1,5-Diaza-2,6-diborabicyclo[3.3.0]octadienes: Products of the Reactions of Trihaloboranes with Ketazines

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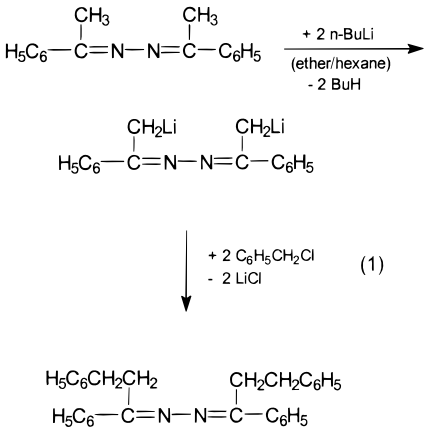
Received February 8, 2000

The 1,5-diazonia-2,6-diboratabicyclo[3.3.0]octa-1[8],4-dienes **1**−**4** were prepared from dilithiated ketazines and trihaloboranes, BX_3 (X = F, Cl, Br, I). Upon elimination of HX the corresponding 1,5-diaza-2,6-diborabicyclo[3.3.0]octa-3,7-dienes were formed and compounds **5** and **6** (X = Cl, Br) were isolated. Treatment of **5** with MeLi and ^{t}BuOLi, respectively, gave **10** and **11**. Monocyclic 1,2,3-azaazoniaborata-5-cyclopentenes (**7**−**9**: X = F, Cl, Br) resulted from monolithiated ketazines and BX_3. The compounds were characterized by NMR spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{19}F), MS, and elemental analyses (CH). X-ray crystal structure determinations are presented for **1**−**4** and **11**.

Introduction

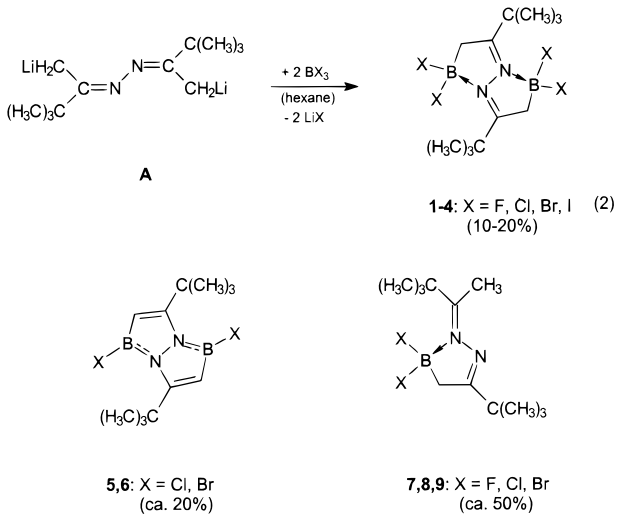
Ketazines are easily lithiated at the α-C atoms.[1] The 1,6-dianions thus formed can be alkylated to give new azine derivatives; see for example eq 1.[2]



It can be expected that such dilithioketazines will react with trihaloboranes to produce diborylated species. Such—so far unknown—compounds contain donor and acceptor centers and may form bicyclic ring systems by intramolecular coordination.

Results and Discussion

In the reactions of the dilithiated *tert*-butylmethylketazine **A** with 2 molar equiv of BX_3 (X = F, Cl, Br, I) in hexane a mixture of products was formed. In any case the bicyclic 1,5-diazonia-2,6-diboratabicyclo[3.3.0]octa-1[8],4-dienes **1**−**4** could be easily isolated in yields between 10 and 20%. Besides these species, the solution contained the corresponding 1,5-diaza-2,6-diborabicyclo[3.3.0]octadienes, characterized for the Cl- and Br-substituted molecules **5** and **6**, and, as the major product, the 1,2,3-azaazoniaborata-5-cyclopentenes, characterized in the case of the fluoride (**7**), chloride (**8**), and bromide (**9**) (eq 2).



The compounds **1**−**4** are easily recrystallized from dichloromethane to give colorless crystals. Single crystals were grown, and the X-ray structure determinations for **1**−**4** confirm their bicyclic structure due to internal coordination. The molecular structures for the fluoro- and the iodo-substituted species are depicted in Figures 1 and 2, respectively.

