Synthesis and Structure of 2-Hydro-, 2-Alkyl-, 2-Alkynyl-, and 2-Stannyl-2,3-dihydro-1*H*-1,3,2-diazaboroles

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Dedicated to Professor Dietmar Seyferth on the occasion of his 70th birthday

Keywords: Boron / Diazaboroles / Hydrides / Tin / Heterocycles

1,3-Di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaborole (**4a**) and 1,3-bis(2,6-dimethylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaborole (**4b**) were formed by the reaction of the corresponding 2-bromo or 2-iodo derivatives **1a** and **2b** with $LiAlH_4$. Treatment of **1a** with *n*-butyllithium afforded 2-*n*-butyl-1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaborole (**5a**), whereas 1,3-di-*tert*-butyl-2-cyano-2,3-dihydro-1*H*-1,3,2-diazaborole (**3a**) was converted into the 2-*tert*-butyl derivative **6a** or the 2-ethynyl-1,3,2-diazaborole **7a** by means of *tert*-butyllithium or by the ethylenediamine adduct of lithium acetylide. Similarly, 1,3-di-*tert*-butyl-2-trimethylstannyl-2,3-dihydro-1*H*-1,3,2-diazaborole (**8a**) and 1,3-bis(2,6-dimethylphenyl)-2-trimethylstannyl-2,3-dihydro-1*H*-1,3,2-diazaborole (**8b**) were accessible from **1a** or **2b** and trimethylstannyllithium. In the complex **9a** the compound **3a** serves as an η^1 ligand towards the $[Cr(CO)_5]$ unit via the cyano group. These novel compounds were characterized by ^1H-, ^{11}B-, ^{13}C-, and ^{119}Sn-NMR spectroscopy, as well as by X-ray structure analyses of **4b**, **8a**, and **9a**.

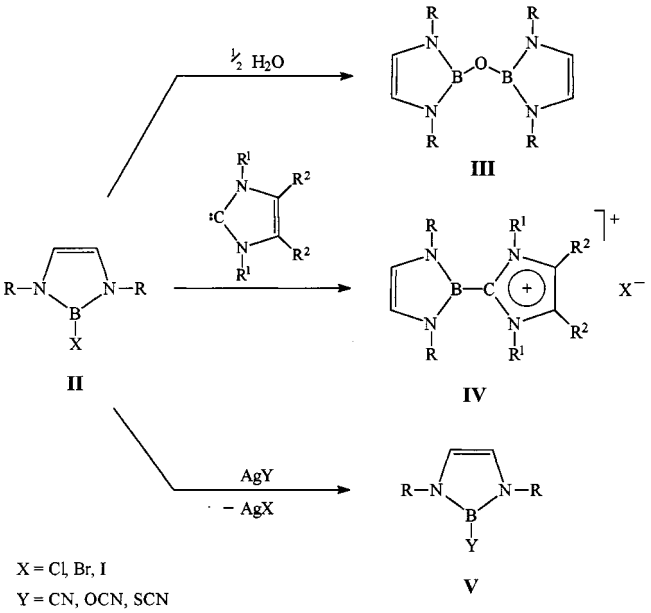
The synthesis of the first 2,3-dihydro-1*H*-1,3,2-diazaboroles **I** dates back to the early 1970s,[1,2] and since then a series of papers concerned with the synthesis, structure, and bonding of such heterocycles has been published.[3,4] A thorough investigation of the chemical reactivity of 2,3-dihydro-1*H*-1,3,2-diazaboroles was primarily hampered by the lack of functionalities at the core of the molecules.[5,6]

Recently, we started a program for the synthesis of the 2-halo-2,3-dihydro-1*H*-1,3,2-diazaboroles **II** as starting materials for further chemical transformations.[7] Treatment of **II** with water, imidazol-2-ylidenes, AgCN, AgOCN, and AgSCN afforded a series of novel 1,3,2-diazaboroles **III**–**V**.[7,8]

The intention of the work described herein is to provide efficient syntheses for 2-hydro-, 2-alkyl-, 2-alkynyl-, and 2-stannyl-2,3-dihydro-1*H*-1,3,2-diazaboroles.

Results and Discussion

One general route to 2,3-dihydro-1*H*-1,3,2-diazaboroles involves the formation of borolium salts from suitable 1,4-diazabutadienes and organoboron halides prior to reduction with sodium amalgam.[2,3,7,8] Accordingly, in the early attempts to synthezise 2,3-dihydro-1*H*-1,3,2-diazaboroles a 1,4-diazabutadiene derivative was treated with $Me_2NH \cdot BH_3$, which led to an inseparable 1:4 mixture of the desired diazaborole **4a** and the corresponding saturated 2-bora-1,3-diazacyclopentane **VI**.[9]



Scheme 1. Chemical transformations of **II**

However, the availability of 2-halo-functionalized 2,3-dihydro-1*H*-1,3,2-diazaboroles provides an alternative approach to 2,3-dihydro-1*H*-1,3,2-diazaboroles. Thus, the treatment of the 2-bromo derivative **1a** and the 2-iodo derivative **2b** with equimolar amounts of $LiAlH_4$ in a hexane/THF mixture or in THF, led cleanly to the 2,3-dihydrodiazaboroles **4a** and **4b**, respectively, in high yields and within a few min.

