

Contribution to the Reactivity of *N,N'*-Diaryl-1,4-diazabutadienes Aryl–N=CH–CH=N–Aryl (Aryl = 2,6-Dimethylphenyl; 2,4,6-Trimethylphenyl) Towards Boron Trichloride

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The reaction of Aryl–N=CH–CH=N–Aryl (**3a**: Aryl = 2,6-Me₂C₆H₃; **3b**: Aryl = 2,4,6-Me₃C₆H₂) with 2 equiv. BCl₃ in a toluene/hexane mixture at –50 °C led to an inseparable mixture of borolium salts [Aryl–N^a=CH–CH=N(Aryl)BCl₂(N^a–B)]⁺BCl₄[–] (**4a**: Aryl = 2,6-Me₂C₆H₃; **9a**: Aryl = 2,4,6-Me₃C₆H₂) and [Aryl–N^a=CH–C(Cl)=N(Aryl)BCl₂(N^a–B)]⁺BCl₄[–] (**4b**: Aryl = 2,6-Me₂C₆H₃; **9b**: Aryl = 2,4,6-Me₃C₆H₂) and the bicyclic species [HC^a=N(Aryl)BCl₂N(Aryl)–C^b=(C^a–C^b)]₂ (**5**: Aryl = 2,6-Me₂C₆H₃; **10**: Aryl = 2,4,6-Me₃C₆H₂). Sodium amalgam reduction of borolium salts **4a,b** and **9a,b** afforded inseparable mixtures of the diazaboroles 2,6-Me₂C₆H₃N^aCH=CR–N^b(2,6-Me₂C₆H₃)BCl(N^a–B) (**1**: R = H; **6**: R = Cl) and 2,4,6-Me₃C₆H₂N^aCH=CR–N^b(2,4,6-Me₃C₆H₂)BCl(N^a–B) (**2**: R = H; **11**: R = Cl). In order to obtain pure **1** and **2**, diazabutadienes

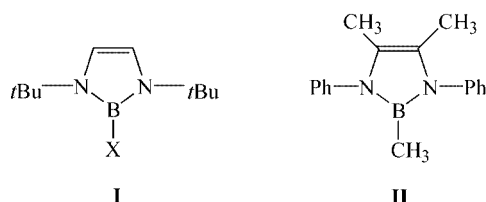
3a and **3b** were slowly combined with 2 equiv. BCl₃ in the same solvents at –78 °C. The acyclic adducts Cl₃BN(Aryl)=CH–CH=N(Aryl)BCl₃ (**7a**: Aryl = 2,6-Me₂C₆H₃; **7b**: Aryl = 2,4,6-Me₃C₆H₂) were reduced with sodium amalgam to furnish the aminoboranes Cl₂BN(Aryl)CH=CH–N(Aryl)BCl₂ (**8**: Aryl = 2,6-Me₂C₆H₃; **12**: Aryl = 2,4,6-Me₃C₆H₂). Stirring solutions of **8** and **12** in the presence of CaH₂ cleanly gave the diazaboroles **1** and **2**, respectively. The novel compounds were characterized by elemental analyses and ¹H-, ¹¹B-, ¹³C NMR and mass spectra. The molecular structures of **1**, **4a**, **5** and **8** were elucidated by single X-ray diffraction analyses.

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Introduction

The synthesis and reactivity of 1,3-dialkyl-2-halo-2,3-dihydro-1*H*-1,3,2-diazaboroles **I** as well as their molecular structures have been thoroughly investigated and documented in the literature.^[1–12] More recently, the electrochemical and optophysical properties of such compounds have attracted our interest. The electrochemical oxidation of 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaboroles by cyclic voltammetry displays clean but irreversible waves, and the oxidation potentials *E*_{ox,1/2} vary strongly with the substitution pattern at the boron atom.^[13] Diazaboroles that are functionalized at the boron center by thienyl-, dithienyl- or biphenyl groups are highly luminescent, emitting bright blue light upon UV irradiation.^[14,15] With respect to this, we planned to extend the scope of our diazaboroles to representatives with aryl groups at both ring nitrogen atoms.

In an early paper, we described the preparation of heterocycle **II** by treatment of diacetyldianil with methylboron dibromide and subsequent reduction of the obtained borolium salt with an excess of sodium amalgam.^[3]



Later this route was followed to synthesize the 2-chloro-1,3-dixylyl-2,3-dihydro-1*H*-1,3,2-diazaborole (**1**).^[10] An alternative route to **1** and to the corresponding 2-bromo derivative was based on the reduction of the corresponding diazabutadiene with lithium metal and the cyclocondensation of the dilithiated species with BX₃ (X = Cl, Br).^[10] In this contribution we report on the reaction of *N,N'*-diaryl-1,4-diazabutadienes with BCl₃. It was found that the reactivity of the *N,N'*-diaryl-1,4-diazabutadienes towards BCl₃ is far less straightforward than that of *N,N'*-di-*tert*-butyl-1,4-diazabutadiene.

Results and Discussion

For the synthesis of **1**, it was obvious to follow the procedure that we previously elaborated.^[10] In only one instance did the combination of diazabutadiene **3a** with two molar equivalents of boron trichloride in a mixture of toluene and hexane at –50 °C and subsequent stirring for 15 h

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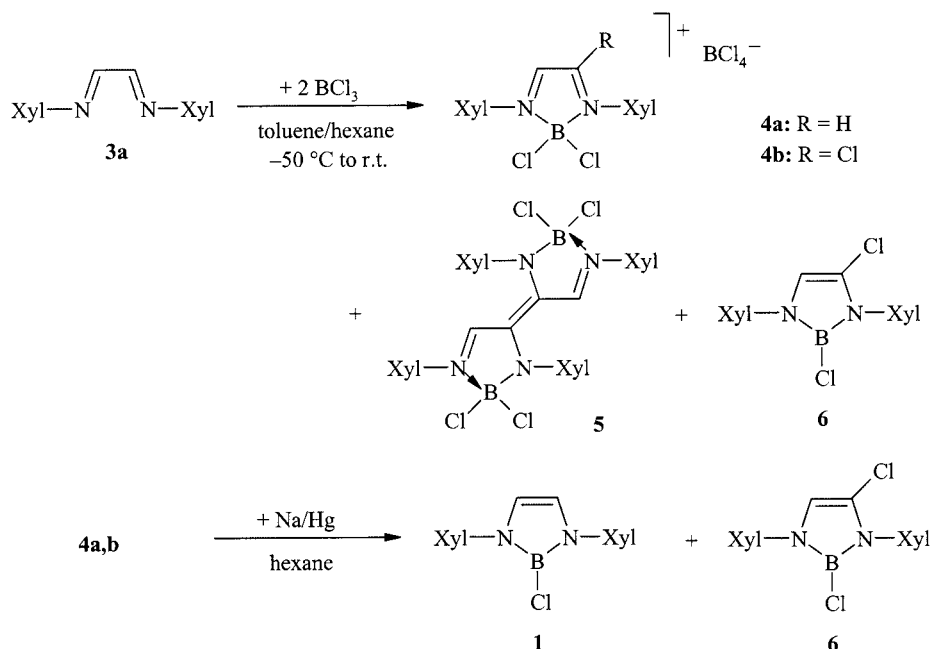
at 20 °C lead to the precipitation of the burgundy-red borolium salt **4a** in about 70% yield. In all the other cases, however, a black solid precipitated, which was identified as an inseparable mixture of **4a** and its analogue **4b** with a chlorine substituent at a ring carbon atom (about 30% yield). After filtration, the mother liquor was placed for 14 d at +4 °C, and compound **5** separated as deep red crystals in 18% yield. When the supernatant solution was decanted and concentrated to one-third of its volume, impure diazaborole **6** was isolated after storing this solution for 2 d at –4 °C. Recrystallization from pentane led to a few crystals of pure compound **6**, which is chlorinated at the C=C double bond.

