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# Mono- and Diboron Corroles: Factors Controlling Stoichiometry and Hydrolytic Reactivity

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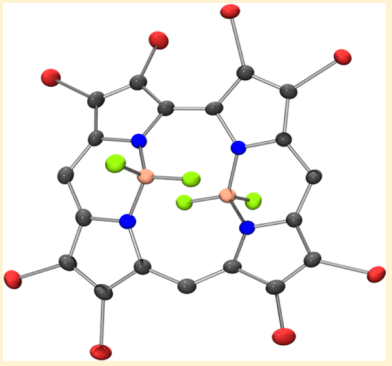
Supporting Information

**ABSTRACT:** The first example of a diboryl corrole complex, $[(BF_2)_2(Br_8T(4\text{-}F\text{-}P)C)]^-$ ($Br_8T(4\text{-}F\text{-}P)C$ = trianion of 2,3,7,8,12,13,17,18-octabromo-5,10,15-tris(4-fluorophenyl)corrole), has been isolated using the strongly electron-withdrawing and sterically crowded triaryl octabromocorrole ligand. Density functional theory (DFT) calculations show that the hydrolysis reaction producing the partially hydrolyzed complexes $[B_2OF_2(Cor)]^-$ is more favored for the less sterically crowded triaryl corrole complexes. Monoboryl complexes $BF_2(H_2Cor)$ (Cor = trianions of 5,10,15-triphenylcorrole (TPC), 5,10,15-tris(4-methylphenyl)corrole ($T(4\text{-}CH_3\text{-}P)C$), 5,10,15-tris(4-trifluoromethylphenyl)corrole ($T(4\text{-}CF_3\text{-}P)C$), and 5,10,15-tris-(pentafluorophenyl)corrole (TPFPC)) were prepared and characterized. The experimental data are consistent with an out-of-plane dipyrrin coordination mode for these complexes, and DFT optimizations suggest that internal BF···HN hydrogen bonding may be significant in stabilizing these complexes. Further examples of the anionic diboron corrole $[B_2OF_2(Cor)]^-$ containing the electron-withdrawing 5,10,15-tris(pentafluorophenyl)corrole (TPFPC) and the sterically hindered 10-(4-methoxyphenyl)-5,15-dimesitylcorrole ($Mes_2(4\text{-}MeOP)C$) trianions are reported.



## INTRODUCTION

Porphyrin and corrole complexes of the element boron provide a beautiful illustration of the more unusual possibilities for coordination complexes of these ubiquitous ligands. The ligands are generally considered to offer four nitrogen donors in a square-planar (porphyrin) or nearly square-planar (corrole) arrangement and have been shown to bind metallic or nonmetallic ions ranging from the very small (phosphorus and silicon) to the very large (lead and bismuth).[1−3] Complexes containing boron, however, have demonstrated that the macrocycles can also serve as binucleating ligands in which two boron atoms are each coordinated to two nitrogen donors (Figure 1).[4,5] Diboron porphyrin and corrole complexes show a range of structural types, stereochemical arrangements, and unusual chemical reactivity. Highlights of the boron porphyrin chemistry include a diboryl porphyrin (Figure 1c), a diboranyl porphyrin (Figure 1d) containing a B−B bond, which forms through spontaneous reductive coupling of the diboryl under certain conditions, and a further diboranyl complex which contains an unusual example of an antiaromatic, 20-electron reduced porphyrin ligand.[6,7]

Recent progress in corrole chemistry has extended the "periodic table of corrole complexes" at an impressive rate, driven in part by the publication of reliable methods for the synthesis of free base corroles.[8−10] In the last five years, new firsts in corrole chemistry[11] have been reported for complexes of the main group elements lithium,[12] lead,[13] and bismuth,[14] the transition metals titanium, zirconium, hafnium,[12,15] tungsten,[16] iridium,[17] and gold,[18−20] lanthanoids lanthanum,

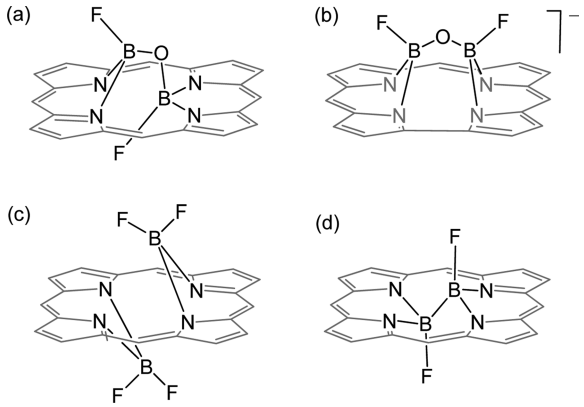



**Figure 1.** (a) Transoid arrangement in $B_2OF_2(Por)$. (b) Cisoid arrangement in $[B_2OF_2(Cor)]^-$. (c) Diboryl porphyrin $(BF_2)_2(Por)$. (d) Diboranyl porphyrin (FBBF)(Por).

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gadolinium, and terbium,[21] and actinoids thorium and uranium.[22]

Our own recent work extends the coordination chemistry of boron to the corrole ligand.[23−25] Although corroles and porphyrins are closely related, we observe some significant differences in the chemistry of their boron complexes. For example, the more constrained corrole hole size leads to cisoid stereochemistry in the FBOBF corrole anion $[B_2OF_2(Cor)]^-$ (Figure 1b), compared to transoid for the related porphyrin $B_2OF_2(Por)$ (Figure 1a) (Cor = unspecified corrole ligand, Por = unspecified porphyrin ligand).[23,24,26] We have also isolated boron hydride corrole complexes, including an unusual example of a complex containing a B−H−B group coordinated within the cavity in the corrole, $Ph_2B_2H(Cor)$.[25]

There are still some missing links in this chemistry, however. Bis(difluoroboryl) and bis(dichloroboryl) porphyrin complexes $(BX_2)_2(Por)$ (X = F, Cl) have been isolated, characterized, and demonstrated to be the precursors to porphyrin complexes containing oxygen-bridged BOB moieties formed by hydrolysis reactions. However, the corresponding bromo- and iodoboryl porphyrin complexes (X = Br, I) were not isolated as they undergo spontaneous reductive coupling reactions to form diboranyl species (XBBX)(Por), and the driving force for this reaction has been shown to derive from the highly sterically constrained environment within the diboryl porphyrins.[7]

The first corrole complex that we reported, $[B_2OF_2(Cor)]^-$, is likely to be formed by hydrolysis of a bis(difluoroboryl) corrole intermediate $[(BF_2)_2(Cor)]^-$ (the corrole analogue of the porphyrin complex in Figure 1c).[23] Similarly, we proposed that the hydride complex $Ph_2B_2H(Cor)$, the product of the reaction of $PhBCl_2$ with free base corrole $H_3Cor$, forms via a spontaneous reductive coupling reaction of a diboryl corrole followed by capture of a proton by an anionic diboranyl intermediate, forming the hydride complex.[25] Although both of these examples involve putative diboryl corrole complex intermediates, $[(BX_2)_2(Cor)]^-$, we have not until now prepared an isolable example, the first of which is reported in this Paper.