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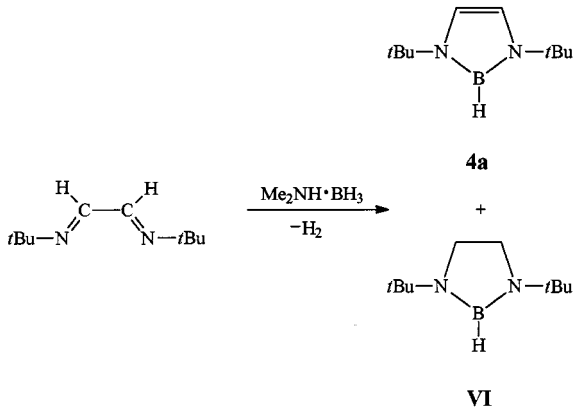
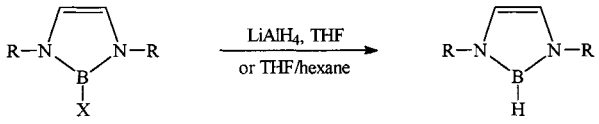


Scheme 2. Borane reduction of a 1,4-diazabutadiene

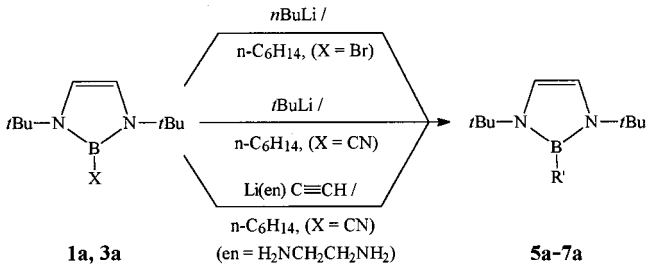


Comp.	R	X
1, 4a	*t*Bu	Br
2, 4b	2,6-$Me_2C_6H_3$	I

Scheme 3. Formation of **4a,b**

The crude products were purified by sublimation at 50°C and 10^{-3} Torr (**4a**) or 210°C and 10^{-4} Torr (**4b**) to give colorless air- and moisture-sensitive solids. In the proton-coupled ^{11}B-NMR spectra (C_6D_6 solution) compounds **4a** and **4b** exhibit doublets at δ = 18.9 ($^1J_{B,H}$ = 149 Hz) and 21.9 ($^1J_{B,H}$ = 158 Hz). The former value compares well with results given in Schulze′s thesis for **4a** (δ = 18.9, d, $^1J_{B,H}$ = 152 Hz), which was dissolved in the four-fold amount of the corresponding saturated compound **VI** (δ = 26.1, d, $^1J_{B,H}$ = 136 Hz).[9] Niedenzu et al. observed for the 1,3,2-diazaboracyclopentane (Me)N^{a}CH$_2$CH$_2$N^b(Me)BH(*N*^{a}−B) and the diazaboracyclohexane (Me)N^{a}CH$_2$CH$_2$CH$_2$N^b-(Me)BH(*N*^{a}−B) ^{11}B-NMR signals at δ = 28.3 (d, $J_{B,H}$ = 131 Hz) and 26.0 (d, $J_{B,H}$ = 132 Hz).[10,11]

The ^{1}H-NMR spectrum of **4a** shows a quadruplet resonance at δ = 4.78 ($^1J_{B,H}$ = 150 Hz) for a boron-ligated hydrogen atom. A medium intense band at $\tilde{\nu}$ = 2594 cm^{-1} and a weak band at $\tilde{\nu}$ = 2623 cm^{-1} in the IR spectrum of **4a** are attributed to the stretching vibrations ν(^{11}B−H) and ν(^{10}B−H). The IR spectrum of **4b** shows a medium intense band at $\tilde{\nu}$ = 2607 cm^{-1} for this mode of vibration. Alkyl substituents at the boron atom of diazaboroles were usually introduced with the organodihaloborane in the condensation step of the synthesis. With 2-halo- and 2-pseudohalo-1,3,2-diazaboroles an inverse approach to such species, namely the replacement of the halide (pseudohalide) by carbanions is now available.



Comp.	R'
5a	*n*-Bu
6a	*t*-Bu
7a	C≡CH

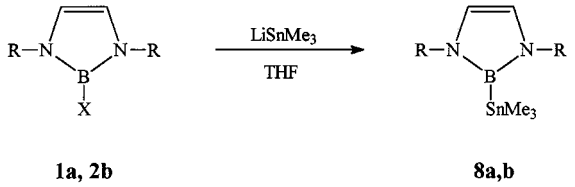
Scheme 4. Nucleophilic substitutions at the B atom of **1a,3a**

The reaction of 2-bromo-1,3,2-diazaborole **1a** with an equimolar amount of *n*-butyllithium in hexane at ambient temp. cleanly afforded **5a** as a colorless hygroscopic solid after distillation at 200−250° and 10^{-3} Torr (84%).

Similarly the 2-cyano-1,3,2-diazaborole **3a** was converted in high yield into the 2-*tert*-butyl- and the 2-ethynyl-1,3,2-diazaboroles **6a** and **7a**, respectively, by treatment with *t*BuLi or the ethylenediamine adduct of lithium acetylide. In the case of **7a** the employment of the 2-cyano-1,3,2-diazaborole as a starting material was crucial since the bromo derivative and the organolithium component gave rise to the formation of (*t*Bu)N^{a}CH=CHN^b(*t*Bu)B^a−N^c(H)CH$_2$-CH$_2$N^d(H)B^{b}N^e(*t*Bu)CH=CH−N^f(*t*Bu)(*N*^{a}−B^a)(*B*^{b}−N^f) instead of **7a**.[12] The ^{11}B{^{1}H}-NMR signals of **5a** (δ = 26.4) compare well with those of (*t*Bu)N^a−CH=CHN^b(*t*Bu)B−CH$_3$(*N*^{a}−B) (δ = 26.2),[3,9] whereas the ^{11}B-NMR resonance of the *tert*-butyl derivative **6a** appeared slightly deshielded (δ = 30.1). In a series of bis(aminoboryl-)acetylenes, the ^{11}B-NMR resonances were registered in the narrow range of δ = 23.8−24.9 regardless of the remaining substituents at the C≡C triple bond.[13] In comparison to this the ^{11}B-NMR signal of **7a** (δ = 15.7) is shielded markedly. This observation may be explained by the aromaticity of the heterocyclic system under discussion. In the ^{1}H-NMR spectrum of **7a** the chemical shift of the ethynyl proton (δ^{1}H = 2.72, s) is identical with those in ($R_2N)_2$B(C≡CH) (R = Me or Et).[13]

The resonance for the α-C atom of the ethynyl unit could not be located in the ^{13}C{^{1}H}-NMR spectrum of the compound. The signal of C_β was registered as a singlet at δ = 96.2, and thus this carbon atom is more deshielded than the corresponding ^{13}C nuclei in Et_2N−B(C≡CH)$_2$ (δ = 85.0), whereas the signal of C_β in (*n*BuO)$_2$B−C≡CH (δ = 91.4) is better comparable with that of **7a**.

