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From *C,N*- and *N,N*-chelated chloroboranes to substituted 1*H*-2,1-benzazaboroles and 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines: A straightforward route to five-membered rings containing B-N or N-B-N moiety†

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A set of 1*H*-2,1-benzazaboroles as B-N analogues of 1*H*-indene and 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines as B-N analogues of 1*H*-pyrrolizine were prepared via nucleophilic addition of selected alkyl(aryl)lithiums (MeLi, tBuLi or PhLi) to, via N→B intramolecular interaction activated, imino C=N functionality in the structure of *C,N*- or *N,N*-chelated chloroboranes. All compounds were characterized by the help of elemental analysis; ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR spectroscopy and molecular structures of isolated compounds were on several occasions established by means of single-crystal X-ray diffraction analysis. The presence of three adjacently bonded substituents and their systematic alternation on five-membered C_3BN (1*H*-2,1-benzazaboroles) or C_2BN_2 (1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines) rings allowed to follow both the influence of the steric repulsion and limits for the formation of respective annulated heterocyclic systems.

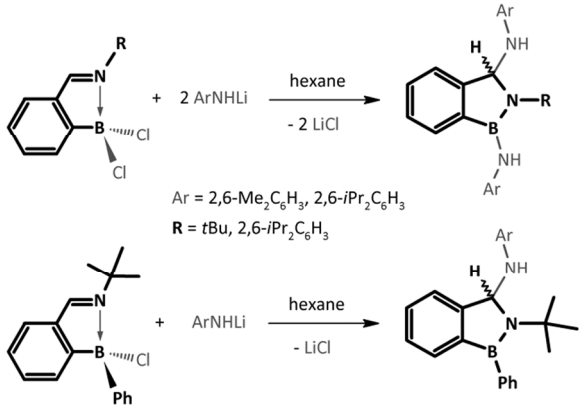
Introduction

The chemistry of intramolecularly *N*-donor coordinated boranes containing various types of ligands has received considerable interest in recent years.[1] These complexes often exhibit desirable and tuneable photophysical and electronic properties such as strong fluorescence with high quantum yields.[2-5] Therefore, they are studied in relation to their utilization as materials for fluorescent labels in biology,[2] laser dyes,[3] organic light-emitting diodes,[4] molecular photoswitches[5] etc. It has also been shown that *N*-donor ligands are able to stabilize borenium cations, which are able to activate molecular hydrogen.[6] Liu *et al.* have recently achieved isolation of 1,2-B-N cyclopentane and 1,2-B-N cyclohexane and some of these compounds have been studied as promising hydrogen storage materials.[7] We have recently reported on an unusual reactivity of *C,N*-chelated (di)chloroboranes with sterically encumbered lithium anilides.[8] These reactions led to the facile formation of highly substituted 1*H*-2,1-benzazaboroles[7] (Scheme 1), which were usually accessible by complicated reaction paths.[9] The plausible mechanism of this reaction involves nucleophilic addition of anilides across the imino C=N bond, that is activated by the strong N→B intramolecular interaction.[8] This procedure has been successfully tested with variety of substrates, thereby suggesting new possible application of *C,N*-chelated boranes i.e. preparation of B-N heterocyclic compounds. In this paper, two major problems are targeted.

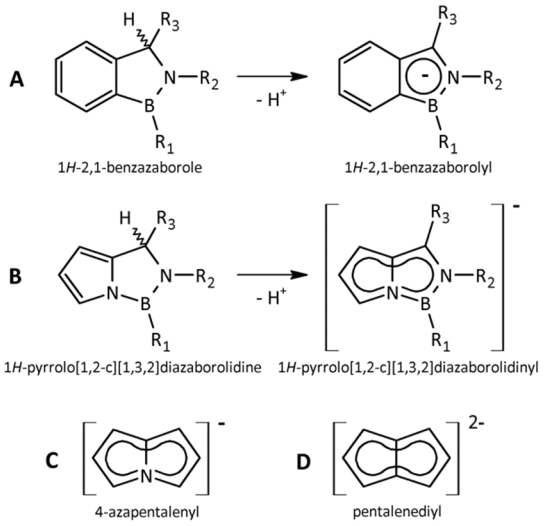
i) Is it possible to use other nucleophiles in similar reactions to that illustrated in Scheme 1? For this purpose, the reactivity of alkyl(aryl)lithiums (MeLi, *t*BuLi or PhLi), as a source of nucleophilic carbanions, toward chloroboranes $L^{1,2}BCl_2$ (**1**, **3**) and $L^{1,2}BPhCl$ (**2**, **4**) (where L^1 = [2-(CH=N*t*Bu)C_6H_4], L^2 = [2-(CH=N-2,6-*i*Pr$_2$$C_6H_3$)$C_6H_4$]) was studied with the aim of the preparation of substituted 1*H*-2,1-benzazaboroles. Intended 1*H*-2,1-benzazaboroles would also be interesting precursors for the preparation of 1*H*-2,1-benzazaborolyl anions as analogues of indenyl anion (Scheme 2A) as we have recently demonstrated.[10]

ii) The second important point is, whether this type of reaction (i.e. nucleophilic attack at the activated imino C=N bond) is

also applicable for the formation of other B-N heterocyclic systems. In this context, the reactivity of *N,N*-chelated boranes $L^{3,4}BPhCl$ (**5**, **6**) derived from the pyrrole backbone (where L^3 = [2-(CH=N*t*Bu)C_4H_3N], L^4 = [2-(CH=N-2,6-*i*$Pr_2C_6H_3$)C_4H_3N]) with alkyl(aryl)lithiums was investigated targeting the formation of 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines (Scheme 2B). To the best of our knowledge, isolated 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines are unknown. These compounds would be B-N analogues[11] of 1*H*-pyrrolizine being isoelectronic. More importantly, their deprotonation should afford 10π-electron 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidinyl anion (Scheme 2B) with potentially interesting coordination behaviour as was proven for analogues namely 4-azapentalenyl anion[12] or pentalenediyl dianion (Scheme 2C, D) earlier.[13]



Scheme 1 Reported reactivity of *C,N*-chelated (di)chloroboranes with lithium anilides (ref. 7).



Scheme 2 Structures of discussed heterocyclic compounds and related anions.

Results and Discussion

Syntheses and structures of starting compounds 1–6

Compounds **1-3** were prepared according to the literature procedure[7] and compound **4** was synthesized in an analogous manner *via* the reaction of $PhBCl_2$ and L^2Li. Compound **4** was observed as a pale yellow crystalline solid in 69 % yield, which is well soluble in dichloromethane and aromatic solvents and shows only limited solubility in hexane and pentane. The identity of **4** was established by the help of elemental analysis, ^1H, ^{11}B, ^{13}C and ^{15}N NMR spectroscopy (see Experimental section and ESI†). Molecular structures of **3** (not determined before) and **4** were determined using single-crystal X-ray diffraction analysis (Figure 1). Compounds **3** crystallized in the chiral $P2_12_12_1$ space group, while **4** crystallized in the $P2_1/c$ space group. The molecular structures of **3** and **4** are closely related to those of **1** and **2**. Intramolecular N→B interactions are characterized by the N(1)-B(1) bond distances 1.620(5) and 1.632(2) Å for **3** and **4**, respectively and both values approach the Σ_{cov}(N,B) = 1.56 Å.[14] The central boron atoms are tetrahedrally coordinated with the percent tetrahedral character (%THC)[15] of 74.7 % (**3**) and 70.0 % (**4**), which are comparable to the values found for **1** (79.0 %) and **2** (66.6 %).[8]

