Synthesis and Properties of Bis(2-heteroaryl)borane Derivatives

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Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

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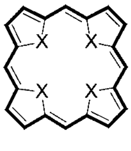
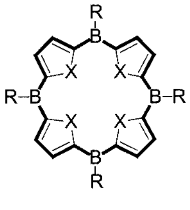
The reaction of (isopropyloxy)bis(2-thienyl)borane (**1d**) with Grignard reagents leads to methylbis(2-thienyl)borane (**1e**) and to phenylbis(2-thienyl)borane (**1f**). Treatment of monolithiated heterocycles with dichloroboranes yields the bis(2-heteroaryl)boranes **1b**, **1c**, and **3a**, which are dibrominated with NBS to give the 5,5′-dibromo products **1b′**, **2a′**, and **3a′**. NMR spectroscopic and MS data confirm the composition of the compounds. The [2+2] cyclization of the dibromo derivatives yields, in the case of **2a′**, the macrocycle **4b**, as confirmed by HR-MS data.

Introduction

We are interested in the electronic structure and ligand properties of tetraboraporphyrinogens **B**, which formally derive from isophlorins (*N*,*N′*-dihydroporphyrins) **A**[1] (X = NR) by exchange of the *meso*-carbon atoms for boron atoms. In **B** the empty p_z orbitals of the boron atoms may allow macrocyclic conjugation when **B** (16 π-electrons) is reduced to the dianion **C**. As a first example of a tetraboraporphyrinogen we recently synthesized the tetrathia macrocycle **B** (X = S; R = N*i*Pr$_2$) in good yield via the bis(2-thienyl)borane **1a**.[2] Attempts to incorporate the corresponding *N*-methylpyrrole derivative **2a** into **B** (X = NMe) were not successful.[3a,3b] The formation of silyl- and stannyl-bridged macrocycles has been reported.[4a,4b]



A
X = NR, O, S



B
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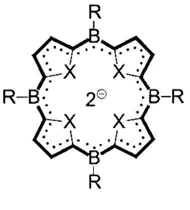
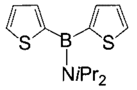
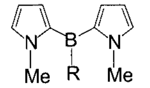


C
X = NR, O, S

Bis(2-heteroaryl)boranes were first prepared via tin/boron exchange and characterized by NMR spectroscopic studies.[5a,5b] Recently, we reported the formation of (diisopropylamino)bis(1-methyl-2-pyrrolyl)borane (**2a**) and its *N*-benzyl analogue.[6] Besides **1a**[2] some bis(2-thienyl)boranes are already known.[7,8] For the synthesis of furan- and *N*-methylpyrrole-containing macrocycles we investigated the 5,5′-dibromination of the corresponding bis(heteroaryl)boranes with *N*-bromosuccinimide. In the following we report on the new derivatives **1b**, **1c**, and **3a** of bis(2-heteroaryl)boranes, as well as on a new synthesis for methylbis(2-thienyl)borane (**1e**) and phenylbis(2-thienyl)borane (**1f**), and a high-yield bromination method for bis(2-heteroaryl)boranes and their reactivity in [2+2] cyclizations.



1a



2a R = N*i*Pr$_2$
2b R = C_4H_3NMe

Results and Discussion

1. Syntheses, Spectra of Aminobis(2-heteroaryl)boranes (1b, 1c, 3a), and Structure of 3b

(Dialkylamino)bis(2-thienyl)boranes are obtained when 2-lithiothiophene is treated at low temperatures with dichloro(diethylamino)borane and dichloro(2,2,6,6-tetramethylpiperidino)borane in a 2:1 ratio to give colorless and moisture-sensitive (diethylamino)bis(2-thienyl)borane (**1b**) and (2,2,6,6-tetramethylpiperidino)bis(2-thienyl)borane (**1c**) in yields of 72 and 85%, respectively. Their compositions follow from spectroscopic data. The ^{1}H NMR spectrum of **1b** exhibits a triplet for the CH_3 and a quadruplet for the CH_2 protons. At low field the thienyl protons appear as doublets of doublets. Sharp ^{13}C NMR signals for the heteroaromatic carbon atoms and a broad signal for the boron-bound car-