The first stannylated 2,3-dihydro-1*H*-1,3,2-diazaboroles were synthesized from **1a** and **2b** and equimolar amounts of trimethylstannyllithium in a THF/hexane mixture at ambient temp.



Comp.	R
1a, 8a	*t*Bu
2b, 8b	2,6-$Me_2C_6H_3$

Scheme 5. Stannylation of **1a,2b**

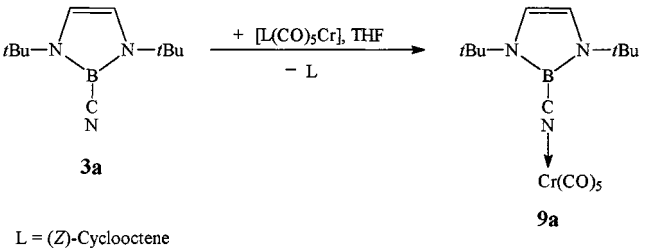
Purification of the colorless solid **8a** was achieved by distillation at 190°C and 10^{-3} Torr and subsequent crystallization of the distillate from *n*-hexane at −30°C (89% yield). The colorless crystalline **8b** precipitated from a hexane solution at −10°C (60% yield).

The $^{11}B\{^1H\}$-NMR spectrum of **8a** is characterized by a singlet at δ = 25.8, with ^{119}Sn satellites ($^1J_{Sn,B}$ = 1031 Hz). In accordance to this, a quadruplet at δ = 152 ($^1J_{Sn,B}$) was encountered in the $^{119}Sn\{^1H\}$-NMR spectrum of the compound. Similarly, the ^{11}B chemical shift of **8b** (δ = 28.2) shows a ^{119}Sn-^{11}B coupling of ^1J = 960 Hz. The $^{119}Sn\{^1H\}$-NMR resonance of **8b** is observed as a quadruplet at δ = 146 with $^1J_{Sn,B}$ = 960 Hz. The saturated compound (Me)-$N^a-CH_2CH_2N^b$(Me)B($SnMe_3$)(N^a−B) displayed a ^{11}B signal at markedly lower field (δ = 36.5, $^1J_{Sn,B}$ = −930 Hz) and a ^{119}Sn-NMR resonance at δ = 152.[14]

The mass spectra of **8a** and **8b** showed, in addition to the peak of the molecular ion, peaks of high intensity at *m*/*z* = 194 (80%) and *m*/*z* = 290 (100%), respectively, which are attributed to the corresponding 2-methyl-2,3-dihydro-1*H*-1,3,2-diazaboroles.

Principally, the 2-cyano-2,3-dihydro-1*H*-1,3,2-diazaborole **3a** is a polyfunctional ligand with different donor sites. Formation of the complex **9a** featuring η^1 coordination of the ligand via the cyano group was achieved by treatment of **3a** with an equimolar amount of [(*Z*)-cyclooctene]$Cr(CO)_5$ in THF at room temp. The product was isolated as yellow needles after crystallization from *n*-hexane at −10°C (83% yield). The ^{11}B-NMR signal of the complex is shielded by Δδ = 2.5 with respect to that of the free ligand. Four ν(CO) bands in the IR spectrum of **9a** ranging from $\tilde{\nu}$ = 2053 to 1888 cm^{-1}, and singlets in the $^{13}C\{^1H\}$-NMR spectrum at δ = 214.4 (CO_{eq}) and 218.9 (CO_{ax}), are consistent with the presence of a $Cr(CO)_5$ group and thus clearly point to a η^1 coordination of **3a**.

In addition to the significant high-field shifts of the ^{11}B-NMR signals of the 2,3-dihydro-1*H*-1,3,2-diazaboroles presented here, in comparison to their saturated analogs, the ^1H- and ^{13}C-NMR resonances of the CH=CH building block (δ^1H = 6.00−6.39 and $\delta^{13}C$ = 112.7−115.5 in **4a−9a**) sustain the argument for the heteroaromatic nature of the rings under discussion.



Scheme 6. Formation of complex **9a**

X-ray Structural Analysis of 8

The molecular structure of **8a** (Figure 1) features a planar 1,3,2-diazaborole ring with a trimethylstannyl substituent which is linked to the boron atom via a B−Sn single bond of 2.274(5) Å. Structurally documented atomic distances between tricoordinate boron and tetravalent tin atoms are rare. The Sn−B bond lengths in the 1,2-bis(organostannylboryl)ethenes **VII** and **VIII** amount to 2.305(7)−2.323(7) and 2.286(17), and 2.277(17) Å, respectively.[15]

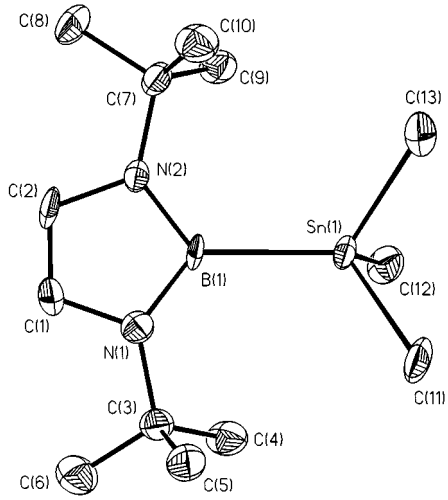
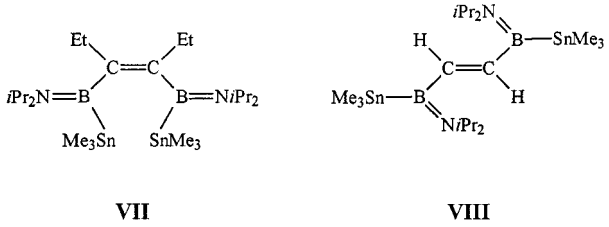


