Substituted C_3BN_2 Heterocycles from Trialkylboranes and Nitriles

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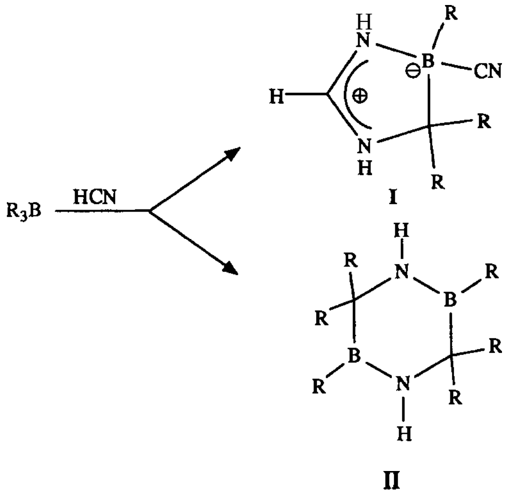
Received July 4, 1991

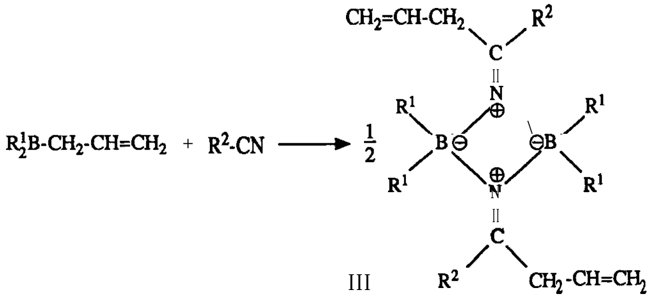
Key Words: Boranes, trialkyl- / Nitriles / Condensation / β-Diketimines

The reaction of trialkylboranes, e.g. triethylborane (Et_3B), tripropylborane (Pr_3B), or 9-alkyl-9-borabicyclo[3.3.1]nonane [alkyl-BBN; alkyl = Et, l-methylpropyl, 1-methybutyl/1-ethylpropyl], with either aceto-, propio-, butyro-, pivalo-, and benzonitrile gives, depending on the reaction conditions used or the nitrile employed, either the substituted diazoniadiboratetidines (1 **a – c**), products of partial hydroboration, or by condensation of two or three nitrile molecules, with or without a concomitant hydroboration, the C_3BN_2 heterocycles 2 **a – c, 8a/b, 9a – d,** and **10a/b** (X-ray structure analyses of 2a and **10b**).

Trialkylboranes (e.g. Et_3B or Pr_3B) readily react with hydrogen cyanide[1] to give mixtures of I and **II.** Both compounds are formed by alkyl group migrations from the boron to the cyanide carbon atom.



Similar alkyl group migrations have been observed in the reactions of trialkylboranes with isonitriles, resulting in the formation of *N,N′*-diorganyl derivatives of II[2–4]. Apparently, the corresponding reactions with nitriles have only been successful for triallylborane or allyldialkylboranes[5–7].



The allyl migration products in these cases are the diazoniadiboratetidines **III.**

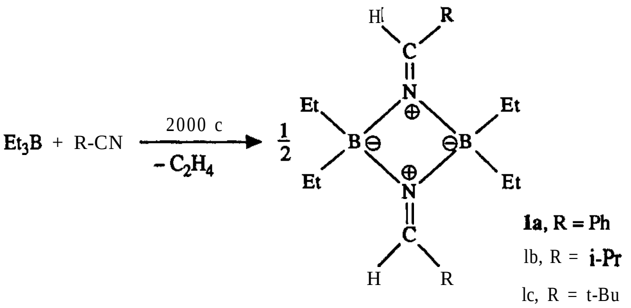
Another case of alkyl migration to a nitrile carbon atom has been observed in the reaction of triisopropylborane with phenyl thiocyanate; again a derivative of **III** is formed[8].

In the reaction of tributylborane with pivalonitrile which gives yet another derivative of **III,** the cyano group has undergone a hydroboration reaction by the intermediately formed dibutylhydroborane[9,10].

On the assumption that the thermal conversion of trialkylboranes to dialkylhydroboranes is unlikely, or at least very slow at the intermediate temperatures of 160 – 200°C[11] with short alkyl groups, it was anticipated that an alkyloboration of a nitrile can be achieved with triethylborane or even with tripropylborane. In this paper we report on some unexpected reactions of trialkylboranes with a number of nitriles.

Results and Discussion

Initially, the ready formation of the diazoniadiboratetidines **la-c** from the reaction of Et_3B with benzo-, 2-propio-, and pivalonitriles at 200°C was disappointing.



la, R = Ph
lb, R = **i-Pr**
lc, R = t-Bu

The relatively good yields of **la** and **b** (70 and 65%, respectively) indicate that already at this temperature through establishement of the equilibrium $Et_3B \rightleftharpoons Et_2BH$ +

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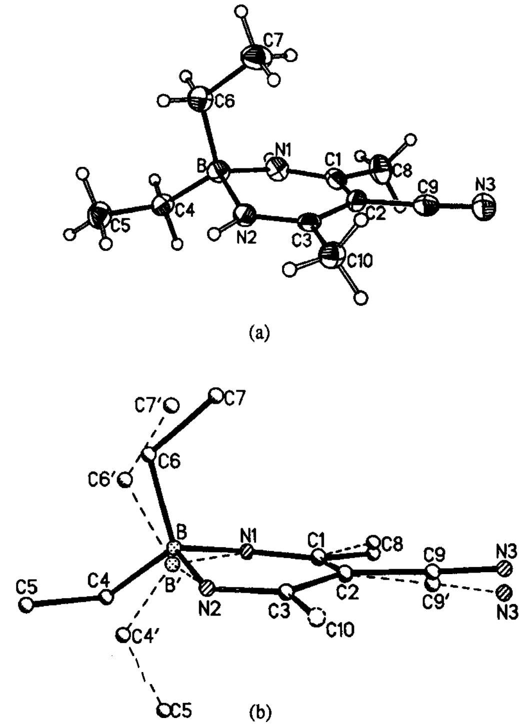
Table 1. NMR data for compounds **2a – c**, **8a**, **b**, and **9b – d**

