general they have an oligonuclear structure.[14] A mononuclear complex with T symmetry and achiral ligands was hitherto unknown. The structure of $[Ba(tbci)_4]^{2+}$ is further unique in that it represents one of the very few examples of a 12-coordinate complex with exclusive formation of six-membered chelate rings. The facile formation of this complex in non-aqueous media may indicate that lipophilic derivatives of symmetrically substituted *cis*-cyclohexane-1,3,5-triols could serve as building blocks for such complexes if sufficiently large metal centers are used.

Experimental Section

tbci[15] was prepared by the reaction of taci[11] and an excess of benzaldehyde in MeOH, followed by $NaBH_4$ reduction. tbmci was obtained from tbci by an Eschweiler–Clarke-type methylation with formaldehyde and formic acid. Both ligands were characterized by ^1H and ^{13}C NMR spectroscopy as well as positive-ion fast-atom bombardment (FAB^+) MS, and gave correct C,H,N analyses (see Supporting Information).

$[Ba(tbci)_4]Br_2\cdot 2CH_3OH$: A solution of $BaBr_2\cdot 2H_2O$ (41 mg) in MeOH (5 mL) was added to a suspension of tbci (220 mg) in MeOH (5 mL). A clear solution was formed from which a crop of colorless crystals deposited within several minutes. Yield: 61% of the air-dried product. Elemental analysis calcd (%) for $C_{110}H_{140}BaBr_2N_{12}O_{14}$ (2151.57): C 61.41, H 6.56, N 7.81; found: C 61.48, H 6.66, N 7.65; ^1H NMR ($CDCl_3$): $\delta = 2.15$ (3H), 3.70 (6H), 3.80 (3H), 7.23–7.36 (15H); ^{13}C NMR: $\delta = 50.7$, 58.4, 66.7, 125.9, 127.1, 128.5, 140.0; MS (FAB^+, 3-nitrobenzylalcohol) m/z (%): 2007.8 (55) $[Ba(tbci)_4Br]^+$, 2005.8 (45) $[Ba(tbci)_3(tbci-H_2)Br]^+$, 1926.3 (7) $[Ba(tbci)_4-H^+]^+$.

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[9] A derivation, based on geometrical and group theory considerations, together with a figure of the five isomers is given in the Supporting Information.

[10] Three of the five possible isomers (T_h, D_3, and D_{3d}) are discussed in ref. [7]; in ref. [5] the total number of possible solutions is erroneously given as six, without specifying the geometry of the individual isomers.

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[12] Crystals of composition $[Ba(tbci)_4]Br_2\cdot 2.5MeOH$ disintegrate rapidly upon exposure to air. A crystal of dimensions 0.30 × 0.18 × 0.12 mm was therefore embedded in a perfluoropolyether and cooled. Data collection was performed at 100(2) K on a SIEMENS SMART-CCD diffractometer, $Mo_{K\alpha}$-radiation ($\lambda = 71.073$ pm): space group $P2_1/n$, $a = 1910.1(5)$, $b = 2650.1(6)$, $c = 2050.1(5)$ pm, $\beta = 95.39(3)^\circ$, $Z = 4$, $V = 10332(4)\times 10^6$ pm^3, $\rho_{calcd} = 1.393$ Mg m^{-3}, $\mu = 1.228$ mm^{-1}, graphite monochromator, numerical absorption correction ($T_{min} = 0.644$, $T_{max} = 0.862$), $2\theta_{max} = 42.0^\circ$. Of 32396 measured reflections, 11083 independent reflections were used for the refinement of 576 parameters, and the structure was solved by direct methods (SHELXS-97). Ba, O, and N atoms were refined with anisotropic displacement parameters (SHELXL-97, full-matrix least-squares calculations on F^2). All other non-hydrogen atoms were refined isotropically. The phenyl groups were modeled as rigid bodies with fixed C–C bond lengths of 1.39 Å and fixed C-C-C angles of 120°. The phenyl groups appeared to be disordered. The disorder could only be partially resolved by using split positions. H(C) atoms were placed at calculated sites (riding model). $R = 0.112$ ($F_o^2 > 2\sigma(F_o^2)$), wR_2 (all data) = 0.267. Max/min residual electron density $+1.11/-1.18$ e Å^{-3}.[16]