The NMR data confirm that the same structures are present in solution. The other products could not be isolated in a pure state, due to their similar solubilities and boiling points. However, they were detected by their mass and NMR spectra. The dehydrohalogenated species **5** and **6** were also prepared as pure compounds from **2** and **3**, respectively, by dehydrohalogenation with an excess of triethylamine (eq 3). Their occurrence among

(1) Kolbah, D., et al. In *Methods of Organic Chemistry (Houben-Weyl)*; Klamann, D., Hagemann, H., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; Vol. E14b (Part 1, Organic Nitrogen Compounds with a Double Bond), pp 640−707.

(2) Henoch, F. E.; Hampton, K. G.; Hauser, C. R. *J. Am. Chem. Soc.* **1969**, *91*, 676.

10.1021/om0001164 CCC: $19.00
Publication on Web 05/19/2000

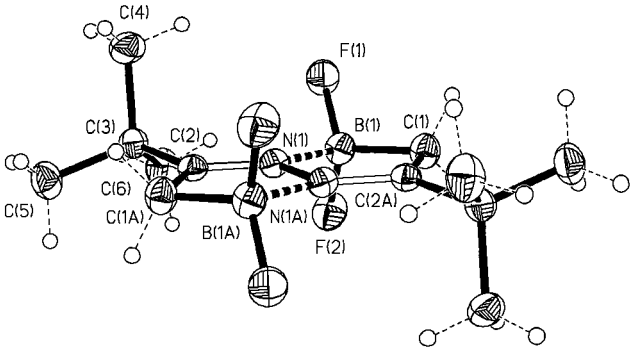


Figure 1. Crystal structure of **1** with anisotropic displacement parameters depicting 50% probability.

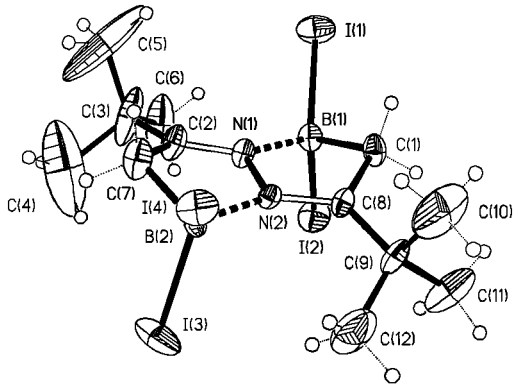
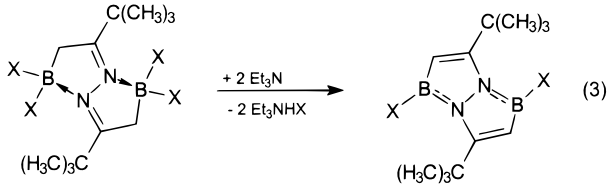


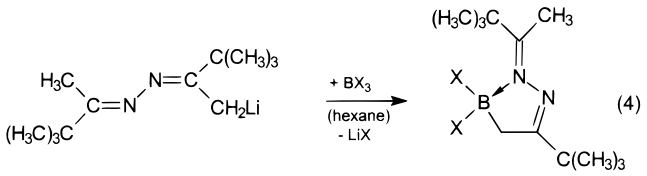
Figure 2. Crystal structure of **4** with anisotropic displacement parameters depicting 50% probability.



2,3 **5,6** X: Cl, Br

the products of the reaction shown in eq 1 can be explained by a reaction of the dilithiated ketazine **A** with **1**−**4**.

Species **7**−**9** were prepared directly from the monolithiated ketazine **B** and an equimolar amount of trihaloborane (eq 4).



B **7, 8, 9**: X = F, Cl, Br

The corresponding saturated ring system 1,2,3-aza-azoniaboratolidine was described earlier by Sucrow et al., who prepared this from open-chain enehydrazones and B_2H_6.[3,4]

(3) Sucrow, W.; Slopinka, M. *Chem. Ber.* **1972**, *105*, 3807.
(4) Sucrow, W.; Zühlke, L.; Slopinka, M.; Pickardt, J. *Chem. Ber.* **1977**, *110*, 2818.
(5) Nöth, H.; Wrackmeyer, B. *Nuclear Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: Berlin, Heidelberg, New York, 1978.