No	$\delta^{13}C$ (50.4 MHz)				$\delta^{11}B$ (64.2 MHz)	$\delta^{1}H$ (200 MHz)				
	R	C^4 R^4	C^5 R^5	C^6 R^6		R	R^4	R^5	R^6	NH
2a	8.5(q) 16.7(t)	167.2(s) 22.8(q)	74.2(s) 120.3(s)	167.2(s) 22.8(q)	-1.9	0.67(t,6H) 0.12(q,6H)	2.15(s,3H)	—	2.15(s,3H)	6.06(2H)
2b	17.8(q) 18.4(t) 29.0(br,t)	167.3(s) 23.1(q)	74.3(s) 120.0(s)	167.3(s) 23.1(q)	-1.3	0.82(t,6H) 1.04(m,4H) 0.12(t,4H)	2.15(s,3H)	—	2.15(s,3H)	5.88(2H)
2c	29.7(t) 23.2(t) 24.0(br,d)	167.2(s) 23.9(q)	75.6(s) 119.9(s)	167.2(s) 23.9(q)	-2.4	1.3 - 1.9(m,2H) 0.58(br,2H)	2.18(s,3H)	—	2.18(s,3H)	6.42(2H)
8a	30.6(br,t) 18.6(q) 17.7(t)	154.4(d) 23.5(q)	87.9(d)	165.3(s)	-1.7	1.10(m,4H) 0.85(t,6H) 0.1(m,4H)	6.95(dd,1H)	4.25(dt,1H)	1.82(s,3H)	5.0(2H)
8b	30.0(t) 24.3(t) 24.3(br,d)	153.8(d) 23.3	88.9(d)	164.9(s)	-3.7	1.3 - 1.8(m) 0.6(br)	7.10(dd,1H)	4.42(dt,1H)	1.94(s,3H)	5.73(2H)
9b	29.9(t) 24.4(t) 24.3(br,d)	163.6(s) 23.5(q)	88.5(d)	163.6(s)	-3.7	1.3 - 1.8(m) 0.6(br)	1.70(s,3H)	4.33(t,1H)	1.70(s,3H)	5.4(2H)
9c	8.8(q) 18.0(t)	167.2(s) 28.2(t) 13.2(q)	88.8(s) 11.3(q)	167.2(s) 28.2(t) 13.2(q)	-2.5	0.67(t,6H) 0.09(q,4H)	2.21(q,2H) 1.12(t,3H)	1.64(s,3H)	2.21(q,2H) 1.12(t,3H)	4.90(2H)
9d	8.9(q) 18.2(t)	166.0(s) 36.2(t) 25.1(t) 13.1(q)	97.4(s) 19.3(t) 16.3(q)	166.0(s) 36.2(t) 13.1(q)	-2.6	0.69(t,6H) 0.09(q,4H)	2.18(t,2H) 1.58(hex,2H) 0.97(t,3H)	2.06(q,2H) 0.94(t,3H)	2.18(t,2H) 1.58(hex,2H) 0.97(t,3H)	4.85(2H)

$CH_2=CH_2$ a significant steady-state concentration of diethylhydroborane develops and should, independent of the nitrile employed, lead to hydroboration, at least as the main reaction path.

It was therefore surprising when the reaction of Et_3B with an excess *of* acetonitrile at 200°C resulted in the liberation of about one equivalent of ethane/ethene (≈ 1:1) mixture and led mainly to the formation of a yellow, microcrystalline solid, m. p. 80 – 81 “C, with a molecular ion peak at m/z = 191 (**B**$_1$) in its mass spectrum, corresponding to a molecular formula of $C_{10}H_{18}BN_3$. The infrared spectrum of this solid reveals an NH band at ṽ = 3300 cm-’ as well as nitrile and C=N stretching frequencies at 2160 and 1630 cm-‘, respectively. The narrow signal in its “B-NMR spectrum at δ = – 1.9 shows the tetravalency of the boron atom. Both the ^1H- and ^{13}C-NMR spectra (see Table 1) reveal only a single type of B – Et and C – Me groups.

These data are consistent with the heterocyclic structure 2a. The structure of 2a was also confirmed by a single-crystal X-ray analysis. Figure la shows one of the two independent molecules found in the asymmetric unit. As can be seen in Figure 1 b the two molecules of 2a differ from each other by the conformation of the BEt_2 groups and of the six-membered heterocycle (in one molecule the ring is clearly folded about the planes made up by the atoms NlBN2 and N1C1C2C3N2 by 19.5°, while in the second molecule this folding is only 2.7”). The extent of these conformational differences point to the importance of packing effects in crystals and the hazards of overemphasizing the chemical significance of molecular conformations in the solid state.



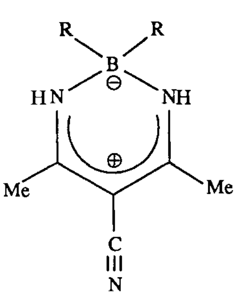
(a)

(b)

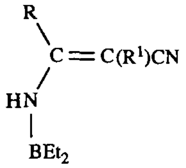
Figure 1 a. Molecular structure of one of the two independent molecules of **2a.** Bond lengths [A]: NIB 1.583(3), N2B 1.582(3), N1C1 1.303(3), N2C3 1.311(3), C1C2 1.419(3), C2C3 1.409(3), C2C9 1.420(3), C9N3 1.159(3), **BC6 1.61** 1(3), **BC4** 1.605(3). – Bond angles [°]: N1BN2 102.4(2), BN1C1 126.9(2), N1C1C2 119.3(2), C1C2C3 121.0(2), C2C3N2 119.5(2), C2C9N3 177.9(2), BC4C5 114.9(2), BC6C7 116.3(2). – Figure 1 b. Superposition of both independent molecules of 2 **a**

The corresponding bond lengths in the two molecules of **2a** are, within the standard deviations, identical and show no abnormalities. Likewise, except for C1N1B and C3N2B, all other bond angles show no noteworthy differences in the two molecules. As in many boron compounds containing ethyl groups[12] the BC4C5 and BC6C7 bond angles in **2a** are at 115.8° (av) significantly widened.

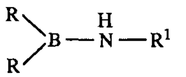
The progress of the above reaction can be monitored by measuring ^{11}B-NMR spectra of aliquots, removed at intervals from the autoclave. It can be seen that the initially formed nitrile – borane addition complex (at the nitrile/borane concentration ratios used in these experiments usually at $\delta^{11}B \approx 42$) rapidly transforms to an intermediate with a chemical shift at $\delta^{11}B = 52.0$ [probably an enaminoborane of the type $R_2BNH{\leftharpoondown}C{=}C{<}$ (**3a**), see below]. The intensity of this peak slowly diminishes, and the peak is replaced by mainly two signals at $\delta^{11}B = 45.0$ and -2.0. The former signal can be assigned to a saturated aminoborane of the type R_2BNHR' (**4**) (see below). The more intense signal at $\delta^{11}B = -2.0$ is due to the final product **2** in the chain of reactions. Finally, when the reaction temperature is raised to 230°C yet another signal at $\delta^{11}B = 35.0$ also develops. The material corresponding to this peak was isolated from the reaction of Pr_3B with acetonitrile and shown to be identical to the known 2,4,6-tripropylborazine[13].