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bon atom are observed. Its ^{11}B NMR shift at $\delta = 35$ ppm is similar to that of other aminobis(2-thienyl)boranes.[7,8] Compound **1c** shows similar NMR shifts to that of **1b** in the heteroaromatic region. The 2,2,6,6-tetramethylpiperidino substituent (tmp) of **1c** yields a multiplet for the ring methylene protons and a singlet for the ring-bound methyl protons. The composition of both compounds was confirmed by HR-EI mass spectra.

	1b	1c	3a	3b
X	S	S	O	O
R	NEt₂	tmp	N*i*Pr₂	C₄H₃O

Addition of a suspension of monolithiated furan to a solution of Cl_2BNiPr_2 yields (diisopropylamino)bis(2-furanyl)borane (**3a**, 45%) as a colorless liquid that is sensitive to air and moisture. When the reaction is carried out by addition of the dichloroborane to monolithiated furan, only a small amount of **3a** is obtained, the main product being tris(2-furanyl)borane (**3b**). The ^1H NMR spectrum of **3a** shows the signals of the isopropyl groups and three doublets of doublets for the ring protons. Because of the coupling constants and the shift, the signal at $\delta = 6.19$ ppm is assigned to 4-H.[5a] Similarly, the ^{13}C NMR signal at $\delta = 110.4$ ppm is assigned to C-4 which is confirmed by a ^1H-^{13}C COSY NMR spectrum. The ^{11}B NMR shift at $\delta = 30$ ppm is in the expected region. The composition of **3a** is confirmed by a high-resolution mass spectrum.

Crystals of **3b** (Figure 1) suitable for X-ray analysis were grown from a hexane solution. Crystal data and structure refinement are shown in Table 1. The B1−C1 bond lengths in **3b** are similar to those in **1g**[9] but significantly shorter than the B−C bonds in triphenylborane[10] (1.585 Å). The O1−C1 bond (1.398 Å) in **3b** is slightly longer than O1−C4 (1.353 Å). This corresponds to **1g**, where the S1−C1 bond is longer than S1−C4. The boron atom in **3b** is tricoordinated and the C−B−C angles are 120°. As in **1g** the bond angle O1−C1−C4 (107.4°) is more acute than O1−C2−C3 (111.0°).

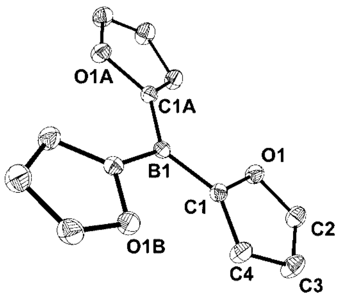
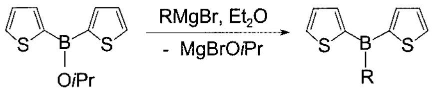


Figure 1. Molecular structure of **3b** in the crystal; selected bond lengths [Å] and angles [°]: O1−C2 1.353(1), O1−C1 1.389(1), B1−C1 1.537 (1), C1−C4 1.368(2), C2−C3 1.338(2), C3−C4 1.415 (2); C1−O1−C2 107.39(9), C4−C1−O1 107.43(9), C4−C1−B1 133.35(9), O1−C1−B1 119.20(8), C3−C2−O1 111.03(10), C2−C3−C4 106.28(11), C1-B1-C1A 120.00(1)