Another key feature of the diboron porphyrin and corrole complexes reported to date is the marked tetragonal elongation of the ligands. For example, in $B_2OF_2(Por)$ and $B_2O_2(BCl_3)_2(Por)$ the nonbonded N···N distance parallel to the B−B axis is over 1.25 Å longer than the N···N distance perpendicular to the B···B axis. This parameter, Δ(N···N), is still around 0.84 Å even in the less sterically constrained diboranyl complexes that contain a B−B bond. This large distortion arises from the constraints of fitting two tetrahedral boron atoms within the confines of the coordination pocket. Corroles have an even smaller "hole" than porphyrins and exhibit a similar degree of tetragonal elongation. The cisoid stereochemistry in the FBOBF corrole anion $[B_2OF_2(Cor)]^-$, compared to the transoid arrangement in the related porphyrin $B_2OF_2(Por)$, is attributed to the smaller binding pocket in the corrole (Figure 1). This suggests that coordination of only one boron atom to the ligand, leaving two of the donor nitrogens unused, might be a more energetically favorable possibility. Such complexes would be macrocyclic analogs of the well-known boron dipyrrin (BODIPY) complexes.[27−29] Although monoboron complexes of N-confused and N-fused porphyrins have been reported,[30] there are no examples of monoboron complexes of the parent porphyrin ligand despite the obvious steric strain imposed by coordinating two boron atoms within the macrocycle. We recently reported a density functional theory (DFT) study on monoboron corroles and N-methyl corroles,[24] and we describe here the first experimental data for monoboron corrole complexes and consider the reasons why they might be observed in corrole but not porphyrin chemistry.

## RESULTS AND DISCUSSION

Our first reported diboron corrole complexes, $[B_2OF_2(Cor)]^-[HNEt^iPr_2]^+$, were prepared from the reaction of the free base corrole $H_3Cor$ with $BF_3{\cdot}Et_2O$ and $NEt^iPr_2$ in a 1:12:20 ratio in $CH_2Cl_2$ (Cor = trianions of 5,10,15-triphenylcorrole (TPC), 5,10,15-tris(4-methylphenyl)corrole (T(4-CH3−P)C), 5,10,15-tris(4-trifluoromethylphenyl)corrole (T(4-$CF_3$−P)C), and 5,10,15-tris(4-fluorophenyl)corrole (T(4-F−P)C)).[23,26] The use of this ratio was optimized for a good yield of the product; other ratios gave incomplete conversion and resulted in difficulties in separating the product from unreacted free base corrole. More recently, we have prepared examples containing the strongly electron-withdrawing 5,10,15-tris(pentafluorophenyl)corrole (TPFPC) and the sterically hindered 10-(4-methoxyphenyl)-5,15-dimesitylcorrole ($Mes_2$(4-MeOP)C), showing that the reaction is quite general. The polar corrole anions $[B_2OF_2(Cor)]^-$ could not be purified by silica gel chromatography, typically sticking at the origin, and were isolated and purified by careful recrystallization. Partial hydrolysis gives rise to the bridging oxygen atom (derived from adventitious water) found in the product. This chemistry parallels that found for the corresponding porphyrin system, in which the reaction of $BF_3{\cdot}Et_2O$ with $H_2Por$ gives $B_2OF_2(Por)$ (Por = dianions of 5,10,15,20-tetraphenylporphyrin (TPP), 5,10,15,20-tetra(4-methylphenyl)porphyrin (TTP), 5,10,15,20-tetra(4-chlorophenyl)porphyrin (T(4-Cl-P)P), 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP)).[31−33]

**Diboryl Corrole.** The diboryl porphyrin complexes $(BX_2)_2(Por)$ (X = F, Cl) were prepared from the reactions of $BF_3{\cdot}OEt_2$ or $BCl_3{\cdot}MeCN$ with either the free base porphyrin $H_2Por$, or, more conveniently, $Li_2Por$, both under strictly anhydrous conditions.[6,7] Even trace adventitious moisture led to formation of the partially hydrolyzed products bearing B−O−B bridges. The sterically crowded octabromo triaryl corrole $H_3(Br_8T(4\text{-}F\text{-}P)C)$,[34] when treated with $BF_3{\cdot}OEt_2$ and $NEt^iPr_2$ in a 1:12:20 ratio in $CH_2Cl_2$, resulted in the diboryl complex $[(BF_2)_2(Br_8T(4\text{-}F\text{-}P)C)]^-[HNEt^iPr_2]^+$, isolated by crystallization from $CH_2Cl_2$/hexane. Although the reactant ratio and conditions were the same as those used for the preparation of $[B_2OF_2(Cor)]^-[HNEt^iPr_2]^+$, the experimental data for the product is consistent with a diboryl corrole product. The $^1H$ and $^{19}F$ NMR spectra of the complex show that the 5,15-$C_6H_4F$ groups are equivalent, while the 10-$C_6H_4F$ group is unique. Two resonances are observed in the $^{19}F$ NMR for the $BF_2$ fluorine atoms, and a single peak is seen in the $^{11}B$ NMR spectrum. High-resolution mass spectrometry (HRMS) also confirms the $[(BF_2)_2(Br_8T(4\text{-}F\text{-}P)C)]^-$ anion.

The formulation of the diboryl complex was confirmed from a crystallographically determined molecular structure (Figure 2). The two boryl groups adopt a transoid arrangement with respect to the mean 23-atom corrole plane, with B1 and B2 displaced by 1.268 and 1.291 Å, respectively, to opposite sides of this plane. The dipyrrin-like half of the molecule defined by N1, N2, and C1−C9 tilts toward B1, and the second dipyrrin fragment (N3, N4, C11−C19) tilts toward B2, with the displacement of the β-pyrrolic carbon atoms above or below the mean 23-atom plane ranging from 0.13 to 0.48 Å. Unlike boron dipyrrin complexes, each boron is not coplanar with the dipyrrin moieties but is markedly bent out of the plane, by 0.76


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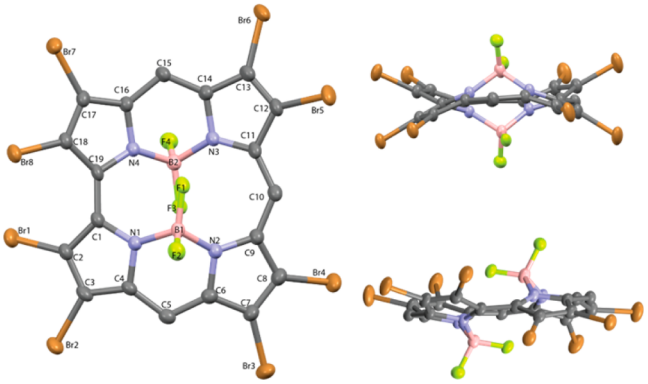
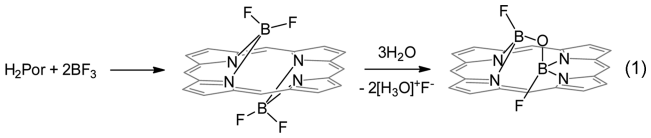