2a, R = Et
2b, R = Pr
2c, $R_2 = 1,5\text{-}C_8H_{14}$



3a, R = Me, R^1 = H
3b, R = Et, R^1 = Me

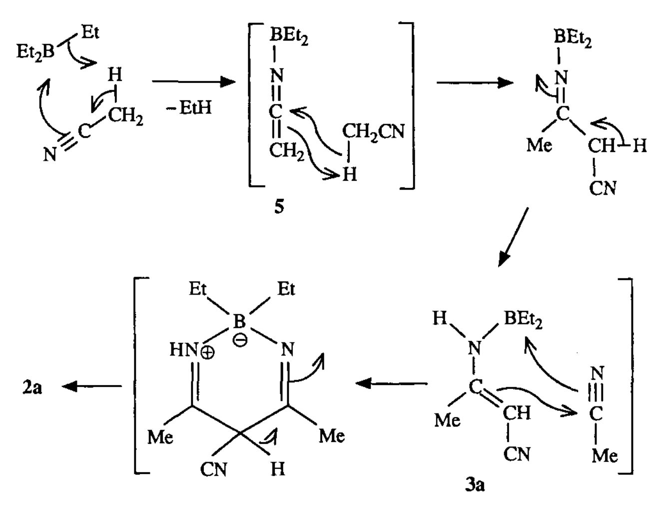


4a, R = R^1 = Et
4b, $R_2 = 1,5\text{-}C_8H_{14}$, R^1 = Et

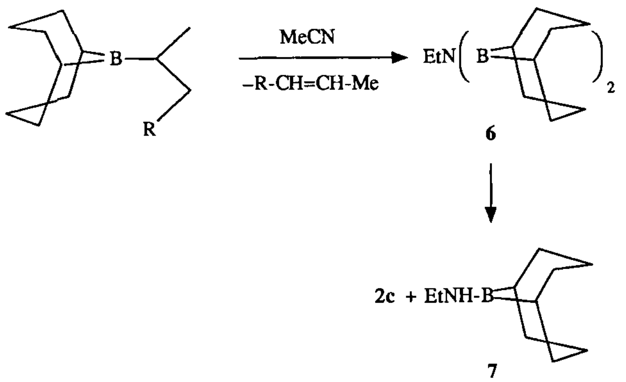
The above information suggests that at least two parallel reaction paths are involved. In one, hydroboration of acetonitrile forms intermediately the substituted enamino- and aminoboranes **3a** and **4**. At higher temperatures, even complete hydrogenolysis of the C – N bond may take place, and a *B*-alkyl-substituted borazine is formed. This pathway results also in the formation of ethene gas. The other path, the main sequence of reactions proceeding at lower temperatures, can be assumed to be initiated by the Lewis acid-promoted or Lewis base-catalyzed evolution of ethane gas and intermediate formation of the keteniminoborane **5**. Further condensation of this species with another two molecules of acetonitrile leads to **2**. Scheme 1 shows the possible steps for this transformation[14].

The condensation of a third acetonitrile molecule with the postulated intermediate **3a** and formation of the stable heterocycle **2** require the abstraction of the two remaining protons of the first nitrile molecule and ring closure at the boron atom. A derivative of intermediate **3a** has been isolated and characterized by reaction with propionitrile which has only two available α-hydrogen atoms (see **3b** below). The nitrile hydroboration product **4** is presumably also further converted to **2** (see below); its concentration decreases with time. Scheme 1 reflects our view that the reaction steps to **2** are Lewis acid (borane)-assisted and by enhancing the proton abstraction can also be Lewis base-catalyzed. Indeed, the addition of catalytic amounts of quinuclidine shortened the reaction time to 2 h at 200°C. However, the best results for the conversion to **2** were achieved by reducing the reaction temperature to 165°C while increasing reaction time to 70 h. When this procedure was applied the ratio of the ethane/ethene gas mixture formed was 3:1. The NMR spectra of the crude reaction product, after removal of excess nitrile and other volatile components, show the presence of nearly pure **2a**.

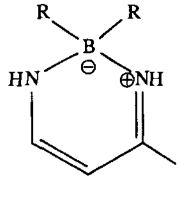
Scheme 1



Heterocycles of the type **2** can also be obtained by reaction of acetonitrile with other trialkylboranes. Thus, Pr_3B reacts at 220°C after 3 h to give the dipropyl derivative **2b** in 25% yield. The 1,5-cyclooctanediyl derivative **2c** can be obtained in low yield from the reaction of 9-ethyl-9-borabicyclo[3.3.1]nonane (Et – BBN) with an excess of acetonitrile. Better yields of this compound can be obtained when either 9-(1-methylpropyl)- or 9-(1-methylbutyl/1-ethylpropyl)-9-borabicyclo[3.3.1]nonane [$C_2H_5C(CH_3)$-BBN or $C_3H_7CH(CH_3)$-/$(C_2H_5)_2CH$-BBN, respectively] is the reacting trialkylborane. The monitoring of the reaction by ^{11}B-NMR spectroscopy reveals also in this case that intermediates accumulate: Initially, the intensity of a peak at $\delta^{11}B \approx 60$ increases rapidly. At later stages this peak slowly decreases in intensity, and two peaks at $\delta^{11}B = 47.7$ and -2.0 emerge. We assign the initially formed peak at $\delta \approx 60$ to bis(9-borabicyclo[3.3.1]non-9-yl)ethylamine (**6**), which with longer reaction times is further converted to **2c** with $\delta^{11}B = -2.4$ and to (9-borabicyclo[3.3.1]non-9-yl)ethylamine (**7**) with $\delta^{11}B = 48.7$. Interestingly, the yield of **2c** is nearly quantitative when **6** is treated in the presence of traces of quinuclidine with an excess of acetonitrile.

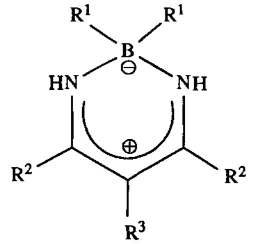


The reaction of acetonitrile with either Pr_3B or with $C_3H_7CH(CH_3)$-/$(C_2H_5)_2CH$-BBN also results in the formation of two other C_3BN_2 heterocycles. From both reactions the distillation fraction containing these heterocycles had similar boiling points and could not be separated. The ^{11}B-NMR spectrum of both fractions showed single sharp signals at $\delta \approx -1.7$ and -3.0, respectively. Analysis by GC followed by GC/MS of the fraction isolated from the reaction of acetonitrile with Pr_3B showed the two components **8a** and **9a** (6.1:1.0) with molecular ions at m/z = 180 and 194, respectively. The corresponding two components **8b** and **9b** (1.2:1.0) from the similar reaction with $C_3H_7CH(CH_3)$-/$(C_2H_5)_2CH$-BBN exhibited molecular ions at m/z = 204 and 218. The ^1H- and ^{13}C-NMR spectra of each of these mixtures (see Table 1) showed similar features in the olefinic regions and agreed well with the pairs **8a**/**8b** and **9a**/**9b**, respectively. In the formation of the heterocycles **8**, one acetonitrile molecule has to undergo hydroboration by in situ formed dipropylhydroborane or, respectively, by 9-BBN prior to the condensation with a second nitrile molecule. The involvement of a hydroborane species is also probable in the formation of the heterocycles **9c** and **9d**. In this case a reductive removal of a cyanide ion is implied.



