Preparation, Structure and Reactivity of 2-Chloro-, 2-Fluoro- and 2-Iodo-2,3-dihydro-1*H*-1,3,2-diazaboroles☆

Lothar Weber*[a], Eckhard Dobbert[a], Roland Boese[b], Michael T. Kirchner[b], and Dieter Bläser[b]

Fakultät für Chemie der Universität Bielefeld[a],
Universitätsstraße 25, D-33615 Bielefeld, Germany,
Fax: (internat.) +49(0)5201-106-6146
E-mail: lothar.weber@uni-bielefeld.de

Institut für Anorganische Chemie der Universität-Gesamthochschule Essen[b],
Universitätsstraße 5−7, D-45117 Essen, Germany

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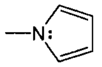
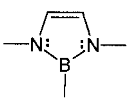
A series of differently substituted 2-chloro-, 2-fluoro- and 2-iodo-2,3-dihydro-1*H*-1,3,2-diazaboroles have been prepared by various methods. 1,3-Di-*tert*-butyl-2-fluoro-2,3-dihydro-1*H*-1,3,2-diazaborole (**3a**), 1,3-di-*tert*-butyl-2-chloro-2,3-dihydro-1*H*-1,3,2-diazaborole (**5a**), 1,3-bis(2,6-dimethylphenyl)-2-chloro-2,3-dihydro-1*H*-1,3,2-diazaborole (**5b**), 2-chloro-4,5-dimethyl-1,3-dineopentyl-2,3-dihydro-1*H*-1,3,2-diazaborole (**5c**), and 1,3-di-*tert*-butyl-2-iodo-2,3-dihydro-1*H*-1,3,2-diazaborole (**6a**) were formed from the corresponding lithiated Z-1,2-diaminoethenes, by treatment with $BF_3 \cdot OEt_2$, BCl_3, or BI_3 in *n*-hexane. Compounds **3a**, **5a**, and **5b** are also available by sodium amalgam reduction of the adduct (tBu)(BF_3)N=CH–CH=N(BF_3)(tBu) (**2a**), and the borolium salts [RN^a=CH–CH=N^b(R)BCl_2]X (N^a–B) (**4a**: R = tBu, X = BCl_4 and **4b**: R = 2,6-$Me_2C_6H_2$, X = Cl) respectively. The iodo derivative (2,6-$Me_2C_6H_2$)–N^a–CH=CH–N^b(2,6-$Me_2C_6H_2$)BI (N^a–B) (**6b**) was synthesized in a redox reaction between the 1,4-diazabutadiene **1b** and BI_3. The novel compounds were characterized by ^{1}H-, ^{11}B- and ^{13}C-NMR spectroscopy, as well as by an X-ray structure analysis of **6b**.

The formal replacement of a C=C fragment in pyrrole **I** by a B−N unit affords 2,3-dihydro-1*H*-1,3,2-diazaboroles **II**.



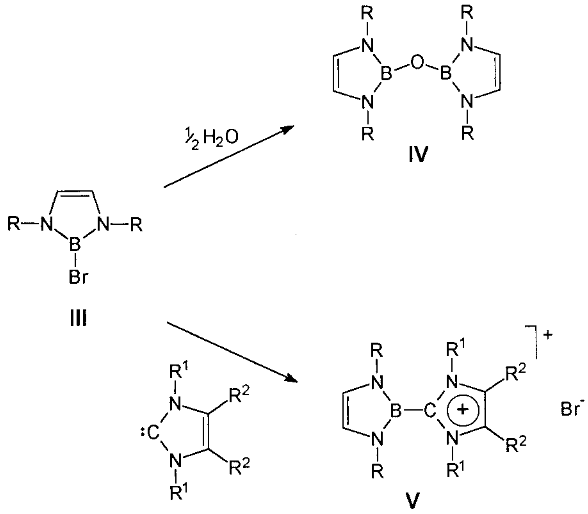
I



II

The first reports on heterocycles of the type **II** date back to the early 1970s[1][2]. Meanwhile, a series of papers concerned with the synthesis, structure, and bonding of such molecules has been published.[3][4] Apart from the synthesis of $[Cr(CO)_3]$ complexes with η^5-1,3,2-diazaborole ligands[5][6] and the cleavage of the N−Si bond in *N*-silylated derivatives by metal amides or alcoholates to yield the corresponding alkali metal 1,3,2-diazaborolides,[7] the chemistry of heterocycles **II** has remained largely unexplored. The lack of functional groups in the 2,3-dihydro-1*H*-1,3,2-diazaboroles examined to date may account for this situation.

Recently we launched a program for the synthesis of 2-halo-2,3-dihydro-1*H*-1,3,2-diazaboroles as precursors for a variety of chemical transformations. In a first account we described the preparation of 2-bromo-2,3-dihydro-1*H*-1,3,2-diazaboroles **III** and their reactions with water and imidazol-2-ylidenes. The resulting salts such as **V** contain the first borylated carbenium ions.[8]



III

IV

V

The intention of the work described herein is to provide efficient syntheses for 2-fluoro-, 2-chloro- and 2-iodo-2,3-dihydro-1*H*-1,3,2-diazaboroles.

Results and Discussion

For the preparation of 2-bromo-2,3-dihydro-1*H*-1,3,2-diazaboroles, as well as the corresponding fluoro, chloro and iodo derivatives, two synthetic approaches are generally available. The first pathway [Scheme 1 (a)], involves the gen-

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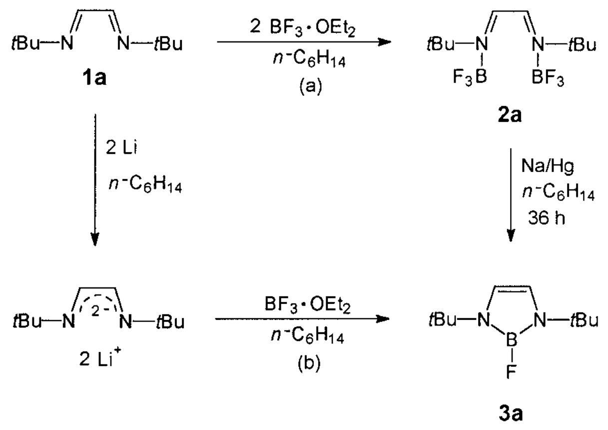
eration of the bis(trifluoroborane) adduct **2a**, by the combination of 1,4-diazabutadiene **1a** with two molar equivalents of $BF_3 \cdot Et_2O$ in *n*-hexane.