**Figure 2.** Three orthogonal views of the crystal structure of $[(BF_2)_2(Br_8T(4\text{-}F\text{-}P)C)]^-$ anion with thermal ellipsoids calculated at the 50% probability level. The 4-$C_6H_4F$ groups have been removed for clarity. Important bond lengths (Å) and angles (deg): F1–B1 1.359(7), F2–B1 1.406(8), F3–B2 1.374(6), F4–B2 1.403(7), N1–B1 1.563(7), N2–B1 1.564(7), N3–B2 1.538(7), N4–B2 1.562(7), F1–B1–F2 109.2(5), F3–B2–F4 107.7(4), N1–B1–N2 101.9(4), N3–B2–N4 102.6(4).

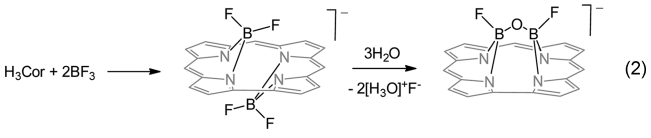
(B1) or 0.79 (B2) Å relative to the plane defined by the 5-atom chelating portion of each dipyrrin group (for example, B1 relative to the N1–C4–C5–C6–N2 plane). The B–N average (av) distances (1.557 Å) are very similar to those of four $[B_2OF_2(Cor)]^-$ structures. However, the B–F av distances (endo, B1–F1 and B2–F3, 1.366 Å; exo, B1–F2 and B2–F4, 1.405 Å) are shorter than the av of those observed in the $[B_2OF_2(Cor)]^-$ anions (1.44 Å).[23] The mean F–B–F and N–B–N angles are close to 108° and 102°, respectively. The related diboron porphyrin complexes $(BF_2)_2(Por)$ were not characterized by X-ray crystallography, but the DFT optimized geometry of $(BF_2)_2$(porphine) was calculated to have very similar B–F (endo, 1.376; exo, 1.396 Å) and B–N (1.580 Å) distances and F–B–F angle (110.3°) to those observed for the $[(BF_2)_2(Br_8T(4\text{-}F\text{-}P)C)]^-$ anion.[7]

The diboryl corrole complex $[(BF_2)_2(Br_8T(4\text{-}F\text{-}P)C)]^-[HNEt{}^iPr_2]^+$ appears to have features very similar to those of the corresponding diboryl porphyrins $(BF_2)_2(Por)$ and represents the first example from this family of complexes to be characterized by a molecular structure determination. We have established that hydrolysis of the diboryl porphyrins $(BF_2)_2(Por)$ leads to the partially hydrolyzed $[B_2OF_2(Por)]$ complexes, as shown in Eq. 1.[7] The question remains as to why




(1)

the diboryl complex could be isolated when the octabromotriarylcorrole $H_3(Br_8T(4\text{-}F\text{-}P)C)$ was used, whereas even under apparently anhydrous conditions the reactions of $BF_3{\cdot}OEt_2$ with the simpler triarylcorroles led to partially hydrolyzed products, indicating that hydrolysis is very facile for these complexes (Eq. 2).




(2)

To test this, the energetics of the hydrolysis reaction for the diboryl complexes of two different corroles, the triarylcorrole T(4-F–P)C and the octabromotriarylcorrole $Br_8T(4\text{-}F\text{-}P)C$, were calculated and are in agreement with the experimental observations (Eq. 3 and Table 1). For Cor = T(4-F–P)C in

**Table 1. ΔG Values (eV) for Eq. 3 for Two Corroles in Different Media**

| | ΔG, eV | ΔG, eV |
|---|---|---|
| medium | Cor = T(4-F–P)C | Cor = $Br_8$T(4-F–P)C |
| gas phase | 0.30 | 0.74 |
| dichloromethane | 0.03 | 0.57 |
| water | 0.05 | 0.48 |

$CH_2Cl_2$ and in water the value of $\Delta G$ is essentially 0.0 eV, meaning the reaction is thermodynamically neutral; experimentally the $B_2F_2O(T(4\text{-}F\text{-}P)C)$ product is isolated. For Cor = $Br_8T(4\text{-}F\text{-}P)C$ in $CH_2Cl_2$ and in water the value of $\Delta G$ is around +0.5 eV, and hydrolysis of the diboryl corrole is not favored, which is in accord with the isolation of $[(BF_2)_2(Br_8T\text{-}(4\text{-}F\text{-}P)C)]^-$ from the reaction of $H_3(Br_8T(4\text{-}F\text{-}P)C)$ in Eq. 2. Both theoretical and experimental results thus suggest that an octabromotriarylcorrole ligand retards the hydrolysis reaction shown in Eq. 3.

$$[(BF_2)_2(Cor)]^- + H_2O \rightarrow [B_2F_2O(Cor)]^- + 2HF$$
$$(Cor = T(4\text{-}F\text{-}P)C,\ Br_8T(4\text{-}F\text{-}P)C) \qquad \text{(Eq. 3)}$$

The above results appear to fit into our growing understanding of corrole stereochemistry. Because of the relative rigidity of the direct pyrrole $C_\alpha$–$C_\alpha$ linkage, corroles are considerably more resistant toward nonplanar distortions than porphyrins.[35] Ruffling is essentially forbidden, and saddling is uncommon for corroles, being largely limited to copper complexes.[36] Thus, even sterically hindered, undecasubstituted corroles typically feature planar cores. The formation of an FBOBF complex would necessarily lead to strong doming of the corrole macrocycle, as observed for the $[B_2OF_2(TPC)]^-$ anion.[23] Strong doming, however, seems inconsistent with the steric requirements of an octabromotriarylcorrole ligand. This would explain the formation of the bis($BF_2$) complex instead with the wave-like $Br_8T(4\text{-}F\text{-}P)C$ ligand.

**Monoboryl Corrole.** The optimized ratio of reactants for the preparation of $[B_2OF_2(Cor)]^-[HNEt(^iPr)_2]^+$ required the free base corrole $H_3Cor$ with $BF_3{\cdot}Et_2O$ and $NEt^iPr_2$ in a 1:12:20 ratio in $CH_2Cl_2$.[23] In the course of studying this reaction, it was observed that, by reducing the number of equivalents of $BF_3{\cdot}Et_2O$ and $NEt(^iPr)_2$ to a ratio of 1:2:4, a different boron corrole product was produced in addition to the anionic $[B_2OF_2(Cor)]^-$. The first indication of the presence of this new species was thin layer chromatography (TLC) on silica of the reaction mixture. A neutral compound was identified as a distinctive bright green spot, which eluted slightly slower ($CH_2Cl_2$/hexane 1:1) than the free base corrole starting material. It was clearly different than the partially hydrolyzed salt $[B_2OF_2(Cor)]^-[HNEt(^iPr)_2]^+$, which remains at the origin under these conditions.