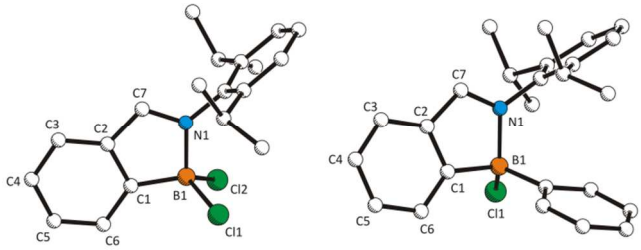


Figure 1 Molecular structures of **3** (left) and **4** (right). Hydrogen atoms and the dichloromethane molecule (in both cases) are omitted for clarity. Selected bond lengths [Å] and bonding angles [deg]: For **3**: B(1)-C(1) 1.587(6), B(1)-N(1) 1.620(5), B(1)-Cl(1) 1.852(5), B(1)-Cl(2) 1.849(4), N(1)-B(1)-C(1) 98.7(3), N(1)-B(1)-Cl(1) 109.9(3), N(1)-B(1)-Cl(2) 109.7(2), C(1)-B(1)-Cl(1) 114.3(3), C(1)-B(1)-Cl(2) 115.0(3), Cl(1)-B(1)-Cl(2) 108.7(2). For **4**: B(1)-C(1) 1.595(4), B(1)-N(1) 1.632(2), B(1)-Cl(1) 1.897(3), B(1)-C(20) 1.598(3), N(1)-B(1)-C(1) 97.44(18), N(1)-B(1)-Cl(1) 108.53(16), N(1)-B(1)-C(20) 111.18(19), C(1)-B(1)-Cl(1) 108.52(17), C(1)-B(1)-C(20) 119.7(2), Cl(1)-B(1)-C(20) 109.62(17).

N,N-chelated boranes **5** and **6** were obtained in reasonable yields of 72% and 78%, respectively, by the treatment of lithium precursors $L^{3,4}Li$ with $PhBCl_2$ in hexane and subsequent workup. Compounds **5** and **6** are crystalline solids well soluble in aromatic solvents, but show only limited solubility in hexane. Both compounds slowly decompose in dichloromethane solutions. Their identity was approved by the help of elemental analysis, ^1H, ^{11}B, ^{13}C and ^{15}N NMR spectroscopy (see Experimental section and ESI†) and the molecular structure of **5** was established using single-crystal X-ray diffraction analysis (Figure 2). **5** crystallized as a racemate in the $P2_1/c$ space group as a consequence of the stereogenic centre at the B(1) atom. The central boron atom is chelated by two nitrogen atoms. The bond distance B(1)-N(1) 1.536(3) Å is significantly shorter than the B(1)-N(2) bond 1.607(4) Å. Nevertheless, both values approach the sum of respective covalent radii [Σ_{cov}(N,B) = 1.56 Å].[14] These values are comparable to those found in related *N,N*-chelated boranes

reported earlier.[16] The coordination polyhedron of the boron atom is a distorted tetrahedron with the %THC[14] value 72.1 %. The results of UV/Vis absorption spectroscopy of **1-6** are summarized in Table 1. All compounds show two main absorption bands in the region 230 – 368 nm. These data are comparable to those found in related *C,N*-chelated boranes.[1k,l]

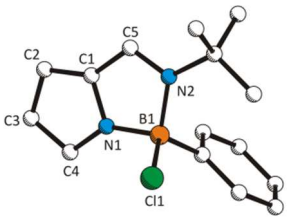
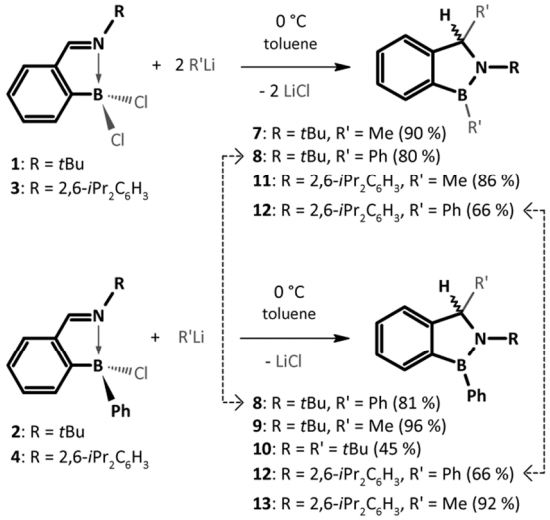


Figure 2 Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Only one position of the disordered *t*Bu group is shown. Selected bond lengths [Å] and bonding angles [deg]: B(1)-N(1) 1.536(2), B(1)-N(2) 1.606(3), B(1)-C(10) 1.596(3), B(1)-Cl(1) 1.876(3), N(1)-B(1)-N(2) 97.10(16), N(1)-B(1)-Cl(1) 109.20(15), N(1)-B(1)-C(10) 112.75(15), N(2)-B(1)-Cl(1) 108.91(13), N(2)-B(1)-C(10) 113.59(18), Cl(1)-B(1)-C(10) 113.99(16).

Reactivity of 1–6 toward lithium reagents

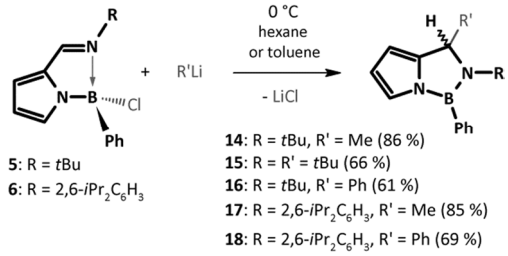
The reaction of boranes **1-4** with one or two equivalents of respective lithium reagents (MeLi, *t*BuLi or PhLi) smoothly afforded substituted 1*H*-2,1-benzazaboroles **7-13** according to Scheme 3. All compounds were obtained in reasonable to excellent isolated yields (45-96%) as oily products (**7** and **11**) or crystalline solids, which are well soluble in aromatic solvents and are stable for a long time under an inert atmosphere. Importantly, it turned out that the reactions between **1** (or **3**) and two equivalents of *t*BuLi or **4** and one equivalent of *t*BuLi did not afforded expected 1*H*-2,1-benzazaboroles.[17] This is probably a result of a significant steric repulsion between the bulky *t*Bu groups or *t*Bu and 2,6-iPr$_2$C$_6$H$_3$ group (*vide infra*). Compounds **7-13** were characterized using elemental analysis, ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR spectroscopy (for a detailed assignment of the NMR spectra see the Experimental section and ESI†). All observed NMR data are entirely consistent with the proposed structures of **7-13** and are similar to those reported before by us for related compounds.[7] Thus, the ^{1}H NMR spectra of **7-13** revealed one signal with expected multiplicity for the aliphatic C*H*(R´) (Table 2) of the 1*H*-2,1-benzazaborole core (in the range 4.41-5.58 ppm). These values are significantly upfield shifted in comparison with the imine C*H* group in the starting compounds **1-4** (observed in the range 7.55-8.45 ppm). Similarly, the ^{13}C NMR spectra established the presence of this *C*H(R´) group by a signal with the chemical shift laying in the interval 63.6-77.1 ppm for **7-13**. The ^{11}B NMR spectra showed in each case one signal (in the range 38.8-43.8 ppm), that are upfield shifted (Δδ ~ 33 ppm) in comparison with the starting compounds **1-4** reflecting a change of the hybridization of the boron atom from sp^3 (**1-4**) to sp^2 (**7-13**).[18] As expected, one signal also appeared in the ^{15}N NMR spectra of **7-13** (in the range from -242.1 to -222.9 ppm) and the obtained values of ^{15}N NMR chemical shifts are comparable to those reported by us for related 1*H*-2,1-benzazaboroles earlier.[8] The results of UV/Vis absorption spectroscopy of **7-13** are summarized in Table 1. All compounds show two or three absorption bands in the region 207 - 271 nm.