Scheme 1

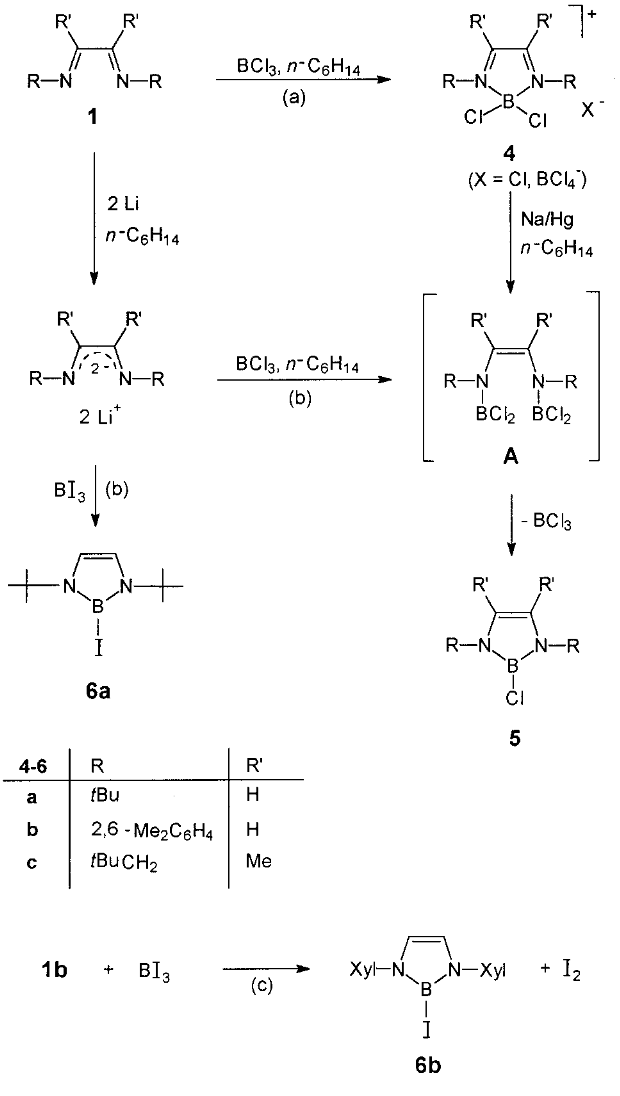


The adduct was obtained as a yellow amorphous solid in 74% yield. Its $^{11}B\{^1H\}$-NMR spectrum in CD_3CN shows only one singlet (at $\delta = 0.4$) for the two chemically and magnetically equivalent boron atoms. Similarly, only one resonance was observed in the $^{19}F\{^1H\}$-NMR spectrum of **2a** (at $\delta = 73.0$) for the six fluorine atoms. The synthesis of 2-fluoro-1,3,2-diazaborole (**3a**) was accomplished by the reduction of **2a** with an excess of sodium amalgam in an *n*-hexane slurry (Scheme 1). After 36 h, the ^{11}B-NMR spectrum only showed the resonance for **3a** at $\delta^{11}B = 20.8$. The crude yellow **3a** was purified by fractional condensation at 40°C and 0.01 Torr to give colorless crystals. At temperatures above 40°C the 2-fluoro-1,3,2-diazaborole decomposed with liberation of **1a**. Compound **3a** is soluble in common aprotic organic solvents. In solution complete decomposition of the heterocycle occurred within 2 days.

A second approach to **3a** [Scheme 1 (b)] made use of the reduction of **1a** by two equivalents of lithium in hexane, prior to the condensation with $BF_3 \cdot Et_2O$.

In contrast to the symmetrical adduct **2a**, the treatment of **1a** with two molar equivalents of BCl_3 in *n*-hexane at −30°C afforded the colorless amorphous borolium tetrachloroborate **4a** in 71% yield. Accordingly, the ^{11}B-NMR spectrum of the salt gave rise to two singlets for the BCl_4^- ion[9] and the boron atom of the ring at $\delta = 1.6$ and 7.7 respectively. The analogous borolium chloride, described in the literature, gave a boron resonance at $\delta = 7.2$ (in $CDCl_3$).[3] The reduction of **4a** with sodium amalgam in *n*-hexane led to the formation of 2-chloro-1,3,2-diazaborole (**5a**) as a colorless solid after sublimation (40−60°C, 0.01 Torr, 91%). The course of the reduction was followed by ^{11}B-NMR spectroscopy. After 5 h, the spectrum of the supernatant solution showed signals at $\delta = 32.3$ and 21.0 in a ratio of 2:1. A small resonance at $\delta = 47.0$ was assigned to BCl_3. After 14 h, the spectrum was dominated by two intense singlets at $\delta = 21.1$ and 47.0, in addition to a weak singlet at $\delta = 31.8$. This observation may be rationalized by the initial formation of the intermediate acyclic aminoborane $(tBu)N(BCl_2){-}CH{=}CH{-}N(BCl_2)(tBu)$ (**A**)[10] which subsequently disproportionated into **5a** and BCl_3 (Scheme 2). The synthesis of **5a** can also be effected by the reaction of the lithiated diazabutadiene with BCl_3 [Scheme 2 (b)].

Scheme 2



4-6	R	R'
a	tBu	H
b	2,6-$Me_2C_6H_4$	H
c	$tBuCH_2$	Me

The reaction of 1,4-diazabutadiene **1b** with an equimolar amount of BCl_3 in a hexane/dichloromethane mixture, led to the violet borolium chloride **4b** (38%) and the corresponding black tetrachloroborate **4b′** (7%). The ^{11}B-NMR spectra of the salts displayed signals at $\delta = 7.2$ for **4b**, and at $\delta = 7.7$ and 1.5 for **4b′**.

Reduction of **4b** by an excess of sodium amalgam in *n*-hexane afforded the 2-chloro-1,3,2-diazaborole **5b** (55% yield). Treatment of 1,4-diazabutadiene **1b** with lithium sand and condensation of the lithium derivative with BCl_3 gave 1,3,2-diazaborole **5b** (53%) as the final product after 3 d. After 1 h, the ^{11}B-NMR spectrum of the yellow solution showed a resonance at $\delta = 32.5$ for an intermediate. Minor resonances at $\delta = 22.0$ and 47.0 were attributed to **5b** and BCl_3, respectively. After 14 h, a spectrum of the same sample displayed only the singlets of **5b** and BCl_3. In an additional experiment, the reaction mixture was filtered after 1 h of stirring at ambient temperature and the concentrated hexane solution was stored overnight at -80°C to give a tan precipitate. The ^{11}B-NMR spectrum of the tan precipitate in $CDCl_3$ showed a major resonance at $\delta = 32.6$ and an impurity of **5b** at $\delta = 21.8$. The ^{1}H-NMR spectrum of the tan solid in C_6D_6 was dominated by singlets at $\delta = 1.99$ (s, 12 H, CH_3), 6.40 (s, 2 H, N=CH), and 6.93 (m, 6 H, aryl-H), in addition to the resonances of **5b**. A 2:1 ratio of the intermediate to **5b** was determined. Based on the spectroscopic data and its good solubility in non-polar solvents, we attributed the formula $(Xyl)(Cl_2B)N-CH=CH-N(BCl_2)(Xyl)$ to this intermediate (Scheme 2).

Lithium reduction of 1,4-diazabutadiene **1c** for 10 d in *n*-hexane, and the subsequent quenching of the lithium derivative with BCl_3 furnished 1,3,2-diazaborole **5c** as a dark brown oil, which slowly solidified to a tan wax (60%).

The synthesis of the 2-iodo-1,3,2-diazaborole (tBu)-$N^a-CH=CH-N^b$(tBu)BI(N^a-B) (**6a**) was achieved by allowing Li_2[(tBu)NCH=CHN(tBu)] to react with an equimolar amount of BI_3 to give a colorless, light-sensitive oil (83%), which completely decomposed within 5 h at room temperature. In contrast, 2-iodo-1,3,2-diazaborole **6b**, accessible by the redox reaction between **1b** and BI_3, was sublimed at 380°C/0.01 Torr without significant decomposition.

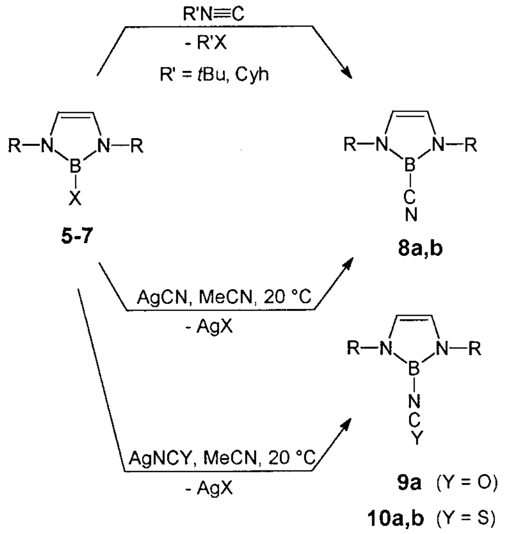
As previously shown, 2-bromo-2,3-dihydro-1*H*-1,3,2-diazaborole (**7a**) can be brought to reaction with imidazolylidenes to give borylated imidazolium salts (eq. 1). In the light of these data, an analogous synthesis of borylated nitrilium salts seemed possible, by reaction of compounds **5**−**7** with organic isocyanides.