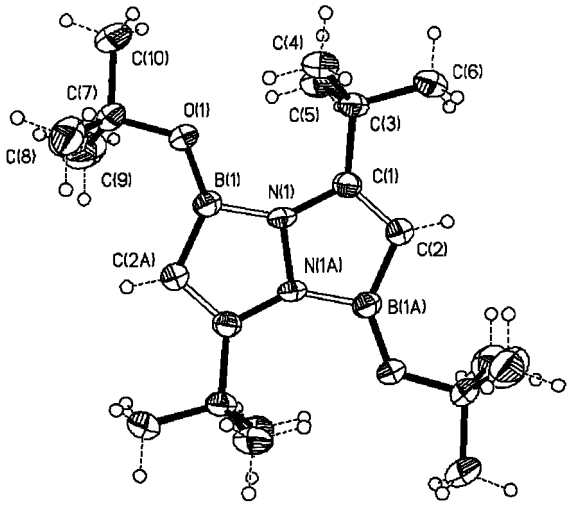
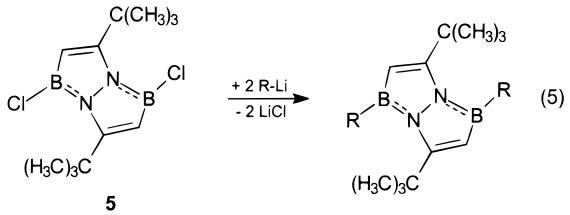


Figure 3. Crystal structure of **11** with anisotropic displacement parameters depicting 50% probability.

As single crystals could not be grown from the halo-substituted 1,5-diaza-2,6-diborabicyclo[3.3.0]octa-3,7-dienes **5** and **6**, the compounds **10** and **11** were prepared according to eq 5. An X-ray structure determination of



5 **10**: R = Me
11: R = O-^{t}Bu

11 confirmed its structure as a planar bicyclic system. Its molecular structure is depicted in Figure 3.

NMR Data. The ^{11}B chemical shifts for the tetracoordinated species **1**−**4** are δ 6.7 (**1**, X = F), δ 4.1 (**2**, X = Cl), δ −5.9 (**3**, X = Br) and δ −34.2 (**4**, X = I): with the exception of $\delta(^{11}B)$ in the compound **1** (X = F), all the shifts are in the expected range. The same is true for **7**−**9**.[5] For **1**, $\delta(^{11}B)$ would be expected at slightly higher field than that for **2**. In the three-coordinate compounds **5**, **6**, **10**, and **11**, the $\delta(^{11}B)$ values are also in the expected range, with **10** (R = Me) at the lowest (δ 39.0) and **11** (R = O^{t}Bu) at the highest field positions (δ 27.3).

Crystal Structures. Selected bond lengths and angles are compiled in Table 1. The comparison of their data demonstrates a good accord between the structures of **1**−**3**. The five-membered-ring systems are (nearly) planar, and the angle sum is close to 540°. Only **4** shows a distortion from planarity and appears to be unsymmetrical. This is depicted in Figure 4, where the molecular structures of **1** and **4** are drawn one upon the other. The coordinative N→B bond length decreases steadily from **1** to **4** from 1.666(2) to 1.584(10) Å. In the 1,5-diaza-2,6-diborabicyclo[3.3.0]octa-3,7-diene **11** the covalent B−N bond length is reduced to 1.456(2) Å and therefore must contain a distinct π-contribution,[6] while the N−C bond length is increased from 1.300(2) Å to 1.400(2) Å and the C−C distance is decreased from

(6) Paetzold, P. Iminoboranes. *Adv. Inorg. Chem.* **1987**, *31*, 123−170.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1−4 and 11

Compounds **1**−**4**

	1 (X = F)	**2** (X = Cl)	**3** (X = Br)	**4** (X = I)
X(1)−B(1)	1.382(2)	1.855(2)	2.025(5)	2.239(9)
N(1)−N(1)#1	1.443(2)	1.460(2)	1.475(6)	1.488(8)
C(1)−C(2)#1	1.485(2)	1.487(2)	1.484(6)	1.493(11)
N(1)−C(2)	1.300(2)	1.306(2)	1.302(6)	1.302(10)
N(1)−B(1)	1.666(2)	1.608(2)	1.594(6)	1.584(10)
C(1)−B(1)	1.600(2)	1.588(2)	1.590(6)	1.588(12)
N(1)−N(1)#−B(1)	107.80(11)	107.71(13)	107.3(4)	106.6(5)
C(1)−B(1)−N(1)	97.97(10)	99.86(11)	100.7(3)	99.0(6)
N(1)−B(1)−X(1)	108.74(11)	109.02(9)	112.0(3)	114.4(5)
C(2)#1−C(1)−B(1)	106.76(11)	106.54(11)	105.9(4)	104.5(6)
C(1)−B(1)−X(1)	116.16(11)	111.65(11)	111.4(3)	109.7(6)
sum of inner angles	539.36	538.61	539.6	532.9
angle sum of N(1)	359.88	359.88	359.9	360.0