Figure 1. Molecular structure of **8a** in the crystal; selected bond lengths [Å] and angles [°]: B(1)−Sn(1) 2.274(5), B(1)−N(1) 1.439(7), N(1)−C(1) 1.379(7), C(1)−C(2) 1.344(8), N(2)−C(2) 1.399(7), B(1)−N(2) 1.450(7), N(1)−C(3) 1.500 (7), N(2)−C(7) 1.497(7); N(1)−B(1)−N(2) 105.0(4), N(1)−B(1)−Sn(1) 127.5(4), N(2)−B(1)−Sn(1) 127.5(4), B(1)−N(1)−C(1) 108.1(4), B(1)−N(2)−C(2) 107.1(4), B(1)−N(1)−C(3) 131.1(5), B(1)−N(2)−C(7) 130.7(4), N(1)−C(1)−C(2) 110.2(5), N(2)−C(2)−C(1) 109.7(5), B(1)−Sn(1)−C(11) 116.7(2), B(1)−Sn(1)−C(12) 111.7(3), B(1)−Sn(1)−C(13) 119.2(3)



VII **VIII**

Scheme 7. Stannylboranes **VII** and **VIII**

A boron−tin bond length of 2.237(5) Å was measured in the boratobenzene complex (C_5Me_5)Fe(C_5H_5B−$SnMe_3$).[16] In the anion $[B_{11}H_{11}SnMe]^-$ boron−tin con-

tacts of comparable lengths [2.288(3)−2.306(3) Å] were encountered.[17]

Atomic distances and valence angles within the diazaborole ring are in good agreement with the equivalent data for the borolylimidazolium cation **IV**.[7] In **8a** the B−N bond lengths [1.439(7), 1.450(7) Å] indicate multiple bond character. In a series of diazaboroles the B−N bond lengths range from 1.407(3) to 1.450(2) Å. The atomic distance C(1)−C(2) [1.344(8) Å] and the N−C(sp^2) bond lengths [1.379(7) and 1.399(7) Å] also indicate multiple bonding. For the N(sp^2)−C(sp^3) single bonds N(1)−C(3) and N(2)−C(7) bond lengths of 1.500(7) and 1.497(7) Å are measured. The endocyclic angles in **8a** N(1)−B(1)−N(2) [105.0(4)°], B(1)−N(1)−C(1) [108.1(4)°], B(1)−N(2)−C(2) [107.1(4)°], N(1)−C(1)−C(2) [110.2(5)°], and N(2)−C(2)−C(1) [109.7(5)°] resemble those in **2b**:[8] N−B−N [106.9(4)°], B−N−C [107.5(3)°], and N−C−C [109.1(2)°] and **IV** [107.1(6), 105.9(4) and 110.5(3)°]. This also applies to the exocyclic angles N(1)−B(1)−Sn(1) and N(2)−B(1)−Sn(1) [127.5(4)°] in **8a**, and the corresponding angle in **2b** [126.6(2)°]. The angles B(1)−Sn(1)−C(13) [119.2(3)°] and B(1)−Sn(1)−C(11) [116.7(2)°] are significantly widened as compared to the angle B(1)−Sn(1)−C(12) [111.7(3)°], which reflects steric interactions between the *tert*-butyl substituents and methyl groups C(11)H_3 and C(13)H_3.

X-ray Structural Analysis of 4

The molecular structure of **4b** (Figure 2) features a planar 1,3,2-diazaborole ring with two nearly orthogonally oriented *ortho*-xylyl substituents at the nitrogen atoms (interplanar angles between the heterocycle and the arene rings: ψ = 85.9 and 86.5°). Atomic distances and valence angles within the diazaborole ring (see caption of Figure 2) are in excellent agreement with those of **8a**, **2b**, and **IV**.

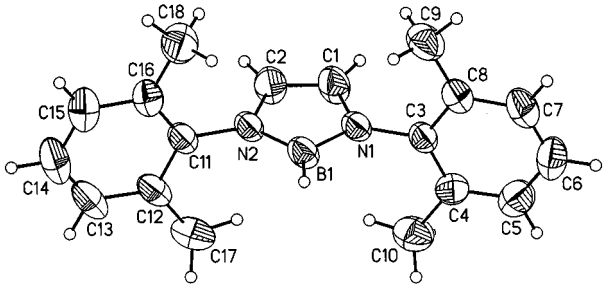


Figure 2. Molecular structure of **4b** in the crystal; selected bond lengths [Å] and angles [°]: B(1)−H(1A) 1.04(3), B(1)−N(1) 1.395(4), N(1)−C(1) 1.377(3), N(1)−C(3) 1.427(3), B(1)−N(2) 1.398(4), N(2)−C(2) 1.374(3), N(2)−C(11) 1.421(3), C(1)−C(2) 1.323(4); N(1)−B(1)−N(2) 106.8(2), N(1)−B(1)−H(1A) 124(2), N(2)−B(1)−H(1A) 129(2), B(1)−N(1)−C(1) 106.9(2), B(1)−N(1)−C(3) 130.9(2), N(1)−C(1)−C(2) 109.8(3), C(1)−N(1)−C(3) 122.1(2), B(1)−N(2)−C(2) 107.3(2), B(1)−N(2)−C(11) 130.6(2), C(2)−N(2)−C(11) 122.1(2), N(2)−C(2)−C(1) 109.2(3)

X-ray Structural Analysis of 9

The molecular structure determination of the pentacarbonylchromium adduct **9a** reveals a nearly undistorted octahedron, one apex of which is occupied by the η^1-2-cyano-2,3-dihydro-1*H*-1,3,2-diazaborole. Thus the atoms B(1), C(1), N(1), Cr(1), C(14), and O(14) are in a linear arrangement. The plane of the heterocycle is staggered with respect to the plane defined by the metal center and the four equatorial carbonyl groups. The bond Cr(1)−C(14) in *trans* disposition to the ligand [1.825(7) Å] is markedly shortened as compared to the remaining Cr(1)−C(CO) bond lengths [1.899(6)−1.917(6) Å], which reveals the 2-cyanodiazaborole as a donor ligand without appreciable π-back bonding. The bond Cr(1)−N(1) of 2.051(5) Å is close to sum of the covalent radii of Cr^0 (1.48 Å)[18] and sp-hybridized N (0.55 Å)[19a]. The C(1)−N(1) bond length of 1.140(6) Å resembles that in cyanogen (1.15 Å).[19b] Due to the presence of an sp-hybridized carbon atom, the bond length B(1)−C(1) [1.547(8) Å] is shorter than the B(sp^2)−C(sp^2) bond in the borolylimidazolium ion **IV** [1.580(11) Å], and it is comparable with the C(sp^2)−B(sp) distance in Li^+-[2,4,6-$Me_3C_6H_2$−B=C−B(2,4,6-$Me_3C_6H_2$)CH($SiMe_3$)$_2$]$^-$ [1.543(6) Å].[20] The bonding parameters within the 1,3,2-diazaborole ring largely resemble those of **4b**, **IV**, and **2b**, and merit no further discussion.

