Syntheses, Structures, and Reactivity of 2,5-Diboryl-1-alkylpyrroles and Di(1-alkyl-2-pyrrolyl)boranes

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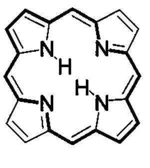
Dedicated to Prof. Wolfgang Sundermeyer on the occasion of his 70th birthday

Keywords: Boranes / 1-Alkylpyrroles / Porphyrinogenes / Lithiation / Tin–boron exchange

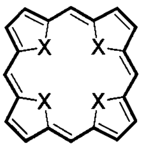
Reactions of 2,5-dilithiated 1-methylpyrrole (**1a**) with $\mathrm{ClB(NR_2)_2}$ lead to the novel 2,5-diboryl-1-methylpyrroles **2a** and **2b**. Accordingly, 2,5-diboryl-1-benzylpyrrole **2d** is obtained. **1a** and $\mathrm{Cl_2BN}i\mathrm{Pr_2}$ form the aminochloroboryl-substituted derivative **2c** and the di(5-boryl-2-pyrrolyl)borane **4** in 29% and 15% yield, respectively. The 2,5-distannyl-1-methylpyrrole **1c** is used for the synthesis of the aryloxy-boryl derivative **2e**. Reacting monolithiated 1-methyl- and 1-benzylpyrroles with $\mathrm{Cl_2BN}i\mathrm{Pr_2}$ yields the di(2-pyrrolyl)boranes **3e** and **3f**, respectively. NMR and MS data are in agreement with the compositions of the compounds, which are confirmed by X-ray structure analyses for **2a**, **2b**, **2d**, und **3e.**

Introduction

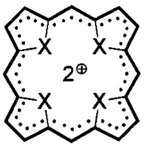
Since 1960 the hypothetical isophlorin (*N,N'*-dihydroporphyrin) **B**, X = NH,[1] as well as its heteroatom analogs have become a matter of interest. They may be regarded as bridged [20]annulenes. While the [18]annulene porphyrin **A** is very stable and shows a diatropic ring current[2] the tetraoxa macrocycle **B**, X = O, is less stable and exhibits a paratropic ring current.[3] Its dicationic precursor **C**, X = O, is an aromatic compound with a diatropic ring current.[4] In the octaethyl, tetramethyl derivatives of the tetraaza compounds **B** and **C**, X = NMe, the steric interference of the methyl groups causes non-planarity of both molecules. This yields for **C**, X = NMe, only to a small diatropic ring current,[5] whereas the paratropic ring current of **B**, X = NMe, is almost zero.[3]



A

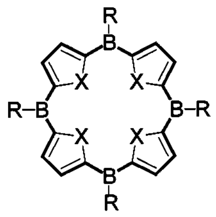


B
X = NH, NR, O, S

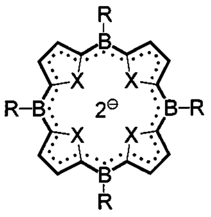


C
X = NH, NR, O, S

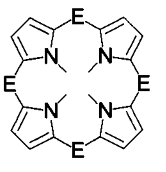
We are interested in the electronic structure and ligand properties of the tetrabora porphyrinogenes **D**, which formally derive from **B** by exchange of the *meso*-carbon for boron atoms. In **D** the empty p_z orbitals of the boron atoms may allow macrocyclic conjugation, when **D** (16 π electrons) is reduced to the dianion **E**. As a first example of a tetrabora porphyrinogene **D** we recently synthesized the tetrathia macrocycle **D**, X = S, R = N*i*$\mathrm{Pr_2}$.[6] The formation of the silyl- and stannyl-bridged macrocycles **F**, E = $\mathrm{SiMe_2}$, $\mathrm{SnMe_2}$, has been reported.[7]



D
X = NH, NR, O, S

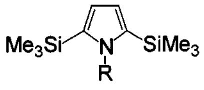


E
X = NH, NR, O, S

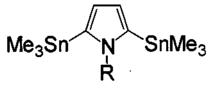


F
E = $\mathrm{SiMe_2}$, $\mathrm{SnMe_2}$

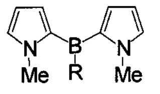
Possible building blocks for the synthesis of **D**, X = NR, may be 2,5-diborylpyrroles **2** and di(2-pyrrolyl)boranes **3**, which when suitably functionalized should be precursors for ring-closure reactions. However, 2,5-diborylpyrroles **2** are not yet known. Only a few 2,5-disilylpyrroles **G**[8] and the 2,5-distannylpyrrole **H**[9] have been reported. The di(1-methyl-2-pyrrolyl)boranes **3a−d** were synthesized via tin−boron exchange and characterized by NMR.[10] In the following we report on the syntheses of novel 2,5-diborylpyrroles **2** as well as the preparation of the di(2-pyrrolyl)boranes **3e** and **3f** via lithiated 1-alkylpyrroles.



