

Synthesis, structures and reactivity of macrocyclic imidazolylboranes

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Dedicated to Professor Frederick Hawthorne on the occasion of his 75th birthday

Abstract

New macrocyclic imidazolylboranes $[\text{imidazolylB}(\text{R}^1)_2]_n$, where selected carbon atoms of imidazolyl rings may bear substituents other than hydrogen, and where $n = 4$ or 5 , are obtained from 1-trimethylsilylimidazoles and haloboranes $\text{XB}(\text{R}^1)_2$ by boron/silicon exchange using 2-bromoimidazole and benzimidazole. These macrocycles are formally zwitterionic and contain imidazolyl rings linked through their nitrogen atoms by BH_2 , $\text{B}(\text{R}^1)_2$ or BR^1X units. Despite the sterical demand of these derivatives tetrameric macrocycles are formed. A new synthetic strategy to macrocyclic imidazolylboranes includes the preparation and cyclization of bis(imidazolyl)boronium chlorides. In addition dihaloboranes have been tested for cyclization to yield halogen-containing macrocycles. The new compounds are spectroscopically characterized and X-ray structure analyses of tetrameric- (**2a**) and pentameric 1-imidazolylborane (**2a'**), tetrameric 1-imidazolyl dimethylborane (**2b**), tetrameric 1-(2-bromo)imidazolylborane (**2d**) and bis(2-bromoimidazolyl)boronium chloride (**3d**) are reported.

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Keywords: Boranes; Cyclooligomerizations; Imidazoles; Macrocycles

1. Introduction

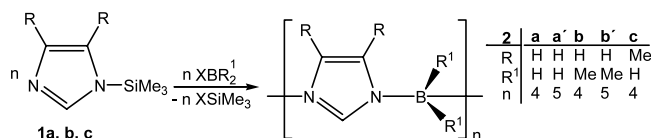
Intermolecular donor/acceptor interactions of 1-imidazolyl diethylborane and 1-imidazolyl diphenylborane cause the formation of polymeric imidazolylboranes [1–3]. For the same reason, cyanoborane $[\text{BH}_2\text{CN}]$ formed from sodium cyanoborate and hydrogen chloride yields a mixture of polymeric products and oligomeric macrocycles [4].

Recently, we reported on a specific method for the synthesis of macrocyclic imidazolylboranes **2** by reaction of 1-trimethylsilylimidazoles **1** with haloboranes under high dilution [5] (Scheme 1).

Depending on the nature of the substituents at the imidazole ring and at the boron atom, the formation of different ring sizes was observed. By column chromatography the tetrameric (**2a**, **b**) and pentameric com-

pounds (**2a'**, **b'**) could be separated and the solid state structures of **2b'**, **c** were analyzed.

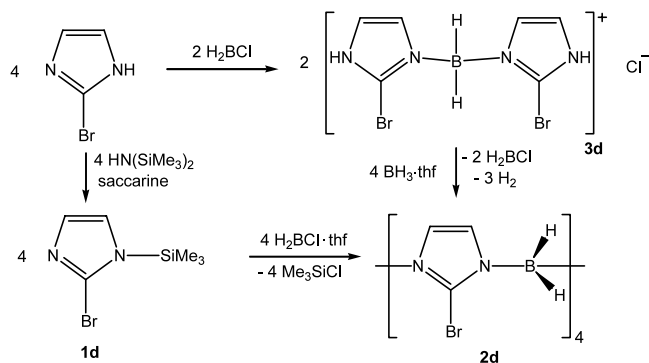
As the deprotonation of the tetrameric compounds **2a**, **b**, **c** with different bases failed due to the low acidity of the C2 position of the imidazole rings we extended our studies to 2-bromoimidazolylboranes. The presence of a bromine atom should increase the reactivity towards bases to give anionic carbenes, useful for host–guest chemistry via the formation of metal–carbene complexes. In the following, we report on cyclization reactions of 2-bromoimidazolyl- and benzimidazolylborane derivatives, as well as on X-ray structure analyses of several macrocycles.



Scheme 1.

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Scheme 2.