The usual reduction of the mixture of **4a** and **4b** with sodium amalgam in hexane afforded an inseparable mixture of the diazaboroles **1** and **6**. A 1/6 ratio of 10:1 was determined by ¹H NMR spectroscopy. Although the reaction of

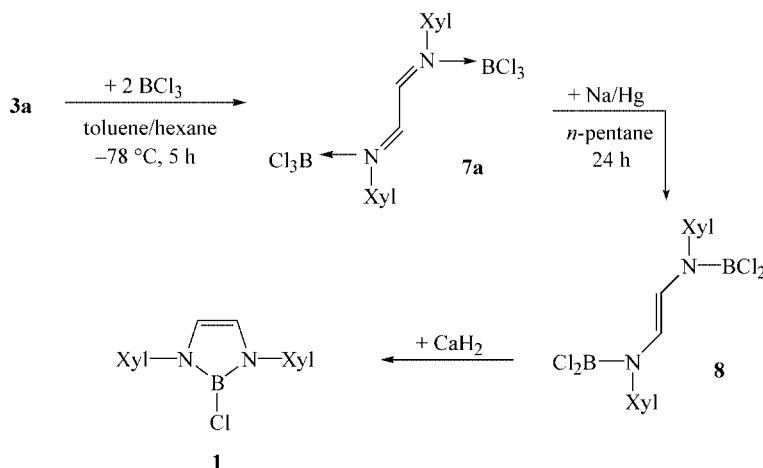
pure salt **4a** gave a sample of pure **1** in one case, this synthetic pathway was discarded because of its poor reproducibility (Scheme 1).

Slow combination (4–5 h) of a toluene solution of **3a** with a cold (–78 °C) solution of BCl₃ in pentane in a molar ratio of 1:2 gave a precipitate of the red-brown adduct **7a** (60% yield). A slurry of this material in *n*-pentane was treated with sodium amalgam at 20 °C. From the supernatant solution, the acyclic doubly borylated (*E*)-*N,N'*-diaminoethene **8** was isolated as colorless crystals in about 70% yield. Stirring a solution of **8** in pentane in the presence of CaH₂ led to cyclization and the formation of diazaborole **1** (46% yield) (Scheme 2).

The reaction of diazabutadiene **3b** with 2 equiv. BCl₃ at –50 °C in a toluene/hexane mixture was performed analogously. A 1:1 mixture of the borolium salts **9a** (R = H) and **9b** (R = Cl) precipitated as a black solid (about 20% yield).



Scheme 1.



Scheme 2.

The mother liquor was concentrated and stored at +4 °C for 14 d, after which product **10** separated as deep green crystals in 14% yield (Scheme 3).

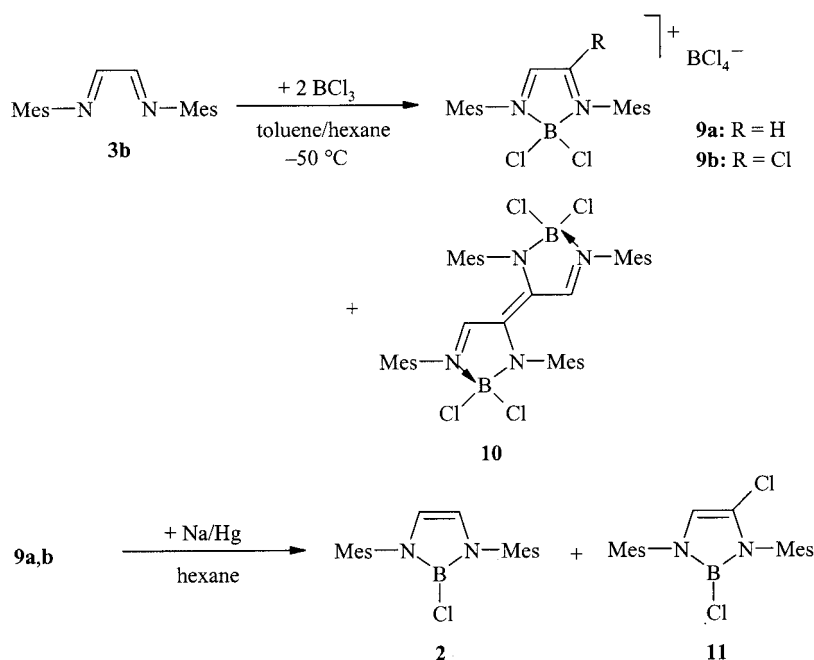
In the ^{11}B NMR spectrum of the mother liquor, a small singlet at $\delta = 21.8$ ppm indicates small amounts of a 1,3,2-diazaborole. Its isolation, however, failed. The reduction of **9a,b** with sodium amalgam led to an inseparable mixture of the diazaboroles **2** and **11**. The generation of pure **2** first required the preparation of the violet adduct **7b** from the reaction of **3b** and 2 equiv. BCl_3 at -78 °C for 4–5 h (70% yield). The sodium amalgam reduction of **7b** afforded the acyclic aminoborane **12**, which upon treatment with CaH_2 cyclized to **2** in 54% yield (Scheme 4).