8a, $R = Pr$

8b, $R_2 = 1{,}5\text{-}C_8H_{14}$



9a, $R^1 = Pr$; $R^2 = Me$; $R^3 = H$

9b, $R^1 = 1{,}5\text{-}C_8H_{14}$; $R^2 = Me$; $R^3 = H$

9c, $R^{1,2} = Et$; $R^3 = Me$

9d, $R^{1,3} = Et$; $R^2 = Pr$

As mentioned above, a prerequisite for the formation of heterocycles of the type **2** is the presence of three α-hydrogen atoms in the nitrile employed. This, unfortunately, strictly limits the choice of the starting nitrile. The reactivity is however not limited to acetonitrile. When an excess of the higher nitriles, e.g. propio- or butyronitrile, which possess only two α-hydrogen atoms is allowed to react under the above conditions ($\approx$ 200°C) with Et_3B, instead of the expected derivatives of **1** two other types of C_3BN_2 heterocycles are obtained. Thus, treatment of an excess of propionitrile with Et_3B leads after heating at 210°C for 17 h to the formation of four main products. The ^{11}B-NMR spectrum taken at different times during the reaction showed peaks at $\delta \approx$ 51.0, 46.0, 31, and -3.0. To isolate and identify these products, the reaction was repeated at 165°C, and the products were worked up initially after a reaction time of 20 h. The main product that could be isolated in pure form by distillation showed a chemical shift at δ = 51.2 in its ^{11}B-NMR spectrum, and also the other spectroscopic results correspond to the E/Z isomeric mixture **3b**, a homolog of **3a**, discussed above. Longer reaction times changed the spectrum of the products formed. After 114 h at 165°C the heterocycles **9c** and **10a** could be isolated by fractional distillation of the reaction product. Compound **9c** formed in $\approx$25% yield possesses NH and C=N groups as seen in its IR spectrum. The ^{11}B-NMR signal at δ = -2.5 indicates a tetravalent boron atom. The presence of a single type of BEt, =C–Et and =C–Me groups (^1H and ^{13}C NMR) in ratio of 2:2:1 together with other analytical data are in agreement with the structure shown. In the formation of **9c** one of the propionitrile molecules has lost a cyanide group (see discussion above for **9a**/**b**). The spectroscopic results accumulated for the second crystalline solid component (**10a**) obtained in this reaction like its homolog **10b**, from a similar reaction involving butyronitrile and Et_3B, proved to be too complex for arriving at a structural solution (for NMR data see Table 2).

Table 2. NMR data for compounds **10a** and **b**

No	$\delta^{13}C$ (50.4 MHz)						$\delta^{11}B$ (64.2 MHz)	δ^1H (200 MHz)				
	Et	C^1 R^1	C^2 R^2	C^3	C^4 R^4	C^5		Et	R^1	R^2	R^4	NH
10a	7.9(q) 6.1(t)	152.7(s)$^{\#}$ 27.0(t) 12.0(q)	68.9(s) 14.6(q)^{x}	146.1(s)$^{\#}$	104.0(s) 16.0(q)^{x}	126.0(s)	31.5	0.8 - 0.9(m, 5H)	2.27(q, 2H) 1.09(t, 3H)	1.82(s, 3H)	2.15(s, 3H)	5.81(1H) 5.73(1H)
10b	8.0(q) 6.2(t)	150.7(s)$^{\#}$ 35.1(t) 23.1(t)* 12.0(q)^{x}	72.3(s) 21.9(t)* 13.8(q)	145.4(s)$^{\#}$	111.5(s) 23.9(t)* 15.2(q)^{x}	124.7(s)	31.5	0.8 - 1.0(m, 5H)	2.25(t, 2H) 1.54(hex, 2H) 0.94(t, 3H)	2.15(q, 2H)* 1.08(t, 3H)^{x}	2.64(q, 2H)* 1.13(t, 3H)^{x}	5.94(1H) 5.66(1H)

$^{\#}$ * ^{x} assignments are uncertain

A single-crystal X-ray analysis of **10b** revealed the molecular structure as shown in Figure 2. (Selected bond lengths and angles are given in the caption.)

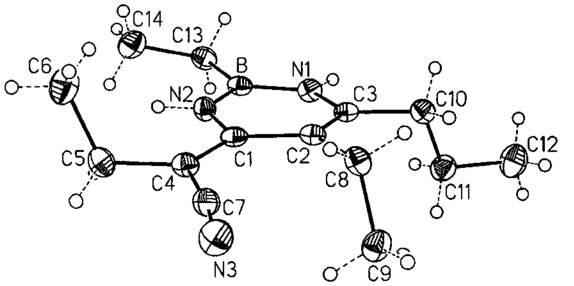
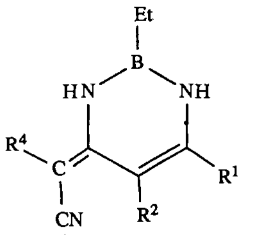


Figure 2. Molecular structure of **10b**. Bond lengths [Å]: N1B 1.406(2), N2B 1.414(2), N2C1 1.390(2), C1C2 1.459(2), C2C3 1.360(2), C3N1 1.383(2), BC13 1.573(2), C3C10 1.502(2), C2C8 1.510(2), C1C4 1.377(2), C4C7 1.420(2), C7N3 1.155(2), C4C5 1.516(2). — Bond angles [°]: N1BN2 113.9(1), BN1C3 122.6(1), N1C3C2 121.7(1), C3C2C1 120.0(1), C2C1N2 114.9(1), C1N2B 126.7(1), N1C3C10 112.4(1), C2C3C10 125.9(1), C3C2C8 120.3(1), C1C2C8 119.7(1), C2C1C4 128.4(1), N2C1C4 116.7(1), C4C7N3 172.6(1)

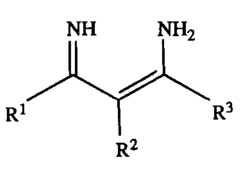
The C_3BN_2 heterocycle is nearly planar (maximum deviation from the mean plane 0.03 Å). Some of the angle deformations due to steric crowding of the substituents are noteworthy. Foremost, the unusual bending of the cyano group: The C4H7N3 angle is 172.6°. Similarly, both of the substituents at C1 and C3 are bent away from the ethyl group at C2. The *B*-ethyl group and the exocyclic substituent at C1 both lie nearly in the plane of the six-membered heterocycle (torsion angles N1BC13C14 = 168.7° and N2C1C4C5 = −1.4°, respectively) while the ethyl group at C2 and the propyl group at C3 adapt a nearly perpendicular conformation with respect to the ring (torsion angles C1C2C8C9 = 88.8° and C2C3C10C11 = 105.1°, respectively).

