2)	10026(2)	2674(2)	303(9)*
C(20)	4217(2)	11546(2)	2925(2)	270(9)*
C(21)	4751(2)	12284(2)	4068(2)	246(8)*
C(22)	4176(2)	11516(2)	4954(2)	207(8)*

* Equivalent isotropic *U* defined as one third of the trace of orthogonalized U_{ij} tensor.

angles 109.5 and 120°C, respectively). The isotropic displacement parameters (IDPs) of all H atoms were refined without constraints.

Structure Data for **2a**: Crystal size 0.47 × 0.31 × 0.26 mm, space group $P\bar{1}$, $Z = 2$, $a = 9.963(2)$, $b = 10.077(2)$, $c = 11.730(3)$ Å, $V = 993.5(4)$ Å^3, $\beta = 105.54(2)°$, $d_{calc.} = 1.160$ g/cm, $\mu = 0.06$ (mm^{-1}), radiation Mo-K_α, $2\Theta = 50$ deg, number of unique reflections 3463, observed reflections 2429 [$F_o \geqslant 4\sigma(F)$], $R = 0.0383$, $R_w = 0.0414$ [$w^{-1} = \sigma^2(F_o) + gF_o^2$] with $g = 0.00264$, residual electron density = 0.165 e/Å^3. The atomic coordinates for **2a** are listed in Table 1[13].

9-(2,2-Dimethylpropylideneamino)-9-borabicyclo[3.3.1]nonane—**9H-9-BBN** *Addition Complex* **2d**: A solution of 4.8 g (23.4 mmol) of **1d** and 2.3 g (11.7 mmol) of **(9H-9-BBN)**$_2$ in 15 ml of toluene was stirred and heated at 50°C for 18 h. After cooling to room temp. the very fine colorless crystals of **2d** that separated were collected, 5.4 g (70%), m.p. 94—95°C. — IR (nujol): ν(BHB) 1900 br and ν(C=N) 1625 s cm^{-1}. — ^{11}B NMR: δ = 36.8 ($h_{1/2}$ = 50 Hz), 27.9 ($h_{1/2}$ = 50 Hz), 3.3 ($h_{1/2}$ = 100 Hz), −8.4 ($h_{1/2}$ = 50 Hz) (in ca. 1:1:2:2 ratios). — ^{13}C NMR [signals assigned to **2d** after subtraction of those for **1d** and for **(9H-9-BBN)**$_2$]: δ = 151.6 (d, 1C), 37.7 (t, 2C), 36.9 (s, 1C), 35.5 (t, t, 2C), 30.5 (t, 4C), 27.6 (q, 3C), 25.4 (t, 1C), 25.2 (t, 1C), 23.9 (t, 2C), 21.2 (br, d, 4C).

N,N-Bis(9-borabicyclo[3.3.1]non-9-yl)benzylamine (**3a**): A solution of 1.5 g (4.3 mmol) of **2a** in 10 ml of mesitylene was refluxed for 48 h. The solvent was evaporated in vacuo. The colorless viscous liquid residue, **3a**, could not be purified by vacuum distillation without decomposition. — MS (70 eV), *m/z* (%): 347 [M$^+$, B$_2$] (70), 256 (15), 236 (40), 90 (100). — ^{1}H NMR: δ = 7.33 (m, 2H), 7.21 (m, 3H), 4.73 (s, 2H), 1.79 (m, 24H), 1.36 (m, 4H). — ^{11}B NMR: δ = 62.6 ($h_{1/2}$ = 600 Hz). — ^{13}C NMR: δ = 142.7 s, 127.9 d, 125.9 d, 125.8 d, 50.1 t, 33.4 t, 27.0 br, d, 22.8 t.

2,2-(1,5-Cyclooctandiyl)-1,3-bis(2,2-dimethylpropylidene)-4,4-difluoro-1,3,2,4-diazoniadiboratetine (**5d**): A solution of 4.5 g (22.0 mmol) of **1d** and 6.3 g (44.4 mmol) of diethyl ether—trifluoroborane in 15 ml of toluene was stirred at room temp. overnight. The toluene was evaporated in vacuo. ^{11}B NMR: δ = 64.1 d, 1.1 m, 0.4 s. To the residue was added pentane, and the solution was allowed to stand at room temp. overnight. Colorless crystals of **5d** separated, m.p. 135—136°C, 4.2 g (67%). — IR (nujol): ν(C=N) 1630 cm^{-1}. — MS (70 eV), *m/z* (%): 338 [M$^+$, B$_2$] (14), 281 (65), 148 (50), 121 (100). — ^{1}H NMR: δ = 7.9 (m, 2H), 1.70 (m, 12H), 1.15 (s, 18H), 0.78 (br. s, 2H). — ^{11}B NMR: δ = 3.1 ($h_{1/2}$ = 100 Hz), 2.4 (m). — ^{13}C NMR: δ = 177.6 d, 38.1 s, 29.6 t, 26.5 q, 23.0 t, 22.8 br, d.

$C_{18}H_{34}B_2F_2N_2$ (338.1) Calcd. C 63.95 H 10.14 B 6.39
Found C 64.19 H 9.98 B 6.63

The residue remaining after evaporating the solvent from the filtrate above, showed identical ^{1}H-, ^{11}B- and ^{13}C NMR spectra as authentic **4**[11].

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[9] A very recent publication describes the preparation of aldiminoboranes by the reaction of hydrodiorganoborane reagents (S. Itsuno, C. Hachisuka, K. Kitano, K. Ito, *Tetrahedron Lett.* **1992**, *33*, 627—630). The authors claim these compounds to be stable enough to withstand TLC analysis as single spots. Furthermore, they did not observe any absorptions due to the C=N group in the IR spectra.

[10] The 1:1 adduct of **9-amino-9-BBN** with **9H-9-BBN** forms a similar NB$_2$H four-membered ring. This adduct is thermally unstable and decomposes above its melting point by releasing H$_2$ and forming crystalline **(9-BBN)**$_2$**NH** (R. Köster, G. Seidel, *Liebigs Ann. Chem.* **1977**, 1837—1846).

[11] R. Köster, W. Schüßler, R. Boese, *Chem. Ber.* **1990**, *123*, 1945—1952.

[12] G. M. Sheldrick, *SHELXTL-PLUS* (Version 2, 1987), an *Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, University of Göttingen.

[13] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-320496, the names of the authors, and the journal citation.

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1a: 143122-91-2 / **1b**: 143122-92-3 / **1c**: 143122-93-4 / **1d**: 143122-94-5 / **2a**: 143122-97-8 / **2d**: 143122-98-9 / **3a**: 143122-95-6 / **5d**: 143122-99-0 / **6d**: 143122-96-7 / **(9H-9-BBN)**$_2$: 21205-91-4 / *p*-MeC$_6$H$_4$CN: 104-85-8 / PhCN: 100-47-0 / *p*-MeOC$_6$H$_4$CN: 874-90-8 / *t*BuCN: 630-18-2