In order to suppress undesired side reactions at the carbon atom of the heterocycle, diacetyl[bis(2,6-dimethylphenylimine)] **13** was subjected to reaction with 2 equiv. BCl_3 in *n*-hexane. The green borolium salt **14** (yield 63%) was re-

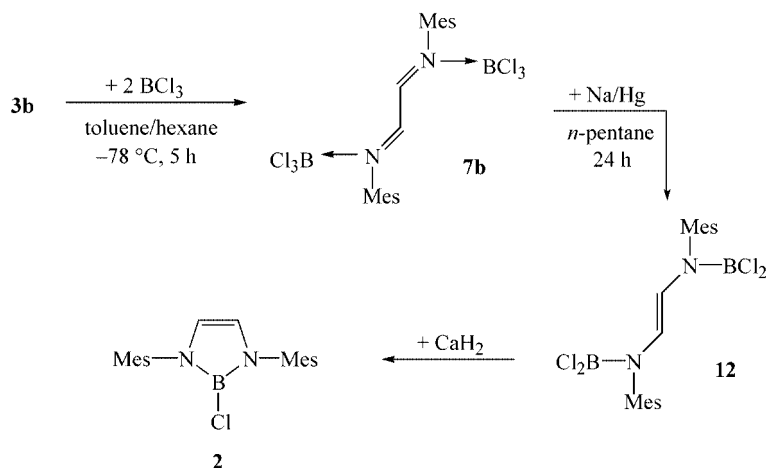
duced with sodium amalgam to furnish, near quantitatively, the expected diazaborole **15** (Scheme 5).

Because of the pronounced thermolability of the 2-chloro-1,3,2-diazaborole **15**, this compound was converted immediately into the more stable 2-cyano-1,3,2-diazaborole **16** by reaction with silver cyanide in acetonitrile (Scheme 5).

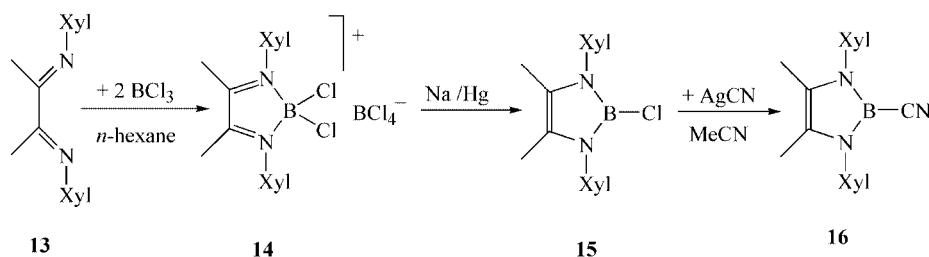
The ^{11}B NMR spectra of the borolium salts show singlets ($\delta = 7.7$ ppm) in the typical region for tetracoordinate boron atoms. For the tetracoordinate boron atoms in the binuclear compounds **5** and **10**, singlets are observed at $\delta = 8.6$ and 8.5 ppm, respectively. The 2-chloroboroles **1**, **2**, **6** and **11** give rise to ^{11}B NMR signals at $\delta = 21.1$ –21.8 ppm. An influence of the Cl substituent at the C=C bond is not visible. In the ^{11}B NMR spectra of 2-cyanoborole **16**, the ^{11}B resonance appears as a singlet at $\delta = 13.5$ ppm. The ^{11}B NMR resonances of the acyclic aminodichloroboranes **8** and **12** are at $\delta = 32.5$ ppm. The signals for the ring protons



Scheme 3.



Scheme 4.



Scheme 5.

in the diazaboroles **1**, **2**, **6** and **11** are observed in the range from 5.51 to 5.93 ppm. The protons at the 1,6-diazahexatriene backbone of **5** and **10** are assigned as singlets at $\delta = 6.85$ ppm. In the (*E*)-configured diaminoethenes **7** and **12**, the protons at the double bond give rise to singlets at $\delta = 6.40$ ppm.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of diazaboroles **1** and **2**, singlets at $\delta = 117.7$ and 117.8 ppm, respectively, are assigned to the identical carbon atoms of the C=C group of the rings. The corresponding carbon atoms in the chlorinated derivative **6** give rise to two singlets at $\delta(^{13}\text{C}) = 113.7$ and 126.8 ppm. The carbon atoms of the N_2C_4 backbone of **5** and **10** are attributed to singlets at $\delta = 161.3$ and 170.3 ppm, respectively.

X-ray Structural Analysis of **1**

Single crystals of **1** were grown from the crude reaction mixture at +4 °C. The molecular structure of **1** (Figure 1, Table 1) features a planar 1,3,2-diazaborole ring with two almost orthogonally oriented *ortho*-xylyl substituents at the

nitrogen atoms (interplanar angle between the heterocycle and arene ring $\varphi = 82.2^\circ$). A C_2 axis bisects the molecule along the B(1)–Cl(1) vector. The bond length B(1)–Cl(1) [1.768(2) Å] is close to the sum of the covalent radii of bo-

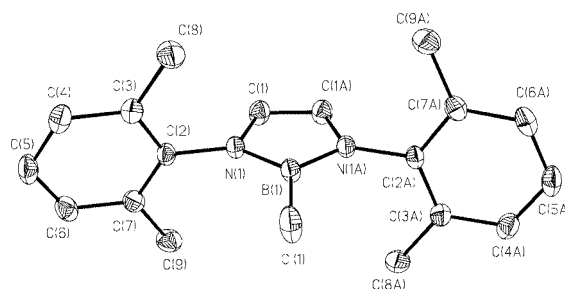


Figure 1. Molecular structure of **1** in the crystal; H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: B(1)–Cl(1) 1.768(2), B(1)–N(1) 1.419(1), N(1)–C(1) 1.401(2), C(1)–C(1A) 1.349(2), N(1)–C(2) 1.433(2); N(1)–B(1)–N(1A) 106.9(1), N(1)–B(1)–Cl(1) 126.6(1), B(1)–N(1)–C(1) 107.2(1), B(1)–N(1)–C(2) 130.3(1), C(1)–N(1)–C(2) 122.5(1), N(1)–C(1)–C(1A) 109.4(1).

Table 1. Crystal data and collection parameters.