G
R = Me, $\mathrm{CO_2}t$Bu,
CONH*t*Bu



H
R = $\mathrm{CO_2}t$Bu



3a-d
R = $\mathrm{NMe_2}$, Et, Cl,
$\mathrm{C_4H_3NMe}$

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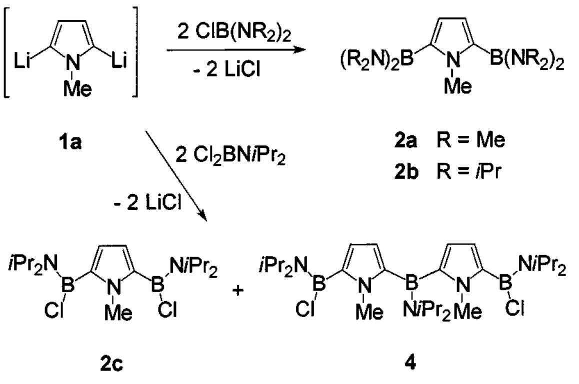
Results and Discussion

Syntheses and Reactivity

2,5-Dilithio-1-methylpyrrole (**1a**) is formed by treating 1-methylpyrrole with 2.4 equivalents of *n*-butyllithium in the presence of *N,N,N',N'*-tetramethylethylendiamine (tmeda) in refluxing hexane. The grey-brown suspension of **1a** is very sensitive and immediately turns dark on air contact. Due to its high reacticity **1a** was used in situ for the preparation of the compounds **2a−c**. Presumably the lithium centers of **1a** are coordinated and stabilized with tmeda.

The reaction of **1a** with $ClB(NMe_2)_2$ leads to the novel 2,5-bis[bis(dimethylamino)boryl]-1-methylpyrrol (**2a**) in 47% yield as colorless, crystalline solid, which is sensitive to air and moisture. The composition of **2a** follows from spectroscopic data and is confirmed by an X-ray structure analysis (see below). The ^{1}H-NMR spectrum shows the expected three singulets. The ^{11}B-NMR spectrum exhibits a signal at $\delta = 30.1$, which corresponds with that of 2-bis(dimethylamino)boryl-1-methylpyrrole ($\delta = 29.8$).[10a] In the ^{13}C-NMR spectrum the signals of the ring carbon atoms appear at $\delta = 116.2$ for those in 3- and 4-position and at $\delta = 137$ as a broadened signal[11] for the boron-bound ring atoms. The ^{13}C signals of the ring atoms reveal a low-field shift of 7 and 15 ppm compared with those of 1-methylpyrrole,[12] which may be explained by π-interaction of the heterocycle with the boryl substituent as discussed by Nöth et al.[10] A thermogravimetric analysis of **2a** shows a continuous loss of mass with no hint for condensation reactions, expected to be accompanied with elimination of $B(NMe_2)_3$. An analogous reaction is known to occur with 2,5-bis(dimethylboryl)thiophene[13] even at room temperature. Treatment of **2a** with $AlMe_3$, MeOH, or PCl_5 did not lead to the projected exchange of substituents at the boron atoms.



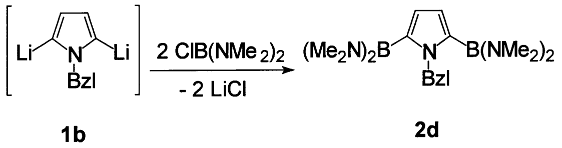
Scheme 1

The reaction of **1a** with $ClB(NiPr_2)_2$ yields only 6% of 2,5-bis[bis(diisopropylamino)boryl]-1-methylpyrrole (**2b**) as a colorless, crystalline solid, which is sensitive to air and moisture. The difference in the yield of **2a** and **2b** is probably caused by the greater steric impact of the diisopropylamino in comparison to the dimethylamino group. The spectroscopic and structural data of **2b** are similar to those of **2a**. Treatment of **2b** with BCl_3 did not yield the appropriate bis(dichloroboryl) derivative.

By adding the suspension of **1a** slowly into a cooled solution of Cl_2BNiPr_2 the 2,5-bis(chlorodiisopropylaminoboryl)-1-methylpyrrole (**2c**) is obtained in 29% together with 15% of bis[5-(chlorodiisopropylaminoboryl)-1-methyl-2-pyrrolyl]diisopropylaminoborane (**4**). Most likely the latter is formed, when the intermediate 5-(chlorodiisopropylamino)-2-lithio-1-methylpyrrole reacts with **2c** to give **4**.

2c is a colorless, crystalline solid, sensitive to air and moisture. Its ^{1}H-, ^{11}B-, and ^{13}C-NMR shifts are very similar to that of **2b** with exception of the shifts for the isopropyl groups. They appear in the ^{1}H-NMR spectrum as two sets of broadened signals with equal intensity, which indicates a B−N double bond.

4 is a colorless, air- and moisture-sensitive crystalline solid, which decomposes when heated to 130°C. The ^{1}H-NMR spectrum of **4** shows three sets of isopropyl groups in equal intensity. The signals for the aminochloroboryl substituents are identical with that of **2c**, the third set belongs to the isopropylamino group between the two heterocycles and is resolved as doublet and septet. The ring protons appear as two doublets at $\delta = 6.51$ and 6.63 with a coupling constant of 3.5 Hz. The ^{11}B-NMR spectrum shows one broad unsymmetrical signal at $\delta = 35$, formed by superposition of the two signals of the different boron atoms. In the ^{13}C-NMR spectrum only one broad signal at $\delta = 23$ for the two methyl groups of the outer isopropyl group is found, the corresponding methyne signals are separated. For the heterocycles four signals are found, two at $\delta = 114.1$ and 116.7 for the carbon atoms in 3- and 4-position and two broad ones[11] at $\delta = 137$ and 141 for the two different boron-bound carbon atoms. The composition of **4** is confirmed by a high resolution mass spectrum.

