sensitive test case of Harata's rule, since the transition moment of the localized azo chromophore is insensitive to the alkyl substitution pattern. The present "structural test" is distinct, compared to earlier studies,[6, 13–16] since a whole chromophore is actually flipped around in the chiral cavity. Most importantly and in contrast to related studies,[17, 18] different orientations of the same chromophore (−N=N−) could be explored within the same host (β-CD).

Experimental Section

β-CD (Fluka) and >99.8% D_2O (Glaser AG, Basel, Switzerland) were used as received. All experiments were performed at ambient temperature in D_2O for consistency with the NMR measurements. The azoalkane **2** was synthesized by cycloaddition of α-terpinene with *N*-methyltriazolinedione (both from Aldrich), subsequent hydrogenation, hydrolysis, and oxidation, in analogy to literature methods for the known azoalkane **1**.[22]

2: M.p. 34–35 °C; UV (D_2O): $\lambda_{max} = 373$ nm ($\varepsilon = 54\,cm^{-1}M^{-1}$); ^1H NMR (300 MHz, D_2O): $\delta = 2.43$ (sept, 1 H, $J = 6.9$ Hz), 1.74 (s, 3 H), 1.54–1.51 (m, 4 H, *anti*), 1.24 (d, 6 H, 6.9 Hz), 1.11–1.08 (m, 4 H, *syn*); ^{13}C NMR (75 MHz, D_2O): $\delta = 69.03$, 63.75, 34.50, 28.74, 25.33, 23.70, 17.81; GC–MS [column SE-30, 70 °C (for 10 min)–10 K min^{-1}–270 °C (for 10 min)]: 13.82 min; MS: 166.16 (M^+), 138 ($M^+ - N_2$), 123 (138 − CH_3), 109, 95 (138 − iC_3H_7), 81, 67, 55, 41; elemental analysis calcd for $C_{10}H_{18}N_2$ (%): C 72.24, H 10.91, N 16.85; found: C 72.13, H 10.68, N 17.08.

ICD spectra were recorded with a Jasco J-720 circular dichrograph (0.2 nm resolution, 25 accumulations, 1 cm cell). Blank measurements of D_2O and solutions of β-CD, **1**, and **2** provided no ICD effects in the region examined. The ^1H NMR (300 MHz) CIS values were determined under conditions of nearly quantitative (>90%) complexation (2.5 mM azoalkane, 8.8 mM β-CD). 2D-ROESY spectra (600 MHz) were obtained for solutions of 9.6 mM azoalkane and 4.6 mM β-CD in D_2O.

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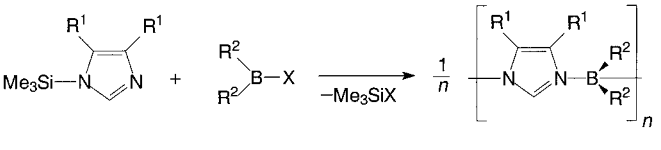
Macrocyclic Imidazolylboranes[**]

Andre Weiss, Hans Pritzkow, and Walter Siebert[*]

Dedicated to Professor Gerhard Fritz on the occasion of his 80th birthday

Polymeric structures have been described for 1-imidazolyldiethylborane[1a] and 1-imidazolyldiphenylborane,[1b] in which a chainlike arrangement results from intermolecular N→B donor/acceptor interactions. An analogous behavior is observed in the cyanoborane $(NC{-}BH_2)_n$ synthesized from $NaBH_3CN$ and HCl.[2] Besides polymeric compounds cyclic cyanoboranes were found consisting of four to ten monomers and showing a maximum of product distribution at $n = 5$. In the following we report on macrocyclic imidazolylboranes.

Initial evidence for the formation of macrocyclic imidazolylboranes occurred in an attempt to prepare bis(3-borane-imidazolyl)boranes from 1-trimethylsilyl-3-borane-imidazole and $RBCl_2$ (R = $NiPr_2$, C_6H_5). Astonishingly, the mass spectra of the products contained a signal group around *m*/*z* 319 and indicated tetrameric imidazolylborane **3a**. Therefore we allowed 1-trimethylsilylimidazole (**1a**) to react with the chloroborane **2a** under high dilution and obtained a mixture of oligomeric imidazolylboranes.