	1	4a	5	8
Empirical formula	$\text{C}_{18}\text{H}_{20}\text{BClN}_2$	$\text{C}_{18}\text{H}_{20}\text{B}_2\text{Cl}_6 \cdot 0.5\text{C}_7\text{H}_8$	$\text{C}_{36}\text{H}_{38}\text{B}_2\text{Cl}_4\text{N}_4$	$\text{C}_{18}\text{H}_{20}\text{B}_2\text{Cl}_4\text{N}_2$
M_r [mg mol $^{-1}$]	310.62	544.75	690.12	427.78
Crystal dimensions [mm]	$0.30 \times 0.12 \times 0.06$	$0.24 \times 0.17 \times 0.04$	$0.15 \times 0.15 \times 0.14$	$0.30 \times 0.30 \times 0.24$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$
a [Å]	14.5730(4)	26.9130(6)	10.3100(3)	7.54300(10)
b [Å]	7.4850(2)	10.7970(2)	14.8210(3)	14.4950(2)
c [Å]	16.6840(4)	17.6110(3)	11.4650(4)	10.1860(2)
β [°]	114.9510(16)	90.8770(12)	93.6320(14)	109.3190(10)
V [Å 3]	1650.02(7)	5116.80(17)	1748.39(9)	1050.98(3)
Z	4	8	2	2
ρ_{calcd} [mg m $^{-3}$]	1.250	1.414	1.311	1.352
μ [mm $^{-1}$]	0.229	0.685	0.371	0.568
$F(000)$	656	2232	720	440
θ [°]	3–30	3–27.5	3–27.5	3–30
Collected reflections	22930	49724	21040	28834
Unique reflections	2417	5848	4002	3061
$R(\text{int})$	0.043	0.052	0.040	0.030
Refined parameters	141	293	262	120
Gof	1.035	1.020	1.017	1.045
R_F [$I > 2\sigma(I)$]	0.0402	0.0311	0.0354	0.0261
wR_F^2 [all data]	0.1125	0.0788	0.0923	0.0708
$\Delta\rho_{\text{max/min}}$ [e Å $^{-3}$]	0.281/–0.352	0.279/–0.248	0.274/–0.265	0.327/–0.310
Remarks	–	disorder of toluene on an inversion centre	disorder of hydrogens at C(17) and C(18)	–
CCDC number	616595	616596	616597	616598

ron (0.81 Å) and chlorine (0.99 Å)^[16] and compares well with the corresponding value in solid B₂Cl₄ (1.75 Å).^[17] Atomic distances and valence angles within the diazaborole ring are in good agreement with the corresponding data for XylN^a-CH=CH-N^b(Xyl)BI(N^a-B)^[10] and need no particular discussion at this point.

X-ray Structural Analysis of 4a

Red plates of **4a** suitable for an X-ray diffraction study (Table 1) were grown from the toluene/hexane mother liquor after removal of solid **4a**. The analysis features a planar diazaborolium cation [sum of bond angles 539.3°(1)], in addition to a tetrachloroborate anion (Figure 2).

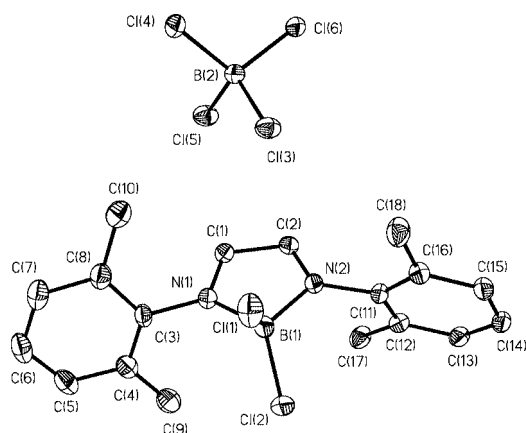
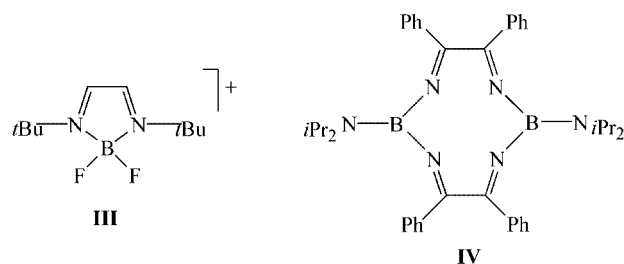


Figure 2. Molecular structure of **4a** in the crystal; H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: B(1)–Cl(1) 1.813(2), B(1)–Cl(2) 1.791(2), B(2)–Cl(3) 1.872(2), B(2)–Cl(4) 1.830(2), B(2)–Cl(5) 1.844(2), B(2)–Cl(6) 1.866(2), B(1)–N(1) 1.615(2), B(1)–N(2) 1.594(2), N(1)=C(1) 1.276(2), N(1)–C(3) 1.462(2), N(2)=C(2) 1.279(2), N(2)–C(11) 1.464(2), C(1)–C(2) 1.477(2); N(1)–B(1)–N(2) 95.8(1), B(1)–N(1)–C(1) 110.7(1), B(1)–N(1)–C(3) 127.4(1), B(1)–N(2)–C(2) 111.5(1), B(1)–N(2)–C(11) 125.9(1), C(1)–N(1)–C(3) 121.2(1), C(2)–N(2)–C(11) 121.7(1), N(1)–C(1)–C(2) 110.7(1), N(2)–C(2)–C(1) 110.6(1), Cl(1)–B(1)–Cl(2) 113.3(1), B(2)–Cl(3–6) 107.4(1)–111.2(1).

There are no bonding contacts between the cation and the anion. The bond lengths B(1)–Cl(1) [1.813(2) Å] and B(1)–Cl(2) [1.791(2) Å] are slightly shorter than the B–Cl bonds in BCl₄[–], which range from 1.830(2) to 1.872(2) Å. The boron–nitrogen bond lengths [B(1)–N(1) 1.615(2) Å, B(1)–N(2) 1.594(2) Å] slightly exceed the average value for the B–N single bond (1.59 Å) found in aminoboranes^[18] and compare well with the corresponding bond lengths in cation **III** [1.607(3) and 1.611(3) Å].^[19]

In 1,3,2-diazaboroles B–N bond lengths range from 1.40 to 1.45 Å. The endocyclic C–N bond lengths [C(1)–N(1) 1.276(2) Å, C(2)–N(2) 1.279(2) Å] are characteristic for double bonds and compare well with those in the cyclic ketiminoborane **IV** [1.273(3)–1.277(2) Å].^[20]



The carbon–carbon bond length in the cation [1.477(2) Å] indicates a bond order of unity, whereas in diazaboroles, double bonds [1.362(8) Å in **1**] are typical. In comparison with **1** [106.9(4)°], the angle at the boron atom is compressed to 95.8(1)°, whereas the endocyclic angles B(1)–N(1)–C(1) [110.7(1)°], B(1)–N(1)–C(2) [111.5(1)°], N(1)–C(1)–C(2) [110.7(1)°] and N(2)–C(2)–C(1) [110.6(1)°] are slightly more obtuse than that in **1** [107.2(1), 109.4(1)°].

X-ray Structural Analysis of 5

The X-ray analysis (Figure 3, Table 1) discloses a molecule in which two planar BN₂C₂ rings (sum of angles 539.7°) are fused by an elongated C(1)–C(1A) multiple bond [1.398(3) Å] (C=C_{calcd.} = 1.33 Å) with an inversion center in the middle of the bond. The bond C(1)–N(1) [1.387(2) Å] is between the double bond N(2)=C(2) [1.300(2) Å] on the one hand and the single bonds N(1)–C(3) [1.440(2) Å] and N(2)–C(11) [1.447(2) Å] on the other hand. The distance C(1)–C(2) [1.437(2) Å] corresponds to a single bond.