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Coordinated B_2 Bridges in Porphyrins—Unexpected Formation of a Diborane(4)- from a Diborylporphyrin**

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and Walter Siebert*

Dedicated to Professor Max Herberhold
on the occasion of his 65th birthday

Free-base porphyrins react with haloboranes to yield diborylporphyrins in which the porphyrin ligands show marked rectangular distortions.[1] The reaction of **1a**-H_2 with $F_3B \leftarrow OEt_2$ in the presence of trace water leads to green **1a**-

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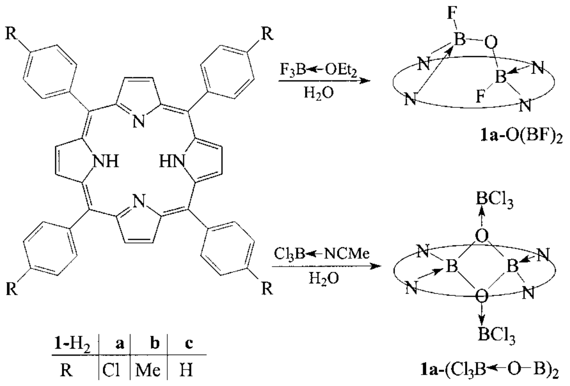
$O(BF)_2$ (Scheme 1), in which each of the boron atoms of the FB–O–BF moiety is connected to two adjacent nitrogen atoms. In contrast **1a**-H_2 reacts with an excess of $MeCN \rightarrow BCl_3$ to yield green **1a**-$(Cl_3B \leftarrow O{-}B)_2$, which contains a coordinated four-membered B_2O_2 ring.[2] The distances between two adjacent nitrogen atoms in the rectangularly distorted porphyrin **1a**-$(Cl_3B \leftarrow O{-}B)_2$ are 2.49 and 3.63 Å ($\Delta = 1.14$ Å). Since this distortion allows the coordination of the two boron atoms in the N_4 plane, we have investigated the synthesis of such compounds. This proved to be possible either by direct insertion of a B–B-bonded fragment into a porphyrin ligand or, surprisingly, by the formation of a B–B bond caused by spontaneous elimination of two butyl radicals from a diborylporphyrin, as we report in the following.

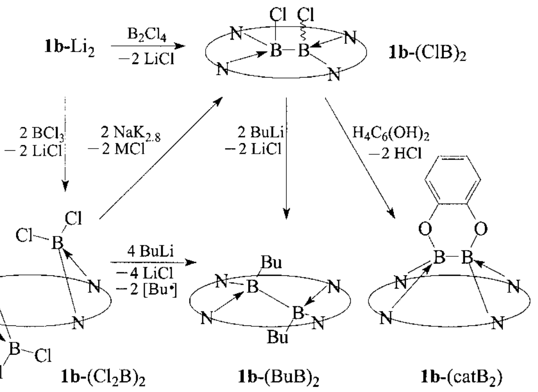


Scheme 1.

The reaction of **1b**-Li_2[3] with B_2Cl_4 led to dark violet, extremely air- and moisture-sensitive **1b**-$(ClB)_2$ in 80% yield. The ^1H NMR spectrum of **1b**-$(ClB)_2$ showed a double set of signals compared to the free porphyrin **1b**-H_2: two singlets for the methyl groups of *para*-tolyl substituents, four doublets, two each for the tolyl *ortho* and *meta* protons, and a typical AB quartet pattern for the pyrrolic protons, consistent with a rectangular distortion of the porphyrin framework and an associated lowering of the symmetry.[2] The ^{11}B signal at $\delta = -12$ is evidence for the tetragonal coordination of the boron atoms. Overall, the spectroscopic data for **1b**-$(ClB)_2$ are consistent with a complex containing a Cl-B-B-Cl fragment in which each B atom is coordinated to two porphyrin nitrogen atoms, and the two chlorine atoms are either *syn* (C_{2v}) or *anti* (C_2) with respect to the porphyrin plane.

Alternatively, **1b**-$(ClB)_2$ can be prepared by the reaction of **1b**-Li_2 with two equivalents of BCl_3 followed by a reductive coupling of the boron atoms (Scheme 2). The first step yields moisture-sensitive green **1b**-$(Cl_2B)_2$ ($\delta(^{11}B) = 5.6$), in which the two Cl_2B moieties are likely to be coordinated on opposite faces of the porphyrin plane for steric reasons.[4] Reduction of **1b**-$(Cl_2B)_2$ with $NaK_{2.8}$ alloy led to **1b**-$(ClB)_2$ in 30% yield.