2. Syntheses of Alkylbis(2-thienyl)boranes (1e, 1f)

Methylbis[2-(5-methyl)thienyl]borane[8] (**1e**) was obtained from a redox reaction between 2-iodo-5-methylthiophene and $MeBI_2$ with elimination of elemental iodine. Because of the low yield an alternative approach to **1e** was developed. (Isopropyloxy)bis(2-thienyl)borane[7] (**1d**) was treated with methylmagnesium bromide in diethyl ether to give **1e** in almost quantitative yield. Its NMR spectroscopic and mass spectrometric data are in accordance with those reported previously.[5b,11] The reaction of phenylmagnesium bromide with **1d** analogously yielded phenylbis(2-thienyl)borane (**1f**) (53%). The composition of the colorless air-sensitive solid follows from ^{11}B and ^1H NMR spectroscopic data, the ^{13}C NMR spectrum exhibits six sharp signals for aryl and thienyl carbon atoms and two broad signals for the boron-bound carbon atoms.[12] Attempts to obtain the corresponding furan and pyrrole derivatives were not successful, because the reactions led to tris(1-methyl-2-pyrrolyl)borane (**2b**) and tris(2-furanyl)borane (**3b**), respectively.

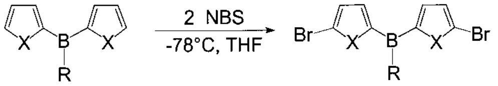


1d

1	e	f	g
R	Me	Ph	C₄H₃S

3. 5,5′-Dibromination of 1b, 2a, and 3a with *N*-Bromosuccinimide

For the syntheses of new macrocycles we need reactive *N*-methylpyrrole and furan derivatives as building blocks. Because of the very low tendency of the bis(2-pyrrolyl)borane **2a** and bis(2-furanyl)borane **3a** to yield dilithiated products[3a,3b] the bromination of the heterocycles at C-5 and C-5′ was investigated by using *N*-bromosuccinimide in THF. The bis(2-heteroaryl)boranes **1b**, **2a**, and **3a** react at −78 °C with *N*-bromosuccinimide in THF to give the dibromo derivatives **1b′**, **2a′**, and **3a′** in 89, 75, and 70% yield, respectively. Compound **3a′** is a yellow oil, which decomposes rapidly at room temperature. The ^{11}B NMR spectra exhibit signals for **1b′** at $\delta = 34$ ppm, for **2a′** at $\delta = 35$ ppm, and for **3a′** at $\delta = 29$ ppm. The shifts for the heteroaromatic protons of each compound show a coupling pattern of two doublets (AB spectrum). The three dibromo compounds **1b′**, **2a′**, and **3a′** were identified by EI-mass and HR EI-mass spectrometry.

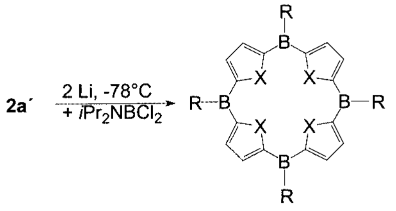


	1b	2a	3a
X	S	NMe	O
R	NEt₂	N*i*Pr₂	N*i*Pr₂

	1b′	2a′	3a′
X	S	NMe	O
R	NEt₂	N*i*Pr₂	N*i*Pr₂

4. Formation of 4b

As the [2+2] cyclization of **1b** led only to products with a quaternary boron atom, **1b′** was treated with lithium at low temperatures and quenched with Cl_2BNiPr_2. However, cyclization did not take place, and only decomposition was noticed. Compound **2a′** reacted in a [2+2] cyclization to yield the first *N*-methylpyrrole-containing tetraboraporphyrinogen **4b**. The ^{11}B NMR shift of δ = 33 ppm and the HR-EI mass spectrometric analysis confirm the existence of macrocycle **4b**, however, purification of the dark brown oil was not successful. The oily residue obtained by performing the same reaction with the furan derivative **3a′** did not contain the macrocycle **4c**.