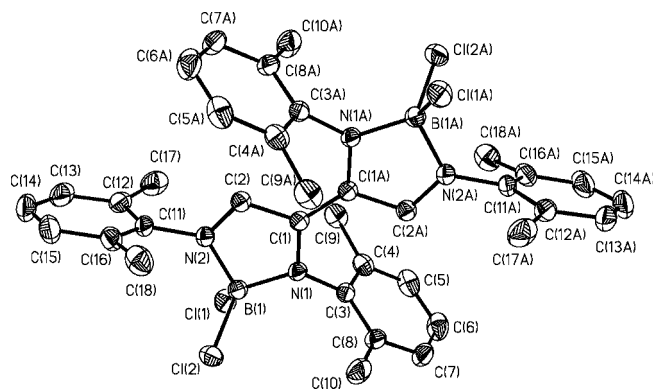
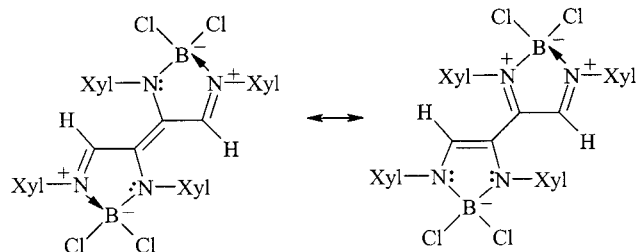


Figure 3. Molecular structure of **5** in the crystal. Selected bond lengths [Å] and angles [°]: B(1)–Cl(1) 1.840(2), B(1)–Cl(2) 1.878(2), B(1)–N(1) 1.518(2), B(1)–N(2) 1.576(2), N(1)–C(1) 1.387(2), N(1)–C(3) 1.440(2), N(2)=C(2) 1.300(2), N(2)–C(11) 1.447(2), C(1)–C(2) 1.437(2), C(1)=C(1A) 1.398(3); Cl(1)–B(1)–Cl(2) 106.6(1), N(1)–B(1)–N(2) 98.5(1), B(1)–N(1)–C(1) 111.4(1), B(1)–N(2)–C(2) 110.2(1), B(1)–N(1)–C(3) 125.4(1), B(1)–N(2)–C(11) 129.1(1), N(1)–C(1)–C(2) 107.0(1), N(1)–C(1)–C(1A) 128.7(2), N(2)–C(2)–C(1) 112.6(1), C(2)–N(2)–C(11) 120.3(1).

The boron–nitrogen bond B(1)–N(1) [1.518(2) Å] reflects a single bond between a tetracoordinate boron atom and an sp²-hybridized nitrogen atom. It is markedly shorter than the coordinative bond B(1)–N(2) [1.576(2) Å]. The B–Cl bond lengths [1.840(2) and 1.878(2) Å] are longer than

those in ring **4** [1.791(2) and 1.813(2) Å] and compare with the B–Cl bond lengths in the BCl_4^- ion.

The shortening of bond N(1)–C(1) and the elongation of bond C(1)=C(1A) are consistent with an extensive delocalization of charge as indicated by the two limiting formulae (Scheme 6).



Scheme 6.

The xylyl rings are oriented in a near perpendicular fashion to the plane defined by the two heterocycles, with interplanar angles of $\varphi = 99.3^\circ$ at N(1) and $\varphi = 88.1^\circ$ at N(2). The angle B(1)–N(1)–N(2) [98.5(1)°] is markedly more acute than those in 1,3,2-diazaboroles [cf. 106.9(1) in **1**]. The angles B(1)–N(1)–C(1) [111.4(1)°] and B(1)–N(2)–C(2) [110.2(1)°] compare with those in the chloroborolium cation of **4a** [110.7(1) and 111.5(1)°] and are slightly more obtuse than that in diazaborole **1** [107.2(1)°].

X-ray Structural Analysis of **8**

Single crystals of **8**, suitable for an X-ray structural study, were grown from a toluene/hexane mixture at 4 °C. The analysis shows the features of a planar 2,5-diaza-1,6-dibora-hexa-1,3,5-triene with an inversion center in the middle of the C=C bond (Figure 4, Table 1). The planes of the two xylyl substituents at the nitrogen atoms are perpendicularly oriented to the plane of the chain ($\varphi = 85.8^\circ$). The chlorine atoms at the boron are located in the plane of the molecule and feature single bonds with lengths of 1.766(1) and 1.767(1) Å. The B–N bond length of 1.395(1) Å is consistent with a double bond, as is the central bond length C(1)–C(1A) of 1.333(2) Å. The distances N(1)–C(1) [1.422(1) Å] and N(1)–C(2) [1.451(1) Å] reflect single bonds.

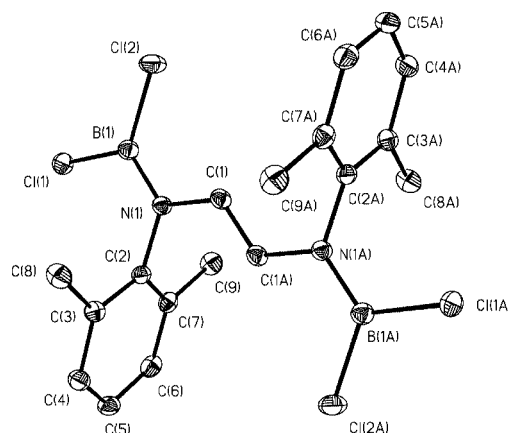
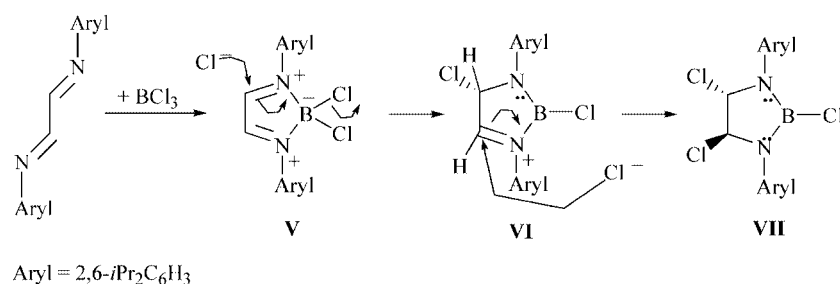