Scheme 3 Preparation of **7–13** together with isolated yields.

In a similar way, *N,N*-chelated boranes **5** and **6** were treated with one equivalent of lithium reagents (Scheme 4). These reactions involved the nucleophilic attack of the respective carbanion to the imino C=N functionality, thus, giving a set of 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines **14-18** in good isolated yields (61-86%) as crystalline solids (except **14**, which was obtained only as a honey-like material and was characterized mainly by NMR spectroscopy, see the Experimental section and ESI†). All compounds are well soluble in aromatic solvents and are stable for a long time under an inert atmosphere. Analogously to the attempted synthesis of sterically overcrowded 1*H*-2,1-benzazaboroles, the reaction between the borane **6** and *t*BuLi did not lead to the formation of expected 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines instead a complicated mixture of products was obtained. The formation of 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines backbones was unambiguously proven by the help of ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR spectroscopy (for a detailed assignment of the NMR spectra see the Experimental section and ESI†). The presence of the *CH*(R´) group 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine core (Table 2) was reflected by the observation of one signal (in the range 4.24-5.74 ppm for **14-18**) with expected multiplicity in the ^{1}H NMR spectra and also one signal (in the range 55.5-68.5 ppm) was detected in corresponding ^{13}C NMR spectra. All these signals are significantly upfield shifted in comparison with the imine C*H* group found in the parent boranes **5** and **6**. The ^{11}B NMR spectra showed one signal (in the range 29.8-34.0 ppm for **14-18**) that is upfield shifted in comparison with values observed for 1*H*-2,1-benzazaboroles **7-13** (38.8-43.8

ppm). This fact should be ascribed to the presence of two adjacently bonded nitrogen atoms resulting in a higher electron density at the boron atom in **14-18**.[18] Two signals were detected in the ^{15}N NMR spectra of **14-18** (in the range from -198.1 to -186.8 ppm for the pyrrole nitrogen atom and from -264.3 to -246.3 ppm for the second nitrogen atom). This distinction between chemical shifts of both nitrogen atoms in **14-18** is remarkable and probably stems from a different degree of π interaction between them and the boron atom. The chemical shifts for the pyrrole nitrogen atom suggest rather week π interaction with the boron centre, which is also corroborated by corresponding B(1)-N(1) bond lengths found in the solid state (*vide infra*). Similar conclusion was made by Wrackmeyer *et al*. on related *N*-pyrrolyl boranes.[19] Nevertheless, chemical shifts of the pyrrole nitrogen atom in **14-18** are similar to those observed in the starting compounds **5** and **6** (-174.4 and -178.5 ppm, respectively). On the contrary, the signals of the second nitrogen atom in **14-18** are significantly shifted in comparison with corresponding imino nitrogen atom in the starting compound **5** (-150.1 ppm)[20], reflecting closure of the 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine core. The results of UV/Vis absorption spectroscopy of **15–18** are summarized in Table 1. All compounds show two or three absorption bands in the region 211 – 260 nm.



Scheme 4 Preparation of **14–18** together with isolated yields.

Solid state structures

Molecular structures of **9**, **10**, **12**, **13**, **15**, **17** and **18** were determined by the help of single-crystal X-ray diffraction analysis and are depicted in Figures 3-5 together with relevant structural parameters. The crystallographic data are summarized in the Experimental section. All compounds (except **9**) crystalized in the centrosymmetric $P2_1/c$ space group as racemates reflecting the presence of the stereogenic carbon centres at C(7) (in **10**, **12** and **13**) and C(5) (in **15**, **17** and **18**), respectively. Compound **9** crystallized in *P-1* space group. The unit cell in the case of **12** contained three independent molecules, but they are structurally closely related so only one of them is discussed below in more detail.

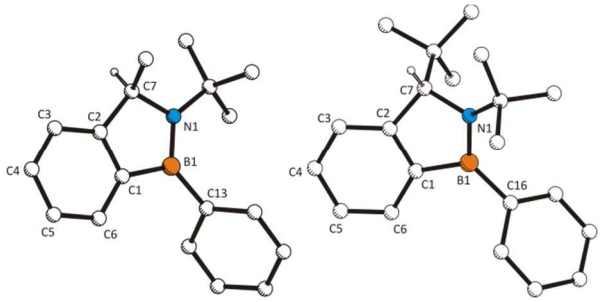


Figure 3 Molecular structures of **9** (left) and **10** (right). Hydrogen atoms, except C(7)H, are omitted for clarity. Selected bond lengths [Å] and bonding angles [deg]: For **9**: B(1)-C(1) 1.560(2), B(1)-N(1) 1.418(2), B(1)-C(13) 1.574(2), C(1)-C(2) 1.397(2), C(2)-C(7) 1.507(2), C(7)-N(1) 1.4889(19), C(1)-B(1)-C(13) 122.55(14), C(1)-B(1)-N(1) 106.16(13), C(13)-B(1)-N(1) 131.26(14), C(7)-N(1)-B(1) 111.23(13). For **10**: B(1)-C(1) 1.564(2), B(1)-N(1) 1.419(2), B(1)-C(16) 1.573(2), C(1)-C(2) 1.399(2), C(2)-C(7) 1.519(2), C(7)-N(1) 1.4953(19), C(1)-B(1)-C(16) 123.00(13), C(1)-B(1)-N(1) 106.13(13), C(16)-B(1)-N(1) 130.84(14), C(7)-N(1)-B(1) 110.03(11).

The molecular structures of **9**, **10**, **12** and **13** proved the formation of benzene fused azaborole ring. The central rings are essentially planar in all cases (except for **10**, *vide infra*). Both boron B(1) and nitrogen N(1) atoms adopt planar environment consistent with the sp^2 hybridization within the five-membered ring as the sum of the angles around both atoms is close to the ideal value of 360°. The B(1)-N(1) bond lengths laying in the interval 1.403(4)-1.419(2) Å for **9**, **10**, **12** and **13** are apparently shorter than the sum of covalent radii for single bond Σ_{cov}(N,B) = 1.56 Å[14] and correspond to the value for the respective double bond (1.48 Å).[14] This fact proves a multiple character of these bonds and reflects strong π-π interaction between both bonding partners. The geometry around the C(7) atom is tetrahedral and, thus, the C(7) bonded substituents are bent out of the plane defined by the benzazaborole core. On the contrary, the C-*ipso* carbon atoms of the substituents bonded to the B(1) and N(1) remain coplanar with the center benzazaborole core, but this situation changes significantly in **10**, where two bulky *t*Bu groups are bonded in neighbouring positions (*vide infra*).