Compounds **10a** and **b** are, besides the byproduct borazine, the only boron-nitrogen heterocycles with a trivalent boron atom obtained so far in this study. They are like the derivatives of **2** and **9**, formally formed by condensation of three nitrile molecules and one borane molecule. In this case the heterocycle is not symmetrical and one of the nitrile molecules has become condensed onto the six-membered heterocycle by an exocyclic double bond.



10a, R^1 = Et, $R^{2,4}$ = Me

10b, R^1 = Pr, $R^{2,4}$ = Et



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The common feature of all these reactions, except for that which leads to **10a** and **b**, is the formation of a very stable 1,3,2-azaazoniaboratine structure. Several other C_3BN_2 heterocycles have previously been prepared by the reaction of a Schiff's base with a suitable organoborane and a nitrile, or more directly from a dialkylenaminoborane and a nitrile[15a]. Examples of other similar stable C_3BNO, C_3BO_2, and C_2BN_3 heterocycles are numerous[15b]. The C_3BN_2 heterocycles **2**, **8**, and **9** presented here should in principle be readily available from the diimines **11** of the corresponding β-diketone. Unfortunately such derivatives are unknown.

Experimental

Melting points: Büchi apparatus, sealed capillary tubes. — MS: MAT CH 5. — ^1H, ^{11}B, and ^{13}C NMR: Bruker AC 200 with Me_4Si as internal and Et_2O-BF_3 as external standards. — GC: Siemens Sichromat 1, OV-1 capillary column (30 m) programmed at 6°C/min, 80–290°C, carrier gas H_2/0.5 bar. — GC/MS: Perkin-Elmer F 22/Varian MAT CH 7 A. — All operations were carried out under dry oxygen-free argon. All solvents were freshly distilled under argon from appropriate drying agents. All reactions at high temperatures were carried out in a 100-ml stainless steel autoclave. Gas samples were removed and analyzed by MS.

1,3-Dibenzylidene-2,2,4,4-tetraethyl-1,3,2,4-diazoniadiboratetidine (**1a**): A mixture of 14.0 g (142.9 mmol) of Et_3B and 45.0 g (436.9 mmol) of benzonitrile was heated at 200°C for 16 h in a stainless steel autoclave. The gas (≈ 2 l, C_2H_4 88%, C_2H_6 12%) was vented. From the yellow-orange solution the volatile components were removed in vacuo at room temp. The residue was distilled at 10^{-3} Torr and the fraction with b.p. 100–118°C collected, 16.3 g (66%). Recrystallization from toluene/hexane gave colorless crystals of **1a**, m.p. 113–114°C. — IR (paraffin film): ν(C=C) = 1630 cm^{-1}. — MS: *m/z* (%) = 317 (55) [M^+ − Et], 144 (100), 116 (40). — ^1H NMR ($CDCl_3$): δ = 8.20, 8.18 (s, 2H), 7.76 (m, 4H), 7.45 (m, 6H), 0.9 (m, 20H). — ^{11}B NMR ($CDCl_3$): δ = 7.9 ($h_{1/2}$ = 200 Hz). — ^{13}C NMR ($CDCl_3$): δ = 157.6 (d), 133.5 (s), 130.7(d), 129.7(d), 14.6 (br, t), 9.6 (q).

$C_{22}H_{32}B_2N_2$ (346.1) Calcd. C 76.34 H 9.32 B 6.25
Found C 76.27 H 9.51 B 6.38

1,3-Diisobutylidene-2,2,4,4-tetraethyl-1,3,2,4-diazoniadiboratetidine (**1b**): A mixture of 11.2 g (114.6 mmol) of Et_3B and 30.5 g (440.9 mmol) of isobutyronitrile was heated at 200°C for 16 h, as above. The gas evolated (1.6 l, C_2H_4 95%, C_2H_6 2%, H_2 3%) was vented. Distillation of the product at 10^{-3} Torr gave a fraction with b.p. 105–113°C, 9.3 g (58%) of **1b**. — IR (film): ν(C=N) = 1630 cm^{-1}. — MS: *m/z* (%) = 278 (1) [M^+], 249 (100), 140 (15), 110 (35), 82 (30). — ^1H NMR ($CDCl_3$): δ = 7.05, 6.95 (d, 2H), 2.45 (dd, 2H), 0.95 (d, 12H), 0.75 (t, 12H), 0.45 (m, 8H). — ^{11}B NMR ($CDCl_3$): δ = 5.4 ($h_{1/2}$ = 200 Hz). — ^{13}C NMR ($CDCl_3$): δ = 166.5, 166.4 (d), 33.0, 32.6 (d), 19.2, 19.1 (q), 14.4 (br, t), 9.8, 9.2, 8.8 (q).

$C_{16}H_{36}B_2N_2$ (278.1) Calcd. C 69.10 H 13.05 N 7.77
Found C 68.95 H 13.12 N 7.91

1,3-Bis(2,2-dimethylpropylidene)-2,2,4,4-tetraethyl-1,3,2,4-diazoniadiboratetidine (**1c**): A mixture of 10.5 g (107.1 mmol) of Et_3B and 38 g (457.8 mmol) of pivalonitrile was heated as above at 200°C for 24 h. The gas (1.3 l) was vented, and after removal of the volatile components at reduced pressure the residue was distilled at 10^{-2} Torr. The fraction with b.p. 57–61°C, 3.5 g (21.4%), a slightly yellow liquid (**1c**), was crystallized from very little hexane at −60°C, m.p. 76–77°C. — IR (paraffin film): ν(C=N) = 1650^{-1}. — MS: *m/z* (%) = 277 (100) [M^+ − 29, B_2], 124 (85) [B_1], 96 (30). — ^1H NMR ($CDCl_3$): δ = 7.21 (s, 2H), 1.09 (s, 18H), 0.64 (t, 12H), 0.48

(q, 8 H). – ^{11}B NMR ($CDCl_3$): δ = 6.6 ($h_{1/2}$ = 150 Hz). – ^{13}C NMR ($CDCl_3$): δ = 169.7 (d), 36.7 (s), 27.1 (q), 15–8 (br, t), 9.3 (q).