The reaction of **1b**-$(ClB)_2$ with pyrocatechol (H_2cat) and **1b**-H_2 as auxiliary base gives **1b**-$H_2 \cdot 2HCl$ and the *syn* compound[5] **1b**-$(catB_2)$, whose ^1H NMR spectrum shows markedly high-field shifted multiplets at $\delta = 5.3$ (*meta*) and $\delta = 4.1$ (*ortho*) for the catechol aromatic protons, which results from the diamagnetic ring current of the porphyrin system. The synthesis of **1b**-$(catB_2)$ indicates that an inversion of the configuration must take place in the reaction of **1b**-$(ClB)_2$ with an *anti* arrangement (see below) of the Cl atoms.



Scheme 2.

Treatment of **1b**-$(ClB)_2$ with two equivalents of butyllithium led to the crystalline, olive-green *anti*-dibutyl derivative **1b**-$(BuB)_2$. The ^1H NMR signals of the porhyrin protons are slightly shifted in comparison with those of **1b**-$(ClB)_2$ and show the same multiplicity (symmetry). The proton signals of the butyl groups are shifted strongly upfield by the diamagnetic ring current of the porphyrin π system. The methylene protons are observed at $\delta = -5.64$, -3.54, and -1.22, which reflects the increasing distance from the porphyrin core, and the protons of the methyl group appear as a triplet at $\delta = -0.63$. Similar chemical shifts are observed for the butyl groups in the butylmetalloporphyrin complexes **1c**-(BuAl)[6a] and **1c**-(BuGa).[6b]

Surprisingly, we observed the formation of **1b**-$(BuB)_2$ (20% yield in a mixture of products) by treatment of **1b**-$(Cl_2B)_2$ with four equivalents of butyllithium, rather than the expected product **1b**-$(Bu_2B)_2$. We propose that this occurs through the intermediate formation of **1b**-$(Bu_2B)_2$, from which, because of the steric overcrowding, two butyl radicals are eliminated and the two boron atoms are linked. Unidentified products (observed by NMR spectroscopy) might be formed by the reaction of the postulated butyl radicals with **1b**-$(Cl_2B)_2$ and **1b**-$(BuB)_2$. Attempts to react **1b**-Li_2 with Bu_2BCl yielded neither **1b**-$(Bu_2B)_2$ nor **1b**-$(BuB)_2$.

The X-ray structure analyses[7] of single crystals of **1b**-$(BuB)_2$ and **1b**-$(BuB)_2 \cdot CH_2Cl_2$ indicate that the butyl groups are arranged *anti* relative to the porphyrin plane (Figure 1). The boron atoms are located 0.44 Å above and below the N_4 plane, which results in a tetrahedral coordination geometry (angles at B1, and at B1B 104.0–111.9°). The molecule displays an inversion center, the *p*-tolyl rings are almost perpendicular to the porphyrin plane. The B–B distance is 1.77 Å, which is typical for adducts of diborane(4) compounds.[8] As expected, the rectangular distortion of the porphyrin framework is not as marked (distance between adjacent N atoms: 3.28 and 2.49 Å, $\Delta = 0.8$ Å) as in **1a**-$(Cl_3B \leftarrow O{-}B)_2$.

Our results demonstrate both the direct insertion of a $(BCl)_2$ moiety into a porphyrin and also its formation by the reductive dehalogenation of a bis(dichloroboryl)porphyrin.