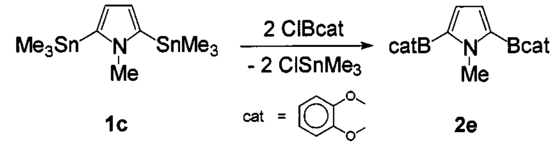


Scheme 2

Treating 1-benzylpyrrole with 2.4 equivalents of *n*-butyllithium and tmeda in refluxing hexane leads to the formation of 1-benzyl-2,5-dilithiopyrrole (**1b**). It is in situ treated with $ClB(NMe_2)_2$ to yield 34% of 2,5-bis[bis(dimethylamino)boryl]-1-benzylpyrrole (**2d**) as a colorless, crystalline solid, which is sensitive to air and moisture. Beside the benzyl group its spectroscopic data are similar to **2a**. A high resolution mass spectrum and an X-ray structure analysis confirm the composition of **2d**.

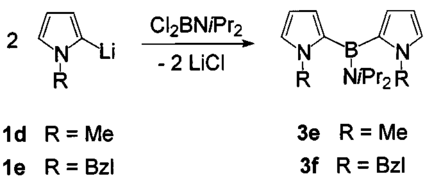
Attempts to synthesize 2,5-bis(dimethylboryl)-1-methylpyrrole (**2f**) from **1a** and Me_2BBr failed. The alternative route via the ditin derivative **1c** was tested to obtain **2e** as precursor for **2f**. Reaction of **1a** with trimethyltinbromide leads to the formation of 2,5-bis(trimethylstannyl)-1-methylpyrrole (**1c**), a colorless solid, characterized by multinuclear NMR spectroscopy (^{1}H, ^{13}C, and ^{119}Sn) and mass spectrometry. It is transformed into 2,5-bis(1,3,2-benzodioxaborol-2-yl)-1-methylpyrrole (**2e**) by the reaction of **1c** with 2-chloro-1,3,2-benzodioxaborole. The tin−boron exchange leads to colorless **2e** in 75% yield.

The 200-MHz ^{1}H-NMR spectrum of **2e** shows only two multiplets in the aromatic region. A 300-MHz spectrum reveals that the singulet for the pyrrole ring protons (δ = 7.09) superposes with one of the multiplets of the benzo ring protons at δ = 7.11. The ^{11}B-NMR shift of **2e** is δ = 30. In the ^{13}C-NMR spectrum a signal for the boron-bound carbon atoms could not be observed.[11] As recently shown the benzodioxaborole ring is easily cleaved by LiMe or $AlMe_3$ to yield dimethylboryl groups.[14] The reaction of **2e** with $AlMe_3$ at −70°C indicated the formation of 2,5-bis(dimethylboryl)-1-methylpyrrole (**2f**), which could not be isolated. Most likely a polycondensation of the projected **2f** occured with elimination of BMe_3.



Scheme 3

The reaction of monolithiated 1-methylpyrrole (**1d**) with $Cl_2BN\textit{i}Pr_2$ yields diisopropylaminodi(1-methyl-2-pyrrolyl)-borane (**3e**) as a colorless, crystalline solid. **3e** is stable up to 210°C, but sensitive to air and moisture. The ^{1}H-NMR spectrum shows next to the signals of the isopropyl group and the ring methyl group three multiplets for the ring protons at δ = 6.31, 6.48, and 6.56. The signal at δ = 6.31 is resolved as doublet of doublets with coupling constants of 2.4 and 3.5 Hz. They are ^3J coupling constants and hence the signal is assigned to the ring proton in 4-position. According to Nöth et al.[10b] the signals for the ring atoms in 4-position (proton and carbon atom) appear at high field, compared with those of the other ring atoms. This fact is based on the mesomeric effect of the boryl group in 2-position, which leads to partially postive charged 1-, 3-, and 5-positions. Accordingly, in the ^{13}C-NMR spectrum the signal for the carbon atom in 4-position appears at δ = 107.7 with the other ring signals at δ = 116.7, 125.4, and 138, the latter being the broadened signal[11] for the boron-bound carbon atoms. The ^{11}B-NMR spectrum shows a signal at δ = 35.6, which is comparable to dimethylamino derivative **3a** (δ = 31.8).[10a] The composition of **3e** is confirmed by a high resolution mass spectrum and an X-ray structure analysis.



Scheme 4

Analogously, di(1-benzyl-2-pyrrolyl)diisopropylaminoborane (**3f**) is synthesized from **1e**. The colorless solid is sensitive to air and moisture. Its chemical shifts are very similar to those of **3e** with exception of the benzyl group.

Crystal Structures

To elucidate the structure of the novel 2,5-diborylpyrroles **2** X-ray diffraction studies of the amino-substituted derivatives **2a**, **2b**, and **2d** were carried out (crystal data and structure refinement including **3e** are shown in Table 1).

The molecule of **2a** has almost C_s-symmetry with the mirror plane perpendicular to the ring plane. The bond lengths and angles are equal within the *esd*s.