2. Results and discussion

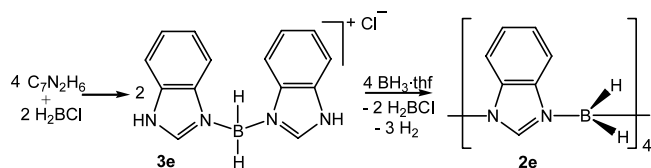
2.1. Syntheses and spectra of oligomeric imidazolylboranes 2d, e

Following the procedure described previously [5], the tetrameric compound **2d** was synthesized from 1-trimethylsilyl-2-bromoimidazole [7] (**1d**) and one equivalent of $\text{H}_2\text{BCl}\cdot\text{thf}$ (Scheme 2). An air-sensitive white solid was obtained in 63% yield. Attempts to obtain **2d** by reacting 2-bromoimidazole with one equivalent of H_2BCl failed due to the formation of bis(2-bromoimidazolyl)boronium chloride (**3d**) in low amount (25%). Using two equivalents of 2-bromoimidazole, **3d** is formed in 67% yield as a colorless crystalline solid, sensitive to air. Its transformation into the tetrameric compound **2d** occurs when **3d** is reacted with two equivalents of $\text{BH}_3\cdot\text{thf}$ (Scheme 2).

Compounds **2d** and **3d** have been characterized by spectroscopic methods and their structures were confirmed by X-ray structure analyses. For compound **2d**, the ^1H -NMR spectrum reveals a symmetric geometry in solution showing a singlet for the imidazole hydrogens in 4,5-position at $\delta = 7.12$ ppm.

As expected, two doublets were observed at 7.36 and 7.56 ppm for the hydrogens in 4,5-position of **3d**. The ^{11}B -NMR spectrum shows one broad signal at $\delta = -8$ for **2d** and the signal for **3d** is observed at $\delta = -9$ ppm. This indicates for both compounds a tetrahedral arrangement at the boron atoms [8]. The EI mass spectrum confirms the formation of the tetrameric species **2d**: the molecular ion is found at $m/z = 632$ [M^+] and the molecule is fragmented by successive loss of monomeric moieties (M').

The reactivity of tetrameric **2d** has been studied in order to prepare metal–carbene complexes. We examined the possibility for direct lithiation of **2d** with bases like *n*-BuLi and *t*-BuLi in different solvents (diethyl ether, THF, hexane) with or without addition of TMEDA. The expected anionic organolithium compounds were then reacted with MX_2 (NiCl_2 , $\text{Ni}(\text{OAc})_2$, $\text{Pd}(\text{OAc})_2$ and $[(\text{Ph}_3\text{P})_2\text{PtCl}_2]$), however, metal–carbene



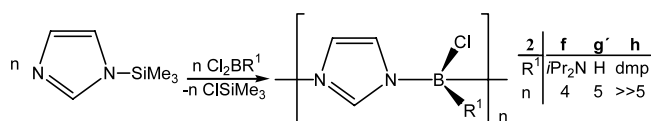
Scheme 3.

complexes were not formed, only decomposition was detected.

Analogously to the preparation of **3d**, the reaction of H_2BCl with benzimidazole yields the bis(benzimidazolyl)boronium chloride (**3e**) as a white solid (Scheme 3). The ^{11}B -NMR signal is shifted to lower frequencies ($\delta = -13.2$ ppm) compared to compound **3d**. In the ^1H -NMR spectrum a singlet at $\delta = 9.48$ ppm is assigned to the hydrogen in 2-position. This signal is observed at higher frequency due to the partial positive charge, which also affects the position of the corresponding signal in the ^{13}C -NMR spectrum ($\delta = 145.1$ ppm).

Addition of a solution of $\text{BH}_3\cdot\text{thf}$ to a suspension of **3e** gives a white solid that is insoluble in all organic solvents (Scheme 3). The product is stable at room temperature and decomposes above 140°C . Due to its insolubility it was not possible to obtain NMR data, but the base pattern at $m/z = 519$ in the mass spectrum corresponds to tetrameric benzimidazolylborane (**2e**) [$\text{M}-\text{H}$] $^+$. A high resolution mass spectrum confirms the molecular formula. Attempts to deprotonate tetrameric **2e** with various bases in different solvents did not lead to formation of any anionic carbene.