The new product was identified by multinuclear NMR spectroscopy and HRMS as the monoboryl corrole $BF_2(H_2Cor)$ (Cor = trianions of 5,10,15-tris(4-methylphenyl)-corrole (T(4-$CH_3$–P)C), TPC, T(4-$CF_3$–P)C, and TPFPC). The isolated yield of each complex was close to 25%. Unlike the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diboryl corrole complex described above and the diboryl porphyrins, which are all very labile toward hydrolysis, the monoboryl corrole is sufficiently inert to hydrolysis that it can be isolated and purified by column chromatography on silica gel, in air. The BODIPY-type boron dipyrrins are also inert to hydrolysis, suggesting that the steric crowding and close proximity of two $BF_2$ groups evident in the diboryl complexes increases their hydrolytic lability and the formation of products containing B−O−B groups. The presence of only one boryl group in $BF_2(H_2Cor)$ reduces this steric crowding.

We first considered the possibility of monoboryl corroles in a DFT survey of boron corrole complexes.[24] The lower symmetry of the corrole ligand (relative to porphyrin) means that three regioisomers are possible for coordination of a single boryl group to two adjacent pyrroles. In two of these the boron is coordinated in a dipyrrin-like site (two pyrroles connected by a meso carbon), the dipyrrin(A) site adjacent to the bipyrrole and the dipyrrin(B) site opposite the bipyrrole; in the third the boron is in a bipyrrole site (two pyrroles directly connected by a pyrrole $C_\alpha$−$C_\alpha$ bond) (Figure 3). In addition, both in-plane

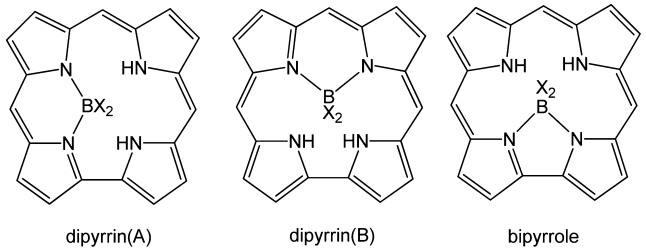


**Figure 3.** Possible regioisomers of monoboryl corrole: dipyrrin(A), dipyrrin(B), and bipyrrole.

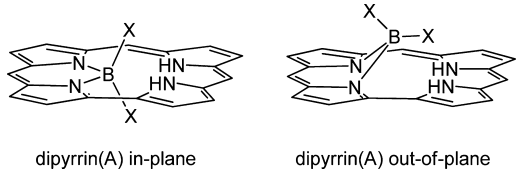


**Figure 4.** Stereoisomers of the dipyrrin(A) monoboryl corrole.

and out-of-plane stereochemistry is possible (shown in Figure 4 for the dipyrrin(A) regioisomer). The electronegative fluorine substituents on boron in the $BF_2(H_2Cor)$ complexes can potentially participate in BF···HN hydrogen bonding to the internal pyrrole NH hydrogens, which might influence the relative stability of the regio- and stereochemical options.[24]

All three regioisomers and both the in-plane and out-of-plane stereoisomers were considered as starting points for the DFT optimizations, giving six possible arrangements. All the out-of-plane isomers were more stable than the in-plane isomers. The lowest energy optimized structure was the less symmetrical out-of-plane dipyrrin(A) regioisomer (Figure 4), which was 7.4 and 10.6 kcal $mol^{-1}$ more stable than the bipyrrole and dipyrrin(B) isomers, respectively. The lowest energy in-plane isomer was dipyrrin(A), 16.6 kcal $mol^{-1}$ above the most stable isomer (OLYP/TZ2P).[24] An analysis of the metrical data calculated for all six possible structures showed that the most stable isomer, the out-of-plane dipyrrin(A), has the least distorted corrole NCC and CCC angles and chelate ring NBN angle. The calculated structure for this isomer also shows BF···HN hydrogen bonding (F···H distance 1.597 Å) between the endo fluorine and a pyrrole NH group (Figure 5a) (BP86-D/TZ2P). The higher energy isomers showed F···H distances too long to support effective hydrogen bonds.[24]

The experimental data for the three $BF_2(H_2Cor)$ complexes is consistent with the dipyrrin(A) regioisomer and out-of-plane boron. This is apparent from the $^1$H NMR spectrum from the lower symmetry of the $\beta$-pyrrolic protons relative to the $[B_2OF_2(Cor)]^-$ anions ($C_s$ symmetry) and the presence of three chemically unique meso aryl groups. The pyrrole N−H protons are observed upfield, close to −0.9 and −1.0 ppm. The $^1$H NMR spectra were fully assigned from the correlation spectroscopy (COSY) and nuclear Overhauser enhancement spectroscopy (NOESY) experiments. The $^{19}$F NMR spectra showed two chemically different fluorine atoms with multiplets at −137 ppm and −157 ppm attributed to F−F and B−F coupling.

The role of the internal BF···HN hydrogen bonding in stabilizing the monoboryl corrole was tested experimentally by using the free base N-21 methyl corrole $H_2$(N-21-$CH_3$)TTC as starting material for the insertion of boron. With one of the N−H protons replaced by a methyl group, formation of a diboron corrole should be blocked as only three pyrrole nitrogens are available. The reaction of $H_2$(N-21-$CH_3$)TTC, $BF_3{\cdot}OEt_2$, and $NEt^iPr_2$ in a 1:8:16 ratio in $CH_2Cl_2$ gave the monoboryl complex $(BF_2)$(H(N-21-$CH_3$)TTC) in 42% yield. A DFT optimization of the structure $(BF_2)$(H(N-21-$CH_3$)Cor) confirmed the isomer equivalent to dipyrrin(A) as the lowest energy structure (Figure 5b), and the experimental data is consistent with this. In the $^1$H NMR spectrum the N−$CH_3$ and NH protons occur at −2.91 and 0.45 ppm, respectively, and the fluorine atoms in the $^{19}$F NMR spectrum occur at −137 and −162 ppm. In the optimized structure of $(BF_2)$(H(N-21-$CH_3$)TTC) the N−$CH_3$ group lies on the opposite face of the corrole from the $BF_2$ group, and BF···HN hydrogen bonding still occurs, with the F···H distance calculated to be 1.590 Å (Figure 5b). The closest crystallography-analyzed analogue of the monoboryl corroles is the CO-bridged corrole (CO)(HTPFPC), which contains a carbonyl group bridged between two adjacent nitrogens in the dipyrrin(A) configuration.[37] Like the $BF_2$ group in the monoboryl corroles, the CO is tilted out of the mean plane of the dipyrrin fragment by 36°, and a short intramolecular CO···HN distance is indicative of hydrogen bonding.