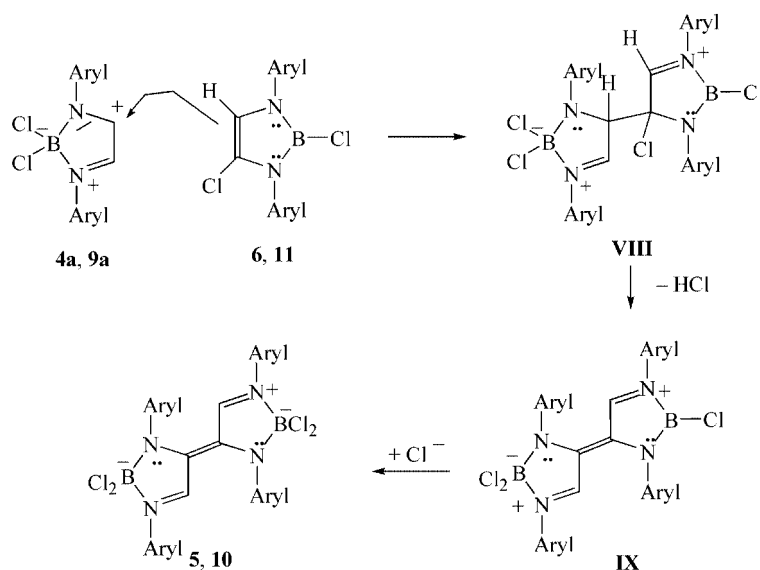
Figure 4. Molecular structure of **8** in the crystal; H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: B(1)–Cl(1) 1.766(1), B(1)–Cl(2) 1.767(1), B(1)–N(1) 1.395(1), N(1)–C(1) 1.422(1), N(1)–C(2) 1.451(1), C(1)=C(1A) 1.333(2); Cl(1)–B(1)–Cl(2) 118.1(1), Cl(1)–B(1)–N(1) 120.2(8), Cl(2)–B(1)–N(1) 121.7(1), B(1)–N(1)–C(1) 123.2(1), B(1)–N(1)–C(2) 121.1(1), C(1)–N(1)–C(2) 115.7(1), N(1)–C(1)–C(1A) 123.2(1).

In going from diazaboroles with various alkyl substituents at the ring atoms to xylyl and mesityl units, the generation of diazaboroles with one chlorine atom at the C=C bond was unexpected. In the case of compound **15** in which the double bond is substituted by two methyl groups, such a behavior could not be observed. Here, a recent paper on the reactivity of BCl_3 towards glyoxal[bis(2,6-diisopropylphenylimine)] by Mair et al. seems relevant.^[21] He postulated the initial formation of a borolium salt **V**, the cation of which undergoes a twofold nucleophilic attack by chloride ions to eventually yield the trichlorinated diazaborolidine **VII** (Scheme 7). If, in our case, transient diazaborolidines are dehydrochlorinated by a base, diazaboroles such as **6** and **11** would be the products. It is conceivable that the carbon chlorination of diaryldiazabutadienes is favored by bulky arene groups.

The initial step in the formation of **5** and **10** is most likely the electrophilic attack of one immonium carbon atom of **4a** or **9a** at the C=C bond of **6** or **11** to give intermediate **VIII**. Elimination of HCl leads to cation **IX**, which finally adds a chloride ion at the tricoordinate boron atom to yield products **5** or **10** (Scheme 8).



Scheme 7.



Scheme 8.

Conclusions

The extension of methodologies for the synthesis of 1,3-dialkyl-2,3-dihydro-1H-1,3,2-diazaboroles to the construction of 1,3-diaryl-2,3-dihydro-1H-1,3,2-diazaboroles is not straightforward. The direct combination of *N,N'*-diaryl-1,4-diazabutadienes with 2 equiv. boron trichloride and the reduction of the obtained borolium salts by sodium amalgam invariably afforded mixtures of singly and doubly chlorinated products. Thus, a detour to pure 2-chloro-1,3-diaryl-2,3-dihydro-1H-1,3,2-diazaboroles was developed. Reaction of the components at -78°C gave a 1:2 adduct, the reduction of which furnished aminoboranes $\text{Cl}_2\text{BN}(\text{Aryl})\text{CH}=\text{CHN}(\text{Aryl})\text{BCl}_2$. Cyclization of these molecules to 2-chloro-1,3,2-diazaboroles was effected by solid calcium hydride.

Experimental Section

General: All experiments were performed under dry, oxygen-free dinitrogen by using standard Schlenk techniques. Solvents were dried with appropriate drying agents and freshly distilled under N_2 before use. The following compounds were prepared according to literature procedures: 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{CHCH}=\text{NC}_6\text{H}_3\text{Me}_2$ -2,6 (**3a**)^[22], 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{N}=\text{CHCH}=\text{NC}_6\text{H}_2\text{Me}_3$ -2,4,6 (**3b**)^[23] and 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{N}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NC}_6\text{H}_3\text{Me}_2$ -2,6 (**13**)^[24,25]. ^1H , ^{11}B and ^{13}C NMR spectra were recorded at ambient temperature in C_6D_6 except for **5** and **10**, which were investigated in CD_2Cl_2 with a Bruker AM Avance DRX 500 instrument (^1H : 500.13 MHz; ^{11}B : 160.46 MHz; ^{13}C : 125.75 MHz). The spectra were referenced versus SiMe_4 (^1H , ^{13}C) and $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B) standards. Boron trichloride, glyoxal, 2,6-dimethylaniline and 2,4,6-trimethylaniline were purchased commercially.

Reaction of Glyoxal-bis(2,6-dimethylphenylimine) (3a) with Boron Trichloride: A solution of **3a** (18.2 g, 69.0 mmol) in a mixture of toluene (300 mL) and hexane (100 mL) was added over 4.5 h to a chilled solution (-50°C) of boron trichloride (16.4 g, 140.0 mmol) in hexane (250 mL). After stirring at -50°C for another hour, it

was warmed up to ambient temperature and stirring was continued for 15 h. A microcrystalline solid was filtered off, washed with hexane and dried in vacuo to give 11.0 g of a mixture of borolium salts **4a** and **4b**. The filtrate was stored for 14 d at $+4^\circ\text{C}$, and dark red crystals of **5** (4.2 g, 18%) separated. In the supernatant liquid, the presence of a 1,3,2-diazaborole was evidenced by ^{11}B NMR spectroscopy ($\delta = 21.6$ ppm). The filtrate was concentrated to 30% of its volume and stored for 2 d at -4°C , from which crystals of impure **6** were formed. Recrystallization from pentane yielded a few crystals of pure **6**.

In only one case did the reaction of **3a** and BCl_3 cleanly afford the burgundy red borolium salt **4a** in about 70% yield. A slurry of the borolium salts **4a** and **4b** (11.0 g) in a mixture of toluene (150 mL) and hexane (300 mL) was treated with sodium amalgam (300 g of a 1% alloy) and vigorously stirred for 20 h. The solution was decanted, filtered, and the solvents evaporated to dryness to give 4.8 g of an inseparable mixture of **1** and **6**. If the solution, after having been separated from mercury, was kept for 14 d at $+4^\circ\text{C}$, a few crystals of pure **1**^[10] could be separated.