4b X = NMe, R = N*i*Pr$_2$

Conclusion

Quenching of 2 equiv. of 2-lithioheteroarenes with dichloro(2,2,6,6-tetramethylpiperidino)borane and dichloro(diisopropylamino)borane yields the corresponding aminobis(2-heteroaryl)boranes **1b**, **1c**, and **3a**. Interestingly, the bromination of the aminobis(2-heteroaryl)boranes **1b**, **2a**, and **3a** with 2 equiv. of *N*-bromosuccinimide leads to new dibromo derivatives **1b′**, **2a′**, and **3a′**. Methyl- and phenylmagnesium bromide were treated with (isopropoxy)bis(2-thienyl)borane (**1d**) to give the organyl-substituted bis(2-thienyl)boranes **1e** and **1f**. In summary, new organyl- and amino-substituted building blocks containing heteroarenes of the new tetraboraporphyrinogens are obtained in good yields. The [2+2] cyclization of the dibromo derivatives **1b′**, **2a′**, **3a′** give in the case of **2a′** the first *N*-methylpyrrole-containing tetraboraporphyrinogen **4b**.

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 under high vacuum. ^1H, ^{11}B, ^{13}C NMR: Bruker DRX 200 spectrometer, shift references are $(CH_3)_4Si$ and $F_3B\cdot OEt_2$. Mass spectra were obtained with a ZAB-2F VH Micromass CTD spectrometer, HR mass spectra with a JEOL MS Station JMS 700 spectrometer both using the EI ionization technique. (Isopropyloxy)bis(2-thienyl)borane (**1d**),[7] dichloro(diisopropylamino)borane,[13] dichloro(diethylamino)borane,[14] and dichloro(2,2,6,6-tetramethylpiperidino)borane[15] were prepared according to literature procedures.

(Diethylamino)bis(2-thienyl)borane (1b): *n*-Butyllithium (2.5 M in hexane; 6 mL, 15 mmol) was added to a solution of thiophene (1.3 g, 15 mmol) in diethyl ether (30 mL) at −25 °C. After warming to room temperature, the reaction mixture was stirred for 1 h and then cooled to −50 °C. Dichloro(diethylamino)borane (1.2 g, 7.6 mmol) in diethyl ether (15 mL) was added dropwise to this solution. The mixture was allowed to warm to room temperature and was stirred overnight. Volatile compounds were removed under vacuum, the residue dissolved in pentane and filtered. The solvent was evaporated under vacuum and the colorless oil crystallized at −15 °C. Yield: 1.4 g (5.5 mmol, 72%) of colorless **1b**, m.p. 103 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.21 (t, CH_3CH_2, $^3J_{H,H}$ = 7.0 Hz, 6 H), 3.38 (q, CH_3CH_2, $^3J_{H,H}$ = 7.0 Hz), 4 H, 7.10 (m, 4 H, CH_{th}), 7.50 ppm (m, 2 H, CH_{th}). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 35 ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 16.1 (CH_3CH_2), 44.3 (CH_3CH_2), 127.7, 129.8, 135.2 (CH_{th}), 142 ppm (br, CB). MS: *m*/*z* (%) = 249 (28) [M^+], 234 (78) [$M^+ - CH_3$]. HR-MS: *m*/*z* (%) = 249.0845 [M^+]; calcd. for $^{12}C_{12}{}^1H_{16}{}^{11}B^{14}N^{32}S_2$ 249.0817 (Δmmu = 2.8).

(2,2,6,6-Tetramethylpiperidino)bis(2-thienyl)borane (1c): *n*-Butyllithium (2.5 M in hexane; 6 mL, 15.0 mmol) was added to a solution of thiophene (1.3 g, 15 mmol) in diethyl ether (30 mL) at −25 °C. The reaction mixture was stirred for 1 h at room temperature. At −20 °C a solution of dichloro(2,2,6,6-tetramethylpiperidino)borane (1.7 g, 7.6 mmol) in diethyl ether (15 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. Volatile compounds were removed under vacuum, and the residue was dissolved in pentane and filtered. The solvent was evaporated under vacuum leaving a white solid. Yield: 2.1 g (6.5 mmol, 85%) of colorless **1c**, m.p. 116−118 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.28 (s, 12 H, $CH_{3,tmp}$), 1.68 (m, 6 H, $CH_{2,tmp}$), 6.98 (m, 2 H, CH_{th}), 7.08 (m, 2 H, CH_{th}), 7.41 ppm (m, 2 H, CH_{th}). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 42 ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 16.1 ($CH_{2,tmp}$), 35.0 ($CH_{3,tmp}$), 37.7 ($CH_{2,tmp}$), 56.3 (C_{tmp}), 127.0, 130.7, 133.5 (CH_{th}), 151 ppm (br, CB). MS: *m*/*z* (%) = 317 (4) [M^+], 302 (100) [$M^+ - CH_3$]. HR-MS: *m*/*z* (%) = 317.1413 [M^+]; calcd. for $^{12}C_{17}{}^1H_{24}{}^{11}B^{14}N^{32}S_2$ 317.1444 (Δmmu = 3.1).