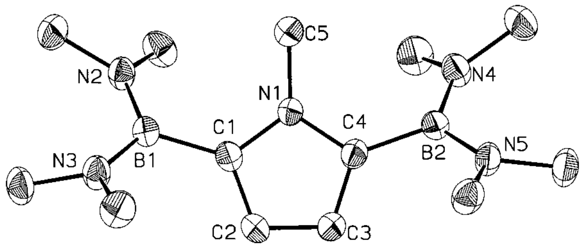


Figure 1. Molecular structure of **2a** in the crystal; selected bond lengths [Å] and angles [°]: N1−C1 1.390(2), N1−C4 1.391(2), C1−C2 1.383(3), C4−C3 1.381(3), C2−C3 1.402(3), N1−C5 1.457(2), C1−B1 1.577(3), C4−B2 1.575(3), B1−N2 1.419(2), B1−N3 1.429(3), B2−N4 1.429(3), B2−N5 1.424(3), C4−N1−C1 111.0(1), N1−C1−C2 105.6(1), C1−C2−C3 108.8(2), C2−C3−C4 108.8(2), C3−C4−N1 105.7(1), N1−C1−B1 127.8(1), N1−C4−B2 127.4(1).

2b has a crystallographic two-fold axis through the molecule and **2d** a crystallographic mirror plane perpendicular to the pyrrole ring.

The geometries of the three molecules are very similar. The distances and angles of the pyrrole rings are almost equal (within 3σ), but show significant deviations from the unsubstituted pyrrole ring,[12] especially for the endocyclic angles (values for the unsubstituted pyrrole in parantheses): C−N−C 111.0−111.6° (109.8°), N−C−C 105.4−105.7° (107.7°), C−C−C 108.7−108.8° (107.4°). The reason for this difference is not clear.

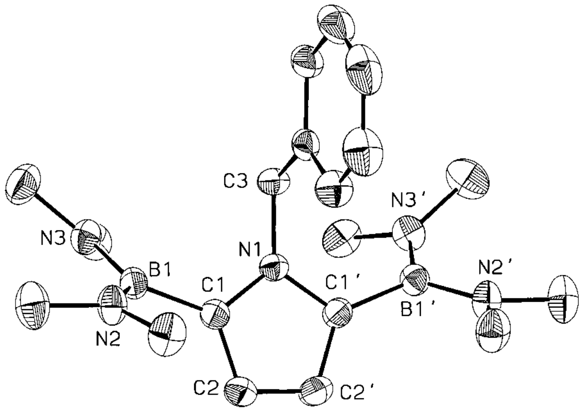


Figure 2. Molecular structure of **2d** in the crystal. − Selected bond lengths [Å] and angles [°] of **2d**: N1−C1 1.390(2), C1−C2 1.382(2), C2−C2′ 1.411(4), N1−C3 1.456(3), C1−B1 1.578(2), B1−N2 1.419(2), B1−N3 1.427(2), C1′−N1−C1 111.4(2), N1−C1−C2 105.6(1), C1−C2−C2′ 108.7(1), N1−C1−B1 125.5(1). − Selected bond lengths [Å] and angles [°] of **2b**: N1−C1 1.384(3), C1−C2 1.373(3), C2−C2′ 1.405(5), N1−C3 1.447(4), C1−B1 1.584(4), B1−N2 1.425(4), B1−N3 1.438(4), C1′−N1−C1 111.6(3), N1−C1−C2 105.4(2), C1−C2−C2′ 108.7(1), N1−C1−B1 127.0(2).

The pyrrole rings are almost planar with max. deviations of 0.006 Å for **2a** and 0.010 Å for **2b** and **2d**. The substituents deviate only slightly from the ring plane. The boron atoms have an almost planar coordination, but the CBNN planes are twisted against the ring planes. The interplanar angles increase from 43.0 and 48.2° for **2a** to 57.8° for **2d** (caused by the benzyl ligand) and up to 71.5° for **2b** with the bulky isopropyl groups. The planes through the amino groups are not coplanar with the CBNN planes, but rotated by 19.0−35.1°. The B−N distances (1.419−1.438 Å) are somewhat greater than in other aminoboranes.[15]

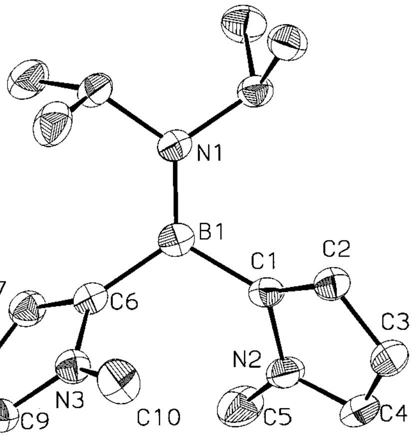


Figure 3. Molecular structure of **3e** in the crystal; selected bond lengths [Å] and angles [°]: N2−C1 1.389(2), N3−C6 1.392(2), C1−C2 1.387(2), C6−C7 1.384(2), C2−C3 1.409(3), C7−C8 1.406(3), C3−C4 1.357(3), C8−C9 1.363(3), C4−N2 1.366(2), C9−N3 1.367(2), N2−C5 1.456(3), N3−C10 1.456(3), C1−B1 1.577(3), C6−B1 1.574(3), B1−N1 1.406(2), C4−N2−C1 109.7(1), C9−N3−C6 110.3(1), N2−C1−C2 105.3(1), N3−C6−C7 105.0(2), C1−C2−C3 109.2(2), C6−C7−C8 109.5(2), C2−C3−C4 106.5(2), C7−C8−C9 106.9(2), C3−C4−N2 109.1(2), C8−C9−N3 108.3(2), N2−C1−B1 124.6(1), N3−C6−B1 122.5(1).