Treatment of **5a**, **6a**, and **7a** with an equimolar amount of *tert*-butyl isocyanide in *n*-hexane, led to the formation of the 2-cyano-1,3,2-diazaborole (**8a**). The expected nitrilium salt could not be detected spectroscopically. The formation of *tert*-butylbromide as a byproduct was proven by ^{1}H-NMR spectroscopy ($\delta = 1.78$) and by comparison with an authentic sample.

The corresponding reaction of **7a** with cyclohexyl isocyanide afforded **8a** in 38% yield after 5 days. No intermediates were observed spectroscopically. Similarly, **5b** and **6b** were converted into **8b** by *tert*-butyl isocyanide in 70% and 55% yield, respectively (Scheme 3).

No reaction was observed between 2-halo-1,3,2-diazaboroles **5**−**7** and $2,6\text{-}Me_2C_6H_3N{\equiv}C$. The cyano compound **8a** was also synthesized in high yield by treatment of the diazaboroles **5a** or **7a** with a slight excess of silver cyanide in acetonitrile at room temperature. The 2-bromo compound was found to be more reactive than the 2-chloro analogue. Similarly, compound **8b** was obtained by treatment of **6b** with AgCN over a period of 2 days (79%).

Scheme 3



	X	R
5	Cl	
6	I	
7	Br	
a		*t*Bu
b		*o*-Xyl

In line with the synthetic approach to isocyanatoboranes and isothiocyanatoboranes devised by Lappert et al.,[11] diazaborole **5a** was converted by silver cyanate in acetonitrile into the isocyanato diazaborole **9a**, which was isolated after 30 min as a colorless thermolabile oil in 78% yield. The analogous reaction between **7a** and AgOCN to afford **9a** was complete after 5 min (83%). The corresponding isothiocyanato diazaborole **10a**, resulted from the reaction of **5a** or **7a** with AgSCN under similar conditions. Again, the reactivity of **7a** exceeded that of **5a**. Derivative **10b** was synthesized from **6b**, **5b**, or $(2,6\text{-}Me_2C_6H_3)N^a-CH=CH-N^b(2,6\text{-}Me_2C_6H_3)BBr(N^a-B)$ (**7b**) (78−93% yield). The reactivity of the 2-halo-1,3,2-diazaboroles was found to be: **7b** > **5b** > **6b**.

It was not possible to unambiguously identify the B−X stretching frequencies in the IR-spectra of the 2-halo-1,3,2-diazaboroles **3**, **5**, **6**, and **7**. In the IR spectra (KBr) of **8a** and **8b**, weak bands at $\nu = 2207$ and 2218 cm^{-1} are attributed to the stretching frequency of the C≡N group. In the IR spectra of $MeN^a-CH_2-CH_2-N^b(Me)BCN(N^a-B)$[12] and $MeN^a-N^b=N^c-N^d(Me)BCN(N^a-B)$[13] the ν(CN) mode was observed as weak bands at 2225 and 2239 cm^{-1}, respectively. A very intense band in the IR spectrum of **9a** at $\nu = 2317$ cm^{-1} was assigned to the asymmetric stretching frequency of the isocyanato group, which is consistent with the data for compounds $(R_2N)_2B-N=C=O$ [$\nu_{as}(NCO) = 2290 \pm 15$ cm^{-1}],[11c] and the IR spectrum of $Me_2B-N=C=O$ [$\nu_{as}(NCO) = 2285$ cm^{-1} vs].[14] These frequencies also underline the presence of an isocyanatoborane $R_2BN=C=O$, and disfavor the isomeric cyanatoborane structure $R_2BOC{\equiv}N$. Similar arguments support an isothiocyanatoborane structure in the 1,3,2-diazaboroles **10a** and **10b**, where very strong bands at 2121 and 2114 cm^{-1}, respectively, are assigned to the ν_{as}(NCS) mode. Intense bands at 871 and 856 cm^{-1} are due to the symmetric stretching frequency of the NCS group. The ν_{as}(NCS) of a series of isothiocyanatoboranes occurs in the range 2089 ± 31 cm^{-1}.[11]

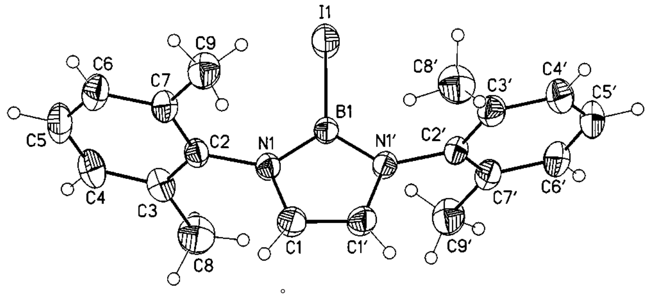
The ^{11}B{^{1}H}-NMR spectra of the halo- and pseudohalodiazaboroles display an increased shielding as follows: **3a** ≈ **5a** (δ = 20.2) > **7a** (16.2) > **9a** ≈ **10a** (14.7) > **8a** (12.0) > **6a** (6.5). Similarly, the ^{11}B-NMR signals of **5b**, **7b**, **10b**, **8b**, and **6b** range from δ = 21.1 to 11.8. The significant highfield shift of **8a** relative to the saturated analogue Me-N^{a}−CH$_2$CH$_2$−N^{b}(Me)BCN*(N*^{a}−B) (δ = 21.0)[12] sustains the heteroaromatic nature of the rings under discussion. The ring protons in **3a** and **5a**−**10a** are observed at δ = 5.99−6.40, whereas in the dixylyl-substituted derivatives **5b**−**8b** and **10b**, singlets at δ = 5.71−5.99 are assigned to these protons. In the ^{13}C{^{1}H}-NMR spectra of **3a** and **5a**−**10a**, singlets at δ = 109.9−114.6 were assigned to the C=C group of the rings. The respective ^{13}C-nuclei of **5b**−**8b**, and **10b** gave rise to resonances at δ = 117.2−120.0.

X-ray Structural Analysis of 6b

The molecular structure of **6b** (Figure 1) features a planar 1,3,2-diazaborole ring with two nearly orthogonally oriented *ortho*-xylyl substituents at the nitrogen atoms (interplanar angle between the heterocycle and an arene ring ψ = 85.6°). A C_2 axis bisects the molecule along the B(1)−I(1) vector. The bond length B(1)−I(1) [2.119(5) A] is close to the sum of the covalent radii of boron (0.81 A) and iodine (1.33 A)[15] and compares well with the atomic distance between the tricoordinate boron and an iodine atom in the dimer of IB^{a}−C(Et)=C(Et)−B^{b}(I)S*(B*^{a}−S) [2.13(2) A][16]. B−I bond lengths involving sp^{2}-hybridized boron atoms range from 2.10(4) A in BI$_3$[17] to 2.237(6) A in the triborane [(Me$_2$N)(I)B]$_2$BNMe$_2$[18]. Atomic distances and valence angles within the diazaborole ring are in good agreement with the respective data for EtN^{a}−CH=CH−N^{b}(Et)BMe*(N*^{a}−B).[4] In **6b**, the B−N bond length [1.418(4) A] indicates multiple-bond character. In a series of diazaboroles the B−N bond lengths range from 1.407(3) to 1.450(2) A. The atomic distance C(1)−C(1′) [1.362(8) A], and the N−C(sp^{2}) bond length [1.401(4) A] also indicate multiple bonding. For the N(sp^{2})−C(sp^{2}) single bond, N(1)−C(2) bond lenghths of 1.438(4) A were measured. The endocyclic angles in **6b**: N(1)−B(1)−N(1)′ [106.9(4)°], B(1)−N(1)−C(1) [107.5(3)°], and N(1)−C(1)−C(1)′ [109.1(2)°] resemble those in the borylimidazolium cation **V** [107.1(6), 105.9(4), and 110.5(3)°, respectively].[1] This also applies to the exocyclic angle N(1)−B(1)−I(1) [126.6(2)°] in **6b**, and the corresponding angle N(1)−B(1)−C(6) in **V** [126.5(3)°].