Methylbis(2-thienyl)borane (1e): Methylmagnesium bromide (3.0 M in diethyl ether; 1.7 mL, 5.1 mmol) was added dropwise to a solution of **1d** (1.1 g, 4.7 mmol) in diethyl ether (50 mL) at −25 °C. The mixture was allowed to warm for 30 min and stirred at room temp. for 3 h until a colorless solid was formed. Volatile compounds were removed under vacuum, the residue was dissolved in diethyl ether and filtered. The solvent was evaporated under vacuum and the wax-like residue dried. Yield: 0.9 g (4.5 mmol, 95%) of colorless **1e**. ^1H NMR (C_6D_6, 200.1 MHz): δ = 1.37 (s, 3 H, BCH_3), 6.96 (dd, $^3J_{H,H}$ = 3.6, $^3J_{H,H}$ = 4.7 Hz, 2 H, C4-H_{th}), 7.37 (dd, $^3J_{H,H}$ = 4.7, $^4J_{H,H}$ = 0.9 Hz, 2 H, CH_{th}), 7.87 ppm (dd, $^3J_{H,H}$ = 3.6, $^4J_{H,H}$ = 0.9 Hz, 2 H, CH_{th}). ^{11}B NMR (C_6D_6, 64 MHz): δ = 57. ^{13}C NMR (C_6D_6, 50 MHz): δ = 12.3 (CB), 129.1 [CH_{th} (C-4)], 136.1, 140.0 ppm (CH_{th}), $C_{th}B$ signal not observed. EI-MS: *m*/*z* (%) = 192 (62) [M^+], 177 (100) [$M^+ - CH_3$].

Phenylbis(2-thienyl)borane (1f): Phenylmagnesium bromide (3.0 M in diethyl ether; 1.7 mL, 5.1 mmol) was added dropwise to a solution of **1d** (1.2 g, 5.1 mmol) in diethyl ether (50 mL) at −20 °C. The mixture was allowed to warm for 20 min and stirred at room temperature for 26 h. Volatile compounds were removed under vacuum, the residue was dissolved in hexane/CH_2Cl_2 (1:4) and filtered. The solvent was evaporated under vacuum and the solid recrystallized from hexane at −80 °C. Yield: 0.7 g (2.7 mmol, 53%) of colorless **1f**, m.p. 85 °C. ^1H NMR (C_6D_6, 200 MHz): δ = 7.04 (m, 2 H, CH_{th}), 7.28 (m, 2 H, CH_{th}), 7.59−8.01 ppm (m, 7 H, CH_{ar}). ^{11}B NMR (C_6D_6, 64 MHz): δ = 49 ppm. ^{13}C NMR (C_6D_6, 50 MHz): δ = 128.1, 129.6, 130.5, 136.7, 136.8, 141.8 (CH_{ar}), 146, 149 ppm (2 × br, CB). EI-MS: *m*/*z* (%) = 254 (100) [M^+].