3e is the first di(2-pyrrolyl)borane, whose structure was determined. The coordination at the boron and the N1 nitrogen center is almost planar, but the molecule ist twisted by 17.8° around the B−N bond. The B−N distance is smaller than in the 2,5-diborylpyrroles **2**. The two pyrrole rings show only small deviations (max. 0.008 Å) from planarity and are rotated by 45.9 and 58.1° against the plane through B1, C1, C6, and N1. The pyrrole rings are not symmetrically substituted and show significant differences of the distances and angles compared with the unsubstituted pyrrole[12] and the 2,5-diborylpyrroles **2**.

Experimental Section

General: Reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents and chemicals were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat-gun in high vacuum. − ^{1}H, ^{11}B, ^{13}C, ^{119}Sn NMR: Bruker AC 200 spectrometer, shift references are $(CH_3)_4Si$, $BF_3 \cdot Et_2O$, and $(CH_3)_4Sn$. − Mass spectra were obtained with a Varian MAT CH7 spectrometer, high resolution mass spectra with a Jeol JMS-700 spectrometer both using the EI technique. − Melting points (uncorrected) were measured with a Büchi apparatus using a capillary, which was filled under nitrogen and sealed. − 1-Benzylpyrrole,[16a] $ClB(NMe_2)_2$,[16b] ClB(N*i*Pr$_{22}$,[16c] Cl$_2$BN*i*Pr$_2$,[16d] 2-chloro-1,3,2-benzodioxaborole (ClBcat),[16e] and $(CH_3)_3SnBr$[16f] were prepared according to literature procedures.

2,5-Dilithio-1-methylpyrrole (1a): To a solution of 3.6 mL (24.0 mmol) of tmeda in 40 mL of hexane 9.6 mL (24.0 mmol) of *n*-butyllithium (2.5 M in hexane) were added with cooling and stirred for 15 min at room temp. After the addition of 0.9 mL (10.1 mmol) of 1-methylpyrrole the mixture was refluxed for 9 h. A grey-brown suspension was formed.

2,5-Bis(trimethylstannyl)-1-methylpyrrole (1c): To a suspension of **1a** (10.3 mmol) in 50 mL of hexane a solution of 5.86 g (24.0 mmol) of $(CH_3)_3SnBr$ in 10 mL of hexane was added dropwise at −30°C. The mixture was allowed to warm to room temp. and stirred for 15 h. Volatile compounds were removed in vacuum, the residue was dissolved in hexane and filtered. The solvent was evaporated in vacuum and the colorless solid obtained was recrystallized from hexane at −80°C. Yield: 2.88 g (69%) colorless **1c**. − ^{1}H NMR (C_6D_6, 200.1 MHz): δ = 0.22 [s, 18 H, $^{2}J(H,^{117}Sn)$ = 53.4 Hz (7,1%), $^{2}J(H,^{119}Sn)$ = 55.9 Hz (7,7%), SnC*H*$_3$], 3.41 (s, 3 H, $^{4}J_{H,Sn}$ = 2.4 Hz, NC*H*$_3$), 6.65 (s, 2 H, $^{3}J_{H,Sn}$ = 10.5 Hz, C*H*). − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = −8.8 ($^{1}J_{C,Sn}$ = 348.3 Hz and 364.3 Hz, Sn*C*H$_3$), 39.4 (N*C*H$_3$), 120.1 ($^{2}J_{C,Sn}$ = 50.5 Hz and 60.5 Hz, *C*H), 136.3 (ring-*C*Sn). − ^{119}Sn NMR (C_6D_6, 74.6 MHz): δ = −33.0. − MS: *m/z* (%): 407 (26) [M$^+$], 392 (62) [M$^+$ − Me], 230 (100).

2,5-Bis[bis(dimethylamino)boryl]-1-methylpyrrole (2a): To a suspension of **1a** (10.1 mmol) in 50 mL of hexane a solution of 2.75 g (20.5 mmol) of $ClB(NMe_2)_2$ in 15 mL of hexane was added within 25 min at −30°C. The mixture was allowed to warm to room temp. and stirred for 14 h. After 20 min of refluxing the volatile compounds were evaporated in vacuum, the residue was dissolved in hexane and filtered. The solvent was removed in vacuum and **2a** was sublimed. A single crystal was grown from a pentane solution at −30°C. Yield: 1.32 g (47%) colorless **2a**, subl.p.: 72°C/5·10^{-2} mbar. − ^{1}H NMR (C_6D_6, 200.1 MHz): δ = 2.65 (s, 24 H, BNC*H*$_3$), 3.44 (s, 3 H, CNC*H*$_3$), 6.52 (s, 2 H, C*H*). − ^{11}B NMR (C_6D_6, 64.2 MHz): δ = 30.1. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 34.4 (CN*C*H$_3$), 40.8 (BN*C*H$_3$), 116.2 (*C*H), 137 (br, *C*B). − MS: *m/z* (%): 277 (7) [M$^+$], 233 (3) [M$^+$ − NMe$_2$], 58 (100).