Oligomeric compounds were also synthesized from trimethylsilylimidazole and dichloroboranes (R^1BCl_2 , $\text{R}^1 = \text{H}$, *i*Pr $_2$ N, DMP) (Scheme 4). The products possess BCl groups, and reactions with *n*-BuLi could lead to neutral macrocyclic carbenes by loss of *n*-BuH and LiCl. The reaction of 1-trimethylsilylimidazole (**1a**) with (diisopropylamino)dichloroborane (*i*Pr $_2$ NBCl $_2$) results in the formation of tetrameric **2f**. In the proton NMR spectrum two signals for the imidazole protons in a 1:2 ratio at $\delta = 7.50$ and 6.88 are observed, which confirm the equivalence of the hydrogens attached to C4 and C5. The ^{11}B -NMR signal of **2f** at 1.0 ppm is shifted to higher frequencies compared to the corresponding signals observed for the compounds **2a**, **b**, **c** and **d**. The mass spectrum exhibits a peak at $m/z = 712$ corresponding to the cation [$\text{M}-4\text{Cl}$] $^+$. Tetrameric **2f** was also reacted with various organolithium compounds for macrocyclic tetracarbene formation, however, only decomposition occurred.



Scheme 4.

The reaction of 1-trimethylsilylimidazole with $\text{HBCl}_2 \cdot \text{SMe}_2$ yields a white solid that is insoluble in all organic solvents. Hydrolysis was observed for protonic solvents like alcohols and water. The molecular peak in the ESI mass spectrum is found at $m/z = 571$ indicating the presence of pentameric imidazolylchloroborane (**2g'**). In the EI mass spectrum the peak at $m/z = 430$ is assigned to the cation $[\text{M}-4\text{Cl}]^+$ corresponding to a pentameric species minus four chlorine atoms. 1-Trimethylsilylimidazole and 2,6-dimethylpiperidylchloroborane $[(\text{dmp})\text{BCl}_2]$ reacted to give of an oligomeric product **2h**. The white solid has a high melting point ($> 300^\circ\text{C}$) and is insoluble in all organic solvents.

2.2. Structure analyses of **2d** and **3d**

X-ray diffraction studies allowed a complete characterization for compounds **2d** and **3d**, the crystal data and details of the structure determination are listed in Table 1. Fig. 1 shows the molecular structure of the tetrameric compound **2d**, which has three independent molecules in the asymmetric unit. The boron atoms are tetracoordinated by two hydrogen and two nitrogen atoms, resulting in the formation of a 16-membered heterocycle. The alternating orientation of the imidazole rings

Table 1
Crystal data and details of structure determination for **3d** and **2d**

Identification code	3d	2d
Empirical formula	$\text{C}_8\text{H}_8\text{B}_1\text{Br}_2\text{N}_4\text{Cl}_1 \cdot \text{thf}$	$\text{C}_{12}\text{H}_{16}\text{B}_4\text{Br}_4\text{N}_8$
Formula weight	414.35	635.21
Temperature (K)	190	190
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
Unit cell dimensions		
<i>a</i> (Å)	10.6049(6)	16.1812(11)
<i>b</i> (Å)	15.4406(10)	41.041(3)
<i>c</i> (Å)	9.788(6)	9.6858(6)
β (°)	103.678(1)	94.068(2)
<i>V</i> [Å ³]	1557.3(2)	6416.0(7)
<i>Z</i>	4	12
<i>D</i> _{calc} (g cm ⁻³)	1.767	1.973
Absorption coefficient (mm ⁻¹)	5.374	7.543
<i>F</i> (000)	816	3648
Crystal size (mm ³)	0.39 × 0.20 × 0.14	0.42 × 0.27 × 0.21
Theta range (°)	2.4–32	1.3–28.3
Index ranges	–15/14, 0/22, 0/14	–21/21, 0/54, 0/12
Reflections collected	7259	49 150
Independent reflections	2594	15 854
	$[R_{\text{int}} = 0.025]$	$[R_{\text{int}} = 0.053]$
Max/min transmission	1.0000, 0.5986	1.0000, 0.3277
Parameters	120	949
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	$R_1 = 0.0345$	$R_1 = 0.0490$
<i>R</i> indices (all data)	$wR_2 = 0.0925$	$wR_2 = 0.1075$
Largest difference peak and hole [e Å ⁻³]	1.739 and –0.256	0.996 and –1.083