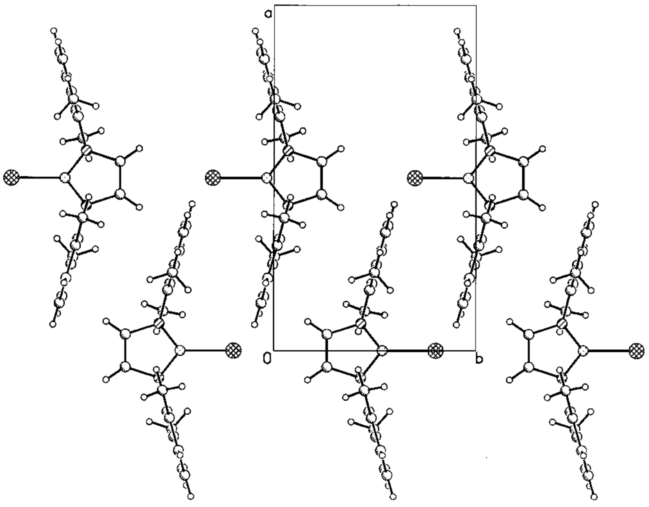
The packing of **6b** shows some interesting features. The molecules are arranged in a pattern with the iodine atoms pointing to the centers of the carbon−carbon double bonds (distance from the iodine atom to the center of the bond 3.17 A), such that each iodine atom is in contact with two hydrogen atoms (distance from iodine to hydrogen 3.093 A, with a normalized 1.08 A distance for C−H). This linkage produces chains of molecules with adjacent chains running in opposite directions, and with the phenyl groups interlocked (Figure 2).

Figure 1. Crystal molecular structure of **6b**[a]



[a] Selected bond lengths [A] and bond angles [°]: B(1)−I(1) 2.119(5), B(1)−N(1) 1.418(4), N(1)−C(1) 1.401(4), C(1)−C(1′) 1.362(8), N(1)−C(2) 1.438(4); N(1)−B(1)-N(1′) 106.9(4), N(1)−B(1)−I(1) 126.6(2), B(1)−N(1)−C(1) 107.5(3), B(1)−N(1)−C(2) 130.0(3), C(1)−N(1)−C(2) 122.5(3), N(1)−C(1)−C(1′) 109.1(2). [B(1), N(1),C(1)−C(1′)−N(1′)−C(2), C(3), C(4), C(5), C(6), C(7)] 85.6.

Figure 2. View of the crystal structure of **6b** along the *c* axis; depicted are two adjacent chains with three molecules each



In the layer depicted in Figure 2, one of the methyl groups is oriented so that a hydrogen atom points towards the aromatic ring system of the adjacent chain. A cheletropic intermolecular interaction of iodine with two hydrogen atoms bonded to sp^{2}-carbon atoms is expected to be mostly electrostatic in nature, and seems to dominate the molecular packing of **6b**. An analysis of specific packing motifs is possible with the help of a statistical approach which involves plots of intermolecular distances and angles for groups of crystals structures that contain the motif under investigation (scatter-plots). The more frequent certain short contacts with reasonable angles occur, the more likely it is that this represents a "supramolecular synthon".[19] Therefore we performed a search in the CSD,[20] which revealed 5703 structures that possess: (1) a *cis*-1,2-dihydro group, attached to a double or aromatic bond of two carbon atoms, and (2) an uncharged halogen (not fluorine) atom with a single bond. Amongst these, 426 structures and 1079 fragments have an intermolecular distance from the halogen atom to the hydrogen atoms of less than the sum of van der Waals radii plus 1 A (H···Cl 3.95 A; H···Br 4.05 A; H···I 4.18 A). A characteristic cheletropic interaction is evident from the polar scatter diagrams, given in Figures 3 and 4. Figure 3 represents the positions of the halogen atoms relative to the aromatic carbon−carbon double bond, with this bond at the equator, and the *cis*-oriented hydrogen atoms situated in the northern hemisphere. An accumulation of structures at a distance of 4 A from the center of the aromatic C=C bond and perpendicular to this bond axis demonstrates that the halogen atoms prefer to be located in the same manner as we found for **6b**. In our case, the intermolecular distance with iodine, and even with bromine, is amongst the smallest found for all the given fragments.

Figure 3. Polar scatter plot of the distance from the halogen to the center of the carbon−carbon double bond, the angle between the carbon−carbon double bond, and the projection of the intermolecular vector to the plane for 1079 fragments in the Cambridge Data Base that contain the halogen···HC=CH motif as defined

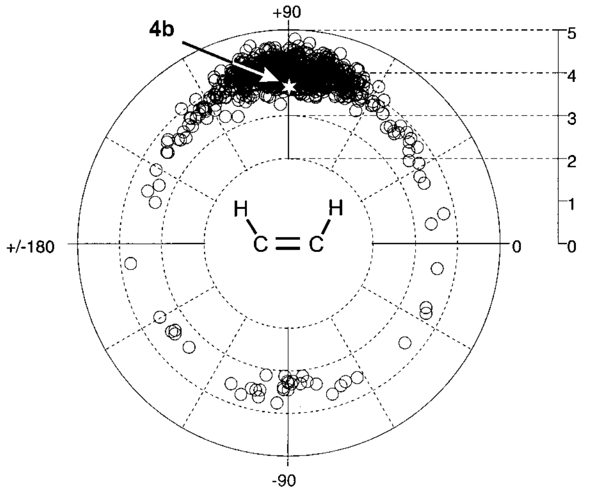
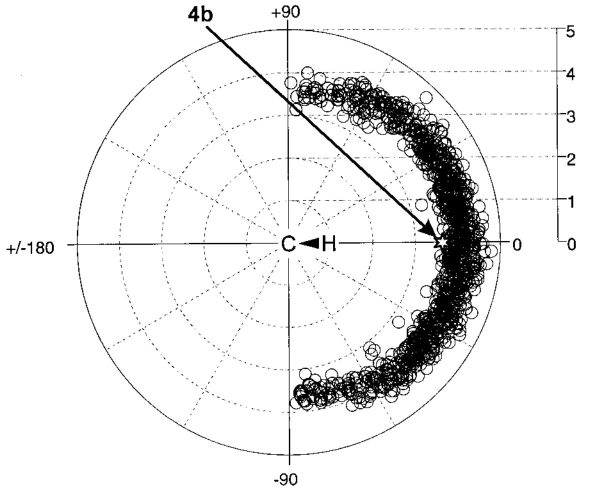


Figure 4. Polar scatter plot of the distance from the halogen to the center of the carbon−carbon double bond and the angle between the molecular plane and the intermolecular vector (section perpendicular to Figure 3)



The distribution of halogen positions below and above the one in Figure 3 is shown in Figure 4. Here the equator of the pole scatter diagram intercepts the center of the double (aromatic) C=C bond, with the hydrogen atoms below and above the plane of the diagram. An accumulation, albeit not so pronounced, of halogen atoms in the plane of the carbon and hydrogen atoms (at 0°) again demonstrates the cheletropic character of the interaction in **6b**. The angles used in Figures 3 and 4 were obtained from the *LP2 method in Quest3D[21], where the positions of one hydrogen atom, the nearest carbon atom, the center of the carbon−carbon bond, and the halogen atom were used as the parameters. The scatter plot was produced by the distance between the halogen atom and the center of the carbon−carbon double bond. Equivalent scatter plots produced for iodine, bromine, and chlorine are available as supporting information on the WWW or from the author.