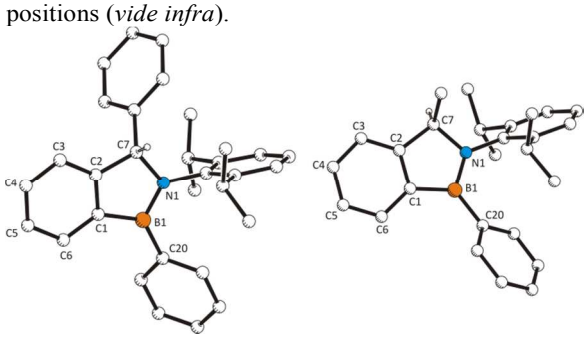


Figure 4 Molecular structures of **12** (left - one of three independent molecules obtained in the unit cell) and **13** (right). Hydrogen atoms, except C(7)H, are omitted for clarity. Selected bond lengths [Å] and bonding angles [deg]: For **12** – data for only one of three independent molecules within the unit cell: B(1)-C(1) 1.559(4), B(1)-N(1) 1.403(4), B(1)-C(20) 1.555(4), C(1)-C(2) 1.401(3), C(2)-C(7) 1.513(3), C(7)-N(1) 1.490(3), C(1)-B(1)-C(20) 129.2(2), C(1)-B(1)-N(1) 105.7(2), C(20)-B(1)-N(1) 125.1(2), C(7)-N(1)-B(1) 113.02(19). For **13**: B(1)-C(1) 1.562(2), B(1)-N(1) 1.404(2), B(1)-C(20) 1.561(2), C(1)-C(2) 1.397(2), C(2)-C(7) 1.509(2), C(7)-N(1) 1.479(2), C(1)-B(1)-C(20) 128.40(14), C(1)-B(1)-N(1) 105.54(14), C(20)-B(1)-N(1) 125.87(14), C(7)-N(1)-B(1) 112.91(12).

The molecular structures of **15**, **17** and **18** unambiguously established the formation of 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine cores. The B(1)-N(1) and B(1)-N(2) bond lengths laying in the intervals 1.459(2)-1.4608(17) Å and 1.403(2)-1.4164(17) Å, respectively, are different and it probably reflects stronger π-π interaction between both bonding partners in the case of B(1)-N(2) bonds (as suggested before in solution based on the ^{15}N NMR data). Nevertheless, all B-N bond lengths correspond to the value for the respective double bond (1.48 Å).[14] The geometry around the boron B(1) as well as N(1) and N(2) atoms is trigonal planar, while the tetrahedral geometry is found around the C(5) atom. The whole central 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine cores in **17** and **18** remain essentially planar, while this is significantly puckered in the case of **15** (*vide infra*).

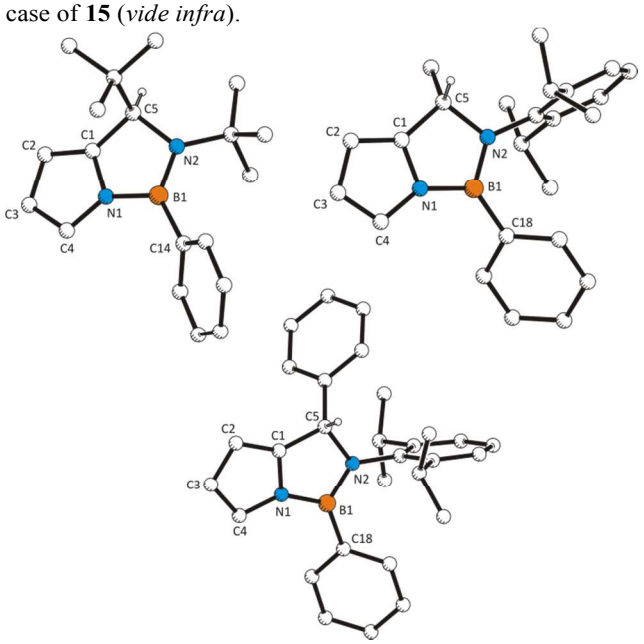


Figure 5 Molecular structures of **15** (left), **17** (right) and **18** (bottom). Hydrogen atoms, except C(5)H, are omitted for clarity. Selected bond lengths [Å] and bonding angles [deg]: For **15**: B(1)-N(1) 1.4608(17), B(1)-N(2) 1.4164(17), B(1)-C(14) 1.574(2), N(2)-C(5) 1.4957(16), C(5)-C(1) 1.5065(17), C(1)-N(1) 1.3778(17), N(1)-B(1)-N(2) 106.74(14), N(1)-B(1)-C(14) 120.70(11), N(2)-B(1)-C(14) 132.54(11), B(1)-N(2)-C(5) 109.23(10), B(1)-N(1)-C(1) 109.92(10). For **17**: B(1)-N(1) 1.460(2), B(1)-N(2) 1.404(2), B(1)-C(18) 1.555(3), N(2)-C(5) 1.488(2), C(5)-C(1) 1.502(2), C(1)-N(1) 1.380(2), N(1)-B(1)-N(2) 105.90(16), N(1)-B(1)-C(18) 126.35(16), N(2)-B(1)-C(18) 127.45(16), B(1)-N(2)-C(5) 112.06(14), B(1)-N(1)-C(1) 110.07(15). For **18**: B(1)-N(1) 1.459(2), B(1)-N(2) 1.403(2), B(1)-C(18) 1.555(2), N(2)-C(5) 1.4947(18), C(5)-C(1) 1.502(2), C(1)-N(1) 1.3760(19), N(1)-B(1)-N(2) 105.90(13), N(1)-B(1)-C(18) 126.44(14), N(2)-B(1)-C(18) 127.66(14), B(1)-N(2)-C(5) 112.33(12), B(1)-N(1)-C(1) 109.99(13).

As mentioned above, molecular structures of **10** and **15** are of particular interest as they contain two *t*Bu groups bonded in adjacent positions. This leads to a significant distortion of the central heterocyclic cores as illustrated in Figure 6. This is obviously a result of slight pyramidalization of the coordination geometry around the nitrogen atoms N(1) (**10**) and N(2) (**15**). Similarly, B(1) and C(12) atoms in the case of **10** and B(1), C(5) and C(10) atoms for **15** are bent out of the mean planes defined by atoms of annulated benzene and pyrrole ring, respectively. This distortion obviously helps to relax the steric stress between the *t*Bu moieties. This phenomenon is also evident in the corresponding ^{11}B and ^{15}N NMR spectra of **10** and **15** (Table 2), where the values of chemical shifts observed for **10** and **15** in comparison with other compounds suggest lower degree of π-π interaction between boron and nitrogen atoms. This steric repulsion is also most probably responsible for the fact that other 1*H*-2,1-benzazaboroles and 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine with adjacently bonded bulky group (*t*Bu or 2,6-*i*Pr$_2$C$_6$H$_3$) couldn't be prepared as mentioned above or were obtained as non-separable mixtures of isomers.[17]

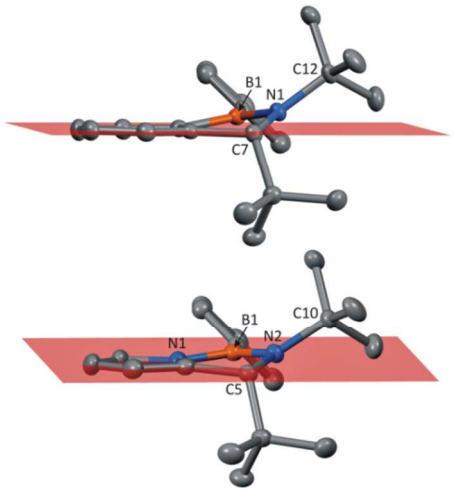


Figure 6 Views on the central cores of **10** (top) and **15** (bottom) demonstrating their significant puckering caused by the presence of adjacently bonded bulky *t*Bu moieties. Molecules are intersected by the plane (red colour) defined by atoms of the benzene (**10**) and pyrrole (**15**) annulated ring.