$C_{18}H_{40}B_2N_2$ (306.2) Calcd. C 70.62 H 13.17 B 7.07
Found C 70.54 H 13.06 B 7.18

5-Cyano-2,2-diethyl-1,2-dihydro-4,6-dimethyl-1,3,2-azaazoniaboratine (**2a**): A mixture of 7.0 g (71.4 mmol) of Et_3B, 15.6 g (159.2 mmol) of acetonitrile, and 0.2 g (2 mmol) of quinuclidine was placed in a 100-ml stainless steel autoclave and heated to 165°C for 70 h. The gas formed (1.5 l, 66.9 mmol) consisted of 70.0% ethane and 24.5% ethene. The volatile components from the deep-red product solution were removed in high vacuum at room temp. The residue, on treatment with hot hexane, gave on cooling the yellow microcrystalline solid **2a**, 7.2 g (53%), m.p. 81–82°C. – IR (paraffin film): ν(NH) = 3300, ν(C≡N) = 2160, ν(C=N) = 1630 cm^{-1}. – MS: *m/z* (%) = 191 (1) [M$^+$], 162 (100) [B_1], 147 (15), 134 (15). – For NMR data see Table 1.

$C_{10}H_{18}BN_3$ (191.1) Calcd. C 62.86 H 9.50 B 5.66
Found C 62.80 H 9.75 B 5.57

5-Cyano-1,2-dihydro-4,6-dimethyl-2,2-dipropyl-1,3,2-azaazoniaboratine (**2b**): A mixture of 40.5 g (289.1 mmol) of Pr_3B and 47.5 g (1.16 mol) of acetonitrile was placed in a 100 ml stainless steel autoclave and heated to 220°C for 3 h. The gas formed (5.4 l) was vented, and from the dark red product solution the volatile compounds were removed in high vacuum at room temp. The residue was distilled at 10^{-3} Torr and the fraction with b.p. 90–150°C collected. The suspension was filtered and the yellow solid washed with cold hexane. Recrystallization from hexane gave 15.9 g (25%) of **2b**, m.p. 158–159°C. – IR (paraffin film): ν(NH) = 3300, ν(C≡N) = 2180, ν(C=N) = 1628 cm^{-1}. – MS: *m/z* (%) = 219 (1) [M$^+$], 176 (100) [B_1], 134 (15). – For NMR data see Table 1.

$C_{12}H_{22}BN_3$ (219.1) Calcd. C 65.78 H 10.12 B 4.93
Found C 65.91 H 10.18 B 4.81

5-Cyano-2,2-(1,5-cyclooctanediyl)-1,2-dihydro-4,6-dimethyl-1,3,2-azaazoniaboratine (**2c**)

Method A: A mixture of 14.03 g (73.0 mmol) of $C_3H_7CH(CH_3)$-/$(C_2H_5)_2CH$-BBN (mixture of 1-methylbutyl and 1-ethylpropyl isomers) and 34.4 g (838 mmol) of acetonitrile was heated at 200°C for 8.5 h. After removal of the volatile components in vacuo at room temp. the ^{11}B-NMR spectrum of the orange-red product solution showed peaks at δ = 62.0, 47.0. –2.3, and –3.6. The slightly turbid orange-red solution was filtered. About 0.3 g of a colorless solid remained on the filter. After washing with small amounts of pentane it melted at 170–171°C. – MS: *m/z* (%) = 274 (100) [M$^+$, B2], 163 (45), 137 (45). – ^{11}B NMR: δ = –1.2. – IR: Identical to that of bis(9-amino-9-borabicyclo[3.3.1]nonane)[16].

To the filtrate above 20 ml of hexane was added and the suspension filtered. The orange solid was recrystallized from heptane, 5.1 g (29%) of **2c**, m.p. 197–198°C. – IR (paraffin film): ν(NH) = 3380 (w), 3280 (s); ν(C≡N) = 2180 and ν(C=N) = 1605 cm^{-1}. – MS: *m/z* (%) = 243 (65) [M$^+$, B1], 229 (20), 214 (30), 200 (55), 186 (100), 160 (85), 147 (45), 134 (40). – For NMR data see Table 1.

$C_{14}H_{22}BN_3$ (243.2) Calcd. C 69.15 H 9.12 B 4.44
Found C 69.20 H 9.19 B 4.23

After removal of the solvent in vacuo the filtrate above was distilled at 10^{-3} bar. Fraction I: b.p. ≈40°C, 1.3 g. – ^{11}B NMR: δ = 47.0, identical to authentic 9-(ethylamino)-9-borabicyclo[3.3.1]nonane (**7**). – MS: *m/z* (%) = 165 (100) [M$^+$, B1] with a small amount of contamination with *m/z* = 193 [probably 9-(diethylamino)-9-borabicyclo[3.3.1]nonane]. Fraction II: b.p. ≈102°C, 2.5 g. – ^{11}B NMR: δ = 62.0. – IR: identical to authentic bis(9-borabicyclo[3.3.1]non-9-yl)ethylamine (**6**) (see below). Fraction III: b.p. ≈140°C, an orange viscous liquid, dissolved in hot heptane, formed on cooling to –60°C a yellow crystalline solid, 3.5 g. – IR (paraffin film): ν(NH) = 3400, 3380; ν(C=N) = 1600 cm^{-1}. – The mass spectrum showed the presence of the two components **8b** and **9b**: *m/z* = 204 and 218 (see also alternative procedure below).

Method B: A mixture of 10.5 g (36.8 mmol) of bis(9-borabicyclo-[3.3.1]non-9-yl)ethylamine (**6**) [prepared from hydroboration of acetonitril with bis(9-borabicyclo[3.3.1]nonane)[17]], 15.6 g (381 mmol) of acetonitrile, and 0.2 g (2.0 mmol) of quinuclidine was heated in the autoclave at 220°C for 10 h. The product suspension was removed from the autoclave, traces were washed out with toluene, and from the combined material the volatile components were removed in vacuo at room temp. The sticky residue was triturated with small amounts of hexane and filtered. The orange-red solid sublimed at 130°C/10^{-3} Torr, 8.5 g (95%) of **2c**. The filtrate was distilled at 39–40°C/10^{-3} Torr, 3.7 g (61%) of 9-(ethylamino)-9-borabicyclo[3.3.1]nonane (**7**) (see above).