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Experimental Section

General: All manipulations were performed under dry argon. Solvents were rigorously dried with an appropriate drying agent and distilled before use. − The following compounds were prepared as described in the literature: *t*BuN=CH−CH=N*t*Bu (**1a**),[22] 2,6-$Me_2C_6H_3N=CH-CH=NC_6H_3Me_2$-2,6 (**1b**),[23] *t*Bu$CH_2N=C(Me)-C(Me)=NCH_2$*t*Bu (**1c**),[24] and BI_3.[25] Boron trichloride, boron trifluoride−diethyl ether, *t*BuNC, cyclohexyl isocyanide, AgCN, AgOCN, and AgSCN were purchased. − IR spectra: Bruker FTIR IFS66. − ^{1}H-, ^{11}B-, ^{13}C-, and ^{19}F-NMR spectra: Bruker AC 100 (^{1}H, 100.13 MHz; ^{13}C, 25.18 MHz), and Bruker AM Avance DRX 500 (^{1}H, 500.13 MHz; ^{11}B, 160.46 MHz; ^{13}C, 125.75 MHz; ^{19}F, 470.60 MHz). References: $SiMe_4$ (^{1}H, ^{13}C), $BF_3 \cdot OEt_2$ (^{11}B), $CFCl_3$ (^{19}F). − Mass spectra (EI): VG Autospec sector-field mass spectrometer (Micromass) 70 eV.

(tBu)(BF$_3$)N=CH−CH=N(tBu)(BF$_3$) (**2a**): A solution of *t*BuN=CH−CH=N*t*Bu (**1a**) (10.0 g, 59.0 mmol) in 200 ml of *n*-hexane, and an emulsion of $BF_3 \cdot OEt_2$ (18.6 g, 118.0 mmol) in 200 ml of *n*-hexane were added separately, dropwise, into a flask filled with chilled *n*-hexane (1000 ml, −10°C). After 24 h of stirring at room temp., a yellow solid was filtered off and washed with *n*-hexane (4 × 30 ml). Drying at 0.01 Torr for 2 h gave **2a** as a bright yellow powder (13.2 g, 74%). − IR (KBr): ν = 3206cm^{-1} w, 3102 w, 2984 vs, 2892 s, 2796 m, 2695 m, 2585 m, 2486 m, 2034 m, 1950 w, 1608 w, 1509 w, 1476 w, 1404 m, 1378 m, 1299 m, 1214 m, 1055 vs, br. [ν(BF)], 534 m, 522 m, 444 m, 419 w. − ^{1}H NMR (CD_3CN): δ = 1.48 (s, 18 H, *t*Bu), 8.90 (s, 2 H, CH). − ^{13}C{^{1}H} NMR (CD_3CN): δ = 28.5 [s, C(CH_3)$_3$], 66.3 [s, *C*(CH_3)$_3$], 163.2 (s, CH). − ^{11}B{^{1}H} NMR (CD_3CN): δ = 0.4 (s). − ^{19}F{^{1}H} NMR (CD_3CN): δ = 73.0 (s). − $C_{10}H_{20}B_2F_6N_2$ (303.86): calcd. C 39.52, H 6.65, N 9.21; found C 39.40, H 6.83, N 9.23.

(tBu)N^a−CH=CH−N^b(tBu)BF(N^a−B) (**3a**). − *Path (a):* A slurry of adduct **2a** (5.0 g, 16.5 mmol) in *n*-hexane (100 ml) was treated at 20°C with sodium amalgam prepared from 3.8 g (165.2 mmol) of sodium and 500 g of mercury. After 36 h of stirring, the yellow hexane phase was decanted. Solvent and volatile components were removed in vacuo (0.1 Torr, 10°C) to give a yellow solid residue. Purification of crude **3a** was achieved by fractional condensation at 40°C and 0.01 Torr (yield 2.38 g, 73%).

Path (b): 1.4-Diazabutadiene **1a** (1.67 g, 10.0 mmol) was reduced with lithium sand (0.139 g, 20.0 mmol) in 70 ml of *n*-hexane for 7 d at 20°C. The yellow slurry obtained was treated with 1.58 g (10.0 mmol) of $BF_3 \cdot Et_2O$, and the mixture was stirred for 10 min. The red solution was filtered, concentrated to ca. 10 ml, and stored overnight at −78°C to afford 1.1 g (56%) of colorless crystalline **3a**. − IR (nujol): ν = 1631cm^{-1} w, 1489 sh, 1428 s, 1395 sh, 1366 s, 1293 m, 1273 w, 1244 s, 1224 m, 1211 m, 1136 s, 1062 w, 1028 w, 951 w, 933 w, 879 w, 822 w, 746 w, 658 w, 623 s. − ^{1}H NMR (C_6D_6): δ = 1.26 (d, $^{5}J_{FH}$ = 1.1 Hz, 18 H, *t*Bu), 5.99 (d, $^{4}J_{FH}$ = 2.3 Hz, 2 H, CH). − $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 30.9 [s, C(*C*H$_3$)$_3$], 51.6 [s, *C*(CH$_3$)$_3$], 109.9 (s, CH). − $^{11}B\{^{1}H\}$ NMR (C_6D_6): δ = 20.3 (s). − $^{19}F\{^{1}H\}$ NMR (C_6D_6): δ = 57.9 (s). − MS/EI (70 eV); *m/z*: 199 [M$^+$]. − $C_{10}H_{20}BFN_2$ (198.09): calcd. C 60.63, H 10.18, N 14.14; found C 60.44, H 10.59, N 14.17.

$[tBuN^a{=}CH{-}CH{=}N^b(tBu)BCl_2]^+BCl_4^-(N^a{-}B)$ (**4a**): A three-necked 2-l flask was filled with 900 ml of *n*-hexane and cooled to −30°C. Solutions of **1a** (8.10 g, 48.0 mmol) in 200 ml of *n*-hexane and BCl_3 (11.30 g, 96.0 mmol) in 200 ml of *n*-hexane were added dropwise at a similar rate into the well-stirred *n*-hexane. The resulting mixture was stirred overnight. The colorless precipitate was filtered off and washed with *n*-hexane (2 × 50 ml) and *n*-pentane (2 × 50 ml) before drying in vacuo to give 13.7 g (71%) of **4a**. − IR (KBr): ν = 2985 cm^{-1} m, 2360 w, 1580 m, 1465 s, br., 1405 s, 1385 s, 1232 m, 1191 s, 1119 w, 1071 m, 1036 w, 920 w, 898 m, 821 s, 804 s, 711 m, 657 m, 547 w, 481 w. − ^{1}H NMR (CD_3CN): δ = 1.70 (s, 18 H, *t*Bu), 8.90 (s, br., 2 H, CH). − $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ = 30.0 [s, C(*C*H$_3$)$_3$], 67.3 [s, *C*(CH$_3$)$_3$], 162.7 (s, CH). − $^{11}B\{^{1}H\}$ NMR (CH_3CN): δ = 1.6 (s, BCl_4^-), 7.7 (s, N_2BCl_2). − $C_{10}H_{20}B_2Cl_6N_2$ (402.62): calcd. C 29.83, H 5.01, N 6.96; found C 29.91, H 5.00, N 6.80.