1	**a**	**b**
R^1	H	Me

2	**a**	**b**
R^2	H	Me
X	Cl	Br

	3a	**b**	**4a**	**b**	**5a**	**6**
R^1	H	H	H	H	Me	Me
R^2	H	H	Me	Me	H	Me
n	4	5	4	5	4	>5

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The mass spectrum of the reaction product shows the molecular ions from the monomer to the pentamer, and the GC-MS analysis confirms the formation of tetrameric **3a** and pentameric **3b** in a ratio of 2.3:1 and excludes the appearance of the units from $n = 1-3$; the corresponding signals in the mass spectrum indicate the fragment ions of higher membered species. After separation of the two macrocycles by column chromatography we obtained crystals of **3b** suitable for X-ray structure analysis[3] from a saturated solution in CH_2Cl_2. Compound **3b** displays a funnellike conformation (Figure 1).

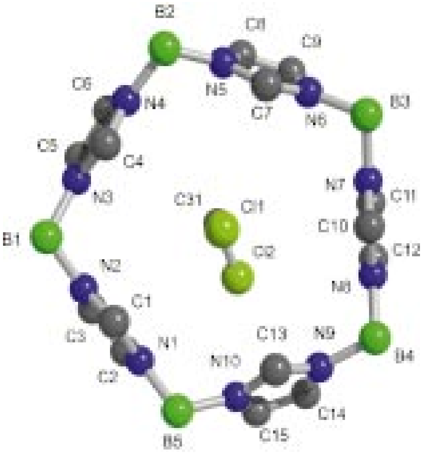

Figure 1. Structure of **3b** in the crystal. Selected average bond lengths [Å] and angles [°]: N-B 1.558(10), N1-C2 1.373(9), N2-C3 1.368(8), C2-C3 1.343(10), N2-C1 1.323(8), N1-C1 1.322(8); C2-N1-B5 127.5(7), C1-N1-B5 127.0(6), C1-N1-C2 105.4(6), C1-N2-C3 105.8(6), C2-C3-N2 108.0(7), C3-C2-N1 108.3(7), N1-C1-N2 112.4(6), N10-B5-N1 109.3(6).

In contrast to **5a** (see below) all imidazole rings are almost perpendicular to the plane of the molecule. The unit cell contains two independent molecules that differ with respect to the CH_2Cl_2 molecule.

Under the influence of the CH_2Cl_2 molecule in the center of the cycle, one of the imidazole rings is more tilted than the others. Apart from this all imidazolylborane units of **3b** are almost identical. The measured average N-B-N angle of 109.3(6)° corresponds to a sp^3-hybridized boron atom; the internal angles barely deviate from those of a perfect pentagon (108°).

Compounds **3a**, **b** are remarkably stable. After successful cyclization no ring opening and subsequent aggregation to higher membered species is observed at different concentrations. Under influence of air and moisture noticeable decomposition occurs after a few days.

The analogous reaction of dimethylbromoborane (**2b**) with **1a** leads to tetrameric **4a** and pentameric **4b** as a by-product (17:1). Compound **4a** crystallized from a saturated solution in CH_2Cl_2. The respective product distribution shows that the favored ring size is dependent on the steric demand of the substituents on the boron atom. The substituents in the 4,5-positions of the imidazole ring display such an influence, as shown from the reactions of 4,5-dimethyl-1-trimethylsilylimidazole (**1b**) with **2a**, **b**: The reaction with **2b** does not lead to cyclic but to higher molecular products **6** as a result of the steric overcrowding. By way of contrast **1b** reacts with chloroborane (**2a**) exclusively to give the tetramer **5a**.

In agreement with these observations is the preferred formation of a pentameric adduct in the case of the sterically undemanding cyanoborane.[2] The X-ray structure analysis[3] of a single crystal of **5a** shows that the unit cell contains two independent molecules; both have an inversion center (Figure 2). Two opposite imidazole rings lie in the plane of the molecule, the other two are perpendicular to it. The average N-B-N angles of 107.4° are slightly less than the value for an ideal tetrahedral angle. The average B–N bond length is 1.564 Å and is consistent with the expected data for a B–N bond at an sp^3-hybridized boron atom.