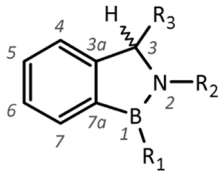
Table 1 UV/Vis absorption maxima of **1**-**13** and **15**-**18** (in CH_2Cl_2 for **1**-**4**, CCl_4 for **5** and **6** and hexane for **7**-**13**, **15**–**18**) (λ = [nm], ε = [l·mol^{-1}·cm^{-1}], sh = shoulder).

Compound	λ_{max1} (ε)	λ_{max2} (ε)	λ_{max3} (ε)
1	230 (8700)	296 (9500)	330 sh (2400)
2	230 (13600)	292 (9500)	330 sh (2300)
3	231 (9000)	301 (8900)	-
4	231 (10800)	296 (12100)	-
5	303 sh (5700)	362 (13800)	-
6	298 (5500)	368 (16600)	-
7	211 (13300)	245 (8200)	-
8	214 (27500)	251 sh (7900)	-
9	209 (32000)	235 (16800)	249 sh (12400)
10	207 (21800)	241 (10400)	271 (4300)
11	215 (14900)	243 (12100)	-
12	207 (38800)	237 (22600)	261 (7400)
13	207 (38200)	239 (26300)	260 (10800)
15	217 (9800)	256 (3600)	-
16	216 (12700)	245 (5500)	-
17	211 (14300)	229 sh (10500)	259 (4200)
18	215 (27400)	229 sh (24700)	260 (8800)

Conclusions

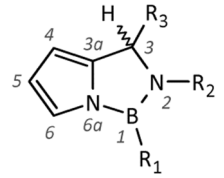
We have recognized new and facile synthetic protocol for the formation of 1*H*-2,1-benzazaboroles and 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidines, which were accessible by quite complicated reaction procedures or were not known at all in the latter case. The detailed study also revealed an important dependence of the formation of these heterocyclic compounds on the bulkiness of attached organic substituents. All here reported derivatives hold a remarkable potential to become ligands for the coordination of transition metals after their deprotonation. The investigation targeting this field as well as dealing with the preparation of related p-block element containing heterocycles is currently underway in our labs.

Table 2 ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR data (δ = [ppm]) of the central cores of **7**-**18** in C_6D_6 at 298 K with numbering schemes of the 1*H*-2,1-benzazaborole and the 1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine cycle.



7: $R_1 = R_3 = Me$, $R_2 = tBu$
8: $R_1 = R_3 = Ph$, $R_2 = tBu$
9: $R_1 = Ph$, $R_2 = tBu$, $R_3 = Me$
10: $R_1 = Ph$, $R_2 = R_3 = tBu$
11: $R_1 = R_3 = Me$, $R_2 = 2,6\text{-}iPr_2C_6H_3$
12: $R_1 = R_3 = Ph$, $R_2 = 2,6\text{-}iPr_2C_6H_3$
13: $R_1 = Ph$, $R_2 = 2,6\text{-}iPr_2C_6H_3$, $R_3 = Me$

		Compound						
Position	Nucleus	**7**	**8**	**9**	**10**	**11**	**12**	**13**
1	δ ^{11}B	41.8	41.9	40.2	43.8	42.0	39.0	38.8
2	δ ^{15}N	-227.5	-225.8	-222.9	-230.9	-241.9	-239.5	-242.1
3	δ ^{1}H	4.41 (q)	5.58 (s)	4.54 (q)	4.53 (s)	4.53 (q)	5.86 (s)	4.78 (q)
	(δ ^{13}C)	(63.6)	(72.8)	(64.0)	(75.8)	(67.7)	(77.1)	(67.9)
3a	δ ^{13}C	156.6	156.2	156.7	156.4	155.9	155.4	156.7
4	δ ^{1}H	7.13 (m)	6.97 (dq)	7.15 (dq)	7.24 (m)	7.20 (d)	7.20 (dq)	7.27 (dq)
	(δ ^{13}C)	(121.2)	(122.7)	(121.2)	(123.6)	(122.1)	(124.3)	(122.4)
5	δ ^{1}H	7.30 (td)	7.10 (m)	7.29 (td)	7.14 (m)	7.34 (m)	7.30 (td)	7.37 (t)
	(δ ^{13}C)	(129.1)	(130.0)	(129.4)	(127.7)	(129.8)	(130.2)	(129.8)
6	δ ^{1}H	7.26 (td)	7.10 (m)	7.17 (tt)	7.16 (m)	7.32 (m)	7.38 (tq)	7.34 (t)
	(δ ^{13}C)	(126.8)	(127.2)	(127.1)	(126.8)	(127.5)	(127.9)	(127.7)
7	δ ^{1}H	7.70 (m)	7.52 (m)	7.50 (dt)	7.56 (m)	7.83 (m)	8.23 (dt)	8.13 (dt)
	(δ ^{13}C)	(130.2)	(131.3)	(131.5)	(130.7)	(131.3)	(132.3)	(132.5)
7a	δ ^{13}C	143.4[b]	[a]	[a]	[a]	142.0[b]	[a]	[a]



14: $R_1 = Ph$, $R_2 = tBu$, $R_3 = Me$
15: $R_1 = Ph$, $R_2 = R_3 = tBu$,
16: $R_1 = R_3 = Ph$, $R_2 = tBu$
17: $R_1 = Ph$, $R_2 = 2,6\text{-}iPr_2C_6H_3$, $R_3 = Me$
18: $R_1 = R_3 = Ph$, $R_2 = 2,6\text{-}iPr_2C_6H_3$

		Compound				
Position	Nucleus	**14**	**15**	**16**	**17**	**18**
1	δ ^{11}B	30.8	34.0	31.9	29.8	30.2
2	δ ^{15}N	-244.9	-255.8	-246.3	-264.3	-261.1
3	δ ^{1}H	4.39 (q)	4.24 (s)	5.44 (s)	4.67 (q)	5.74 (s)
	(δ ^{13}C)	(55.5)	(68.4)	(63.9)	(59.9)	(68.5)
3a	δ ^{13}C	145.5	144.4	145.1	145.9	143.4
4	δ ^{1}H	6.12 (m)	6.16 (d)	5.96 (dt)	6.30 (m)	6.26 (m)
	(δ ^{13}C)	(101.2)	(105.5)	(102.9)	(102.5)	(104.9)
5	δ ^{1}H	6.51 (t)	6.45 (t)	6.42 (t)	6.67 (t)	6.70 (t)
	(δ ^{13}C)	(114.9)	(114.4)	(115.6)	(115.8)	(116.2)
6	δ ^{1}H	6.69 (d)	6.78 (d)	6.71 (dt)	7.30 (d)	7.40 (d)
	(δ ^{13}C)	(116.5)	(116.8)	(116.6)	(117.7)	(118.4)
6a	δ ^{15}N	-191.9	-186.8	-192.1	-198.1	-195.8

[a] signal of the carbon atom *7a* was not observed, [b] observation of signal of the carbon atom *7a* required application of 10^5 pulses due to its broadening.
s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets, tt = triplet of triplets, m = multiplet

Experimental

General procedures

All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube technique. All solvents were dried using Pure Solv–Innovative Technology equipment. The starting compounds: BCl_3 (1 M solution in hexane) and $PhBCl_2$ (97%) were obtained from the commercial suppliers and used as delivered. The ligand-precursors $L^{1,2}Br$ and $L^{3,4}H$ were prepared according to published procedures.[21] Compounds **1-3** were synthesized according to the literature.[8] Compound **9** has also been recently prepared by an alternative reaction.[10]