$[2,6\text{-}Me_2C_6H_3N^a{=}CH{-}CH{=}N^b(2,6\text{-}Me_2C_6H_3)BCl_2]^+Cl^-(N^a{-}B)$ (**4b**) *and $[2,6\text{-}Me_2C_6H_3N^a{=}CH{-}CH{=}N^b(2,6\text{-}Me_2C_6H_3)BCl_2]^+BCl_4^-(N^a{-}B)$* (**4b′**): A three-necked 2-l flask was charged with 1200 ml of *n*-hexane and chilled to −20°C. As described before the solutions of BCl_3 (5.90 g, 50.0 mmol) in 200 ml of *n*-hexane and **1b** (13.2 g, 50.0 mmol) in a mixture of *n*-hexane (150 ml) and CH_2Cl_2 (50 ml) were added dropwise into the flask. After warming up to ambient temp., a violet precipitate was filtered off, washed with *n*-hexane (3 × 30 ml) and dried in vacuo to give 7.2 g (38%) of **4b**. The mother liquor was concentrated to ca 500 ml and stored at 5°C overnight to yield 1.7 g (7%) of black crystalline **4b′**.

4b: IR (KBr): $\tilde{\nu}$ = 2567 cm^{-1} w, 1585 w, 1473 s, br., 1197 m, 1095 w, 884 w, 821 m, 775 m, 656 w, 548 w. − Due to the poor solubility and due to decomposition no reliable ^{1}H- and ^{13}C-NMR spectra were available. − $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ = 7.2 (s). − $C_{18}H_{20}BCl_3N_2$ (381.54): calcd. C 56.66, H 5.28, N 7.34; found C 57.87, H 5.20, N 6.95.

4b′: IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} w, 2922 w, 1608 sh, 1535 sh, 1473 s, 1444 s, 1374 s, 1252 sh, 1227 m, 1094 s, 1000 s, 933 m, 908 w, 771 s, 722 w, 668w, 542 w. − $^{11}B\{^{1}H\}$ NMR (CD_3CN): δ 7.7 (s, BN_2), 1.5 (s, BCl_4^-). − $C_{18}H_{20}B_2Cl_6N_2$ (498.71): calcd. C 43.35, H 4.04, N 5.62; found C 38.6, H 4.31, N 4.77. − Repeated attempts to purify the crude product by recrystallization failed.

$(tBu)N^a{-}CH{=}CH{-}N^b(tBu)BCl(N^a{-}B)$ (**5a**). − *Path (a):* A sample of 4.46 g (11.0 mmol) of borolium salt **4a** was stirred overnight with 305.2 g of sodium amalgam (96.0 mmol sodium) in 120 ml of hexane. The reaction mixture was protected from light. The slightly yellow solution was decanted from a yellow precipitate. Filtration and removal of volatile components in vacuo afforded an orange-yellow oil, which slowly solidified to give orange crystalline **5a**. The crude material was sublimed at 40−60°C (0.01 Torr) to yield 2.18 g (91%) of colorless product.

Path (b): A sample of 1,4-diazabutadiene **1a** (2.50 g, 14.8 mmol) was stirred with lithium sand (0.21 g, 29.6 mmol) in 70 ml of *n*-hexane for 7 d at 20°C. A solution of 1.75 g (14.8 mmol) of BCl_3 in 30 ml of *n*-hexane was added dropwise to the chilled yellow slurry (−50°C). The mixture was allowed to warm up to room temp., and stirring was continued overnight. Filtration and removal of solvent from the filtrate in vacuo gave 1.74 g (55%) of **5a**. − IR (CsI, film): ν = 1515 cm^{-1} w, 1464 m, 1399 s, 1367 s, 1347 sh, 1327 s, 1285 m, 1237 s, 1209 m, 1136 m, 1030 w, 987 m, 943 w, 893 w, 822 w, 696 w, 662 m. − ^{1}H NMR (C_6D_6): δ = 1.35 (s, 18 H, *t*Bu), 6.19 (s, 2 H, CH). − $^{13}C\{^{1}H\}$ NMR (C_6D_6: δ = 30.9 [s, C(*C*H$_3$)$_3$], 53.2 [s, *C*(CH$_3$)$_3$], 112.0 (s, CH). − $^{11}B\{^{1}H\}$ NMR (C_6D_6): δ = 20.2 (s). − MS/EI; *m/z* (%): 214 (20) [M$^+$], 158 (8.5) [M$^+$ − C_4H_8], 143 (13) [M$^+$ − C_4H_8 − CH_3], 102 (100) [M$^+$ − 2 C_4H_8]. − $C_{10}H_{20}BClN_2$ (214.55): calcd. C 55.99, H 9.39, N 13.05; found C 55.11, H 9.42, N 12.85.

$2,6\text{-}Me_2C_6H_3N^a{-}CH{=}CH{-}N^b(2,6\text{-}Me_2C_6H_3)BCl(N^a{-}B)$ (**5b**). − *Path (a):* A slurry of 4.00 g of **4b** (10.5 mmol) in 150 ml of *n*-hexane was treated with sodium amalgam obtained from 1.38 g of Na (60.0 mmol) and 200 g of mercury. Stirring at ambient temp. was maintained for 5 d. The solution was decanted from the metal, and volatile components were removed in vacuo to yield 1.80 g (55%) of **5b** as a colorless solid.

Path (b): A solution of the 1,4-diazabutadiene **1b** (4.00 g, 15.0 mmol) in 80 ml of *n*-hexane was reduced by 0.21 g (30.0 mmol) of lithium sand during 7 d at 20°C. The resulting brown slurry was chilled to −30°C and a solution of 1.76 g (15.0 mmol) of BCl_3 in 50 ml of *n*-hexane was added dropwise. Stirring at room temp. was continued for 3 d. Filtration was followed by removing volatile components in vacuo to afford a colorless solid. Recrystallization from *n*-hexane gave 2.48 g (53%) of pure **5b**. − ^{1}H NMR (C_6D_6): δ = 2.17 (s, 12 H, CH$_3$), 5.86 (s, 2 H, HC=N), 6.99 (m, 6 H, aryl-H). − $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 18.1 (s, CH$_3$), 117.7 (s, HC=N), 127.3 (s, *p*-C aryl), 135.8 (s, *o*-C aryl), 139.9 (*i*-C aryl). − $^{11}B\{^{1}H\}$ NMR (C_6D_6): δ = 21.1 (s). − MS/EI; *m/z*: 310 [M$^+$]. − $C_{18}H_{20}BClN_2$ (310.63): calcd. C 69.60, H 6.49, N 9.02; found C 68.78, H 6.45 N 8.87.

$(tBuCH_2)N^a{-}C(Me){=}C(Me){-}N^b(CH_2tBu)BCl(N^a{-}B)$ (**5c**): Lithium sand (0.32 g, 46.8 mmol) was added to a solution of 3.50 g (15.0 mmol) of 1,4-diazabutadiene (**1c**) in 100 ml of *n*-hexane. After stirring the mixture for 10 d at room temp., the resulting green slurry was chilled to −30°C, and a solution of 1.76 g (15.0 mmol) of BCl_3 in 50 ml of *n*-hexane was added dropwise. After 2 h of stirring, the slurry was filtered, and the solvent was removed in vacuo to afford 2.53 g (60%) of **5c** as a dark brown oil, which solidified to a tan wax. − Due to the lability of the product no reliable IR spectrum was available. − ^{1}H NMR (C_6D_6): δ = 0.89 (s, 18 H, *t*Bu), 1.77 (s, 6 H, CH$_3$), 3.21 (s, 4 H, CH$_2$). − $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 10.9 (s, =C−*C*H$_3$), 28.4 [s, C(*C*H$_3$)$_3$], 34.3 (s, CH$_2$), 53.7 [s, *C*(CH$_3$)$_3$], 118.9 (s, C=C). − $^{11}B\{^{1}H\}$ NMR (C_6D_6): δ = 22.7 (s). − MS/EI; *m/z*: 270 [M$^+$ in relation to ^{11}B and ^{35}Cl]. − $C_{14}H_{28}BClN_2$ (270.65): calcd. C 62.13, H 10.43, N 10.35; found C 62.02, H 10.56, N 10.31.