Compound **11**

B(1)−O(1)	1.357(2)	N(1)−C(1)	1.400(2)
N(1)−N(1)#1	1.420(2)	N(1)−B(1)	1.456(2)
C(1)−C(2)#1	1.352(2)	C(2)#1−B(1)	1.526(2)
N(1)#1−N(1)−B(1)	108.76(11)	C(2)#1−B(1)−O(1)	135.63(12)
N(1)−B(1)−C(2)#1	103.59(10)	sum of inner angles	540.0
N(1)−B(1)−O(1)	120.78(11)	angle sum of N(1)	360.0
C(1)−C(2)−B(1)#1	107.82(11)		

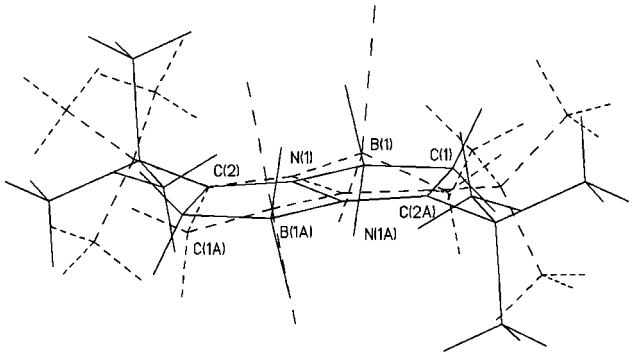


Figure 4. Molecular structures of **1** (solid line) and **4** (dashed line) drawn one upon the other.

1.485(2) Å to 1.352(2) Å in accordance with the double-bond character of these bonds in **1** and **11**, respectively.

Experimental Section

All reactions were performed in an atmosphere of dry nitrogen in dry solvents. Sublimation point (sublp) temperatures are those of the oil bath. Melting points were determined in sealed capillaries. Elemental analyses were performed by the Analytical Laboratory of the University of Göttingen, Institute of Inorganic Chemistry. NMR spectra were recorded on a Bruker AM 250 instrument. Solvent and standards used: ^{1}H and ^{13}C, $CDCl_3$/TMS internal; ^{11}B, $CDCl_3/F_3B{\cdot}OEt_2$ external; ^{19}F, $CDCl_3/C_6F_6$ internal. Mass spectra were obtained with a Finnigan MAT 8230 spectrometer (EI, 70 eV).

tert-Butylmethylketazine was prepared from pinacolone and hydrazine using a catalytic amount of HCl.[1]

4,8-Di-*tert*-butyl-2,2,6,6-tetrahalo-1,5-diazonia-2,6-diboratabicyclo[3.3.0]octa-1^{8},4-dienes, 1−4. General Procedure. A solution of 9.8 g (0.05 mol) of the *tert*-butylmethylketazine in 150 mL of hexane was mixed with 43.5 g (0.01 mol) of a solution containing 15% *n*-BuLi in hexane. The reaction mixture (slurry) was heated at reflux for 4 h and transferred to a dropping funnel in due course. The corresponding trihaloborane (0.1 mol: 14.2 g of $BF_3{\cdot}OEt_2$,11.8 g of BCl_3, 25.0 g of BBr_3, 39.2 g of BI_3) was dissolved in 100 mL of toluene (for $BF_3{\cdot}OEt_2$) or in 100 mL of hexane (all others) and cooled to −50 °C. The dilithiated azine (**A**) was added dropwise with stirring, and the mixture was held at ambient temperature overnight. The remaining solvent was removed under reduced pressure. The yellow-brown residue was sublimed under high vacuum and recrystallized from hexane/dichloromethane (3:1) and gave a yield of 2.2 g (15%) of **1** (X = F), 3.8 g (21%) of **2**, (X = Cl) 4.6 g (17%) of **3** (X = Br), and 4.0 g (11%) of **4**.

4,8-Di-*tert*-butyl-2,2,6,6-tetrafluoro-1,5-diazonia-2,6-diboratabicyclo[3.3.0]octa-1^{8},4-diene (1): colorless crystals; sublp 95 °C (0.01 Torr); mp 108 °C. Anal. Calcd for $C_{12}H_{22}B_2F_4N_2$ (291.93): C, 49.37; H, 9.60. Found: C, 49.66; H, 9.66. MS: EI *m/e* (relative intensity) 277 (3) [$M^+ - CH_3$], 273(5) [$M^+ - F$], 235 (30) [$M^+ - C_4H_9$], 57 (100) [$C_4H_9^+$]. ^{1}H NMR: δ 1.39 (s, Me, 18H), 2.08 (t, $^{3}J_{HF} = 8.4$ Hz,CH_2, 4H). ^{13}C NMR: δ 28.6 (t, C*Me*$_3$, $^{5}J_{HF} = 3.8$ Hz), 39.4 (t, *C*Me$_3$, $^{4}J_{CF} = 0.7$ Hz), 30.0 (br, B*C*), 199.8 (t, $^{3}J_{CF} = 3.1$ Hz, CN). ^{19}F NMR: δ 20.7. ^{11}B NMR: δ 6.7.