(Z/E)-3-[(Diethylboryl)amino]-2-methyl-2-pentenenitrile (**3b**): A mixture of 22.7 g (411.7 mmol) of propionitrile and 9.8 g (100.0 mmol) of Et_3B was heated at 165°C for 20 h. 1.63 l (73%) of gas (69% ethane, 31% ethene) was vented. From the red liquid product all volatile components were removed in vacuo at room temp., and the residue was distilled at 1 Torr. Fraction I: b.p. 88–93°C, 4,4 g (25%) of **3b**. – IR (film): ν(NH) = 3360, 3300, ν(C≡N) = 2195, 2185, and ν(C=N) = 1630, 1610 cm^{-1}. – MS: *m/z* (%) = 178 (5) [M$^+$], 149 (100), 94 (30). – ^{1}H NMR: δ = 5.82, 5.36 (br, 1 H); 2.52, 2.28 (q, 2 H); 1.80, 1.67 (s, 3 H); 1.03, 1.00 (t, 3 H); 0.85 (m, 10 H). – ^{11}B NMR: δ = 51.2. – ^{13}C NMR: 159.2, 158.8 (s, 1 C); 120.2, 119.6 (s, 1 C); 92.3, 91.7 (s, 1 C); 28.7, 24.8 (t, 1 C); 14.6, 14.1 (q, 1 C); 12.1, 11.1 (s, 1 C); 11.9 (br, t, 2 C); 8.0 (q, 2 C).

Table 3. Crystallographic data for compounds **2a** and **10b** and data collection procedures

	2a	**10b**
Formula	$C_{10}H_{18}BN_3$	$C_{14}H_{24}BN_3$
Crystal size (mm)	0.60 x 0.41 x 0.29	0.39 x 0.24 x 0.23
Space group	Pbca	$P\bar{1}$
Z	16	2
a (Å)	14.099(2)	9.003(2)
b (Å)	13.173(2)	9.150(2)
c (Å)	24.869(4)	9.650(2)
α (deg)	90	87.44(2)
β (deg)	90	88.22(2)
γ (deg)	90	68.04(2)
T (K)	110	110
V (Å^3)	4618.7(9)	736.2(3)
d_{calcd} (g/cm^3)	1.097	1.106
μ (cm^{-1})	0.06	0.06
Radiation	Mo-K_α	Mo-K_α
$2\Theta_{max}$ (deg)	40	45
Total no. of unique reflections	3024	1914
Observed reflections	2354	1714
R	0.040	0.0352
R_w [$w = \sigma(F_o + gF^2)$]	0.045	0.0428
g	1.24 x 10^{-3}	5.0 x 10^{-4}
Residual electron density (e/Å^3)	0.21	0.15

Mixture of 1,2-Dihydro-4-methyl-2,2-dipropyl-1,3,2-azaazoniaboratine (**8a**) *and 1,2-Dihydro-4,6-dimethyl-2,2-dipropyl-1,3,2-azaazoniaboratine* (**9a**): A mixture of 11.2 g (79.9 mmol) Pr_3B, 16.4 g (400.0 mmol) of acetonitrile, and 0.2 g of quinuclidine was heated at 150°C for 100 h. The gas, 1.28 l (71%), was vented, and from the orange liquid product the volatile components were removed in water-pump vacuum. The fraction with b.p. 76–80°C/10^{-1}, 4.1 g, was collected. GC showed the two components **8a** and **9a** (6.4:1.0). – GC/MS for **8a**: m/z (%) = 137 (100) [M^+ – 43], 108 (25), 95 (35); for **9a**: 151 (100) [M^+ – 43], 122 (25), 109 (20). – For NMR data of **8a** see Table 1.

Mixture of 2,2-(1,5-Cyclooctanediyl)-1,2-dihydro-4-methyl-1,3,2-azaazoniaboratine (**8b**) *and 2,2-(1,5-Cyclooctanediyl)-1,2-dihydro-4,6-dimethyl-1,3,2-azaazoniaboratine* (**9b**): A mixture of 7.7 g (39.9 mmol) of 9-(1-methylbutyl)-9-borabicyclo[3.3.1]nonane, 5.0 g (121.9 mmol) of acetonitrile, and 0.3 g (2.7 mmol) of quinuclidine was heated at 200°C for 6.5 h. After removal of the volatile components, the residue was distilled. The fraction with b.p. 105 to 108°C/10^{-3} Torr, 3.95 g, was collected. GC showed the two components **8b** and **9b** (≈1.2:1.0). – GC/MS for **8b**: m/z (%) = 204 (70) [M^+], 175 (40), 147 (100), 121 (80); for **9b**: 218 (65) [M^+], 189 (30), 175 (50), 161 (100), 135 (90). – For NMR data see Table 1.

Table 4. Atomic coordinates (× 10^4) and equivalent isotropic displacement factors (Å^2 × 10^4) for compound **2a**

	x	y	z	U_{eq}
N(1)	6892(1)	723(1)	5219(1)	229(6)*
N(2)	8141(1)	2027(1)	5142(1)	199(6)*
N(3)	8666(1)	464(1)	6832(1)	284(7)*
B	7446(2)	1370(2)	4784(1)	209(8)*
C(1)	7159(2)	536(2)	5711(1)	217(7)*
C(2)	7990(2)	1010(2)	5914(1)	190(7)*
C(3)	8448(2)	1786(2)	5623(1)	188(7)*
C(4)	6701(2)	2055(2)	4457(1)	218(7)*
C(5)	7142(2)	2766(2)	4041(1)	280(8)*
C(6)	8080(2)	649(2)	4404(1)	258(7)*
C(7)	8758(2)	-75(2)	4689(1)	333(8)*
C(8)	6600(2)	-162(2)	6057(1)	318(8)*
C(9)	8351(2)	719(2)	6424(1)	211(7)*
C(10)	9282(2)	2329(2)	5857(1)	231(7)*
N(1')	10582(1)	-3178(1)	7198(1)	208(6)*
N(2')	9689(1)	-1765(2)	6787(1)	225(6)*
N(3')	10533(1)	-3918(2)	5334(1)	275(7)*
B'	10047(2)	-2166(2)	7348(1)	221(8)*
C(1')	10667(2)	-3602(2)	6729(1)	187(7)*
C(2')	10256(2)	-3130(2)	6269(1)	184(7)*
C(3')	9768(2)	-2196(2)	6318(1)	197(7)*
C(4')	10777(2)	-1370(2)	7611(1)	270(8)*
C(5')	11607(2)	-1043(2)	7260(1)	334(8)*
C(6')	9155(2)	-2443(2)	7723(1)	268(7)*
C(7')	8432(2)	-3170(2)	7478(1)	365(9)*
C(8')	11199(2)	-4580(2)	6675(1)	250(7)*
C(9')	10397(2)	-3566(2)	5754(1)	204(7)*
C(10')	9330(2)	-1711(2)	5831(1)	286(8)*