1: ^1H NMR: $\delta = 2.17$ (s, 12 H, CH_3), 5.85 (s, 2 H, $\text{HC}=\text{N}$), 6.99 (m, 6 H, aryl-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 18.1$ (s, CH_3), 117.7 (s, $\text{HC}=\text{N}$), 127.3 (s, *p*-aryl-C), 135.8 (s, *o*-aryl-C), 139.9 (s, *i*-aryl-C) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR: $\delta = 21.1$ (s) ppm. EI-MS: m/z (%) = 310 (100) [M^+].

6: ^1H NMR: $\delta = 2.11$ (s, 6 H, CH_3), 2.16 (s, 6 H, CH_3), 5.75 (s, 1 H, $\text{HC}=\text{N}$), 6.98 (m, 6 H, aryl-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 18.02$ (s, CH_3), 18.05 (s, CH_3), 113.7 (s, $\text{HC}=\text{N}$), 126.6 (s, $\text{ClC}=\text{N}$), 127.2 (s, *p*-aryl-C), 127.7 (s, *p*-aryl-C), 127.9 (s, *m*-aryl-C), 129.1 (s, *m*-aryl-C), 135.5 (s, *o*-aryl-C), 136.7 (s, *o*-aryl-C), 138.9 (s, *i*-aryl-C), 138.5 (s, *i*-aryl-C) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR: $\delta = 21.6$ (s) ppm. EI-MS: m/z (%) = 344.1 (100) [M^+], 309.1 (79) [$\text{M}^+ - \text{Cl}$]. $\text{C}_{18}\text{H}_{19}\text{BCl}_2\text{N}_2$ (345.06): calcd. C 62.65, H 5.55, N 8.12; found C 62.67, H 5.44, N 8.15.

5: ^1H NMR: $\delta = 2.24$ (s, 12 H, CH_3), 2.45 (s, 12 H, CH_3), 6.85 (s, 2 H, $\text{HC}=\text{N}$), 7.15 (m, 12 H, aryl-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.1$ (s, CH_3), 19.7 (s, CH_3), 128.9 (s, *p*-aryl-C), 129.2 (s, *p*-aryl-C), 130.9 (s, *m*-aryl-C), 133.7 (s, *o*-aryl-C), 136.8 (s, *o*-aryl-C), 137.7 (s, *i*-aryl-C), 139.1 (s, *i*-aryl-C), 161.3 (s, $\text{HC}=\text{N}$) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR: $\delta = 8.6$ (s) ppm. EI-MS: m/z (%) = 688.2 (2) [M^+], 652.2 (100)

[M⁺ – Cl], 618.2 (82) [M⁺ – 2 Cl]. C₃₆H₃₈B₂Cl₄N₄ (690.12): calcd. C 62.65, H 5.55, N 8.12; found C 62.71, H 5.38, N 8.09. Because of the poor solubility, no reliable NMR spectra of the borolium salts **4a,b** were obtained.

(E)-Cl₂B(*o*-Xyl)N–CH=CH–N(*o*-Xyl)BCl₂ (8): A solution of **3a** (5.29 g, 20.0 mmol) in toluene (100 mL) was added dropwise over 4–5 h to a chilled solution (–78 °C) of BCl₃ (4.67 g, 40 mmol) in pentane (75 mL). Immediately after the addition, the red-brown precipitate of the adduct **7a** was collected by filtration and dried at 10^{–3} bar. Reduction of the adduct was effected by treatment with sodium amalgam (100 g of a 1% alloy) in pentane (150 mL) over 24 h. The supernatant liquid was separated and concentrated to about 100 mL. Storage overnight at +4 °C afforded colorless crystals of **8** (5.13 g, 60%). ¹H NMR: δ = 1.99 (s, 12 H, CH₃), 6.40 (s, 2 H, NCH=), 6.92 (m, 6 H, aryl-H) ppm. ¹³C{¹H} NMR: δ = 17.3 (s, CH₃), 120.5 (s, NCH=), 128.3 (s, *p*-aryl-C), 129.3 (s, *m*-aryl-C), 134.6 (s, *o*-aryl-C), 139.3 (s, *i*-aryl-C) ppm. ¹¹B{¹H} NMR: δ = 32.6 (s) ppm. EI-MS: *m/z* (%) = 428.0 (100) [M⁺], 395.2 (6) [M⁺ – Cl], 310.1 (73) [M⁺ – BCl₃]. C₁₈H₂₀B₂Cl₄N₂ (427.79): calcd. C 50.54, H 4.71, N 6.55; found C 50.26, H 4.82, N 6.43. Because of the low solubility of **7a**, no useful NMR spectra were obtained.

Cyclization of 8 to 1: A sample of **8** (0.50 g, 1.2 mmol) was dissolved in hexane (50 mL). CaH₂ (0.05 g) was added, and the slurry was stirred at ambient temperature for 48 h. It was filtered, and the filtrate concentrated to 10 mL and stored at –4 °C, after which crystalline **1** (0.175 g, 46%) separated.

Reaction of Glyoxal-bis(2,4,6-trimethylphenylimine) (3b) with Boron Trichloride: Analogously to the reaction of **3a** with BCl₃, a solution of **3b** (14.55 g, 50.0 mmol) in a mixture of toluene (200 mL) and hexane (50 mL) was combined with a chilled solution (–50 °C) of BCl₃ (11.8 g, 100.0 mmol) in hexane (250 mL) over a period of 4.5 h. Stirring was continued for 1 h at –50 °C and then for 15 h at 20 °C. The microcrystalline black precipitate was filtered off and dried (5.6 g of a mixture of salts **9a** and **9b**). Storage of the mother liquor for 2 weeks at +4 °C afforded dark green crystals of **10** (2.7 g, 14%). Sodium amalgam (200 g of a 1% alloy) was added to a slurry of the borolium salts (5.6 g) in a mixture of toluene (100 mL) and hexane (200 mL). The mixture was vigorously stirred for 20 h. The organic phase was decanted, and the solvents were removed in vacuo. An inseparable 4:1 mixture (2.4 g) of **2** and **11** as a white powder was obtained.