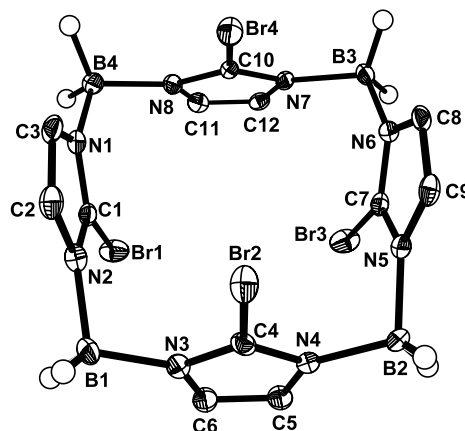


Fig. 1. Molecular structure of **2d** in the crystal (one of three independent molecules). Hydrogen atoms bonded to carbon are omitted for clarity. Selected bond lengths (Å) and angles (°): B1–N2 1.578(8), B1–N3 1.565(7), N2–C1 1.334(7), C1–N1 1.329(7), N1–C3 1.387(7), C2–C3 1.332(8), C2–N2 1.398(7), Br1–C1 1.850(5), N2–B1–N3 107.7(4), C2–N2–B1, 125.2(5), C1–N2–B1 130.5(5), N1–C1–N2 113.2(4), N2–C1–Br1 122.5(4), N1–C1–Br1 124.3(4), C1–N1–C3 105.3(4), N1–C3–C2 108.3(5), C3–C2–N2 108.9(5), C2–N2–C1 104.2(5).

leads to a pseudo D_{2d} symmetry with twofold C_2 axes through B1/B3 and B2/B4 atoms. This symmetry is different compared to the tetrameric compounds **2a**, **b**, **c** owing mainly to the transannular interactions of bromine atoms in 2-positions of the imidazole rings. A similar geometry has been observed in a gallium derivative containing methyl groups at the same position [9]. The boron–nitrogen distances are almost identical (1.57 Å average) and similar to that in **2a**, **b**, **c**. The N–B–N angles have an average value of 107.6° , and the boron atoms exhibit a slightly distorted tetrahedral geometry.

Crystals of bis(2-bromo)imidazoleboronium chloride·thf (**3d**) suitable for X-ray diffraction were grown by slowly cooling of a warm concentrated THF solution. The molecular structure of **3d** is shown in Fig. 2. The N–B distance [1.577(3) Å] is similar to that in com-

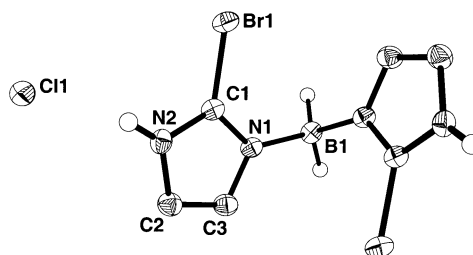


Fig. 2. Structure of **3d** in the crystal. Selected bond lengths (Å) and angles (°): B1–N1 1.577(3), N1–C1 1.328(1), C1–N2 1.326(3), N2–C2 1.375(3), C2–C3 1.344(3), C3–N1 1.385(3), Br1–C1 1.854(2), N1–B1–N1' 107.6(2), N1–B1–H1 112.3(1), C1–N1–B1, 128.3(2), C3–N1–B1 125.3(2), N1–C1–N2 110.3(2), C1–N2–C2 108.3(2), N2–C2–C3 106.4(2), C2–C3–N1 108.7(2), C3–N1–C1 106.3(18), N1–C1–Br1 125.57(2), N2–C1–Br1 124.1(2).

pounds containing two hydrogen atoms and two imidazole rings attached to the boron atom. The angles around the boron atom are close to a tetrahedral geometry with values from 107.6(2) to 112.3(1)°.

2.3. Structure analyses of **2a**, **a'** and **2b**

As discussed in Section 1, the structures of **2b'** and **2c** have already been reported in our communication [5]. Colorless crystals of **2a** [5] were grown by sublimation at 150 °C/10⁻⁴ mbar (crystal data of **2a**, **a'** and **2b** are listed in Table 2). In the solid state, **2a** has an inversion center. Two adjacent pairs of imidazole rings are turned out of the B₄ molecular plane by 66 and -80°, respectively. The range of B–N bond lengths varies from 1.56 to 1.57 Å (Fig. 3).