(Diisopropylamino)bis(2-furanyl)borane (3a): *n*-Butyllithium (2.5 M in hexane; 10.0 mL, 25. mmol) was added at room temperature to a solution of TMEDA (2.7 g, 24. mmol) in hexane (50 mL). The solution was stirred for 30 min and furan (1.4 g, 21 mmol) was added at room temperature. After stirring the mixture for 90 min, it was added to a solution of Cl_2BNiPr_2 (2.2 g, 12. mmol) in hexane (100 mL), within 80 min, at −25 °C. The mixture was allowed to warm to room temperature and stirred for 20 h. Volatile compounds were removed under vacuum, the residue was dissolved in hexane and filtered. The solvent was evaporated under vacuum and the crude product was distilled to give colorless **3a** (1.4 g, 5.5 mmol, 45%), b.p. 65 °C/$5\cdot10^{-3}$ mbar. ^1H NMR (C_6D_6, 200 MHz): δ = 1.21 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 3.95 [sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, $CH(CH_3)_2$], 6.19 (dd, $^3J_{H,H}$ = 1.7, $^3J_{H,H}$ = 3.3 Hz, 2 H, C4-H_{fu}), 6.63 (dd, $^3J_{H,H}$ = 3.3, $^4J_{H,H}$ = 0.7 Hz, 2 H, CH_{fu}), 7.39 ppm (dd, $^3J_{H,H}$ = 1.7, $^4J_{H,H}$ = 0.7 Hz, 2 H, CH_{fu}). ^{11}B NMR (C_6D_6, 64 MHz): δ = 30 ppm. ^{13}C NMR (C_6D_6, 50 MHz): δ = 23.5 [$CH(CH_3)_2$], 49.4 [$CH(CH_3)_2$], 110.4 [CH_{fu} (C-4)], 123.4, 145.2 ppm (CH_{fu}), CB signal not observed. EI-MS: *m/z* (%) = 245 (16) [M^+], 230 (100), [$M^+ - CH_3$]. HR EI-MS: *m/z* (%) = 245.1608 [M^+]; calcd. for $^{12}C_{12}{}^1H_{16}{}^{11}B^{14}N^{32}S_2$ 245.1587 (Δmmu = 2.1).

Bis(5-bromo-2-thienyl)(diethylamino)borane (1b′): A solution of **1b** (1.3 g, 5.0 mmol) in THF (65 mL) was cooled to −78 °C and *N*-bromosuccinimide (1.5 g, 10 mmol) was added in portions. The mixture turned yellow to orange and was allowed to warm to room temperature. The solvent was removed under vacuum and pentane was added to the residue. After filtering the succinimide off, the solvent of the yellow solution was evaporated. The yellow viscous oil was crystallized from pentane at −30 °C to give colorless **1b′** (1.5 g, 3.8 mmol, 75%), m.p. 132 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.15 (t, CH_3CH_2, $^3J_{H,H}$ = 7.0 Hz, 6 H), 3.28 (q, CH_3CH_2, $^3J_{H,H}$ = 7.0 Hz, 4 H), 6.79 (m, 4 H, CH_{th}), 6.90 ppm (m, 2 H, CH_{th}). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 34 ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 16.3 (CH_3CH_2), 44.9 (CH_3CH_2), 114.1, 130.0, 135.4 (C_{th}), 144 ppm (br, CB). MS: *m/z* (%) = 407 (12) [M^+], 392 (15) [$M^+ - CH_3$].

Bis(5-bromo-1-methyl-2-pyrrolyl)(diisopropylamino)borane (2a′): This compound was prepared analogously to **1b′** from **2a** (1.4 g , 5.0 mmol) and *N*-bromosuccinimide (1.5 g, 10 mmol) of. Yield: 1.9 g (4.5 mmol, 89%) of colorless **2a′**, m.p. 145 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.15 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 3.02 (s, 6 H, NCH_3), 3.94 [sept, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, 2 H], 6.08 (d, $^3J_{H,H}$ = 3.7 Hz, 2 H, CH_{py}), 6.22 ppm (d, $^3J_{H,H}$ = 3.7 Hz, 2 H, CH_{py}). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 35 ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 25.0 [$CH(CH_3)_2$], 34.5 ($N-CH_3$), 49.3 [$CH(CH_3)_2$], 105.2, 110.2, 116.4 (CH_{py}), 139 ppm (br, CB). MS: *m/z* (%) = 429 (60) [M^+], 350 (15) [$M^+ - Br$]. HR-MS: *m/z* (%) = 427.0409 [M^+]; calcd. for $^{12}C_{16}{}^1H_{24}{}^{11}B^{79}Br_2{}^{14}N_3$ 427.0430 (Δmmu = 2.1).