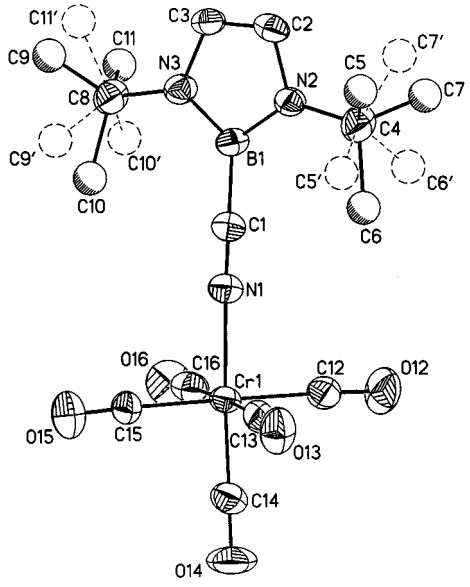


Figure 3. Molecular structure of **9a** in the crystal; selected bond lengths [Å] and angles [°]: B(1)−N(2) 1.416(7), N(2)−C(2) 1.389(7), N(2)−C(4) 1.477(5), B(1)−N(3) 1.433(7), N(3)−C(3) 1.373(6), N(3)−C(8) 1.478(5), C(2)−C(3) 1.312(8), B(1)−C(1) 1.547(8), C(1)−N(1) 1.140(6), Cr(1)−N(1) 2.051(5), Cr(1)−C(12) 1.906(7), Cr(1)−C(13) 1.899(6), Cr(1)−C(14) 1.825(7), Cr(1)−C(15) 1.906(6), Cr(1)−C(16) 1.917(6); N(2)−B(1)−N(3) 107.5(4), B(1)−N(2)−C(4) 133.5(4), B(1)−N(3)−C(8) 132.9(4), B(1)−N(2)−C(2) 105.6(4), C(2)−N(2)−C(4) 120.9(4), B(1)−N(3)−C(3) 105.1(4), C(3)−N(3)−C(8) 122.0(4), N(2)−C(2)−C(3) 110.2(5), N(3)−C(3)−C(2) 111.5(5), B(1)−C(1)−N(1) 178.2(5), C(1)−N(1)−Cr(1) 177.5(5), N(1)−Cr(1)−C(12) 89.0(2), N(1)−Cr(1)−C(13) 90.4(2), N(1)−Cr(1)−C(14) 177.5(3), N(1)−Cr(1)−C(15) 91.7(2), N(1)−Cr(1)−C(16) 92.0(2), Cr(1)−C(14)−O(14) 177.9(6)

Experimental Section

General: All manipulations were performed under dry argon. Solvents were rigorously dried with an appropriate drying agent and freshly distilled before use. − The following compounds were prepared as described in the literature: (*t*Bu)N^a−CH=CH−N^b(*t*Bu)-BBr(*N*^{a}−B) (**1a**),[7] (*t*Bu)N^a−CH=CH−N^b(*t*Bu)BCN(*N*^{a}−B) (**3a**),[8] (2,6-Me$_2$C$_6$H$_3$)N^a−CH=CH−N^b(2,6-Me$_2$C$_6$H$_3$)BI(*N*^{a}−B) (**2b**),[8] [(*Z*)-cyclooctene]Cr(CO)$_5$.[21] LiAlH$_4$, Me$_3$SnCl, Li(H$_2$NCH$_2$CH$_2$NH$_2$)C≡CH, Li metal, *n*-butyllithium, *tert*-butyllithium were purchased. − IR spectra: Bruker FTIR IFS66. − ^{1}H-, ^{11}B-, ^{13}C-, and ^{119}Sn-NMR spectra: C$_6$D$_6$ at room temp.; Bruker AC 100 (^{1}H, 100.13 MHz); Bruker Avance DRX 500 (^{1}H, 500.13 MHz, ^{11}B, 160.46 MHz, ^{13}C, 125.75 MHz, ^{119}Sn, 186.51 MHz); references: SiMe$_4$ (^{1}H, ^{13}C), BF$_3$ · OEt$_2$ (^{11}B), SnMe$_4$ (^{119}Sn). − Mass spectra (EI): VG Autospec sector-field mass spectrometer (Micromass) 70 eV.

(*t*Bu)N^a−CH=CH−N^b(*t*Bu)BH(*N*^{a}−*B*) (4a): A sample of solid LiAlH$_4$ (0.114 g, 3.0 mmol) was added to a solution of **1a** (0.777 g, 3.0 mmol) in a mixture of *n*-hexane (20 mL) and THF (20 mL). After 2 min of stirring at 20°C, the solution was decanted from the solid components and concentrated to dryness. The residue was taken up in *n*-pentane (30 mL) and filtered. The filtrate was freed from solvent, and the colorless residue was sublimed (40−45°C, 10^{-3} Torr) to afford 0.475 g (88%) of colorless solid **4a**. M.p. 51−53°C. − IR (nujol): $\tilde{\nu}$ = 2623 cm^{-1} w [ν(^{10}B−H)], 2594 m [ν(^{11}B−H)], 1410 s, 1366 s, 1316 m, 1290 m, 1282 m, 1247 s, 1221 w, 1147 m, 1092 w, 922 m, 818 w, 664 s, 633 w, 553 m. − ^{1}H NMR: δ = 1.30 (s, 18 H, *t*Bu), 4.78 (q, $^1J_{B,H}$ = 150 Hz, 1 H, BH), 6.39 (s, 2 H, CH). − ^{13}C{^{1}H} NMR: δ = 31.9 [s, C(*C*H$_3$)$_3$], 51.4 [s, *C*(CH$_3$)$_3$], 114.2 (s, CH). − ^{11}B NMR: δ = 18.9 (d, $^1J_{B,H}$ = 149 Hz). − MS/EI: *m*/*z* (%) = 180 (67) [M$^+$], 165 (100) [M$^+$ − CH$_3$]. − C$_{10}$H$_{21}$BN$_2$ (180.12): calcd. C 66.67, H 11.77, N 15.54; found C 66.73, H 12.04, N 15.28.