4,8-Di-*tert*-butyl-2,2,6,6-tetrachloro-1,5-diazonia-2,6-diboratabicyclo[3.3.0]octa-1^{8},4-diene (2): colorless crystals; sublp 120 °C (0.01 Torr); mp 217 °C. Anal. Calcd for $C_{12}H_{22}B_2Cl_4N_2$ (357.75): C, 40.29; H, 6.20. Found: C, 40.30; H, 6.29. MS: EI *m/e* (relative intensity) 358 (1) [M^+ ($C_{12}H_{22}B_2N_2{}^{35}Cl_3{}^{37}Cl$)], 343 (1) [$M^+ - CH_3$], 321 (15) [$M^+ - Cl$], 301 (20) [$M^+ - C_4H_9$], 285 (40) [$M^+ - {}^{35}Cl - H^{37}Cl$], 57 (100) [$C_4H_9^+$]. ^{1}H NMR: δ 1.60 (s, Me, 18H), 2.95 (s, CH_2, 4H). ^{13}C NMR: δ 29.5 (C*Me*$_3$), 40.9 (*C*Me$_3$), 45.7 (br, BC), 202.0 (CN). ^{11}B NMR: δ 4.1.

2,2,6,6-Tetrabromo-4,8-di-*tert*-butyl-1,5-diazonia-2,6-diboratabicyclo[3.3.0]octa-1^{8},4-diene (3): colorless crystals; sublp 135 °C (0.01 Torr); mp 238 °C. Anal. Calcd for $C_{12}H_{22}B_2Br_4N_2$ (535.56); C, 26.91; H, 4.14. Found: C, 27.05; H, 4.31. MS: EI *m/e* (relative intensity) 455 (25) [M^+ − Br ($C_{12}H_{22}B_2N_2{}^{79}Br_2{}^{81}Br$)], 374 (100) [$M^+ - 2HBr$]. ^{1}H NMR: δ 1.67 (s, Me, 18H), 3.38 (s, CH_2, 4H). ^{13}C NMR: δ 29.8 (C*Me*$_3$), 41.2 (*C*Me$_3$), 50.0 (br, BC), 202.6 (CN). ^{11}B NMR: δ −5.9.

4,8-Di-*tert*-butyl-2,2,6,6-tetraiodo-1,5-diazonia-2,6-diborata-bicyclo[3.3.0]octa-1^{8},4-diene (4): colorless crystals; sublp. 168 °C (0.01 Torr); mp 190 °C. Anal. Calcd for $C_{12}H_{22}B_2I_4N_2$ (723.56): C, 19.92; H, 3.06. Found: C, 20.11; H, 3.07. MS: EI *m/e* (relative intensity) 597 (20) [M^+ − I], 468 (100) [$M^+ - 2$ HI]. ^{1}H NMR: δ 1.75 (s, Me, 18H), 3.93 (s, CH_2, 4H). ^{13}C NMR: δ 30.1 (C*Me*$_3$), 40.9 (*C*Me$_3$), 55.7 (br, BC), 201.9 (CN). ^{11}B NMR: δ −34.2.

4,8-Di-*tert*-butyl-2,6-dihalo-1,5-diaza-2,6-diborabicyclo-[3.3.0]octa-3,7-dienes 5 and 6. General Procedure. Into a solution of 0.01 mol of **2** (3.6 g) and **3** (5.4 g), respectively, in 70 mL of hexane was injected 0.04 mol (4 g) of triethylamine in 15 mL of hexane dropwise through a septum. Magnetic stirring was continued for 2 days at ambient temperature, and the solvent was evaporated at reduced pressure. By sublimation under a high vacuum **5** and **6** were obtained as yellowish solids, in yields of 1.7 g (58%) of **5** and 2.3 g (61%) of **6**.