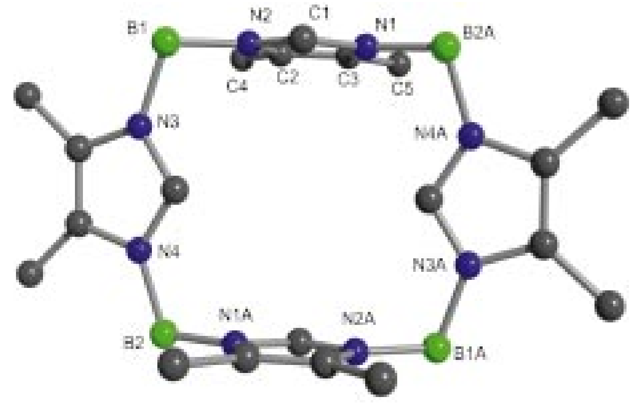

Figure 2. Structure of **5a** in the crystal. Selected average bond lengths [Å] and angles [°]: C1-N1 1.335(1), C2-N2 1.395(1), C2-C4 1.490(2), C2-C3 1.365(1), N2-B1 1.559(2); B1-N2-C1 125.4(1), N2-B1-N3 107.2(1), B1-N2-C2 127.8(1), N2-C2-C4 121.7(1), N1-C1-N2 111.3(1).

In accordance with the work of Arduengo et al.,[4] Herrmann et al.,[5] and Fehlhammer et al.[6] the oligomeric derivatives of **3**–**5** should be of great potential with respect to deprotonation and formation of a carbene, which could subsequently be used to prepare stable metal–carbene complexes. The tetrameric compounds **3a**–**5a** are particularly interesting for porphyrin-like metal complexes. Recently we reported the preparation and characterization of some borane-substituted imidazole-2-ylidene complexes.[7]

Experimental Section

Tetrameric and pentameric 1-imidazolylborane **3a**, **b**: A BH_2Cl solution (50 mL of a 0.55 M solution in THF) was added dropwise to a stirred solution of **1a** (3.76 g, 26.8 mmol) in THF (150 mL) over 2 h at 0 °C and the mixture was stirred for 3 h. After 15 h the resulting solution was concentrated to 20 mL and filtered through a fritted column (G3), filled with SiO_2 (3 cm). After removal of the solvent under vacuum the residue was washed several times with pentane and dried under high vacuum to provide **3a**, **b** (1.83 g, 85%; m.p. 70–80°C) as a colorless mixture. Separation by column chromatography: SiO_2 (0.04–0.06 mesh, dried for 15 h under high vacuum) as stationary phase, Et_2O/hexane (1/1) as eluent at −25 °C. Detection with TLC (SiO_2) and iodine as well as GC-MS. **3a:** EI-MS: m/z (%): 319 (100) $[M_4 - H]^+$, 239 (28) $[M_3 - H]^+$, 173 (34) $[C_6H_{12}B_3N_4]^+$, 159 (34) $[M_2 - H]^+$, 93 (34) $[C_3H_7B_2N_2]^+$; $^1H\{^{11}B\}$ NMR (200 MHz, CD_2Cl_2): $\delta = 3.4$ (s, br., 2 H, BH_2), 7.00 (s, 2 H, 4,5-H), 7.29 (s, 1 H, 2-H); ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta = 124.1$ (s, C-4,5), 137.6 (s, C-2); ^{11}B NMR (64 MHz, CD_2Cl_2): $\delta = -9.1$ (t, $^2J(B,H) = 99.3$ Hz); HR-EI-MS: m/z calcd for $^{12}C_{12}{}^1H_{19}{}^{14}N_8{}^{11}B_4$ $[M^+ - H]$: 319.2105, found: 319.2136, $\Delta m = 3.1$ mmu; **3b**: EI-MS: m/z (%): 398 (100) $[M_5 - H]^+$, 319 (33) $[M_4 - H]^+$, 173 (58) $[C_6H_{12}B_3N_4]^+$, 93 (90) $[C_3H_7B_2N_2]^+$; ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 6.95$ (s, 2H, 4,5-H), 7.56 (s, 1H, 2-H); ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta = 124.6$ (s, C-4,5), 140.0 (s, C-2); ^{11}B NMR (64 MHz, CD_2Cl_2): $\delta = -9.5$ (s).