Crystals of tetrameric **2b** were obtained from a saturated CH₂Cl₂ solution at 4 °C. The unit cell contains two independent molecules, which differ mainly in the angles between the imidazole rings and the B₄ planes. The macrocycle consists of four symmetric imidazole units with their nitrogen atoms bonded to BMe₂ moieties. In both molecules, two opposite imidazole rings are almost perpendicular to the B₄ plane, the remaining imidazole rings form angles of 5 and 49°. In this way, the repulsive interactions between the methyl groups and the imidazole rings are minimized.

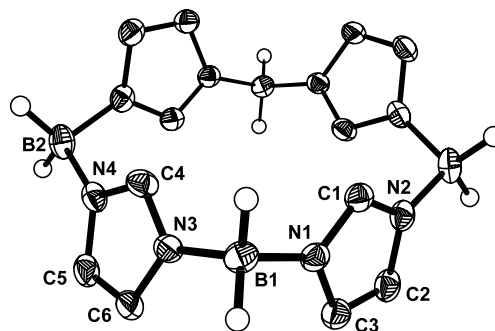


Fig. 3. Molecular structure of **2a** in the crystal. Hydrogen atoms bonded to carbon are omitted for clarity. Selected bond lengths (Å) and angles (°): N1–C1 1.331(1), N1–C3 1.379(1), C2–C3 1.353(1), C2–N2 1.377(1), N2–C1 1.334(1), N1–B1 1.571(1), N2–B2' 1.568(1), B1–N3 1.560(1), B2–N4 1.568(1), C1–N1–C3 106.3(1), C1–N1–B1 126.1(1), N1–C1–N2 111.7(1), N1–B1–N3 107.1(1), N2'–B2–N4 106.0(1).

The average B–N bond lengths (1.60 Å) are remarkably longer than in **2a**, **2a'** and **2c** (bond lengths found between 1.56 and 1.58 Å). The presence of methyl groups attached to boron atoms leads to a strained tetrahedral coordination geometry at the boron atom, as can be seen from the NBN angles. The average N–B–N angle (103.4°) in **2b** is much smaller than in **2a**, **2a'** and **2c** (Fig. 4).

Table 2
Crystal data and details of structure determination for **2a**, **2a'** and **2b**

Identification code	2a	2a'	2b
Empirical formula	C ₁₂ H ₂₀ B ₄ N ₈	C ₁₅ H ₂₅ B ₅ N ₁₀	C ₂₀ H ₃₆ B ₄ N ₈
Formula weight	319.60	399.50	431.81
Temperature	173(2)	173(2)	173(2)
Crystal system	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pnma</i>	<i>P</i> $\bar{1}$
Unit cell dimensions			
<i>a</i> (Å)	9.3506(2)	9.7400(6)	10.3366(2)
<i>b</i> (Å)	12.3406(2)	20.6899(12)	12.3629(2)
<i>c</i> (Å)	7.8260(2)	10.9517(6)	22.3023(2)
α (°)	90	90	97.114(1)
β (°)	100.403(1)	90	100.884(1)
γ (°)	90	90	112.353(1)
<i>V</i> (Å ³)	888.21(3)	2207.0(2)	2527.67(7)
<i>Z</i>	2	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.195	1.202	1.135
Absorption coefficient (mm ⁻¹)	0.075	0.076	0.069
<i>F</i> (000)	336	840	928
Crystal size (mm ³)	0.45 × 0.34 × 0.29	0.46 × 0.37 × 0.28	0.48 × 0.24 × 0.12
Theta range (°)	2.21–28.28	1.97–28.30	0.95–25.35
Index ranges	–12/12, 0/16, 0/10	0/13, 0/26, 0/14	–12/12, –14/14, 0/26
Reflections collected	8811	15 034	33 796
Independent reflections	2168 [<i>R</i> _{int} = 0.022]	2757 [<i>R</i> _{int} = 0.0331]	9260 [<i>R</i> _{int} = 0.0450]
Max/min transmission	0.771, 0.914	1.0000, 0.8967	0.928, 0.835
Parameters	149	192	685
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0372	<i>R</i> ₁ = 0.0378	<i>R</i> ₁ = 0.0444
<i>R</i> indices (all data)	<i>wR</i> ₂ = 0.1069	<i>wR</i> ₂ = 0.1063	<i>wR</i> ₂ = 0.1209
Largest difference peak and hole [e Å ⁻³]	0.221 and –0.133	0.260 and –0.159	0.577 and –0.248