2,5-Bis[bis(diisopropylamino)boryl]-1-methylpyrrole (2b): To a suspension of **1a** (10.1 mmol) in 50 mL of hexane a solution of 5.10 g (20.7 mmol) of ClB(N*i*Pr$_2$)$_2$ in 20 mL of hexane was added within 20 min at room temp. The mixture was stirred for 14 h and refluxed for 8 h. Volatile compounds were removed in vacuum, the residue was dissolved in hexane and filtered. The solvent was evaporated in vacuum and **2b** was sublimed. A single crystal was grown from a hexane solution at −30°C. Yield: 0.30 g (6%) colorless **2b**, subl.p.: 140°C/1.2·10^{-2} mbar. − ^{1}H NMR (C_6D_6, 200.1 MHz): δ = 1.17 [d, 48 H, $^{3}J_{H,H}$ = 6.9 Hz, CH(C*H*$_3$)$_2$], 3.58 [sept, 8 H, $^{3}J_{H,H}$ = 6.9 Hz, C*H*(CH$_3$)$_2$], 3.70 (s, 3 H, NC*H*$_3$), 6.39 (s, 2 H, ring-C*H*). − ^{11}B NMR (C_6D_6, 64.2 MHz): δ = 33.7. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 25.1 [CH(*C*H$_3$)$_2$], 37.3 (N*C*H$_3$), 47.8 [*C*H(CH$_3$)$_2$], 116.7 (ring-*C*H), *C*B signal not observed. − MS: *m/z* (%): 501 (47) [M$^+$], 458 (39) [M$^+$ − *i*Pr], 401 (43) [M$^+$ − N*i*Pr$_2$], 211 (100) [B(N*i*Pr$_2$)$_2$$^+$].

2,5-Bis(chlorodiisopropylaminoboryl)-1-methylpyrrole (2c) and Bis[5-(chlorodiisopropylaminoboryl)-1-methyl-2-pyrrolyl]diisopropylaminoborane (4): To a solution of 4.43 g (24.3 mmol) of Cl$_2$BN*i*Pr$_2$ in 20 mL of hexane a suspension of **1a** (10.3 mmol) in 50 mL hexane was added dropwise at −50°C. The mixture was allowed to warm to room temp. and stirred for 15 h. Volatile compounds were removed in vacuum, the residue was dissolved in hexane and filtered. The solvent was evaporated and the residue treated with 20 mL of hexane. **4** was crystallized from the solution at −30°C, filtered, and dried. The remaining solution was evaporated in vacuum to half the volume and **2c** was crystallized at −30°C, separated, and dried. Yield: 1.12 g (29%) of colorless **2c**. − ^{1}H NMR (C_6D_6, 200.1 MHz): δ = 0.84, 1.34 [each br, 12 H, $CH(CH_3)_2$], 3.38, 4.07 [each br, 2 H, $CH(CH_3)_2$], 3.81 (s, 3 H, NCH_3), 6.48 (s, 2 H, ring-C*H*). − ^{11}B NMR (C_6D_6, 64.2 MHz): δ = 33.8. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 22.1, 23.0 [each $CH(CH_3)_2$], 37.1 (NCH_3), 47.0, 51.6 [each $CH(CH_3)_2$], 115.0 (ring-*C*H), 137 (br, *C*B). − MS: *m*/*z* (%): 371 (13) [M$^+$], 328 (18) [M$^+$ − *i*Pr], 84 (100). − Yield: 422 mg (15%) of colorless **4**, m.p.: 187°C (decomp.). − ^{1}H NMR (C_6D_6, 200.1 MHz): δ = 0.94, 1.32 [each br, 12 H, $CH(CH_3)_2$ (outer)], 1.17 [d, 12 H, $^{3}J_{H,H}$ = 6.8 Hz, $CH(CH_3)_2$ (inner)], 3.31 (s, 6 H, NCH_3), 3.37 [br, 2 H, $CH(CH_3)_2$ (outer)], 4.07 [sept, 2 H, $^{3}J_{H,H}$ = 6.8 Hz, $CH(CH_3)_2$ (inner) and br, 2 H, $CH(CH_3)_2$ (outer)], 6.51, 6.63 (each d, 2 H, $^{3}J_{H,H}$ = 3.5 Hz, ring-C*H*). − ^{11}B NMR (C_6D_6, 64.2 MHz): δ = 35. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 23 [br, both $CH(CH_3)_2$ (outer)], 24.8 [$CH(CH_3)_2$ (inner)], 36.2 (NCH_3), 46.9, 51.5 [each $CH(CH_3)_2$ (outer)), 49.1 ($CH(CH_3)_2$ (inner)], 114.1, 116.7 (each ring-*C*H), 137, 141 (each br, *C*B). − MS: *m*/*z* (%): 561 (56) [M$^+$], 518 (27) [M$^+$ − *i*Pr], 292 (100). − HR-MS: *m*/*z* (%): 561.3915 (9) [M$^+$, calc. for $^{12}C_{28}$ $^{1}H_{52}$ $^{11}B_3$ $^{35}Cl_2$ $^{14}N_5$: 561.3879].