Tetrameric 1-imidazolyldimethylborane **4a**: The reaction was analogous to that of **3a**, **b**, but with CH_2Cl_2 instead of THF. Yield: 97% (contains 5% **4b**).

Tetrameric 1-(4,5-dimethylimidazolyl)borane **5a**: A BH_2Cl solution (40 mL of a 0.45 M solution in THF) was added dropwise to a stirred solution of **1b** (3.02 g, 17.9 mmol) in THF (150 mL) over 4 h at 0°C. The workup procedure was analogous to that of **3a**, **b** and gave colorless **5a** (1.65 g, 85%). EI-MS: m/z (%): 431 (55) $[M_4 - H]^+$, 337 (8) $[C_{15}H_{29}B_4N_6]^+$, 229 (60) $[C_{10}H_{20}B_3N_4]^+$, 216 (28) $[M_2]^+$, 203 (12) $[C_{10}H_{16}BN_4]^+$, 121 (100) $[C_5H_{11}B_2N_2]^+$, 108 (29) $[M]^+$; ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 2.12$ (s, 6H, CH_3), 6.64 (s, 1H, 2-H); ^{13}C NMR (50 MHz, CD_2Cl_2): $\delta = 8.2$ (s, CH_3), 128.1 (s, C-4,5), 135.3 (s, C-2); ^{11}B NMR (64 MHz, CD_2Cl_2): $\delta = -11.8$ (s, br.).

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Nitrophenolate as a Building Block for Lanthanide Chains and Clusters**

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Inorganic clusters continue to attract considerable attention because they represent the bridge linking molecular and solid state chemistry and because they are useful tools for understanding the size-dependent physical properties of electronic material.[1] While the cluster chemistry of the transition metals is now firmly established and huge clusters have been isolated—especially clusters of molybdenum,[2] copper,[3] and silver[4]—the analogous chemistry of the lanthanides is virtually undeveloped.[5] Whereas systematic studies on the lanthanide clusters of sulfur, selenium, and tellurium have recently been reported,[6] most of the lanthanide–oxygen clusters have been obtained by unexpected synthetic routes such as the decomposition of ether solvents,[7] the decomposition of grease,[8] or the reaction with traces of water in the mixture.[9] While we were preparing this paper, a systematic synthesis of pentadecanuclear lanthanide–tyrosine clusters from water was discovered by Zheng et al.[10]

We report here on the systematic preparation of lanthanide–oxygen clusters by partial hydrolysis of a water-sensitive reaction mixture. To reach this synthetic goal we were most interested in using a ligand which features different coordination modes. During our investigations it turned out that this is ideally achieved by using *o*-nitrophenolate. Transmetalation of potassium *o*-nitrophenolate with anhydrous yttrium or lutetium trichloride in THF with rigorous exclusion of air followed by crystallization from THF/pentane (1/4) leads to infinite chains of **1a** (Ln = Y) and **1b** (Ln = Lu). The

$[(\mathrm{THF})_4\{\mathrm{K}(o\text{-}\mathrm{O_2NC_6H_4O})_4\mathrm{Ln}\}_4]_n$ **1**

new complexes have been characterized by standard spectroscopic techniques, and the solid-state structures of **1a** and **1b** (Figure 1a) were established by single-crystal X-ray diffraction.[11] Compounds **1a** and **1b** are isostructural. Each lanthanide ion of **1** is surrounded by four *o*-nitrophenolate anions which act as bidentate ligands. Thus, each lanthanide ion is eightfold coordinated. Nevertheless, two different coordination modes of the *o*-nitrophenolate are realized in **1**; the nitro group may either point to the left side or to the right side of the chain. Thus, the dissimilarities in the coordination spheres of the lanthanide ions in **1** is caused by different orientations of the ligands around the metal center. The Ln−O bond lengths for Ln−OR are: 221.1(8)–231.8(9) (**1a**) and 219.5(12)–232.4(11) pm (**1b**); and for Ln−ONO are: 231.5(8)–249.7(8) (**1a**) and 234.7(11)–250.4(9) pm (**1b**). The potassium cations are located in between the

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