The X-ray crystal structure has been already determined for **2a'** [5]. A different conformation of **2a'** in the solid state is observed when it is crystallized from a saturated THF solution instead of CH_2Cl_2 . The latter includes CH_2Cl_2 solvent molecules in the unit cell, which influence the conformation. From THF, solvent-free crystals are obtained. The macrocycle is puckered and exhibits a mirror plane through B1 and C8. In contrast to **2a**, **b**, **c**, the boron atoms do not lie in a plane. The deviation from tetrahedral geometry at the boron atoms is increased since the average N–B–N angles (107.6°) are smaller compared to the CH_2Cl_2 -containing solid structure (109.3°) (Fig. 5).

3. Conclusion

In conclusion, the reaction of imidazole derivatives with haloboranes leads to the formation of oligomeric macrocyclic products. The preferred ring size is tetrameric, however, pentameric structures are obtained when the substituents in 4,5-position of the imidazole rings and at the boron atoms are small. It was not possible to isolate macrocycles larger than pentameric or smaller than tetrameric compounds. Cyclization also occurs with a bromine atom in C2 position of the imidazole. Transannular interactions of the bromine atoms are avoided as the imidazole rings are turned out of the B_4 molecular plane. Attempts to form anionic carbenes by reactions of tetrameric imidazolylboranes with bases, failed due the low acidity of the C2 proton. Replacing hydrogen for bromine at C2 did not facilitate the formation of anionic macrocycles.

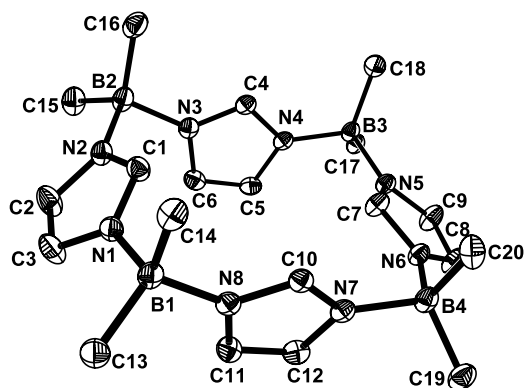


Fig. 4. Molecular structure of **2b** in the crystal (one of two independent molecules). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): N1–C1 1.332(2), N1–C3 1.374(2), C2–C3 1.354(3), C2–N2 1.370(2), N2–C1 1.334(2), N1–B1 1.599(2), N2–B2 1.606(2), B1–C13 1.610(3), C1–N1–C3 105.6(1), C1–N1–B1 125.8(1), N1–C1–N2 112.2(2), N2–B2–N3 103.0(1), C13–B1–C14 114.0(2).

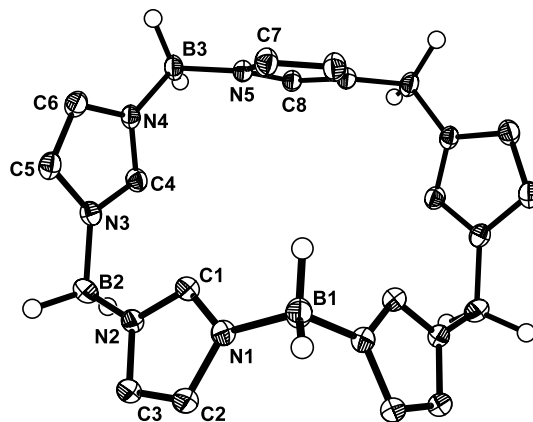


Fig. 5. Molecular structure of **2a'** in the crystal. Hydrogen bonded to carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): N1–C1 1.334(2), N1–C2 1.377(2), N1–B1 1.563(2), N2–C1 1.328(1), N2–C3 1.380(2), N2–B2 1.578(2), C2–C3 1.353(2), C1–N1–C2 106.1(1), N1–C1–N2 111.8(1), N1–B1–N1A 108.3(1), N2–B2–N3 107.3(1), N4–B3–N5 107.5(1).