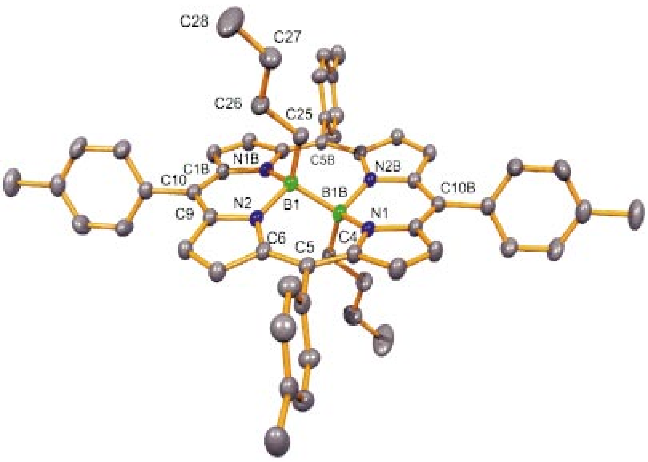


Figure 1. Structure of **1b**-(BuB)$_2$ · CH$_2$Cl$_2$ in the crystal. The CH$_2$Cl$_2$ molecule and the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: B1-B1B 1.769(7), B1-N2 1.584(5), B1-N1B 1.577(4), B1-C25 1.622(5); N1B-B1-N2 104.0(3), C25-B1-B1B 111.9(3), C9-C10-C1B 119.0(3), C4-C5-C6 130.9(3).

The fascinating formation of the diborane(4) derivative **1b**-(BuB)$_2$ from the diborylporphyrin **1b**-(Cl$_2$B)$_2$ will be further investigated with regard to preparative applications.

Experimental Section

1b-(ClB)$_2$: B$_2$Cl$_4$ (290 mg, 1.77 mmol) was condensed onto a suspension of **1b**-Li$_2$ (940 mg, 1.38 mmol) in hexane (80 mL) at −100 °C. The mixture was allowed to warm to room temperature (3 h) and then stirred for 12 h. This yielded a precipitate which was filtered off, washed with hexane, and extracted with toluene. Yield: 940 mg (80 %) dark violet **1b**-(ClB)$_2$ · *n*Tol ($n = 0.5-1$). Low-temperature fast atom bombardment (LT-FAB) MS (toluene): *m/z* (%): 760 (1) [M^+], 725 (7) [$M-\mathrm{Cl}]^+$, 690 (3) [$M-2\,\mathrm{Cl}]^+$; ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 2.71$ (s, 6H; CH$_3$), 2.76 (s, 6H; CH$_3$), 7.62 (d, $^3J = 7.9$ Hz, 4H; *meta*), 7.71 (d, $^3J = 7.9$ Hz, 4H; *meta*), 8.14 (d, $^3J = 7.9$ Hz, 4H; *ortho*), 8.22 (d, $^3J = 7.9$ Hz, 4H; *ortho*), 9.16 (AB-q, 8H; β-pyrrole-H); ^{11}B NMR (64 MHz, CD$_2$Cl$_2$): $\delta = -12$ (br.); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (lgε) = 370 (3.78), 425 (4.86), 559 (3.60), 605 nm (3.70).

1b-(ClB)$_2$ was also obtained by treatment of **1b**-(Cl$_2$B)$_2$ (140 mg, 0.17 mmol) with NaK$_{2.8}$ alloy (0.5 mL) in toluene (20 mL) at −78 °C. After the mixture had been allowed to warm to room temperature (3 h) and stirred for 1 h, it was filtered and the solvent was removed from the filtrate. Yield: 39 mg (30 %) **1b**-(ClB)$_2$ · *n*Tol (n = 0.5−1).

1b-(Cl$_2$B)$_2$: BCl$_3$ (1.00 g, 8.53 mmol) was added to a suspension of **1b**-Li$_2$ (280 mg, 0.41 mmol) in hexane (80 mL) at −78 °C. The mixture was allowed to warm up and stirred for 14 h at room temperature. The precipitate was removed from the solvent and excess BCl$_3$ by filtration, then washed with hexane to yield **1b**-(Cl$_2$B)$_2$ (324 mg; 95 %). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 2.68$ (s, 6H; CH$_3$), 2.77 (s, 6H; CH$_3$), 7.72 (d, br, $^3J = 7.4$ Hz, 8H; *meta*), 8.14 (d, br, $^3J = 7.4$ Hz, 8H; *ortho*), 9.34 (m, br, 8H; β-pyrrole-H); ^{11}B NMR (64 MHz, CD$_2$Cl$_2$): $\delta = 5.6$ (s); UV/Vis (CH$_2$Cl$_2$): at high dilution only decomposition products were detected.