Although the reactions of $BF_3{\cdot}OEt_2$ with free base porphyrins under a wide range of reaction conditions and stoichiometries have been explored in our group, we have never observed evidence for a monoboron porphyrin complex with formulation $(BF_2)$(HPor). Monoboron complexes of other polypyrrole macrocycles are known. The hole size in the subphthalocyanine, subporphyrin, subporphyrazine, and subbenzoporphyrin ligands are optimized for one boron, which coordinates to all three nitrogens.[5] Larger polypyrrole macrocyles such as amethryin and octaphyrin will coordinate one or two borons; these contain uncomplexed N−H bonds, which show long BF···HN hydrogen bonding distances of around 2.0−2.2 Å.[32] However, the two dipyrrin-like boron binding sites in these macrocycles are too far apart to interact via F···H hydrogen bonding. Oxasmaragdyrin is a core-modified expanded porphyrin containing one furan and four pyrrole subunits, which forms a mono-$BF_2$ complex; however, it contains only one dipyrrin-like subunit and hence no site for a second


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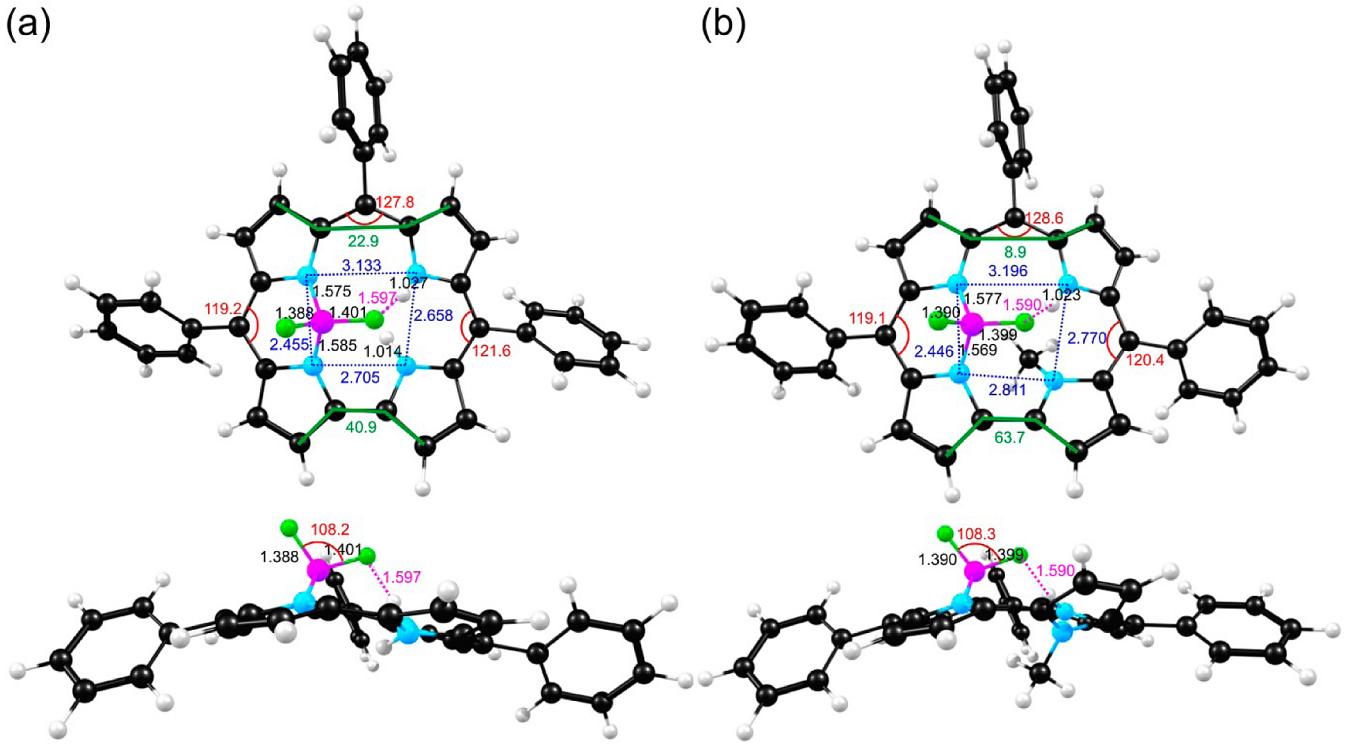


**Figure 5.** Two views each of the optimized (BP86-D/TZ2P) structure of the out-of-plane dipyrrin(A) isomer of (a) $BF_2(H_2TPC)$ and (b) the lowest energy isomer of $(BF_2)(H(N\text{-}21\text{-}CH_3)TPC)$. Bond distances (Å) are shown in black, nonbonded distances in blue, bond angles (deg) in red, dihedral angles in green, and the BF···HN hydrogen bond in magenta. Color code: C black, N blue, H ivory, B pink, F green.

boron.[38] N-confused and N-fused porphyrins bind only one boron as only three of the four nitrogens are available to coordinate to boron.[30] Optimised BP86-D/TZ2P structures calculated for $(BF_2)(H_2TPC)$ and $(BF_2)(HTPP)$ can be compared in Figures 5 and 6. The two uncomplexed pyrroles in the corrole complex $(BF_2)(H_2TPC)$ must twist away from one another to avoid steric hindrance; this results in one of the N−H protons being oriented above the corrole on the same face as the $BF_2$ group and well-positioned to form a strong BF···HN hydrogen bond (1.597 Å) (Figure 5). In the monoboron porphyrin complex $(BF_2)(HTPP)$ the NH proton remains in the porphyrin plane and forms a strong hydrogen bond to the other pyrrole nitrogen (NH···N = 1.898 Å), and the BF···HN bond is not well-oriented and is much longer (2.066 Å) (Figure 6).

## ■ CONCLUSIONS

Two further examples of the anionic diboron corrole $[B_2OF_2(Cor)]^-$ containing 10-(4-methoxyphenyl)-5,15-dimesitylcorrole ($Mes_2$(4-MeOP)C) and the strongly electron-withdrawing 5,10,15-tris(pentafluorophenyl)corrole (TPFPC) have been prepared, suggesting that the hydrolysis reaction that produces these is quite general. Now, however, with a sterically hindered octabromotriarylcorrole ligand, we have obtained the first example of a diboryl corrole complex, $[(BF_2)_2(Br_8T(4\text{-}F\text{-}P)C)]^-$; in other words, the hydrolysis reaction has been prevented altogether. Several examples of monoboryl complexes $BF_2(H_2Cor)$ have been prepared and characterized for which several regio- and stereochemical possibilities can be envisaged; the experimental data is consistent with an out-of-plane dipyrrin(A) ($C_1$) coordination mode. No monoboryl counterpart for these has been isolated in the porphyrin system, and the DFT optimized structural parameters suggest that internal BF···HN hydrogen bonding may be significant in the corrole system. These results continue the trend of opening up new possibilities for the coordination chemistry of the corrole ligand when the small, tetrahedral boron atom is introduced.