10: ¹H NMR: δ = 2.17 (s, 18 H, CH₃), 2.29 (s, 6 H, CH₃), 2.36 (s, 12 H, CH₃), 6.85 (s, 2 H, =CHN), 6.93 (s, 4 H, aryl-H), 6.98 (s, 4 H, aryl-H) ppm. ¹³C{¹H} NMR: δ = 18.6 (s, CH₃), 20.5 (s, CH₃), 20.6 (s, CH₃), 129.4, 130.1, 131.2, 133.0, 134.2, 135.1, 136.0, 136.3, 138.6, 139.0 (10 s, aryl-C), 161.2 (s, =CHN) ppm. ¹¹B{¹H} NMR: δ = 8.5 (s) ppm. EI-MS: *m/z* (%) = 744.2 (2) [M⁺], 710.3 (100) [M⁺ – Cl], 674.4 (66) [M⁺ – 2 Cl]. C₄₀H₄₆B₂Cl₄N₄ (746.27): calcd. C 64.32, H 6.21, N 7.51; found C 64.30, H 6.11, N 7.52.

2 and 11: ¹¹B{¹H} NMR: δ = 21.8 (s) ppm. This mixture was not analyzed further. Because of the poor solubility, no reliable NMR spectra of the borolium salts **9a,b** were obtained.

(E)-Cl₂B(Mes)N–CH=CH–N(Mes)BCl₂ (12): By analogy to the preparation of **8**, compounds **3b** (5.84 g, 20.0 mmol) and BCl₃ (4.67 g, 40 mmol) were combined in a toluene/pentane mixture at –78 °C over 4–5 h. A violet precipitate was filtered off and dried at 10^{–3} mbar. Sodium amalgam reduction of this solid (150 g, 1% Na/Hg) was effected in pentane (150 mL) for 24 h. Concentration of the organic phase to about 100 mL and storage of the liquid overnight at +4 °C afforded colorless crystals of **12** (5.93 g, 65%). ¹H NMR: δ = 2.03 (s, 12 H, *o*-CH₃), 2.04 (s, 6 H, *p*-CH₃), 6.50 [s, 2

H, NC(H)=C], 6.75 (s, 4 H, aryl-H) ppm. ¹³C{¹H} NMR: δ = 17.3 (s, *o*-CH₃), 20.9 (s, *p*-CH₃), 120.9 (s, CH=CH), 130.1 (s, *m*-aryl-C), 134.2 (s, *o*-aryl-C), 136.9 (s, *p*-aryl-C), 137.8 (s, *i*-aryl-C) ppm. ¹¹B{¹H} NMR: δ = 32.6 (s) ppm. EI-MS: *m/z* (%) = 338 (100) [M⁺ – BCl₃]. C₂₀H₂₄B₂Cl₄N₂ (455.85): calcd. C 52.69, H 5.33, N 6.14; found C 52.63, H 5.35, N 6.13.

Cyclization of 12 to 2: A mixture of **12** (0.50 g, 1.1 mmol), CaH₂ (0.05 g) and hexane (50 mL) was stirred at 25 °C for 48 h and then filtered, and the filtrate was concentrated to 10 mL. Crystallization at –4 °C afforded pure **2** (0.20 g, 54%). ¹H NMR: δ = 2.13 (s, 6 H, *p*-aryl-CH₃), 2.19 (s, 12 H, *o*-aryl-CH₃), 5.92 [s, 2 H, NC(H)=C], 6.79 (m, 4 H, aryl-H) ppm. ¹³C{¹H} NMR: δ = 18.0 (s, *o*-aryl-CH₃), 20.9 (s, *p*-aryl-CH₃), 117.8 (s, N–CH), 129.2 (s, *m*-aryl-C), 135.3 (s, *o*-aryl-C), 136.4 (s, *p*-aryl-C), 137.4 (s, *i*-aryl-C) ppm. ¹¹B{¹H} NMR: δ = 21.9 (s) ppm. EI-MS: *m/z* (%) = 338.2 (100) [M⁺]. C₂₀H₂₄BClN₂ (338.68): calcd. C 70.93, H 7.14, N 8.27; found C 70.68, H 7.20, N 8.16.

Xyl–N^aC(CH₃)=C(CH₃)–N^b(Xyl)BCN(N^a–B) (16): A solution of **13** (6.80 g, 23.0 mmol) in hexane (250 mL) was added dropwise over 4.5 h to a chilled solution (–50 °C) of BCl₃ (5.39 g, 46.0 mmol) in hexane (250 mL). Stirring was continued for 1 h at –50 °C and 15 h at ambient temperature. Green borolium salt **14** (7.6 g, 63%) was filtered off and dried at 10^{–1} bar. The slurry of the salt in hexane (350 mL) was reduced with sodium amalgam (150 g of a 1% alloy, 20 h). Decanting of the organic phase was followed by evaporation to dryness to afford crude **15** (4.5 g, 98.6%) as a light grey powder. A sample of solid AgCN (3.2 g, 24.0 mmol) was added to a solution of **15** in acetonitrile (350 mL), and the mixture was stirred for 20 h at 20 °C. It was filtered, and the filtrate was concentrated, after which **16** (3.10 g, 41.0%) was obtained. ¹H NMR: δ = 1.44 [s, 6 H, =C(CH₃)N], 2.03 (s, 12 H, aryl-CH₃), 6.99 (m, 6 H, aryl-H) ppm. ¹³C{¹H} NMR: δ = 9.8 [s, =C(CH₃)N], 17.9 (s, aryl-CH₃), 121.2 [s, C(CH₃)=C(CH₃)], 127.6 (s, *p*-aryl-C), 128.2 (s, BCN), 128.5 (s, *m*-aryl-C), 135.6 (s, *o*-aryl-C), 138.1 (s, *i*-aryl-C) ppm. ¹¹B{¹H} NMR: δ = 13.5 (s) ppm. EI-MS: *m/z* (%) = 329.2 (100) [M⁺], 314.2 (12) [M⁺ – CH₃]. C₂₁H₂₄BN₃ (329.24): calcd. C 76.61, H 7.35, N 12.76; found C 76.59, H 7.42, N 12.65.

15: ¹H NMR: δ = 1.57 [s, 6 H, =C(CH₃)N], 2.15 (s, 12 H, aryl-CH₃), 7.02 (s, 6 H, aryl-H) ppm. ¹³C{¹H} NMR: δ = 10.2 [s, =C(CH₃)N], 18.2 (s, aryl-CH₃), 118.9 [s, =C(CH₃)N], 127.2 (s, *p*-aryl-C), 128.3 (s, *m*-aryl-C), 136.6 (s, *o*-aryl-C), 138.6 (s, *i*-aryl-C) ppm. ¹¹B{¹H} = 21.3 (s) ppm. EI-MS: *m/z* = 338.2 [M⁺].

X-ray Structural Analyses: Crystal data were measured on a Nonius Kappa CCD-diffractometer and are given in Table 1. CCDC-616595 (**1**), -616596 (**4a**), -616597 (**5**) and -616598 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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