$(tBu)N^a{-}CH{=}CH{-}N^b(tBu)BI(N^a{-}B)$ (**6a**): A slurry of 2.50 g (14.8 mmol) of 1,4-diazabutadiene **1a** in 100 ml of *n*-hexane was allowed to react with lithium sand (0.21 g, 29.6 mmol) for 7 d at 20°C. A solution of 5.83 g (14.9 mmol) of BI_3 in 50 ml of *n*-hexane was added dropwise to the chilled slurry (−20°C). Stirring for 2 h was followed by filtration. The filtrate was liberated from volatile components in vacuo to afford 3.78 g (83%) of **6a** as a colorless oil. At room temp. the pure compound decomposed completely within 5 d, whereas in the dark at −30°C a *n*-hexane solution of **6a** remained unaffected. − Due to decomposition a reliable IR spectrum was not available. − ^{1}H NMR (C_6D_6): δ = 1.45 (s, 18 H, *t*Bu), 6.40 (s, 2 H, CH). − $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 31.7 [s,

$C(CH_3)_3$], 54.2 [s, $C(CH_3)_3$], 114.6 (s, C=C). − $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 6.5 (s). − MS /EI; *m/z*: 306 (27) [M^+], 250 (11) [$M^+ - C_4H_8$], 194 (100) [$M^+ - 2\ C_4H_8$], 178 (3) [$M^+ - I$]. − $C_{10}H_{20}BIN_2$ (305.99): calcd. C 39.21, H 6.59, N 9.15; found C 39.35, H 6.48, N 8.99.

$(2,6\text{-}Me_2C_6H_3)N^a{-}CH{=}CH{-}N^b(2,6\text{-}Me_2C_6H_3)BI(N^a{-}B)$ (**6b**): A mixture of CH_2Cl_2 (600 ml) and *n*-hexane (400 ml) was cooled to −10°C and two separate solutions of 6.00 g (22.7 mmol) of 1,4-diazabutadiene **1b** in CH_2Cl_2 (250 ml) and 8.89 g (22.7 mmol) of BI_3 in *n*-hexane (200 ml) were added dropwise. The reaction was filtered after warming up to room temp. and stirring for 5d. The filtrate was concentrated to dryness. The brown-black residue was extracted with 150 ml of *n*-hexane, and the red *n*-hexane solution was decanted from insoluble components. Storing the concentrated filtrate (ca 20 ml) at −4°C for 3 d afforded 2.43 g (26%) of colorless crystalline **6b**. The compound was purified by sublimation at 0.01 Torr and 380°C. − IR (KBr): ν = 1554 cm^{-1} w, 1551 w, 1475 vs, 1439 m, 1397 s, 1340 m, 1279 s, 1263 s, 1244 m, 1197 m, 1162 w, 1105 s, 1032 w, 908 s, 772 vs, 688 s, 621 s, 569 w, 530 w. − ^1H NMR (C_6D_6): δ = 2.16 (s, 6 H, CH_3), 5.99 (s, 2 H, HC=N), 6.98 (m, 6 H, arylH). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 18.3 (s, CH_3), 120.0 (s, HC=N), 126.2 (s, *p*-C-aryl), 135.7 (s, *o*-C-aryl), 140.7(s, *i*-C-aryl), − $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 11.8 (s). − MS/EI; *m/z*: 402 (96) [M^+], 275 (100) [$M^+ - I$]. − $C_{18}H_{20}BIN_2$(402.08): calcd. C 53.72, H 5.01, I 31.56, N 6.97; found C 53.56, H 5.16, I 31.44, N 6.99.

$(tBu)N^a{-}CH{=}CH{-}N^b(tBu)BCN(N^a{-}B)$ (**8a**). − *From Isocyanides:* A solution of **5a** (1.07 g, 5.00 mmol) in 50 ml of *n*-hexane was treated at room temp. with 0.43 g (5.0 mmol) of *tert*-butyl isocyanide. After 4 h of stirring it was filtered, and the volatile components removed from the filtrate in vacuo (0.01 Torr) to give crude **8a** as a colorless solid. Purification was achieved either by recrystallization from *n*-hexane or by sublimation at 0.03 Torr and 55°C, yield 0.61 g (60%). Similarly, 1.30 g (5.00 mmol) of $(tBu)N^a{-}CH{=}CH{-}N^b(tBu)BBr(N^a{-}B)$ (**7a**) was converted into 0.66 g (64%) of **8a**. Starting from **6a** (1.53 g, 5.0 mmol) 0.41 g of **8a** (41%) was obtained analogously. The reaction of 0.78 g (3.0 mmol) of **7a** with 0.33 g (3.0 mmol) of cyclohexyl isocyanide in 50 ml of *n*-hexane at 20°C for 5 d also afforded **8a** (0.23 g, 38%).

From AgCN: A mixture of **5a** (0.43 g, 2.0 mmol) and silver cyanide (0.32 g, 2.4 mmol) was stirred in acetonitrile (50 ml) for 1 h at room temp. After concentration to dryness, the residue was extracted with *n*-hexane (3 × 50 ml) and the combined extracts were filtered. Repeated concentration to dryness gave analytically pure **8a** (0.35 g, 84%). The analogous reaction of **7a** (0.52 g, 2.0 mmol) with AgCN (0.32 g, 2.4 mmol) in 50 ml of CH_3CN for 20 min afforded 0.46 (89%) of **8a**. − IR (KBr): ν = 2207 cm^{-1} w [ν(C≡N)], 1501 w, 1467 m, 1405 s, 1368 s, 1344 m, 1295 m, 1261 m, 1234 s, 1207 m, 1147 s, 1100 w, 1032 w, 953 w, 824 s, 804 s, 694 s, 660 sh, 649 s, 500 m. − ^1H NMR (C_6D_6): δ = 1.29 (s, 18 H, *t*Bu), 6.14 (s, 2 H, CH). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.5 [s, $C(CH_3)_3$], 53.7 [s, $C(CH_3)_3$], 114.6 (s, C=C). − $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 12.0 (s). − MS/EI; *m/z* (%): 205 (27) [M^+], 149 (10) [$M^+ - C_4H_8$], 93 (100) [$M^+ - 2\ C_4H_8$]. − $C_{11}H_{20}BN_3$ (205.12): calcd. C 64.40, H 9.85, N 20.48; found C 63.72, H 9.45, N 19.45.

$(2,6\text{-}Me_2C_6H_3)N^a{-}CH{=}CH{-}N^b(2,6\text{-}Me_2C_6H_3)BCN(N^a{-}B)$ (**8b**). − *From Isocyanides:* Equimolar amounts of **5b** (0.62 g, 2.0 mmol) and *tert*-butyl isocyanide (0.17 g, 2.0 mmol) were allowed to react in 40 ml of *n*-hexane for 8 h at room temp. The solution was filtered and the colorless filtrate was concentrated to dryness. The remaining yellow solid was sublimed at 0.001 Torr and ca. 400°C to give 0.42 g (70%) of **8b**. Similarly, a sample of 0.80 g (2.0 mmol) of **6b** was converted into 0.33 g of **8b** by treatment with 0.17 g (2.0 mmol) of *tert*-butyl isocyanide.