NMR spectroscopy

^{1}H, ^{11}B, ^{13}C and ^{15}N NMR spectra were recorded on a Bruker Avance 500 or a Bruker Avance III 400 MHz spectrometers, using a 5 mm tunable broad-band probe. Appropriate chemical shifts in ^{1}H and ^{13}C NMR spectra were related to the residual signals of the solvent (C_6D_6: δ(^{1}H) = 7.16 ppm and δ(^{13}C) = 128.39 ppm), ^{11}B NMR spectra were related to external standard $B(OMe)_3$ (δ(^{11}B) = 18.1 ppm), ^{15}N NMR spectra were related to external neat nitromethane (δ(^{15}N) = 0.0 ppm). For compounds **1-18** the full assignment of all signals in all measured NMR spectra was managed with the help of various techniques including ^{1}H, $^{13}C\{^{1}H\}$ APT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC and in several cases 1D ^{1}H NOESY has been used. ^{15}N NMR chemical shifts were obtained from ^{1}H-^{15}N HMBC spectra. Table 2 summarizes all NMR data of the central cores for **7-18** including the multiplicities of the signals

in the ^{1}H NMR spectra. The full assignment including assignment of all bonded phenyl/alkyl groups bonded to central cores are available in the ESI†, thus these data are not mentioned in this section.

UV-VIS spectroscopy

Electronic absorption spectra were run on a Black-Comet C-SR-100 concave grating spectrometer in quartz cuvette (region 200 - 1080 nm, optical pathway 1 cm, concentration 10^{-4} - 10^{-5} mol.l^{-1}) in CH_2Cl_2 for **1-4**, CCl_4 for **5** and **6** and hexane for **7-13**, **15-18**. The spectra of **14** could not be obtained as it was not isolated as an analytically pure compound and therefore the results may be confusing. All observed data are summarized in Table 1.

Syntheses

Synthesis of [2-(CH=N-2,6-*i*Pr$_2$C$_6$H$_3$)C$_6$H$_4$]B(Ph)Cl (4). *n*BuLi (30.4 mL of 1.6M solution in hexane, 48.7 mmol) was added to a solution of L^{2}Br (16.759 g, 48.7 mmol) in hexane (150 mL) at 0 °C and stirred for 1 h at this temperature. Additional hexane (50 mL) was added to the resulting yellow-orange suspension of the lithium compound. A solution of $PhBCl_2$ (7.73 g, 48.7 mmol) in hexane (20 mL) was added under intensive stirring to the suspension of lithium compound at 0 °C. The obtained ginger dense mixture was allowed to reach r.t. and stirred overnight. The mixture was filtered in the air *via* the fine frit with layer of Celite and remaining insoluble material was washed by 2x100 mL of undried dichloromethane. Both portion of filtrate were collected and then evaporated to give crude orange product, which was recrystallized from minimal amount of boiling dichloromethane to give **4** as pale-yellow crystalline solid (isolated yield 13.01 g, 69 %), m. p. 174 °C. Compound is air stable.

Anal. calc. for $C_{25}H_{27}BClN$ (MW 387.75): C, 77.4; H, 7.0; Found: C, 77.3; H, 7.0 %. For NMR data see Table 2 and ESI†.

Synthesis of [2-(CH=N-*t*Bu)C$_4$H$_3$N]B(Ph)Cl (5). *n*BuLi (24.2 mL of 1.6M solution in hexane, 38.7 mmol) was added to a solution of L^{3}H (5.82 g, 38.7 mmol) in hexane (160 mL) at -60 °C and stirred for 1 h at this temperature. A solution of $PhBCl_2$ (6.15 g, 38.7 mmol) in hexane (20 mL) was added under intensive stirring to the ivory suspension of lithium compound at -30 °C. The obtained dense dark pink mixture was allowed to reach r.t. and stirred overnight. The mixture was filtered, the pink filtrate with intensive green fluorescence was discarded and the remaining insoluble material was extracted by 200 mL of boiling mixture of hexane and toluene (3:1). The resulting suspension was filtered and the dark pink filtrate was stored at -30 °C which gave **5** as pink crystalline solid (isolated yield 7.61 g, 72 %), m. p. 123 °C.

Anal. calc. for $C_{15}H_{18}BClN_2$ (MW 272.58): C, 66.1; H, 6.7; Found: C, 66.1; H, 6.7 %. For NMR data see Table 2 and ESI†.

Synthesis of [2-(CH=N-2,6-*i*Pr$_2$C$_6$H$_3$)C$_4$H$_3$N]B(Ph)Cl (6). *n*BuLi (10.3 mL of 1.6M solution in hexane, 16.5 mmol) was added to a solution of L^{4}H (4.20 g, 16.5 mmol) in hexane (150 mL) at 0 °C and stirred for 1 h at this temperature. A solution of $PhBCl_2$ (2.62 g, 16.5 mmol) in hexane (10 mL) was added under intensive stirring to the ivory suspension of lithium compound at 0 °C. The obtained dense ginger mixture was allowed to reach r.t. and stirred overnight. Then the mixture was heated to boil and filtered. The remaining insoluble material was extracted by additional 3x50 mL of boiling hexane and then filtered. All filtrates were collected and volume was reduced to one half. Storing at -30 °C gave **6** as ginger crystalline solid (isolated yield 4.88 g, 78 %), decomp. p. 147 °C.

Anal. calc. for $C_{23}H_{26}BClN_2$ (MW 376.73): C, 73.3; H, 7.0; Found: C, 73.2; H, 7.2 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1,3-Me$_2$-2-*t*Bu-1*H*-2,1-benzazaborole (7). MeLi (4.0 mL of 1.6M solution in Et_2O, 6.4 mmol) was added to a solution of **1** (772 mg, 3.2 mmol) in toluene (50 mL) at 0 °C. The obtained fine cream suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and the remaining insoluble material was extracted by additional 10 mL of toluene. Pale-yellow filtrates were collected and evaporated *in vacuo* to give **7** as pale-yellow oil (isolated yield 579 mg, 90 %). This product can be purified by vacuum distillation at 190 °C, 1 mm Hg to give colourless oil.

Anal. calc. for $C_{13}H_{20}BN$ (MW 201.12): C, 77.6; H, 10.0; Found: C, 77.6; H, 9.9 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1,3-Ph$_2$-2-*t*Bu-1*H*-2,1-benzazaborole (8). *Procedure A)* PhLi (2.4 mL of 1.8M solution in nBu_2O, 4.4 mmol) was added to a solution of **1** (528 mg, 2.2 mmol) in toluene (30 mL) at 0 °C. The obtained fine ginger suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and filtrate was evaporated *in vacuo* to give pale-yellow honey-like matter. This matter was dissolved in hot pentane (5 mL). Storing at -30 °C gave **8** as white powder (isolated yield 565 mg, 80 %).

Procedure B) Analogously to the procedure A), using PhLi (1.7 mL of 1.8M solution in nBu_2O, 3.0 mmol) that was reacted with **2** (854 mg, 3.0 mmol). Isolated yield 796 mg, 81 %, m. p. 83 °C.