4,8-Di-*tert*-butyl-2,6-dichloro-1,5-diaza-2,6-diborabicyclo[3.3.0]octa-3,7-diene (5): yellowish solid; sublp. 78 °C (0.01 Torr); mp 144 °C. Anal. Calcd for $C_{12}H_{20}B_2Cl_2N_2$ (284.83): C, 50.60; H, 7.08. Found: C, 50.11; H, 6.98. MS: EI *m/e* (relative intensity) 284 (40) [M^+ ($C_{12}H_{20}B_2{}^{35}Cl_2N_2$)], 269 (100) [$M^+$ − Me]. ^{1}H NMR: δ 1.38 (s, Me, 18H), 5.19 (s, CH, 2H). ^{13}C NMR: δ 29.3 (C*Me*$_3$), 33.7 (*C*Me$_3$), 108 (br, BC), 170.8 (CN). ^{11}B NMR: δ 33.7.

2,6-Dibromo-4,8-di-*tert*-butyl-1,5-diaza-2,6-diborabicyclo[3.3.0]octa-3,7-diene (6): yellowish solid; sublp 95 °C (0.01 Torr); mp 155 °C. Anal. Calcd for $C_{12}H_{20}B_2Br_2N_2$ (373.73): C, 38.57; H, 5.39. Found: C, 38.45; H, 5.34. MS: EI *m/e* (relative intensity) 374 (100) [M^+ ($C_{12}H_{20}B_2{}^{79}Br{}^{81}BrN_2$)], 359 (100) [$M^+$ − Me]. ^{1}H NMR: δ 1.42 (s, Me, 18H), 5.29 (s, CH, 2H). ^{13}C NMR: δ 29.7 (C*Me*$_3$), 33.6 (*C*Me$_3$), 112 (br, BC), 170.4 (CN). ^{11}B NMR: δ 32.1.

5-*tert*-Butyl-3,3-dihalo-2-(1,1-dimethylbutylidene-2)-1,2,3-azaazoniaborata-5-cyclopentenes 7−9. To a solution of 0.1 mol (19.8 g) of *tert*-butylmethylketazine in 150 mL of hexane was added 0.1 mol (43.5 g) of a 15% solution of *n*-BuLi

Table 2. Crystal Data and Structure Refinement Details for 1−4 and 11

	1	2	3	4	11
formula	$C_{12}H_{22}B_2F_4N_2$	$C_{12}H_{22}B_2Cl_4N_2$	$C_{12}H_{22}B_2Br_4N_2$	$C_{12}H_{22}B_2I_4N_2$	$C_{20}H_{38}B_2N_2O_2$
fw	291.94	357.74	535.58	723.54	360.14
temp (K)	153(2)	150(2)	150(2)	150(2)	203(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$C2/c$
a (Å)	5.6886(5)	5.9241(5)	6.151(3)	8.6171(14)	20.753(4)
b (Å)	12.030(2)	18.340(3)	7.955(4)	19.262(5)	9.1072(12)
c (Å)	10.5940(13)	7.8103(10)	9.594(5)	12.972(3)	12.747(2)
α (deg)	90	90	93.38(6)	90	90
β (deg)	92.702(12)	100.416(9)	105.08(3)	108.23(2)	108.059(12)
γ (deg)	90	90	102.39(3)	90	90
vol (Å^3), Z	724.2(2), 2	834.6(2), 2	439.4(4), 1	2045.9(7), 4	2289.4(6), 4
calcd density (Mg m^{-3})	1.339	1.423	2.024	2.350	1.045
abs coeff (mm^{-1})	0.113	0.699	9.150	6.088	0.065
F(000)	308	372	258	1320	792
cryst size (mm)	0.80 × 0.70 × 0.70	1.00 × 1.00 × 0.60	1.00 × 1.00 × 0.30	1.00 × 0.30 × 0.30	0.90 × 0.80 × 0.80
θ range for data collecn (deg)	3.59−25.05	3.67−25.05	3.53−25.01	3.55−25.03	3.77−25.03
limiting indices	$-6 \le h \le 6$	$-7 \le h \le 7$	$-7 \le h \le 7$	$-10 \le h \le 10$	$-24 \le h \le 24$
	$-14 \le k \le 14$	$-21 \le k \le 21$	$-9 \le k \le 9$	$-9 \le k \le 22$	$-10 \le k \le 10$
	$-12 \le l \le 12$	$-9 \le l \le 9$	$-11 \le l \le 11$	$-15 \le l \le 15$	$-8 \le l \le 15$
no. of rflns coll	2570	2944	3108	5673	3418
no. of indep rflns	1285	1472	1554	3615	2024
R(int)	0.0263	0.0392	0.0579	0.0140	0.0241
refinement method	full-matrix least squares on F^2				
no. of data/restraints/ params	1283/0/94	1470/0/94	1554/0/95	3615/0/187	2022/0/124
goodness of fit on F^2	1.0694	1.106	1.059	1.111	1.062
final R indices ($I > 2\sigma(I)$)					
R1	0.0376	0.0249	0.0612	0.0471	0.0445
wR2	0.0988	0.0678	0.1274	0.1099	0.1200
R indices (all data)					
R1	0.0393	0.0261	0.0645	0.0496	0.0478
wR2	0.1024	0.0727	0.1320	0.1122	0.1259
largest diff peak and hole (e Å^{-3})	0.240 and −0.250	0.297 and −0.239	2.288 and −1.262	4.424 and −3.297	0.162 and −0.216