## ■ EXPERIMENTAL SECTION

$BF_3{\cdot}Et_2O$ (Aldrich) and *N*,*N*′-diisopropylethyl amine (Aldrich) were distilled prior to use. All other reagents were used as received (Aldrich, Fluka). Silica (DAVISIL LC150A 35−70 μm) was used for flash chromatography. $H_3TPC$, $H_3T(4\text{-}CH_3{-}P)C$, $H_3T(4\text{-}CF_3{-}P)C$, $H_3TPFPC$, $H_3(Mes_2(4\text{-}MeOP)C$, $(N{-}CH_3)H_2T(4\text{-}CH_3{-}P)C$, and $H_3[Br_8T(pFP)C$ were prepared by literature procedures.[8,10,34,39,40]

$^1H$, $^{13}C$, $^{19}F$, $^{11}B$, COSY, and NOESY spectra were recorded on Bruker Avance 300, Bruker DRX 400, or Mercury Plus Varian spectrometers at 298K. Spectra were recorded in $CDCl_3$ and referenced to tetramethylsilane (TMS) or residual solvent peaks. For $^{19}F$ NMR, 2,2,2-trifluoroethanol-$d_3$ ($\delta$ = −77.8) was used as internal reference, or $CFCl_3$ was used as external reference. For $^{11}B$ NMR, $BF_3{\cdot}Et_2O$ was used as external reference. High resolution mass spectra were recorded on a VG 70-SE spectrometer. Fast atom bombardment (FAB)+ spectra used *m*-nitrobenzyl alcohol as the matrix and a xenon atom gun. Accurate mass calculations were referenced to polyethyleneglycol (PEG). Electrospray ionization (ESI) and laser desorption ionization time-of-flight (LDI-TOF) mass spectra were recorded on Bruker microTOF-QII and Waters Micromass MALDI micro MX, respectively, mass spectrometers. Microanalyses were carried out at the Campbell Microanalytical Laboratory, The University of Otago.

**[FBOBF(TPFPC)][HNEt($^i$Pr)$_2$].** $H_3$(TPFP)Cor (20 mg, 0.025 mmol) was dissolved in $CH_2Cl_2$ (10 mL), and $NEt(^iPr)_2$ (0.089 mL, 0.502 mmol, 20 equiv) was added followed by $BF_3{\cdot}OEt_2$ (0.038 mL, 0.301 mmol, 12 equiv). The reaction mixture was stirred for 1 h at room temperature (RT). The solvent was removed under reduced pressure. The solid was washed with hexane and then recrystallized in $CH_2Cl_2$/*n*-hexane, affording a dark green solid. Yield: 10.5 mg, 44%. $^1H$ NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = 1.44 (d, 12H, $NCH(CH_3)_2$),


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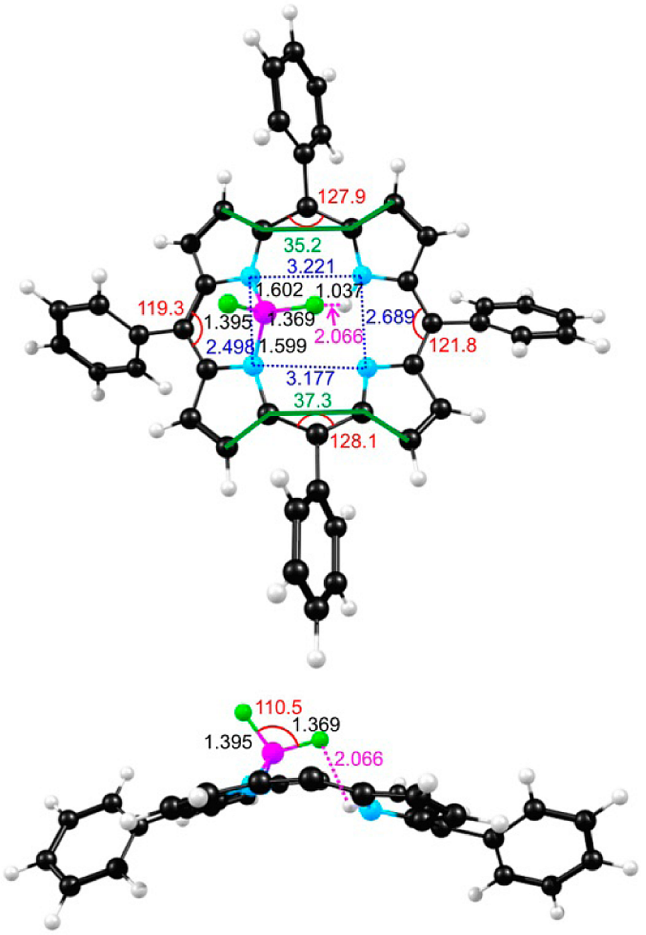


**Figure 6.** Two views of the optimized (BP86-D/TZ2P) structure of the monoboryl porphyrin complex $BF_2$(HTPP). Two phenyl rings were omitted for clarity in the bottom view. Bond distances (Å) are shown in black, nonbonded distances in blue, bond angles (deg) in red, dihedral angles in green, and the BF···HN hydrogen bond in magenta. Color code: C black, N blue, H ivory, B pink, F green.

1.47 (t, 3H, $NCH_2CH_3$), 3.15 (q, 2H, $NCH_2CH_3$), 3.70 (m, 2H, $NCH(CH_3)_2$), 6.60 (br s, 1H, N*H*), 8.26 (d, 2H, CH, $^3J$ = 4.80 Hz), 8.29 (d, 2H, CH, $^3J$ = 4.80 Hz), 8.62 (d, 2H, CH, $^3J$ = 4.80 Hz), 9.34 (d, 2H, CH, $^3J$ = 4.80 Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = −131.6s (br s, 2F, BF), −136.43 (d, 2F, $CF^{ortho}$, $^3J$ = 24.19 Hz), −138.1 (d, 2F, $CF^{ortho}$, $^3J$ = 24.19 Hz), −153.8 (t, 2F, $CF^{para}$, $^3J$ = 20.43 Hz), −153.9 (t, 1F, $CF^{para}$, $^3J$ = 20.43 Hz), −162.04 (t, 2F, $CF^{meta}$, $^3J$ = 24.36 Hz), −162.62 ppm (t, 1F, $CF^{meta}$, $^3J$ = 24.36 Hz). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = −10.7 ppm (br s). $^{13}C$ NMR ($CDCl_3$, 25 °C, 100 MHz): $\delta$ = 10.92 (4C, $NCH(CH_3)_2$), 15.61 (1C, $NCH_2CH_3$), 40.50 (1C, $NCH_2CH_3$), 52.66 (2C, $NCH(CH_3)_2$), 116.92, 117.12, 120.32, 125.65, 128.58, 132.30, 135.25, 135.37, 135.48, 136.06, 137.56, 137.69, 137.79, 137.91, 139.28, 139.60, 143.23, 144.10. UV−vis ($\lambda_{max}$/nm ($\varepsilon$/$M^{-1}$ $mol^{-1}$)): 415 (13.4 × $10^3$), 571, 595. HRMS ($ESI^-$): Calcd for $C_{37}H_8B_2F_{17}N_4O$: 869.0630, found 869.0614.