1b-(BuB)$_2$: A 2.5 M *n*BuLi solution (0.3 mL, 0.75 mmol) was added to a suspension of **1b**-(ClB)$_2$ · *n*Tol (300 mg, 0.35 mmol) in hexane (20 mL) at −78 °C. The reaction mixture was allowed to warm up to room temperature and stirred 16 h. The precipitate was filtered, washed with hexane, and extracted with CH$_2$Cl$_2$ to yield olive-green **1b**-(BuB)$_2$ (200 mg, (71 %). LT-FAB-MS (toluene): *m/z* (%): 804 (3) [M^+], 747 (7) [$M-\mathrm{C_4H_9}]^+$, 690 (15) [$M-2(\mathrm{C_4H_9})]^+$; ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): $\delta = -5.7$ (m, 4H; CH$_2$), −3.47 (m, 4H; CH$_2$), −1.13 (m, 4H; CH$_2$), −0.56 (t, $^3J = 7.3$ Hz, 6H; CH$_3$), 2.63 (s, 6H; CH$_3$), 2.67 (s, 6H; CH$_3$), 7.47 (d, $^3J = 7.4$ Hz, 4H; *meta*), 7.58 (d, $^3J = 7.9$ Hz, 4H; *meta*), 7.93 (d, $^3J = 7.4$ Hz, 4H; *ortho*), 7.99 (d, $^3J = 8.0$ Hz, 4H; *ortho*), 8.34 (AB-q, 8H; β-pyrrole-H); ^{11}B NMR (64 MHz, CD$_2$Cl$_2$): $\delta = -6$ (br.); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (lgε) = 419 (5.28), 443 (4.92), 517 (4.12), 553 nm (4.00).

1b-(BuB)$_2$ was also obtained as one component in a mixture of other, unidentified products from the reaction of **1b**-(Cl$_2$B)$_2$ with four equivalents of *n*BuLi. Its preparation by this method was confirmed by ^{1}H NMR data (about 20 % yield) and by an X-ray structure analysis.[7]

1b-(catB$_2$): Pyrocatechol (34 mg, 0.31 mmol) was added to a mixture of **1b**-(ClB)$_2$ · Tol (260 mg, 0.31 mmol) and **1b**-H$_2$ (208 mg, 0.31 mmol) in toluene (30 mL) at −78 °C. After the mixture had been allowed to warm to room temperature, it was filtered to remove insoluble **1b**-H$_2$ · 2 HCl, and **1b**-(catB$_2$) (98 mg; 40 %) was isolated from the filtrate. FAB-MS (NPOE: 2-nitrophenyloctylether): *m/z* (%): 798 (10) [M^+], 690 (18) [$M-\mathrm{cat}]^+$; ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 2.68$ (s, 6H; CH$_3$), 2.69 (s, 6H; CH$_3$), 4.15 (m, 2H; *ortho*$_{\mathrm{cat}}$), 5.43 (m, 2H; *meta*$_{\mathrm{cat}}$), 7.48 (d, $^3J = 7.8$ Hz, 4H; *meta*), 7.58 (d, $^3J = 7.9$ Hz, 4H; *meta*), 8.10 (d, br, $^3J = 7.9$ Hz, 8H; *ortho*), 9.10 (AB-q, 8H; β-pyrrole-H); ^{11}B NMR (64 MHz, CD$_2$Cl$_2$): $\delta = -15$ (br); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (lgε) = 370 (3.71), 419 (5.12), 516 nm. (4.23)

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[7] Structural data of **1b**-(BuB)$_2$ · CH$_2$Cl$_2$: monoclinic *C*2/*c*, $a = 25.757$ (2), $b = 8.9382$ (9), $c = 23.314$ (2) Å, $\beta = 114.830(2)°$, $V = 4871.3(\ 8)$ Å^3, $Z = 4$. A total of 14615 independent reflections (4291 observed, $I > 2\sigma(I)$), the measurement was carried out on a Bruker AXS diffractometer SMART 1000 (Mo$_{K\alpha}$ radiation, ω scan, $T = 190(2)$ K), $R1 = 0.066$, $wR2 = 0.215$. The structure was solved by direct methods (SHELXS 86) and refined with all measured reflections against F^2 (SHELXL 97).[10] The structure of **1b**-(BuB)$_2$ (synthesized from **1b**-(Cl$_2$B)$_2$) was determined as well and showed good agreement. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167513 (**1b**-(BuB)$_2$ · CH$_2$Cl$_2$) and CCDC-167514 (**1b**-(BuB)$_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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