4. Experimental

General: Reactions were carried out under dry argon, using standard Schlenk techniques. Solvents were dried, distilled and saturated with nitrogen. Glassware was dried with a heat-gun in high vacuum. Compounds **2a**, **b**, **c** were synthesized following a procedure described elsewhere [5]. 2-Bromo-1-trimethylsilyl-imidazole (**1a**) [7] was prepared according to a literature procedure.

4.1. Bis(2-bromoimidazole)boronium chloride (**3d**)

1.70 mmol of a $\text{H}_2\text{BCl}\cdot\text{thf}$ solution (0.9 M) were added dropwise to a solution of 2-bromoimidazole (0.5 g, 3.40 mmol) in 30 ml of THF at -70°C . The mixture was allowed to warm to room temperature (r.t.) and was stirred for 6 h. The formed solid was separated by filtration and washed with hexane to give **3d** (Yield: 0.39 g, 67%), m.p. $>300^\circ\text{C}$. Crystals suitable for X-ray diffraction study were obtained by slowly cooling of a warm concentrated THF solution. $^1\text{H-NMR}$ (200 MHz, $\text{DMSO-}d_6$): $\delta = 7.36$ (d, $^3J_{\text{HH}} = 2$ Hz, H4), 7.56 (d, $^3J_{\text{HH}} = 2$ Hz, H5). $^{13}\text{C-NMR}$ (50 MHz, $\text{DMSO-}d_6$): $\delta = 120.6$ (C2), 122.3 (C4), 128.6 (C5). $^{11}\text{B-NMR}$ (64 MHz, $\text{DMSO-}d_6$): $\delta = -8$ (s, br). EIMS: m/z (%) = 305 [$\text{M}-\text{Cl}$] $^+$ (60), 159 [$\text{M}-\text{C}_3\text{H}_3\text{N}_2\text{BrCl}$] $^+$ (100), 146 [$\text{C}_3\text{H}_3\text{N}_2\text{Br}$] $^+$ (48).

4.2. Tetrameric 1-(2-bromoimidazolyl)borane (**2d**)

2.19 g (10 mmol) of 2-bromo-1-trimethylsilyl-imidazole (**1d**) were dissolved in 100 ml hexane and treated with 1 equiv of $\text{H}_2\text{BCl}\cdot\text{thf}$ solution (0.9 M) at -70°C . After stirring for 4 h at r.t. the solvent was removed, the residue washed with hexane and dried under high vacuum to give colorless **2d** (Yield: 0.1 g, 63%),

m.p. = 160 °C. Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a concentrated THF solution. ¹H-NMR (200 MHz, CD₂Cl₂): δ = 7.12 (s, H4,5). ¹³C-NMR (50 MHz, CD₂Cl₂): δ = 129.5 (C4,5), 122.7 (C-2). ¹¹B-NMR (64 MHz, CD₂Cl₂): δ = -7.9 (s). EIMS: *m/z* (%): 632 [M]⁺ (20), 487 [M - C₃H₂N₂Br]⁺ (28), 474 [M₃]⁺ (10), 329 [M₃ - C₃H₂N₂Br]⁺ (40), 316 [M₂]⁺ (15), 171 [M₂ - C₃H₂N₂Br]⁺ (100), 158 [M']⁺ (28), [M' = monomeric 1-(2-bromoimidazolyl)borane (1/4 **2d**)].

Compound **2d** was also synthesized by the following procedure: To a suspension of **3d** (0.20 g, 0.58 mmol) in 20 ml of THF, 4 equiv of a BH₃·thf solution (1 M) were added dropwise at -60 °C. The mixture was allowed to warm to r.t. and was stirred for 8 h. After removal of the solvent, colorless **2d** was obtained (0.13 g, 75%).

4.3. Bis(benzimidazole)boronium chloride (**3e**)

Compound **3e** was prepared analogously to **3d** from 0.5 g (4.23 mmol) of benzimidazole and 2.11 mmol of a H₂BCl·thf solution (0.9 M). (Yield: 0.55 g, 92%), m.p. = 252 °C. ¹H-NMR (200 MHz, DMSO-*d*₆): δ = 7.35 (m, 4H, H5,6), 7.63 (dd, 2H, *J* = 2.6, 6.8 Hz H4), 7.87 (dd, 2H, *J* = 2.6, 6.8 Hz, H7), 9.48 (s, 2H, H2). ¹³C-NMR (50 MHz, DMSO-*d*₆): δ = 114.8, 115.6 (C6,7), 125.8, 126.0 (C5,8), 132.7, 135.2 (C4,9), 145.1 (C2). ¹¹B-NMR (64 MHz, DMSO-*d*₆): δ = 13.2 (s). EIMS: *m/z*: 249 [M - Cl]⁺ (100), 248 [M - HCl]⁺ (72), 131 [C₇H₈B]⁺ (35).