**[BFOBF(Mes$_2$(4-MeOP)C)][HNEt($^i$Pr)$_2$].** $H_3$(Mes$_2$-*p*-MeOPh)Cor (20 mg, 0.0312 mmol) was dissolved in $CH_2Cl_2$ (10 mL). $NEt(^iPr)_2$ (0.111 mL, 0.625 mmol) was added followed by $BF_3{\cdot}OEt_2$ (0.047 mL, 0.374 mmol). The reaction mixture was stirred for 1 h at RT. The solvent was removed in vacuo, and the crude product was recrystallized in $CH_2Cl_2$/*n*-hexane, yielding a dark solid. Yield: 9.5 mg, 35%.

$^1H$ NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = 0.81 (s, 6H, $CH_3^{para}$), 1.37 (d, 12H, $NCH(CH_3)_2$), 1.39 (t, 3H, $NCH_2CH_3$) 2.52 (s, 6H, $CH_3^{ortho}$), 2.86 (s, 6H, $CH_3^{ortho}$), 3.09 (q, 2H, $NCH_2CH_3$), 3.63 (m, 2H, $NCH(CH_3)_2$), 4.06 (s, 3H, $OCH_3$), 6.47 (br s, 1H, N*H*), 6.96 (s, 2H, $CH^{phenyl}$), 7.17 (d, 2H, $CH^{phenyl}$, $^3J$ = 8.58 Hz), 7.34 (s, 2H, $CH^{phenyl}$), 7.76 (d, 2H, CH, $^3J$ = 4.68 Hz), 7.83 (d, 2H, CH, $^3J$ = 4.68 Hz), 7.91 (d, 2H, $CH^{phenyl}$, $^3J$ = 8.58 Hz), 8.30 (d, 2H, CH, $^3J$ = 4.68 Hz), 8.78 (d, 2H, CH, $^3J$ = 4.68 Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = −128.15 ppm (br s, 2F, BF). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = −8.9 ppm (br s). $^{13}C$ NMR ($CDCl_3$, 25 °C, 100 MHz): $\delta$ = 10.53 (4C, $NCH(CH_3)_2$), 16.83 (1C $NCH_2CH_3$), 20.34 (4C, $CH_3$), 21.12 (2C, $CH_3$), 40.48 (1C, $NCH_2CH_3$), 52.30 (2C, $NCH(CH_3)_2$), 54.45 (1C, $OCH_3$), 110.57, 115.68, 116.04, 116.67, 117.21, 125.55, 126.50, 126.56, 126.66, 133.82, 134.06, 135.20, 135.83, 137.13, 139.09, 140.69, 142.16, 142.93. UV−vis ($\lambda_{max}$/nm ($\varepsilon$/$M^{-1}$ $mol^{-1}$)): 418 (8.8 × $10^3$), 429, 580, 604. HRMS ($ESI^-$): Calcd for $C_{44}H_{37}B_2F_2N_4O_2$: 713.3090, found 713.3065.

**[(BF$_2$)$_2$(Br$_8$T(4-F−P)C)][HNEt$^i$Pr$_2$].** $H_3$($Br_8$T(4-F−P)C) (10 mg, 0.0083 mmol) was dissolved in dry $CH_2Cl_2$ (15 mL), then $BF_3{\cdot}Et_2O$ (12.2 $\mu$L, 0.10 mmol, 12 equiv) and $NEt^iPr_2$ (29 $\mu$L, 0.17 mmol, 20 equiv) were added, and the mixture was stirred under $N_2$ at RT overnight. *n*-Hexane was added, and the resulting white precipitate was removed by filtration. The filtrate was purified by column chromatography ($SiO_2$, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.31 (m, 6H, 5,10,15-*m*-$C_6H_4$), 7.84 (q, $^4J_{FH}$ = 5.5 Hz, $^3J_{HH}$ = 7.2 Hz, 4H, 5,15-*o*-$C_6H_4$), 7.99 (q, $^4J_{FH}$ = 5.5 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, 10-*o*-$C_6H_4$). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 106.0, 107.4, 108.6, 108.8, 111.4, 113.7, 113.9, 114.4, 114.6, 115.6, 118.2, 124.2, 126.9, 130.4, 135.5, 135.6, 138.4, 140.9, 142.2, 142.5, 162.4, 164.9. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): $\delta$ −114.0 (5,15-$C_6H_4F$), −115.2 (10- $C_6H_4F$), −149.7 ($BF_2$), −149.8 ($BF_2$). $^{11}B$ NMR (128 MHz, $CDCl_3$): $\delta$ −1.2. HRMS (ESI): calcd for $C_{37}H_{12}B_2Br_8F_7N_4$: 1306.4545, found 1306.4569. UV−vis ($\lambda_{max}$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$), $CH_2Cl_2$): 453 (17 074), 466 (16 641), 565 (1096), 622 (2007), 672 (4712).

**BF$_2$(H$_2$T(4-CH$_3$−P)C).** $BF_3{\cdot}Et_2O$ (0.0320 mL, 0.260 mmol) was added dropwise via syringe to a solution of $H_3$(T(4-$CH_3$−P)C) (45.0 mg, 0.0792 mmol) in dry $CH_2Cl_2$ (10 mL) under nitrogen. Diisopropylethylamine (0.193 mL, 1.11 mmol) was added dropwise, and the bright green solution was stirred at RT for 1 h. The solvent was removed in vacuo, and then the product was purified by column chromatography ($SiO_2$, $CH_2Cl_2$/*n*-hexane 1:2). Yield: 12.2 mg, 25.0%. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ −0.99 (s, 1H, NH), −0.87 (s, 1H, NH), 2.62 (s, 3H, $C_6H_4CH_3$), 2.67 (s, 3H, $C_6H_4CH_3$), 2.69 (s, 3H, $C_6H_4CH_3$), 7.52−7.54 (d, 2H, $J$ = 8 Hz, *m*-$C_6H_4CH_3$), 7.61 (br s, 2H, *m*-$C_6H_4CH_3$), 7.68−7.70 (d, 2H, *m*-$C_6H_4CH_3$), 8.01−8.03 (d, 2H, $J$ = 7.6 Hz, *o*-$C_6H_4CH_3$), 8.35−8.42 (m, 8H, 2 × *o*-$C_6H_4CH_3$, 4 × $\beta$*H*), 8.53−8.54 (dd, 1H, $J$ = 6.8 Hz, $\beta$*H*), 8.89−8.91 (dd, 1H, $J$ = 6.4 Hz, $\beta$*H*), 8.95−8.96 (d, 1H, $J$ = 4.0 Hz, $\beta$*H*), 9.13−9.14 (d, 1H, $J$ = 4.4 Hz, $\beta$*H*). $^{19}F$ NMR (282.4 MHz, $CDCl_3$): $\delta$ −157.2−(−156.9) (m, 1F, B*F*), −137.4−(−137.2) (m, 1F, B*F*). $^{11}B$ NMR (128 MHz, $CDCl_3$): $\delta$ −8.40. UV−vis ($\lambda_{max}$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$), $CH_2Cl_2$): 426 (196 692), 446 (114 095), 546 (9875), 596 (14 602), 649 (36 892). HRMS (FAB +): Calcd for $C_{40}H_{31}{}^{10}BF_2N_4$: 615.26462, found: 615.26293. Calcd for $C_{40}H_{31}{}^{11}BF_2N_4$: 616.260 98, found: 616.261 82. Elemental analysis: calcd for $C_{40}H_{31}BF_2N_4$: C, 77.93; H, 5.07; N, 9.09. Found: C, 77.80; H, 5.18; N, 8.95%.