(2,6-Me$_2$C$_6$H$_3$)N^a−CH=CH−N^b(2,6-Me$_2$C$_6$H$_3$)BH(*N*^{a}−*B*) (4b): A sample of solid LiAlH$_4$ (0.100 g, 2.6 mmol) was added to a solution of 0.820 g (2.0 mmol) of **2b** in 80 mL of THF at room temp., and the mixture was vigorously stirred. After 5 min, the colorless solution was decanted and liberated from solvent in vacuo. The oily residue was taken up in *n*-hexane (40 mL) and filtered. The solvent was removed from the filtrate, and the residue was sublimed at 210°C (10^{-3} Torr). The product was crystallized from *n*-pentane at −10°C to yield 0.490 g (89%) of colorless **4b**. M.p. 112°C. − IR (KBr): $\tilde{\nu}$ = 3104 cm^{-1} w, 3022 w, 2953 m, 2921 m, 2854 w, 2607 [ν(BH)], 1594 w, 1555 w, 1479 s, 1438 m, 1402 m, 1376 sh, 1281 m, 1258 m, 1246 w, 1190 w, 1126 m, 1107 w, 1089 w, 1033 w, 902 m, 808 w, 770 s, 749 w, 687 s, 583 w, 552 w, 514 w, 455 w. − ^{1}H NMR: δ = 2.20 (s, 12 H, CH$_3$), 6.03 (s, 2 H, CH=CH), 7.01 (s, 6 H, H−aryl). − ^{13}C{^{1}H} NMR: δ = 18.2 (s, CH$_3$), 118.4 (s, CH=CH), 126.5 (s, C-*p* aryl), 135.2 (s, C-*o* aryl), 141.8 (s, C-*i* aryl). − ^{11}B{^{1}H} NMR: δ = 21.9 (d, $^1J_{B,H}$ = 158 Hz). − MS/EI: *m*/*z* (%) = 276 (100) [M$^+$]. − C$_{18}$H$_{21}$BN$_2$ (276.19): calcd. C 78.28, H 7.66, N 10.14; found C 78.28, H 7.86, N 10.12.

(*t*Bu)N^a−CH=CH−N^b(*t*Bu)B(*n*Bu)(*N*^{a}−*B*) (5a): A solution of 0.518 g (2.0 mmol) of **1a** in *n*-hexane (30 mL) was treated with 1.25 mL (2.0 mmol) of a 1.6 M *n*-butyllithium solution in *n*-hexane at room temp. After 30 min of stirring, it was filtered. The filtrate was freed from the solvent, and the residue was distilled (10^{-3} Torr, 200−250°C) to give **5a** as a colorless hygroscopic solid. The crude material was crystallized from *n*-pentane at −10°C (yield 0.400 g, 84%). M.p. 95−100°C. − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} vs, 2929 s, 2913 s, 2869 s, 2766 m, 1628 s, 1610 s, 1464 s, 1437 sh, 1395 m, 1368 s, 1234 s, 1210 s, 1134 w, 1095 w, 967s, 754 w, 558 w, 473 m. − ^{1}H NMR: δ = 0.99 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH$_2$C*H*$_3$), 1.36(s, 18 H, *t*Bu), 1.48 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 1.66 (m, 2 H, BCH$_2$), 6.33 (s, 2 H, CH). − ^{13}C{^{1}H} NMR: δ = 14.0 (s, CH$_2$*C*H$_3$), 26.9 (s, *C*H$_2$CH$_3$), 31.1 (s, *C*H$_2$CH$_2$CH$_3$), 32.1 [s, C(*C*H$_3$)$_3$], 52.9 [s, *C*(CH$_3$)], 112.7 (s, CH). − ^{11}B{^{1}H} NMR: δ = 26.4 s. − MS/EI: *m*/*z* (%) = 236 (65) [M$^+$]. − C$_{14}$H$_{29}$BN$_2$ (236.21): calcd. C 71.19, H 12.37, N 11.86; found C 70.92, H 12.56, N 10.98.

(*t*Bu)N^a−CH=CH−N^b(*t*Bu)B(*t*Bu)(*N*^{a}−*B*) (6a): A chilled solution (−30°C) of **3a** (0.615 g, 3.0 mmol) in *n*-hexane (30 mL) was treated with 2 mL of 1.5 M solution of *tert*-butyllithium (3.0 mmol) in *n*-pentane. It was allowed to warm up to 20°C, and the resultant slurry was filtered. Removal of the solvent and distillation of the residue gave **6a** as a light yellow oil (bp 150−170°C, 10^{-3} Torr), which slowly solidified at 0°C. M.p. 54−56°C. Yield: 0.623 g (88%). − IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, s, 1660 m, 1631 m, 1478 s, 1460 sh, 1419 sh, 1396 s, 1365 s, 1310 m, 1228 m, 1133 w, 1057 m, 934 w, 748 w, 713 w, 631 w. − ^{1}H NMR: δ = 1.41 [s, 9 H, B(*t*Bu)], 1.42 [s, 18 H, N(*t*Bu)], 6.32 (s, 2 H, CH). − ^{13}C{^{1}H} NMR: δ = 33.4 [s, NC(*C*H$_3$)$_3$], 33.9 [s, BC(*C*H$_3$)$_3$], 53.8 [s, N*C*(CH$_3$)$_3$], 113.6 (s, CH)). − ^{11}B{^{1}H} NMR: δ = 30.1 s. − MS/EI: *m*/*z* (%) = 236 (6) [M$^+$], 179 (10) [M$^+$ − *t*Bu]. − C$_{14}$H$_{29}$BN$_2$ (236.21): calcd. C 71.19, H 12.37, N 11.86; found C 70.78, H 12.25, N 11.65.