4.4. Tetrameric 1-benzimidazolylborane (**2e**)

Compound **2e** was prepared analogously to **2d** (2nd procedure) in THF instead hexane as a solvent from 0.3 g (1.05 mmol) of bis(benzimidazole)boronium chloride (**3e**) and 4.20 mmol of a H₃B·thf solution (1 M). (Yield: 0.23 g, 82%), m.p. = 146 °C (dec.). The product is insoluble in organic solvents. EIMS: *m/z* (%): 519 [M - H]⁺ (100), 389 [M₃ - H]⁺ (40), 259 [M₂ - H]⁺ (78). HRMS: *m/z* = 519.2748 [M - H]⁺ Anal. Calc. for ¹²C₂₈H₂₇¹¹B₄¹⁴N₈ = 519.2768. Δ mmu = 2.0, (M' = 1/4M).

4.5. Tetrameric diisopropylamino-1-imidazolylchloroborane (**2f**)

To a solution of 1-trimethylsilylimidazole (0.5 g, 3.56 mmol) in 30 ml of hexane 3.56 mmol of *i*Pr₂NBCl₂ (diluted in hexane) were added dropwise at -70 °C. The mixture was allowed to warm to r.t. and was stirred for 4 h. The white solid was separated by filtration and washed with hexane to give colorless **2f** (Yield: 0.70 g, 92%), m.p. = 260 °C (dec.). ¹H-NMR (200 MHz, DMSO-*d*₆): δ = 0.84 (d, *J* = 6.3 Hz, CH₃), 2.72 (sept, *J* = 6.3 Hz, CHCH₃), 6.88 (s, H4,5), 7.50 (s, H2). ¹³C-

NMR (50 MHz, DMSO-*d*₆): δ = 26.3 (CH₃), 45.3 (CHCH₃), 130.0 (C2), 135.81 (C4,5). ¹¹B-NMR (64 MHz, DMSO-*d*₆): δ = 1.0 (s). EIMS: *m/z* (%): 712 [M - 4Cl]⁺ (60), 596 (40), 510 (100), 327 (80), 231 (66).

4.6. Pentameric 1-imidazolyl-chloroborane (**2g'**)

The compound **2g'** was prepared analogously to **2f** from 0.3 g (2.14 mmol) of 1-trimethylsilylimidazole and 2.14 mmol of HBCl₂·SMe₂ (**2g'**) is obtained as a colorless solid, insoluble in organic solvents (Yield: 0.27 g, 88%), m.p. > 300 °C. ESIMS: *m/z* (%): 571 [M - H]⁺ (10), 467 (36), 399 (25), 319 (100), 294 (25), 227(17), 199 (15). EIMS: *m/z* (%): 430 [M - 4Cl]⁺ (100), 351 (60), 206 (30).

4.7. Tetrameric 2,6-dimethylpiperidyl-1-imidazolylchloroborane (**2h**)

Compound **2h** was prepared analogously to **2f** from 0.3 g (2.14 mmol) of 1-trimethylsilylimidazole and 2.14 mmol of 2,6-dimethylpiperidyl-dichloroborane. The white solid was insoluble in organic solvents (Yield: 85%), m.p. > 300 °C.

4.8. Crystal structure determinations of **2a**, **2a'**, **2b**, **2d** and **3d**

Crystal data and details of the structures determinations are listed in Tables 1 and 2. Intensity data were collected at 173 K (**2a**, **a'** and **2d**), at 190 K (**3d** and **2d**) with a Bruker AXS area detector (Mo-K_α-radiation λ = 0.71073 Å, graphite monochromator, ω-scan). The structures were solved by direct methods and refined by least-squares methods based on *F*² with all measured reflections [SHELXTL NT5.1] [6]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference Fourier maps and refined.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC nos. 199745 for **2a**, 199746 for **2a'**, 199747 for **2b**, 199748 for **3d**, 199749 for **2d**. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk/conts/retreving/html>).

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