Anal. calc. for $C_{23}H_{24}BN$ (MW 325.25): C, 84.9; H, 7.4; Found: C, 84.8; H, 7.4 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1-Ph-2-*t*Bu-3-Me-1*H*-2,1-benzazaborole (9). MeLi (5.7 mL of 1.6M solution in Et_2O, 9.1 mmol) was added to a solution of **2** (2.59 g, 9.1 mmol) in toluene (90 mL) at 0 °C. The obtained fine pale-yellow suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and the remaining insoluble material was extracted by additional 2x10 mL of toluene and then filtered. Pale-yellow filtrates were collected and evaporated *in vacuo* to give crude **9** as pale-yellow crystalline solid. Obtained crude product was recrystallized from hot hexane (40 mL). Storing at -30 °C gave

9 in form of colourless single-crystals (isolated yield 2.31 g, 96 %), m. p. 90 °C.

Anal. calc. for $C_{18}H_{22}BN$ (MW 263.18): C, 82.1; H, 8.4; Found: C, 82.0; H, 8.5 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1-Ph-2,3-*t*Bu$_2$-1*H*-2,1-benzazaborole (10). *t*BuLi (4.2 mL of 1.7M solution in pentane, 7.2 mmol) was added to a solution of **2** (2.04 g, 7.2 mmol) in toluene (90 mL) at 0 °C. The obtained fine orange suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and the remaining insoluble material was extracted by additional 2x10 mL of toluene. Orange filtrates were collected and evaporated *in vacuo* to give orange honey-like matter. This matter was recrystallized from hot hexane (30 mL). Storing at -30 °C gave colourless crystalline solid polluted by yellow oil. Multiple recrystallization of this crude product from hot hexane and storing at -30 °C gave **10** as colourless single-crystals (isolated yield 983 mg, 45 %), m. p. 118 °C. Compound **10** is stable for a long time (several months) in argon atmosphere but decomposes in solution slowly over time.

Anal. calc. for $C_{21}H_{28}BN$ (MW 305.26): C, 82.6; H, 9.3; Found: C, 82.5; H, 9.2 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1,3-Me$_2$-2-(2,6-*i*Pr$_2$C$_6$H$_3$)-1*H*-2,1-benzazaborole (11). MeLi (3.8 mL of 1.6M solution in Et_2O, 6.1 mmol) was added to a solution of **3** (1.05 mg, 3.0 mmol) in toluene (60 mL) at 0 °C. The obtained fine dark ginger suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and the remaining insoluble material was extracted by additional 10 mL of toluene. Pale-orange filtrates were collected and evaporated *in vacuo* to give **11** as pale-orange honey-like matter (isolated yield 802 mg, 86 %). Neither X-ray diffraction analysis nor melting point could be obtained, because any attempt to crystalize **11** failed.

Anal. calc. for $C_{21}H_{28}BN$ (MW 305.26): C, 82.6; H, 9.3; Found: C, 82.3; H, 9.2 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1,3-Ph$_2$-2-(2,6-*i*Pr$_2$C$_6$H$_3$)-1*H*-2,1-benzazaborole (12). *Procedure A)* PhLi (1.3 mL of 1.8M solution in *n*Bu_2O, 2.2 mmol) was added to a solution of **3** (390 mg, 1.1 mmol) in toluene (40 mL) at 0 °C. The obtained fine ginger suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was evaporated *in vacuo* and extracted by boiling hexane (30 mL). Resulting suspension was filtered and obtained ginger filtrate was stored at -30 °C to give **12** as colourless crystalline solid (isolated yield 321 mg, 66 %).

Procedure B) Analogously to the procedure A), using PhLi (0.6 mL of 1.8M solution in *n*Bu_2O, 1.0 mmol) that was reacted with **4** (390 mg, 1.0 mmol). Isolated yield 283 mg, 66 %, m. p. 180 °C.

Anal. calc. for $C_{31}H_{32}BN$ (MW 429.40): C, 86.7; H, 7.5; Found: C, 86.7; H, 7.4 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1-Ph-2-(2,6-*i*Pr$_2$C$_6$H$_3$)-3-Me-1*H*-2,1-benzazaborole (13). MeLi (0.5 mL of 1.6M solution in Et_2O, 0.9 mmol) was added to a solution of **4** (330 mg, 0.9 mmol) in toluene (30 mL) at 0 °C. The obtained fine ivory suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and obtained filtrate was evaporated *in vacuo*. The crude product was recrystallized from hexane (30 mL). Storing at -30 °C gave **13** as colourless single-crystals (isolated yield 289 mg, 92 %), m. p. 185 °C.

Anal. calc. for $C_{26}H_{30}BN$ (MW 367.33): C, 85.0; H, 8.2; Found: C, 84.9; H, 8.3 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1-Ph-2-*t*Bu-3-Me-1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine (14). MeLi (2.4 mL of 1.6M solution in Et_2O, 3.8 mmol) was added to a solution of **5** (1.03 g, 3.8 mmol) in toluene (30 mL) at 0 °C. The obtained pink suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and obtained red filtrate was evaporated *in vacuo* to give reddish honey-like matter, which contained product **14** as the major product (>95%, according to the ^{1}H NMR spectra). Neither X-ray diffraction analysis nor melting point could be obtained, because any attempt to crystalize **14** failed. Isolated yield of crude product 820 mg, 86 %). **14** is unstable under natural daylight conditions. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1-Ph-2,3-*t*Bu$_2$-1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine (15). *t*BuLi (2.4 mL of 1.7M solution in pentane, 4.0 mmol) was added to a solution of **5** (1.10 g, 4.0 mmol) in toluene (30 mL) at 0 °C. The obtained orange suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight, while colour of reaction mixture changed to red. The mixture was filtered and volume of obtained red filtrate was reduced to one half. Storing at -30 °C gave colourless crystalline solid polluted by red oil, which was washed off by hexane (2 mL). Obtained crude product was recrystallized from hexane (30 mL). Storing at -30 °C gave **15** as colourless single-crystals (isolated yield 789 mg, 66 %), m. p. 110 °C.

Anal. calc. for $C_{19}H_{27}BN_2$ (MW 294.24): C, 77.6; H, 9.3; Found: C, 77.5; H, 9.3 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1,3-Ph$_2$-2-*t*Bu-1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine (16). PhLi (2.6 mL of 1.8M solution in *n*Bu_2O, 4.7 mmol) was added to a solution of **5** (1.29 g, 4.7 mmol) in toluene (30 mL) at 0 °C. The obtained pink suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and volume of obtained red filtrate was reduced to one quarter. Storing at -30 °C gave colourless microcrystalline solid **16**. Isolated yield 909 mg, 61 %), m. p. 101 °C.

Anal. calc. for $C_{21}H_{23}BN_2$ (MW 314.23): C, 80.3; H, 7.4; Found: C, 80.5; H, 7.5 %. **16** is unstable under natural daylight conditions. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1-Ph-2-(2,6-*i*Pr$_2$C$_6$H$_3$)-3-Me-1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine (17). MeLi (1.2 mL of 1.6M solution in Et$_2$O, 1.9 mmol) was added to a solution of **6** (715 mg, 1.9 mmol) in hexane (40 mL) at 0 °C. The obtained red suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and obtained red filtrate was evaporated *in vacuo* to give red crystalline solid, which was recrystallized from hexane (20 mL). Storing at -30 °C gave **17** as pink single-crystals (isolated yield 573 mg, 85 %), m. p. 154 °C.

Anal. calc. for $C_{24}H_{29}BN_2$ (MW 356.31): C, 80.9; H, 8.2; Found: C, 80.8; H, 8.1 %. For NMR data see Table 2 and ESI†.