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

2,2,4,6-Tetraethyl-1,2-dihydro-5-methyl-1,3,2-azaazoniaboratine (**9c**) *and 4-(Cyanoethylidene)-2,6-diethyl-1,2,3,4-tetrahydro-5-methyl-1,3,2-diazaborine* (**10a**): A mixture of 21.0 g (214.0 mmol) of triethylborane and 47.5 g (863.0 mmol) of propionitrile was heated in an autoclave at 165°C for 114 h. The gas, 8.3 l (173%), was vented. From the deep-red product solution the volatile components were removed in vacuo at room temp. The residue was distilled at 10^{-3} Torr. Fraction I: Boiling range 60–110°C, 11.2 g (25.1%) of **9c**. It was redistilled, the subfraction with b.p. 65–67°C (8.3 g) was collected. – IR (film): ν(NH) = 3400 and ν(C=N) = 1590 cm^{-1}. – MS: m/z (%) = 208 (1) [M^+], 179 (100) [B_1]. – For NMR data see Table 1. Fraction II: Boiling range 110–140°C, 11.6 g (27%) of **10a**. It was redistilled leading to a subfraction with the boiling range 130–135°C, 6.5 g of a sticky solid. Recrystallization from hot heptane: m.p. 102–103°C. – IR (paraffin film): ν(NH) = 3200; ν(C≡N) = 2150, and ν(C=C) = 1605 cm^{-1}. – MS: m/z (%) = 203 (100) [M^+], 202 (100), 175 (25) 174 (23), 163 (45), 150 (35). – For NMR data see Table 2.

$C_{11}H_{18}BN_3$ (203.1)	Calcd.	C 65.05	H 8.93	B 5.32
	Found	C 65.19	H 8.81	B 5.51

2,2,5-Triethyl-1,3-dihydro-4,6-dipropyl-1,3,2-azaazoniaboratine (**9d**) *and 6-(1-Cyanopropylidene)-2,5-diethyl-1,2,3,4-tetrahydro-6-propyl-1,3,2-diazaborine* (**10b**): A mixture of 10.0 g (102.0 mmol) of Et_3B and 27.7 g (400.8 mmol) of isobutyronitrile was heated as before at 165°C for 65 h. The gas was vented, and the volatile components were removed at reduced pressure. The residue was distilled at 10^{-3} Torr. Fraction I: Boiling range 90–100°C, 5.8 g (23%) of **9d**. – IR (film): ν(NH) = 3390 and ν(C=C) = 1590 cm^{-1}. – MS: m/z (%) = 250 (3) [M^+], 221 (100). – For NMR data see Table 1. Fraction II: Boiling range 105–120°C, 3.5 g (14%). Crystallization from heptane gave **10b**, m.p. 97–98°C. – IR (paraffin film): ν(NH) = 3300; ν(C≡N) = 2155, and ν(C=C) =

Table 5. Atomic coordinates (× 10^4) and equivalent isotropic displacement factors (Å^2 × 10^4) for compound **10b**

	x	y	z	U_{eq}
N(1)	2673(1)	440(1)	179(1)	202(5)*
N(2)	1736(1)	2834(1)	-1149(1)	202(5)*
N(3)	2834(2)	7121(2)	790(1)	323(6)*
B	1837(2)	1255(2)	-1001(2)	207(6)*
C(1)	2373(2)	3603(2)	-268(1)	188(5)*
C(2)	3314(2)	2617(2)	866(1)	192(5)*
C(3)	3412(2)	1102(2)	1060(1)	188(5)*
C(4)	2030(2)	5181(2)	-561(1)	209(5)*
C(5)	1042(2)	6053(2)	-1796(2)	256(6)*
C(6)	1969(2)	5803(2)	-3169(2)	371(7)*
C(7)	2531(2)	6178(2)	234(2)	231(6)*
C(8)	4157(2)	3293(2)	1836(2)	232(5)*
C(9)	3153(2)	4088(2)	3087(2)	289(6)*
C(10)	4250(2)	-16(2)	2227(2)	225(6)*
C(11)	3092(2)	-259(2)	3313(2)	280(6)*
C(12)	3921(2)	-1543(2)	4373(2)	382(7)*
C(13)	1104(2)	485(2)	-2080(2)	247(6)*
C(14)	530(2)	1435(2)	-3419(2)	311(6)*

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

1605 cm^{-1}. – MS: m/z (%) = 245 (30) [M^+], 230 (100). – For NMR data see Table 2.

$C_{14}H_{24}BN_3$ (245.2) Calcd. C 68.59 H 9.87 B 4.41
Found C 68.49 H 9.63 B 4.32

X-ray Single-Crystal Structure Determination of **2a** *and* **10b**: Data collection and calculations were carried out on a Nicolet R 3 m/V four-cycle diffractometer with Microvax II and SHELXTL-PLUS software[18]. The structure solution was performed by direct methods, and all hydrogen atoms were included as rigid groups (C–H bond lengths 0.96 Å, C–C–H and H–C–H angles 109.5 and 120°, respectively). The isotropic displacement parameters (IDP's) of all the hydrogen atoms were refined without constraints. The structural data for compounds **2a** and **10b** are compiled in Table 3, and the atom coordinates in Tables 4 and 5, respectively[19].

CAS Registry Numbers

1a: 20740-10-7 / **1b**: 136676-01-2 / **1c**: 136676-02-3 / **2a** (chelate): 136704-95-5 / **2a** (B^{III}): 136675-94-0 / **2b** (chelate): 136704-96-6 / **2b** (B^{III}): 136675-95-1 / **2c** (chelate): 136704-97-7 / **2c** (B^{III}): 136675-96-2 / (*Z*)-**3b**: 136675-91-7 / (*E*)-**3b**: 136675-92-8 / **6**: 136675-90-6 / **7**≡**4b**: 136675-89-3 / **8a**: 136705-00-5 / **8b**: 136704-98-8 / **9a** (chelate): 136705-01-6 / **9a** (B^{III}): 136675-98-4 / **9b** (chelate): 136704-99-9 / **9b** (B^{III}): 136675-97-3 / **9c** (chelate): 136705-02-7 / **9c** (B^{III}): 136675-99-5 / **9d** (chelate): 136705-03-8 / **9d** (B^{III}): 136676-00-1 / **10a**: 136675-93-9 / **10b**: 136704-94-4 / Et_3B: 97-94-9 / Pr_3B: 1116-61-6 / CH_3CN: 75-05-8 / CH_3CH_2CN: 107-12-0 / $(CH_3)_2CHCN$: 78-82-0 / $(CH_3)_3CCN$: 630-18-2 / PhCN: 100-47-0 / $C_3H_7CH(CH_3)$-9-BBN: 121194-78-3 / $(C_2H_5)_2CH$-9-BBN: 136704-93-3 / $(H_2N$-9-$BBN)_2$: 65938-39-8 / quinuclidine: 100-76-5

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