(*t*Bu)N^a−CH=CH−N^b(*t*Bu)B−C≡CH(*N*^{a}−*B*) (7a): A sample of Li(H$_2$N−CH$_2$CH$_2$−NH$_2$)C≡CH (0.370 g, 2.0 mmol) was added to a solution of 0.420 g (2.0 mmol) of **3a** in *n*-hexane (50 mL). Stirring at ambient temp. was continued for 24 h. Then the colorless hexane phase was decanted from a precipitate, and subsequently concentrated to dryness (10^{-3} Torr). The colorless residue was recrystallized from *n*-hexane to give pure **7a** as colorless needles. M.p. 77−85°C (dec.). Yield 0.347 g (85%). − IR (film, CsI): $\tilde{\nu}$ = 3299 cm^{-1} w [ν(≡CH)], 2972 s, 2936 w, 2910 w, 2872 w, 2067 w [ν(C≡C)], 1629 w, 1478 w, 1463 w, 1398 s, 1367 s, 1345 s, 1284 m, 1235 s, 1143 m, 947 w, 824 w, 652 s. − ^{1}H NMR: δ = 1.47 (s, 18 H, *t*Bu), 2.72 (s, 1 H, ≡C−H), 6.25 (s, 2 H, =CH). − ^{13}C{^{1}H} NMR: δ = 31.7 [s, C(*C*H$_3$)$_3$], 53.3 [s, *C*(CH$_3$)$_3$], 96.2 [s, BC≡*C*H], 112.8 (s, =*C*H). − ^{11}B{^{1}H} NMR: δ = 15.7 s. − MS/EI: *m*/*z* (%) = 204 (27) [M$^+$], 92 (100) [M$^+$ − 2 Me$_2$C=CH$_2$]. − C$_{12}$H$_{21}$BN$_2$ (204.16): calcd. C 70.59, H 10.29, N 13.70; found C 70.14, H 10.15, N 13.82.

(*t*Bu)N^a−CH=CH−N^b(*t*Bu)BSnMe$_3$(*N*^{a}−*B*) (8a): 0.100 g (14.4 mmol) of lithium sand was added to a solution of 0.770 g (3.9 mmol) of chlorotrimethylstannane in THF (40 mL), and the slurry was stirred under ultrasonic activation for 30 min. Then 1.00 g (3.9 mmol) of **1a** was added with vigorous stirring. After 1 h, the reaction mixture was filtered, and the solvent was removed from the filtrate by distillation. The residue was dissolved in 20 mL of *n*-hexane. The cloudy solution was filtered and the filtrate was subjected to distillation. The product was obtained as a fraction at 190°C (10^{-3} Torr). Recrystallization from *n*-hexane at −30°C afforded 0.117 g (89%) of **8a** as a colorless solid. M.p. 59°C. − IR (nujol): $\tilde{\nu}$ = 1630 cm^{-1} w, 1574 w, 1394 m, 1365 s, 1296 s, 1263 w, 1230 s, 1196 w, 1185 w, 1136 m, 1026 w, 953 w, 928 w, 824 w, 772 s, 670 m, 642 w, 615 m, 508 s. − ^{1}H NMR: δ = 0.41 (s, $^2J_{Sn,H}$ = 44 Hz, 9 H, SnMe$_3$), 1.31 (s, 18 H, *t*Bu), 6.50 (s, $^4J_{Sn,H}$ = 14 Hz, 2 H, CH). − ^{13}C{^{1}H} NMR: δ = −4.6 (s, $^1J_{Sn,C}$ = 283 Hz, SnCH$_3$), 33.1 [s, C(*C*H$_3$)$_3$], 53.3 [s, *C*(CH$_3$)$_3$], 114.8 (s, $^3J_{Sn,C}$ = 43 Hz, CH). − ^{11}B{^{1}H} NMR: δ = 25.8 (s, $^1J_{Sn,B}$ = 1031 Hz). − ^{119}Sn{^{1}H} NMR: δ = 152 (q, $^1J_{Sn,B}$ = 1032 Hz). − MS/EI: *m*/*z* (%) = 344 (4) [M$^+$], 329 (75) [M$^+$ − CH$_3$], 194 (80) [(*t*Bu)N^{a}CH=CH−N^b(*t*Bu)BCH$_3$(*N*^{a}−B)$^+$]. − C$_{13}$H$_{29}$BN$_2$Sn (342.89): calcd. C 45.54, H 8.52, N 8.17; found C 45.38, H 8.52, N 7.82.

(2,6-Me$_2$C$_6$H$_3$)N^a−CH=CH−N^b(2,6-Me$_2$C$_6$H$_3$)BSnMe$_3$(*N*^{a}−*B*) (8b): A quantity of 0.297 g (1.5 mmol) of Me$_3$SnCl was treated

Table 1. Crystal data and data collection parameters

Compound	**4b**	**8a**	**9a**
formula	$C_{18}H_{21}BN_2$	$C_{13}H_{29}BN_2Sn$	$C_{16}H_{20}BCrN_3O_5$
M_r	276.18	342.88	397.16
crystal dimensions [mm]	0.33×0.21×0.18	0.9×0.4×0.2	0.15×0.13×0.03
crystal system	monoclinic	triclinic	orthorhombic
space group	$P2(1)/n$	$P\bar{1}$	$P2(1)2(1)2(1)$
a [Å]	8.4986(2)	8.998(5)	6.4166(1)
b [Å]	16.9200(3)	9.357(6)	16.3958(1)
c [Å]	11.7980(1)	11.225(7)	20.0326(2)
α [°]	90	90.71(5)	90
β [°]	98.723(1)	93.26(5)	90
γ [°]	90	116.86(4)	90
V [Å^3]	1676.89(5)	841.0(9)	2107.54(4)
Z	4	2	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.094	1.354	1.252
μ [mm^{-1}]	0.063	1.504	0.570
$F(000)$	592	352	824
T [K]	296	173	296
2θ [°]	2.8−48.4	3.6−55.0	5.4−56.8
no. refl. recorded	8226	3769	18627
no. refl. unique	2437	3551	4388
no. refl. obs. $I > 2\sigma(I)$	1645	3145	3193
R (int)	0.0407	0.0629	0.0488
refined parameters	194	163	232
GOF	1.035	1.108	1.024
$R(2\sigma)$	0.0676	0.0618	0.0699
w$R2$	0.2230	0.1685	0.2101
$\Delta\rho_{max}$ [e Å^{-3}]	0.234	1.88	0.675