in hexane, and the mixture was heated at reflux for 4 h. The monolithiated ketazine thus formed was added dropwise to the stirred solution of 0.1 mol of the corresponding trihaloborane (14.2 g of $BF_3{\cdot}OEt_2$, 11.75 g of BCl_3, 25.1 g of BBr_3) in 100 mL of toluene in the case of $BF_3{\cdot}OEt_2$ or 100 mL of hexane (all others) at −50 °C. The reaction mixture was warmed to room temperature over several hours. After evaporation of the solvent under reduced pressure the remaining solid residues were sublimed at 0.01 Torr to give yields of 11.0 g (43%) (**7**), 15.0 g (54%) (**8**), and 17.2 g (47%) (**9**).

5-*tert*-Butyl-3,3-difluoro-2-(1,1-dimethylbutylidene-2)-1,2,3-azaazoniaborata-5-cyclopentene (7): colorless solid; sublp 45 °C (0.01 Torr); mp 58 °C. Anal. Calcd for $C_{12}H_{23}BF_2N_2$ (244.13): C, 59.04; H, 9.50. Found: C, 59.07; H: 9.74. MS: EI *m/e* (relative intensity) 244 (1) [M^+], 229 (10) [M^+ − Me], 187 (25) [$M^+ - C_4H_9$], 57 (100) [$C_4H_9^+$]. ^{1}H NMR: δ 1.16 (s, Me, 9H), 1.39 (s, Me, 9H), 1.54 (t, $^3J_{HF}$ = 8.5 Hz, CH_2, 2H), 2.42 (s, Me, 3H). ^{13}C NMR: δ 20.6 (Me), 22.0 (br, BCH_2), 27.8 (C*Me*$_3$), 28.6 (t, C*Me*$_3$, $^5J_{CF}$ = 4.4 Hz), 37.4 (*C*Me$_3$, $^4J_{CF}$ = 1 Hz), 40.1 (t, *C*Me$_3$, $^4J_{CF}$ = 0.8 Hz), 187.1 (CN), 190.0 (t, CN, $^3J_{CF}$ = 4.5 Hz). ^{11}B NMR: δ 9.7 (t, $^1J_{BF}$ = 60 Hz). ^{19}F NMR: δ 21.9.

5-*tert*-Butyl-3,3-dichloro-2-(1,1-dimethylbutylidene-2)-1,2,3-azaazoniaborata-5-cyclopentene (8): colorless solid; sublp 76 °C (0.01 Torr); mp 104 °C. Anal. Calcd for $C_{12}H_{23}BCl_2N_2$ (277.04): C, 52.03; H, 8.37. Found: C, 51.95; H, 8.43. MS: EI *m/e* (relative intensity) 276 (5) [M^+ ($C_{12}H_{23}B^{35}Cl_2N_2$)], 261 (10) [$M^+$ − Me], 241 (40) [M^+ − ^{35}Cl], 57 (100) [$C_4H_9^+$]. ^{1}H NMR: δ 1.20 (s, Me, 9H), 1.39 (s, Me, 9H), 2.22 (s, CH_2, 2H), 2.72 (s, Me, 3H). ^{13}C NMR: δ 21.3 (C*Me*), 27.8 (C*Me*$_3$), 28.0 (C*Me*$_3$), 34.0 (br, BCH_2), 36.8 (*C*Me$_3$), 41.2 (*C*Me$_3$), 188.6 (CN), 189.4 (CN). ^{11}B NMR: δ 7.4.