2,5-Bis[bis(dimethylamino)boryl]-1-benzylpyrrole (2d): To a solution of 3.6 mL (24.0 mmol) of tmeda in 50 mL of hexane 9.2 mL (23.0 mmol) of *n*-butyllithium (2.5 M in hexane) was added with cooling. After stirring for 20 min at room temp. 1.58 g (10.0 mmol) of 1-benzylpyrrole was added with cooling and the mixture was heated under reflux for 14 h. To the resulting suspension 2.77 g (20.6 mmol) of $ClB(NMe_2)_2$ in 20 mL of hexane was added dropwise at −30°C. After the mixture was allowed to warm to room temp. and stirred for 4 h, it was refluxed for 2 h. Volatile compounds were evaporated in vacuum, the residue was dissolved in hexane and filtered. The solvent was removed in vacuum and the colorless solid washed with pentane. A single crystal was grown from a solution of pentane and CH_2Cl_2 (4:1) at −30°C. Yield: 1.21 g (34%) colorless **2d**, m.p.: 103°C. − ^{1}H NMR ($CDCl_3$, 200.1 MHz): δ = 2.59 (s, 24 H, CH_3), 4.91 (s, 2 H, CH_2), 6.17 (s, 2 H, pyrrole-C*H*), 6.92 (m, 2 H, phenyl-C*H*), 7.17 (m, 3 H, phenyl-C*H*). − ^{11}B NMR ($CDCl_3$, 64.2 MHz): δ = 30.8. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 40.6 (CH_3), 51.1 (CH_2), 116.1 (pyrrole-*C*H), 126.5, 127.2, 127.9 (each phenyl-*C*H), 141.4 (phenyl-C_{ipso}), *C*B signal not observed. − MS: *m*/*z* (%): 353 (69) [M$^+$], 309 (9) [M$^+$ − NMe_2], 99 (100) [$B(NMe_2)_2^+$]. − HR-MS: *m*/*z* (%): 353.2907 (22) [M$^+$, calc. for $^{12}C_{19}$ $^{1}H_{33}$ $^{11}B_2$ $^{14}N_5$: 353.2922].

2,5-Bis(1,3,2-benzodioxaborol-2-yl)-1-methylpyrrole (2e): A solution of 1.13 g (2.8 mmol) of **1c** in 10 mL of toluene was cooled to −75°C and the solution of 878 mg (5.7 mmol) of ClBcat in 10 mL of toluene was added. The mixture was allowed to warm to room temp. and stirred for 15 h. After 1 h of refluxing the resulting solid was separated by filtration, washed with hexane and CH_2Cl_2, and dried. Yield: 661 mg (75%) colorless **2e**. − ^{1}H NMR ([D_8]thf, 200.1 MHz): δ = 4.38 (s, 3 H, CH_3), 7.09 (s, 2 H, pyrrole-C*H*), 7.11, 7.31 (each m, 4 H, benzo-C*H*). − ^{11}B NMR ([D_8]thf, 64.2 MHz): δ = 30. − ^{13}C NMR ([D_8]thf, 50.3 MHz): δ = 37.3 (CH_3), 113.3, 123.9 (each benzo-*C*H), 124.2 (pyrrole-*C*H), 149.6 (*C*O), *C*B signal not observed. − MS: *m*/*z* (%): 317 (28) [M$^+$], 58 (100).

Diisopropylaminodi(1-methyl-2-pyrrolyl)borane (3e): To a solution of 2.6 mL (29.2 mmol) of 1-methylpyrrole in 20 mL of thf 12.5 mL (31.2 mmol) of *n*-butyllithium (2.5 M in hexane) was added at −35°C. After the mixture was allowed to warm for 1 h, and stirred at room temp. for 3 h. At −70°C a solution of 2.60 g (14.3 mmol) of Cl_2BNiPr_2 in 10 mL of thf was added. The mixture was allowed to warm to room temp. and stirred for 16 h. Volatile compounds were removed in vacuum, the residue was dissolved in hexane and filtered. The solvent was evaporated in vacuum and the colorless

Table 1. Crystal data and structure refinement for **2a**, **2b**, **2d**, and **3e**

	2a	**2b**	**2d**	**3e**
Formula	$C_{13}H_{29}B_2N_5$	$C_{29}H_{61}B_2N_5$	$C_{19}H_{33}B_2N_5$	$C_{16}H_{26}BN_3$
Molecular weight	277.03	501.46	353.13	271.22
Crystal system	orthorhombic	monoclinic	orthorhombic	triclinic
Space group	*P*bca	*C*2/c	*P*bnm	$P\bar{1}$
Unit cell				
a [Å]	12.500(9)	22.925(4)	9.492(5)	7.697(4)
b [Å]	16.070(11)	12.651(2)	13.721(8)	9.678(5)
c [Å]	16.796(15)	12.773(2)	16.263(9)	12.324(6)
α [°]	90	90	90	72.93(3)
β [°]	90	111.03(1)	90	74.62(3)
γ [°]	90	90	90	81.94(3)
Volume [Å^3]	3374(4)	3457.7(11)	2118(2)	844.2(7)
Z	8	4	4	2
Calc. density [g/cm^3]	1.09	0.96	1.11	1.07
Adsorption coeff. [mm^{-1}]	0.07	0.06	0.07	0.06
F(000)	1216	1120	768	296
Crystal size [mm]	0.5×0.5×0.7	0.5×0.55×0.8	0.25×0.5×0.7	0.3×0.4×0.4
Θ_{max} [°]	25	25	30	25
Index ranges	0/+14, 0/+19, 0/+19	0/+29, 0/+16, −16/+15	0/+13, 0/+19, 0/+22	−8/+7, −10/+11, 0/+14
Number of reflections				
unique	2970	3008	3187	2798
observed [$I > 2\sigma(I)$]	2195	1884	1929	2138
Transmission	0.891−0.999	0.736−0.786	0.886−0.999	0.930−0.996
Parameters	201	181	202	285
Final *R* indices				
*R*1 [$I > 2\sigma(I)$]	0.044	0.072	0.053	0.043
*wR*2	0.115	0.207	0.157	0.113
Max. diff. peak / hole [e/Å^3]	+0.15 / −0.20	+0.17 / −0.19	+0.34 / −0.27	+0.15 / −0.23