with 0.100 g (14.4 mmol) of lithium sand in 30 mL of THF with ultrasonic activation. At room temp. a solution of 0.600 g of **2b** in 20 mL of *n*-hexane was added dropwise. After 1 h of stirring, the solvent was removed, and 20 mL of *n*-hexane was added to the residue. It was filtered, and the light yellow filtrate was concentrated to initiate crystallization. Completion of the crystallization was achieved by storing the solution overnight at −10°C. Yield: 0.395 g (60%) of colorless crystalline **8b**. M.p. 43−45°C. − IR (KBr): $\tilde{\nu}$ = 3023 cm^{-1} w, 2976 m, 2911 m, 1621 w, 1594 w, 1477 s, 1438 m, 1378 s, 1277 w, 1263 w, 1246 w, 1183 w, 1102 w, 907 w, 767 s, 695 w, 518 s, 498 m. − ^{1}H NMR: δ = −0.19 (s, $^2J_{Sn,H}$ = 77.4 Hz, 9 H, Sn Me_3), 2.16 (s, 12 H, Me−aryl), 6.13 (s, $J_{Sn,H}$ = 10 Hz, HC=CH), 6.99 (m, 6 H, H−aryl). − ^{13}C{^{1}H} NMR: δ = −12.3 (s, $^1J_{Sn,C}$ = 293 Hz), 18.0 (s, CH_3−aryl), 120.0 (s, $^3J_{Sn,C}$ = 34 Hz, HC=CH), 127.0 (C-*p* aryl), 135.8 (C-*o* aryl), 142.6 (C-*i* aryl). − δ^{11}B{^{1}H} NMR: δ = 28.2 (s, $^1J_{Sn,B}$ = 960 Hz). − δ^{119}Sn{^{1}H} NMR: δ = 146.0 (q, $^1J_{Sn,B}$ = 960 Hz. − MS/EI: *m*/*z* (%) = 425 (45) [$M^+ - CH_3$]; 290 (100) [(2,6-$Me_2C_6H_3$)N^a−CH=CH−N^b(2,6-$Me_2C_6H_3$)BMe(N^a−B)$^+$]. − $C_{21}H_{29}BN_2Sn$ (438.97) calcd. C 57.46, H 6.66, N 6.38; found: C 57.58, H 6.72, N 6.30.

(*t*Bu)N^a−CH=CH−N^b(*t*Bu)BCN→Cr(CO)$_5$(*N*^{a}−*B*) (9a): A solution of [(*Z*)-cyclooctene]Cr(CO)$_5$ (0.440 g, 14.5 mmol) in 5 mL of THF was added dropwise at room temp. to a stirred solution of **3a** (0.300 g, 14.6 mmol) in 30 mL of THF. After 1 h, the brown reaction mixture was concentrated to dryness. The residue was dissolved in 30 mL of hexane. It was filtered, and the filtrate was stored at −10°C. Product **9a** was isolated as yellow needles. Yield: 0.480 g (83%). M.p. 45−50°C (dec.). − IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1} m, 2206 w, 2120 w, 2053 m [ν(CO)], 1987 sh [ν(CO)], 1927 vs [ν(CO)], 1888 sh [ν(CO)], 1632 m, 1529 w, 1467 w, 1432 w, 1404 w, 1369 m, 1305 w, 1262 w, 1208 w, 1170 w, 1067 m, 1027 m, 803 m, 697 m, 663 s, 552 w, 449 w. − ^{1}H NMR: δ = 1.11 (s, 18 H, *t*Bu), 6.00 (s, 2 H, CH). − ^{13}C{^{1}H} NMR: δ = 31.2 [s, C(CH_3)$_3$], 53.8 [s, $C(CH_3)_3$], 115.5 (s, CH), 214.4 (s, CO_{eq}), 218.9 (s, CO_{ax}). − ^{11}B{^{1}H} NMR: δ = 9.4 s. − MS/EI: *m*/*z* (%) = 397 (0.2) [M^+], 285 (0.4) [M^+ − 4 CO], 257 (5) [M^+ − 5 CO], 205 (30) [M^+ − Cr(CO)$_5$]. − $C_{16}H_{20}BCrN_3O_5$ (397.16): calcd. C 48.39, H 5.08, N 10.58; found: C 48.39, H 5.02, N 10.60.

X-ray Crystallography: For **4b** and **9a** crystallographic data were collected with a Siemens CCD-Smart three-axis goniometer using graphite-monochromated Mo-K_α radiation with a full-sphere scan covering more than 98% of the data. An empirical absorption correction (Siemens-SADABS) was applied, for structure solution with Direct Methods and refinements on F^2; Siemens SHELTL-Plus software (Vers. 5.01) was used. Hydrogen atoms were treated as riding groups with U values at the 1.2 fold (1.5 fold for methyl groups) of the corresponding C atoms. − For **8a** the data were collected with a Bruker P2$_1$ four-circle diffractometer. Crystallographic programs used for structure solution and refinement were from SHELXTL PLUS and SHELXL-97. The structure was solved by using Direct Methods and was refined by using full-matrix least squares on F^2 of all unique reflexions with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with U(H) = 1.2 U_{eq} for groups, U(H) = 1.5 U_{eq} for CH_3 groups. Crystal data of the compounds are listed in Table 1.[22]

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[22] Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-410214 (**4b**), -410215 (**9**), and from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK, [Fax: int.code +44-1223/336-0335, E-mail: deposit@ccdc.cam.nc.uk], on quoting the depository numbers CCDC-103177 (**8a**), the names of the authors, and the journal citation.

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