5-*tert*-Butyl-3,3-dibromo-2-(1,1-dimethylbutylidene-2)-1,2,3-azaazoniaborata-5-cyclopentene (9): colorless solid; sublp 93 °C (0.01 Torr); mp 127 °C. Anal. Calcd for $C_{12}H_{23}BBr_2N_2$ (365.95): C, 39.39; H, 6.33. Found: C, 39.72; H, 6.41. MS: EI *m/e* (relative intensity) 351 (15) [M^+ − Me], 285 (100) [$M^+ - {}^{81}$Br], 204 (50) [$M^+ - {}^{81}Br_2$], 57 (38) [$C_4H_9^+$]. ^{1}H NMR: δ 1.21 (s, Me, 9H), 1.39 (s, Me, 9H), 2.58 (s, CH_2, 2H), 2.79 (s, Me, 3H). ^{13}C NMR: δ 23.2 (Me), 27.8 (C*Me*$_3$), 28.0 (C*Me*$_3$), 36.7 (*C*Me$_3$), 37.0 (br, BCH_2), 41.5 (*C*Me$_3$), 189.4 (CN), 190.4 (CN). ^{11}B NMR: δ −1.3.

4,8-Di-*tert*-butyl-2,6-dimethyl-1,5-diaza-2,6-diborabicyclo[3.3.0]octa-3,7-diene (10). Into 0.01 mol (2.8 g) of **5** dissolved in 70 mL of hexane was injected 0.02 mol (8.7 g) of MeLi (5% solution in Et_2O) through a septum at 0 °C. Magnetic stirring was continued for 24 h at ambient temperature, the solvents were evaporated under reduced pressure, and the residue was sublimed at 60 °C (0.01 Torr) to give 1.3 g (53%) of white solid **10** (mp 96 °C). Anal. Calcd for $C_{14}H_{26}B_2N_2$ (243.99): C, 68.92; H, 10.74. Found: C, 69.01; H, 10.84. MS: EI *m/e* (relative intensity) 244 (85) [M^+], 229 (100) [M^+ − Me]. ^{1}H NMR: δ 0.85 (s, Me, 6H), 1.31 (s, Me, 18H), 5.08 (s, CH, 2H). ^{13}C NMR: δ 3.4 (br, BMe), 30.1 (C*Me*$_3$), 33.0 (*C*Me$_3$), 110.4 (br, BC), 168.8 (CN). ^{11}B NMR: δ 39.0.

4,8-Di-*tert*-butyl-2,6-di-*tert*-butoxy-1,5-diaza-2,6-diborabicyclo[3.3.0]octa-3,7-diene (11). A 0.02 mol amount of *tert*-butyl alcohol dissolved in 50 mL of hexane was reacted with 0.02 mol (8.7 g) of *n*-BuLi (15% solution in hexane) at room temperature and then heated at reflux for 2 h. The clear solution thus obtained was injected through a membrane into a solution of **5** (0.01 mol, 2.8 g) in 50 mL of hexane at 0 °C. Magnetic stirring was continued for 12 h at ambient temperature. After evaporation of the solvent the colorless residue was sublimed at 82 °C (0.01 Torr) to give 2.1 g (57%) of **11** (mp. 244 °C). Anal. Calcd for $C_{20}H_{38}B_2N_2O_2$ (360.15): C, 66.70; H, 10.63. Found: C, 66.48; H, 10.45. MS: EI *m/e* (relative intensity) 360 (60) [M^+], 345 (5) [M^+ − Me], 57 (100) [$C_4H_9^+$]. ^{1}H NMR: δ 1.32 (s, Me, 18H), 1.37 (s, Me, 18H), 4.58 (s, CH, 2H). ^{13}C NMR: δ 29.0 (C*Me*$_3$), 30.6 (OC*Me*$_3$), 33.8, 74.3 (O*C*Me$_3$), 94.8 (br, BC), 170.9 (CN). ^{11}B NMR: δ 27.3.

X-ray Structure Determinations for 1−4 and 11. Data were collected on a Stoe-Siemens diffractometer with monochromated Mo Kα radiation (λ = 71.03 pm). The temperatures

of the measurements are listed in Table 2. The structures were solved by direct methods using SHELXS-90.[7] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms the riding model was used. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g^2P$, with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93.[8] The R values are defined as $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$. Figures 1−3 show 50% probability displacement ellipsoids. Crystal data and structure refinement details are listed in Table 2.

(7) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(8) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.

Acknowledgment. Support of this work by the Fond der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of crystal data, complete fractional coordinates and U values, bond lengths and angles, and anisotropic displacement parameters and fully labeled figures of 50% anisotropic displacement parameters of the structures **1**−**4** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0001164