solid recrystallized from hexane at −30°C. A single crystal was grown from a solution of hexane and CH_2Cl_2 (6:1) at room temp.. Yield: 1.50 g (38%) colorless **3e**, m.p. > 210°C. − ^{1}H NMR (C_6D_6, 200.1 MHz): $\delta = 1.17$ [d, 12 H, $^{3}J_{H,H} = 6.7$ Hz, $CH(CH_3)_2$], 2.82 (s, 6 H, NCH_3), 4.07 [sept, 2 H, $^{3}J_{H,H} = 6.7$ Hz, $CH(CH_3)_2$], 6.31 [dd, 2 H, $^{3}J_{H,H} = 2.4$ Hz, $^{3}J_{H,H} = 3.5$ Hz, ring-*CH*(C4)], 6.48 (m, 2 H, ring-C*H*), 6.56 (dd, 2 H, $^{3}J_{H,H} = 3.5$ Hz, $^{4}J_{H,H} = 1.5$ Hz, ring-C*H*). − ^{11}B NMR (C_6D_6, 64.2 MHz): $\delta = 35.6$. − ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 24.8$ [$CH(CH_3)_2$], 35.3 (NCH_3), 49.0 [$CH(CH_3)_2$], 107.7 [ring-*C*H(C4)], 116.7, 125.4 (each ring-*C*H), 138 (br, *C*B). − MS: *m/z* (%): 271 (65) [M^+], 147 (100). − HR-MS: *m/z* (%): 271.2226 (38) [M^+, calc. for $^{12}C_{16}$ $^{1}H_{26}$ ^{11}B $^{14}N_3$: 271.2220].

Di(1-benzyl-2-pyrrolyl)diisopropylaminoborane (3f): To a solution of 1.8 mL (12.0 mmol) of tmeda in 40 mL of hexane 4.8 mL (12.0 mmol) of *n*-butyllithium (2.5 M in hexane) was added with cooling and stirred for 30 min at room temp.. After the addition of 1.55 g (9.9 mmol) of 1-benzylpyrrole the mixture was refluxed for 2 h. To the brown suspension a solution of 1.04 g (5.7 mmol) of Cl_2BNiPr_2 in 25 mL of hexane was added within 45 min at −30°C. After the mixture was allowed to warm to room temp. and stirred for 18 h, it was refluxed for 30 min. Volatile compounds were removed in vacuum, the residue was dissolved in toluene and filtered. The solvent was evaporated in vacuum and the colorless solid recrystallized from pentane at −80°C. Yield: 662 mg (31%) colorless **3f**. − ^{1}H NMR ($CDCl_3$, 200.1 MHz): $\delta = 1.11$ [d, 12 H, $^{3}J_{H,H} = 6.8$ Hz, $CH(CH_3)_2$], 4.04 [sept, 2 H, $^{3}J_{H,H} = 6.8$ Hz, $CH(CH_3)_2$], 4.57 (s, 4 H, CH_2), 6.28 [dd, 2 H, $^{3}J_{H,H} = 2.4$ Hz and 3.4 Hz, pyrrole-C*H*(C4)], 6.47 (dd, 2 H, $J_{H,H} = 3.4$ Hz, $^{4}J_{H,H} = 1.5$ Hz, pyrrole-C*H*), 6.85 (dd, 2 H, $^{3}J_{H,H} = 2.4$ Hz, $^{4}J_{H,H} = 1.5$ Hz, pyrrole-C*H*), 7.08 (m, 4 H, phenyl-C*H*), 7.26 (m, 6 H, phenyl-C*H*). − ^{11}B NMR ($CDCl_3$, 64.2 MHz): $\delta = 36.4$. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 24.6$ [$CH(CH_3)_2$], 48.9 [$CH(CH_3)_2$], 51.7 (CH_2), 107.4 [pyrrole-*C*H(C4)], 116.7, 124.5 (each pyrrole-*C*H), 126.9, 127.3, 128.1 (each phenyl-*C*H), 137 (br, *C*B), 139.5 (phenyl-C_{ipso}). − MS: *m/z* (%): 423 (100) [M^+], 408 (18) [$M^+ - Me$], 91 (88) [$CH_2 - Ph^+$].

X-ray Structure Determinations of 2a, 2b, 2d, and 3e: Crystal data and details of the stucture determinations are listed in Table 1. Unique sets of intensity data for **2a**, **2d**, and **3e** were collected at −70°C with a Siemens Stoe AED2 diffractometer and for **2b** at room temp. with a Syntex R3 diffractometer (Mo-K_α radiation, $\lambda = 0.7107$ Å, graphite monochromator, ω-scan). Empirical absorption corrections (ψ-scans) were applied. The structures were solved by direct methods (SHELXS-86)[17a] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-93)[17b]. All non-hydrogen atoms are refined anisotropically. For **2a** and **2b** hydrogen atoms were inserted in calculated positions, for **2d** and **3e** they were located in difference Fourier maps and refined isotropically.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-102879 (**2a**), CCDC-102880 (**2b**), CCDC-102881 (**2d**), and and CCDC-102882 (**3e**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: int. code +44 (0)1223/ 336-001; E-mail: deposit@ccdc.cam.ac.uk

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