Synthesis of racemic 1,3-Ph$_2$-2-(2,6-*i*Pr$_2$C$_6$H$_3$)-1*H*-pyrrolo[1,2-c][1,3,2]diazaborolidine (18). PhLi (0.6 mL of 1.8M solution in *n*Bu$_2$O, 1.1 mmol) was added to a solution of **6** (432 mg, 1.1 mmol) in hexane (40 mL) at 0 °C. Resulting pink suspension was stirred for 30 min at this temperature and then was allowed to reach r.t. and stirred overnight. The mixture was filtered and volume of pink filtrate was reduced to one half. Storing at -30 °C gave **18** as pink single-crystals (isolated yield 332 mg, 69 %), m. p. 172 °C.

Anal. calc. for $C_{29}H_{31}BN_2$ (MW 418.38): C, 83.3; H, 7.5; Found: C, 83.4; H, 7.6 %. For NMR data see Table 2 and ESI†.

X-ray crystallography

The suitable single crystals were mounted on a glass fibre with an oil and measured on a four-circle diffractometer KappaCCD with a CCD area detector by monochromatized MoK_α radiation (λ = 0.71073 Å) at 150(1) K. The numerical[22] absorption corrections from the crystal shape were applied for all crystals. The structures were solved by the direct method (SIR92)[23] and refined by a full matrix least squares procedure based on F^2 (SHELXL97).[24] Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors H_{iso} (H) = 1.2 Ueq (pivot atom) or of 1.5 U_{eq} for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in the aromatic ring, respectively. The *t*Bu group in **5** is disordered. This disorder of three carbon atoms has been treated by splitting them to two nearly equivalent positions. There is a slightly higher residual electron density peak detected at about 0.8 Å from the Cl(2) atom in the structure of **3**. This particular peak has no chemical significance. Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 999425-999434.

Crystallographic data for 3. $C_{19}H_{22}BCl_2N.CH_2Cl_2$, M = 431.01, monoclinic, $P2_1/c$, a = 12.3332(4), b = 13.0120(2), c = 14.1703(4) Å, β = 108.492(3)°, V = 2156.63(11) Å^3, Z = 4, T = 150(1) K, 18640 total reflections, 3863 independent (R_{int} = 0.039, $R1$ (obs. data) = 0.076, w$R2$ (all data) 0.182), S = 1.050, Δρ, max., min. [e Å^{-3}] 1.235, -0.866, CCDC 999434.

Crystallographic data for 4. $C_{25}H_{27}BClN.CH_2Cl_2$, M = 472.66, orthorhombic, $P2_12_12_1$, a = 10.3590(6), b = 13.0260(12), c = 18.498(2) Å, V = 2496.1(4) Å^3, Z = 4, T = 150(1) K, 16082 total reflections, 4755 independent (R_{int} = 0.038, $R1$ (obs. data) = 0.043, w$R2$ (all data) 0.081), S = 1.196, Δρ, max., min. [e Å^{-3}] 0.262, -0.325, CCDC 999433.

Crystallographic data for 5. $C_{15}H_{18}BClN_2$, M = 272.57, monoclinic, $P2_1/c$, a = 10.9790(8), b = 9.7780(3), c = 17.0041(10) Å, β = 127.218(6)°, V = 1453.67(18) Å^3, Z = 4, T = 150(1) K, 10875 total reflections, 2623 independent (R_{int} = 0.036, $R1$ (obs. data) = 0.045, w$R2$ (all data) 0.095), S = 1.106, Δρ, max., min. [e Å^{-3}] 0.256, -0.300, CCDC 999430.

Crystallographic data for 9. $C_{18}H_{22}BN$, M = 263.18, triclinic, $P\text{-}1$, a = 8.8771(3), b = 9.2700(3), c = 9.7179(3) Å, α = 74.766(3), β = 76.770(4), γ = 82.477(4)°, V = 748.98(4) Å^3, Z = 2, T = 150(1) K, 7972 total reflections, 2747 independent (R_{int} = 0.040, $R1$ (obs. data) = 0.049, w$R2$ (all data) 0.111), S = 1.113, Δρ, max., min. [e Å^{-3}] 0.366, -0.203, CCDC 999426.

Crystallographic data for 10. $C_{21}H_{28}BN$, M = 305.25, monoclinic, $P2_1/c$, a = 13.5601(10), b = 11.2810(9), c = 12.2599(7) Å, β = 107.667(6)°, V = 1787.0(2) Å^3, Z = 4, T = 150(1) K, 26459 total reflections, 3159 independent (R_{int} = 0.031, $R1$ (obs. data) = 0.049, w$R2$ (all data) 0.104), S = 1.099, Δρ, max., min. [e Å^{-3}] 0.306, -0.249, CCDC 999425.

Crystallographic data for 12. $C_{31}H_{32}BN$, M = 429.39, monoclinic, $P2_1/c$, a = 20.1420(19), b = 9.9090(11), c = 37.433(3) Å, β = 97.702(6)°, V = 7403.7(12) Å^3, Z = 12, T = 150(1) K, 45732 total reflections, 9787 independent (R_{int} = 0.046, $R1$ (obs. data) = 0.066, w$R2$ (all data) 0.117), S = 1.180, Δρ, max., min. [e Å^{-3}] 0.363, -0.302, CCDC 999428.

Crystallographic data for 13. $C_{26}H_{30}BN$, M = 367.32, monoclinic, $P2_1/c$, a = 10.4121(8), b = 12.0880(6), c = 17.2750(9) Å, β = 101.555(6)°, V = 2130.2(2) Å^3, Z = 4, T = 150(1) K, 21672 total reflections, 3721 independent (R_{int} = 0.035, $R1$ (obs. data) = 0.052, w$R2$ (all data) 0.106), S = 1.169, Δρ, max., min. [e Å^{-3}] 0.250, -0.240, CCDC 999429.

Crystallographic data for 15. $C_{19}H_{27}BN_2$, M = 294.24, monoclinic, $P2_1/c$, a = 13.3330(7), b = 11.1231(10), c = 12.0420(8) Å, β = 106.788(5)°, V = 1709.8(2) Å^3, Z = 4, T = 150(1) K, 23195 total reflections, 3229 independent (R_{int} = 0.019, $R1$ (obs. data) = 0.042 w$R2$ (all data) 0.101), S = 1.088, Δρ, max., min. [e Å^{-3}] 0.281, -0.211, CCDC 999432.

Crystallographic data for 17. $C_{24}H_{29}BN_2$, M = 356.30, monoclinic, $P2_1/c$, a = 10.3910(9), b = 11.9710(8), c = 17.1839(12) Å, β = 103.239(7)°, V = 2080.7(3) Å^3, Z = 4, T = 150(1) K, 15236 total reflections, 3387 independent (R_{int} = 0.042, $R1$ (obs. data) = 0.056, w$R2$ (all data) 0.111), S = 1.143, Δρ, max., min. [e Å^{-3}] 0.254, -0.217, CCDC 999431.

Crystallographic data for 18. $C_{29}H_{31}BN_2$, M = 418.37, monoclinic, $P2_1/c$, a = 16.5759(8), b = 10.0011(11), c = 14.4270(7) Å, β = 91.314(4)°, V = 2391.0(3) Å^3, Z = 4, T = 150(1) K, 23632 total reflections, 4207 independent (R_{int} = 0.036, $R1$ (obs. data) = 0.051, w$R2$ (all data) 0.106), S = 1.113, Δρ, max., min. [e Å^{-3}] 0.287, -0.251, CCDC 999427.

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Notes and references

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