Bis(5-bromo-2-furanyl)(diisopropylamino)borane (3a′): This compound was prepared analogously to **1b′** from **3a** (1.2 g, 5.0 mmol) and *N*-bromosuccinimide (1.5 g, 10 mmol). The mixture turned dark brown and was allowed to warm to room temp. for 16 h. The solvent was removed under vacuum and pentane was added. After filtering the succinimide off, the solvent of the yellow solution was evaporated. The yellow, viscous oil turned orange and needed no further purification. Yield: 1.4 g (3.5 mmol, 70%) of orange **3a′**. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.16 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 3.82 [sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, $CH(CH_3)_2$], 6.21 (d, $^3J_{H,H}$ = 3.7 Hz, 2 H, CH_{fu}), 6.41 ppm (d, $^3J_{H,H}$ = 3.7 Hz, 2 H, CH_{fu}). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 29 ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 23.8 [$CH(CH_3)_2$], 48.3 [$CH(CH_3)_2$], 112.0, 125.7, 145.5 ppm (CH_{fu}), CB signal not observed . MS: *m/z* (%) = 403 (6) [M^+], 324 (60) [$M^+ - Br$]. HR-MS: *m/z* (%) = 400.9823 [M^+]; calcd. for $^{12}C_{14}{}^1H_{18}{}^{11}B^{79}Br_2{}^{14}N^{16}O_2$ 400.9797 (Δmmu = 2.6).

Macrocycle 4b: A solution of bis(5-bromo-1-methyl-2-pyrrolyl)(diisopropylamino)borane [**2a′**, 481 mg (1.1 mmol)] was added to a suspension of lithium powder (13 mg, 2.2 mmol) in THF (30 mL) at −78 °C. The color of the suspension changed to bright orange. After 2 h of stirring, the mixture was allowed to warm to −20 °C. Excess lithium was filtered off and the solution cooled to −40 °C. A solution of dichloro(diisopropylamino)borane (0.21 g, 1.2 mmol) in pentane (20 mL) was added over 2 h and warmed overnight to room temperature. Insoluble salts were filtered and the volatile compounds evaporated leaving a brown oily residue that could not be purified by column chromatography or crystallization. ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 33 ppm. MS: *m/z* (%) = 760 (13) [M^+], 717 (3) [$M^+ - iPr$]. HR-MS: *m/z* (%) = 760.6600 [M^+]; calcd. for $^{12}C_{44}{}^1H_{76}{}^{11}B_4{}^{14}N_8$ 760.6565 (Δmmu = 3.5).

X-ray Structure Determination of 3b: Crystal data and details of the structure determination are listed in Table 1. Intensity data for **3b** were collected at −83 °C with a Bruker AXS SMART 1000 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scan). An empirical absorption correction was applied. The structure was solved by direct methods (SHELXS-86)[16] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97).[16] All non-hydrogen atoms are refined anisotropically. Hydrogen atoms were located in difference Fourier maps and refined isotropically. CCDC-177342 (**3b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **3b**

Empirical formula	$C_{12}H_9BO_3$
Formula mass	212.00
Crystal system	cubic
Space group	$P2_13$
Unit cell dimensions	a = 10.2961(4) Å
Volume	1091.49(7) Å^3
Z	4
Density (calculated)	1.29 g/cm^3
Absorption coefficient	0.091 mm^{-1}
$F(000)$	440
Crystal size	0.36 × 0.30 × 0.20 mm
θ_{max}	32.40°
Reflections collected	7894
Independent reflections	1272 [R(int) = 0.0332]
Final R indices [$I > \sigma(I)$]	$R1$ = 0.0387, $wR2$ = 0.1004
R indices (all data)	$R1$ = 0.0463, $wR2$ = 0.1084
Largest diff. peak/hole	0.288/-0.124 e·Å^{-3}

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