From AgCN: A mixture of **6b** (0.80 g, 2.0 mmol) and AgCN (0.32 g, 2.4 mmol) was stirred in 50 ml of CH_3CN for 2 d at room temp. Concentration to dryness, extraction with *n*-hexane, filtration and removal of volatile components from the filtrate yielded 0.47 g (79%) of **8b**. − IR (KBr): ν = 2218 cm^{-1} w [ν(C≡N)], 1949 w, 1868 w, 1791 w, 1647 w, 1594 w, 1541 w, 1479 s, 1441 m, 1399 m, 1368 w, 1282 m, 1207 m, 1109 m, 915 m, 775 s, 717 m, 658 m, 421 w. − ^1H NMR (C_6D_6): δ = 2.06 (s, 12 H, CH_3), 5.75 (s, 2 H, CH), 6.95 (m, 6 H, H-aryl). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 17.8 (s, CH_3), 119.4 (s, C=C), 128.6 (s, *p*C-aryl). − $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 13.5 (s). − MS/EI; *m/z* (%): 301 (100) [M^+]. − $C_{19}H_{20}BN_3$ (301.18): calcd. C 75.70 , H 6.69, N 13.95; found C 75.30, H 7.25, N 13.61.

$(tBu)N^a{-}CH{=}CH{-}N^b(tBu)BNCO(N^a{-}B)$ (**9a**): Analogously, the treatment of **5a** (0.43 g, 2.0 mmol) with AgOCN (0.53 g, 2.4 mmol) in 50 ml of CH_3CN for 30 min at 20°C afforded 0.35 g (78%) of **9a** as a colorless viscous oil. Complete decomposition of **9a** occurred within 2 d. Heterocycle **9a** was also prepared from **7a** and AgOCN in CH_3CN (50 ml) for 5 min (83% yield). − IR (CsI): ν = 2972 cm^{-1} s, 2317 vs [ν_{as}(NCO)], 1699 m, 1684 m, 1527 w, 1474 m, 1458 m, 1404 s, 1367 s, 1322 s, 1288 w, 1240 s, 1138 m, 1033 w, 1001 w, 822 w, 807 w, 632 m [ν_{sym}(NCO)], 596 w. − ^1H NMR (C_6D_6): δ = 1.21 (s, 18 H. *t*Bu), 6.04 (s, 2 H, =CH). − $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 14.7 (s). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.0 [s, $C(CH_3)_3$], 52.5 [s, $C(CH_3)_3$], 111.6 (s, =CH), 123.9 (s, br., N=C=O). − MS/EI (70 eV); *m/z* (%): 221 (20) [M^+]. − $C_{11}H_{20}BN_3O$ (221.12): calcd. C 59.74, H 9.13, N 18.99; found C 59.30, H 9.33, N 18.63.

$(tBu)N^a{-}CH{=}CH{-}N^b(tBu)BNCS(N^a{-}B)$ (**10a**): Compound **10a** was prepared analogously from **5a** (0.43 g, 2.0 mmol) and AgSCN (0.40 g, 2.4 mmol) in CH_3CN (50 ml, 20°C, 1 h), yield: 0.42 g (74%). The corresponding reaction of **7a** and AgSCN took place within 10 min to give a 76% yield of **10a**. − IR (CsI): ν = 3133 cm^{-1} w, 2975 s, 2936 sh, 2910 sh, 2875 sh, 2122 vs, br. [ν_{as}(NCS)], 1475 m, 1406 s, 1375 s, 1291 m, 1241 s, 1205 m, 1141 s, 1029 w, 948 w, 871 s [ν_{sym}(NCS)], 822 w, 802 m, 683 w, 632 s. − ^1H NMR (C_6D_6): δ = 1.20 (s, 18 H, *t*Bu), 5.99 (s, 2 H, =CH); ($CDCl_3$): δ = 1.42 (s, 18 H, *t*Bu), 6.16 (s, 2 H, =CH). − $^{11}B\{^1H\}$ NMR (C_6D_6): δ 14.7 (s). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.1 [s, $C(CH_3)_3$], 53.0 [s, $C(CH_3)_3$], 111.8 (s, =CH), 140.5 (s, NCS), (C_6D_6): δ = 31.0 [s, $C(CH_3)_3$], 52.9 [s, $C(CH_3)_3$], 112.1 (s, =CH). − MS/EI (70 eV); *m/z* (%): 237 (70) [M^+], 125 (100) [$M^+ - 2\ tBu$]. − $C_{11}H_{20}BN_3S$ (237.17): calcd. C 55.71, H 8.50, N 17.72; found C 54.89, H 8.78, N 17.24.

$(2,6\text{-}Me_2C_6H_3)N^a{-}CH{=}CH{-}N^b(2,6\text{-}Me_2C_6H_3)BNCS(N^a{-}B)$ (**10b**): A sample of solid AgSCN (0.41 g, 3.0 mmol) was added to a slurry of **6b** (1.00 g, 2.5 mmol) in CH_3CN (40 ml) and stirred for 5 h at 20°C. The slurry was filtered, and the filtrate concentrated to dryness. The residue was extracted with *n*-hexane (3 × 50 ml) and the combined extracts were filtered. The volatile components were removed from the filtrate to give pure **10b** (0.77 g, 93%) as a waxy solid. Analogously, **5b** was converted into **10b** within 3 h in 78% yield. The corresponding bromide gave **10b** after 1 h in 87% yield. − IR (KBr): ν = 2918 cm^{-1} w, 2177 sh, 2114 vs [ν_{as}(NCS)], 2038 sh, 1516 w, 1479 s, 1441 s, 1402 s, 1390 s, 1303 w, 1285 m, 1201 w, 1111 s, 1032 w, 992 w, 909 m, 856 s [ν_{sym}(NCS)], 768 s, 702 w, 656 w, 643 s. − ^1H NMR (C_6D_6): δ = 2.10 (s, 12 H, CH_3), 5.71 (s, 2 H, =CHN), 6.97 (m, 6 H, aryl-H). − $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 14.5 (s). −$^{13}C\{^1H\}$ NMR (C_6D_6): δ = 17.9 (s, CH_3), 117.2 (s, =CHN), 127.3 (s, *p*-aryl-C), 128.6 (s, *m*-aryl-C), 135.2 (s, *o*-aryl-C), 139.2 (s, *i*-aryl-C). − MS/EI (70 eV); *m/z* (%):

333 (100) [M$^+$]. − $C_{19}H_{20}BN_3S$ (333.15): calcd. C 68.44, H 6.05, N 12.61; found C 68.38, H 6.30, N 12.38.

X-ray Structural Analysis of **6b**: Colorless single crystals from *n*-hexane; 0.42 × 0.37 × 0.32 mm; $T = 293$ K; Siemens P4 four-circle diffractometer; Mo-K_α (graphite monochromator, $\lambda = 0.71073$ A), empirical formula $C_{18}H_{20}BIN_2$, monoclinic space group *C*2/*c*; unit cell dimensions: $a = 14.911(2)$, $b = 7.9706(8)$, $c = 16.9105(12)$ A; $\beta = 114.360(6)°$; $V = 1830.9(3)$ A^3, $d_{calcd.} = 1.459$ g cm^{-3}, $Z = 4$; μ(Mo-K_α) = 1.747 mm^{-1}; range for data collection: $5.3° \leq 2\Theta \leq 60.1°$; ω-scan, index ranges: $-20 \leq h \leq 0$, $-11 \leq k \leq 0$, $-21 \leq l \leq 23$; reflections collected 2769 ($R_{int} = 0.017$); independent reflections 2675; parameters 102; absorption correction: empirical φ-scans, min/max transmission 0.94/0.79 [R_{merg}(before/after) = 0.0333/0.0136]. Program used: Siemens SHELXTL Ver. 5.03. Structure solution: Direct Methods; structure refinement: Full-matrix least-squares on F^2, $R1 = 0.042$, $wR2 = 0.1043$ based on 1884 reflections with $I > 2\sigma(I)$, $wR2$ (all data) = 0.1189 with $w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 3.11P]$, where $P = (F_o^2 + 2F_c^2)/3$; GOOF (F^2) = 1.029, maximum residual electron density 0.922 eA^{-3}, hydrogen atoms treated as riding groups with the 1.2-fold isotropic *U* value of the corresponding C atom and 1.5-fold for methyl groups.[26]

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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