**BF$_2$(H$_2$TPC).** Prepared as described for $BF_2$($H_2$T(4-$CH_3$−P)C), using $H_3$(TPC) (31.7 mg, 0.0604 mmol), $BF_3{\cdot}Et_2O$ (0.0149 mL, 0.121 mmol), and $NEt(^iPr)_2$ (0.0420 mL, 0.242 mmol). Yield: 9.5 mg, 26.6%.

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ −1.05 (br s, 1H, N*H*), −0.89 (br s, 1H, N*H*), 7.65−7.84 (m, 6H, *m*-$C_6H_5$/ 3H, *p*-$C_6H_5$), 8.15−8.17 (d, 2H, $J$ = 7.0 Hz, *o*-$C_6H_5$), 8.37−8.38 (m, 2H, *o*-$C_6H_5$), 8.39 (s, 4H, $\beta$*H*), 8.44−8.46 (d, 1H, $J$ = 4.6 Hz, $\beta$*H*), 8.48−8.49 (m, 2H, *o*-$C_6H_5$), 8.54−8.56 (dd, 1H, $J$ = 4.6 Hz, $\beta$*H*), 8.90−8.93 (dd, 1H, $J$ = 4.8 Hz, $\beta$*H*), 8.95−8.97 (dd, 1H, $J$ = 4.4 Hz, $\beta$*H*), 9.15−9.16 (d, 1H, $J$ = 4.5 Hz, $\beta$*H*). $^{19}F$ NMR (282.4 MHz, $CDCl_3$): $\delta$ −157.2−(−156.7)(m, 1F, B*F*), −137.7−(−136.9) (m, 1F, B*F*). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 111.33, 111.79, 119.94, 120.25, 120.58, 120.85, 121.55, 121.69, 123.96, 125.07, 127.43, 127.58, 127.68, 127.74, 128.20, 128.84, 132.57, 133.68, 134.52, 135.73, 135.87, 137.14, 137.26, 137.58, 138.02, 143.16, 144.71, 145.41, 147.11, 155, 157.24. HRMS (FAB+): Calcd for $C_{37}H_{25}{}^{11}BF_2N_4$: 574.214 03, found: 574.214 71. $^{11}B$ NMR (128


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MHz, $CDCl_3$): $\delta$ −8.43. UV−vis ($\lambda_{max}$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$), $CH_2Cl_2$): 428 (15 136), 449 (8699), 554 (922), 598 (1380), 649 (2800).

**$BF_2$(H$_2$T(4-$CF_3$−P)C).** Prepared as described for $BF_2$($H_2$T(4-$CH_3$−P)C), using $H_3$(T(4-$CF_3$−P)C) (40.1 mg, 0.0549 mmol), $BF_3$·$Et_2O$ (0.0135 mL, 0.120 mmol), and NEt($^i$Pr)$_2$ (0.0382 mL, 0.220 mmol). Yield: 9.9 mg, 23.2%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −1.05 (br s, 1H, N*H*), −0.928 (br s, 1H, N*H*), 8.01−8.03 (d, 2H, $J$ = 8.2 Hz, $C_6H_4CF_3$), 8.10 (br s, 2H, $C_6H_4CF_3$), 8.15−8.17 (d, 2H, $J$ = 8.3 Hz, $C_6H_4CF_3$), 8.24−8.26 (d, 2H, $J$ = 7.6 Hz, $C_6H_4CF_3$), 8.34−8.35 (d, 1H, $J$ = 4.6 Hz, *βH*), 8.39−8.40 (d, 1H, $J$ = 4.6 Hz, *βH*), 8.43 (m, 2H, $C_6H_4CF_3$), 8.43−8.44 (d, 1H, $J$ = 4.5 Hz, *βH*), 8.55−8.57 (dd, 1H, $J$ = 2.0 Hz, *βH*), 8.64−8.66 (d, 2H, $J$ = 6.2 Hz, $C_6H_4CF_3$), 8.95−8.96 (dd, 1H, $J$ = 2.0 Hz, *βH*), 9.04−9.05 (dd, 1H, $J$ = 1.4 Hz, *βH*), 9.21−9.22 (d, 1H, $J$ = 4.5 Hz, *βH*). $^{19}$F NMR (282.4 MHz, $CDCl_3$): $\delta$ −157.13−(−156.73) (m, 1F, $BF_2$), −137.27−(−136.88) (m, 1F, $BF_2$), −63.36 (s, 3F, $C_6H_4CF_3$), −63.20 (s, 3F, $C_6H_4CF_3$), −63.11 (s, 3F, $C_6H_4CF_3$). $^{11}$B NMR (128 MHz, $CDCl_3$): $\delta$ −8.735. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 110.33, 110.48, 120.16, 120.50, 120.80, 120.92, 121.86, 121.16, 124.15, 124.31, 124.44, 124.51, 125.05, 125.18, 125.22, 125.25, 125.86, 125.89, 128.92, 129.59, 129.92, 130.25, 132.98, 133.78, 134.11, 135.68, 135.87, 136.47, 138.40, 140.83, 141.49, 144.12, 146.04, 147.13. HRMS (FAB+): Calcd for $C_{40}H_{22}{}^{10}BF_{11}N_4$: 777.179 82, found: 777.182 52. Calcd for $C_{10}H_{22}{}^{11}BF_{11}N_4$: 778.17619, found: 778.17676.

**$BF_2$(H$_2$TPFPC).** $H_3$(TPFP)C (30 mg, 0.038 mmol) was dissolved in dry $CH_2Cl_2$ (10 mL). NEt($^i$Pr)$_2$ (0.027 mL, 0.151 mmol, 4 equiv) was added under nitrogen, followed by $BF_3$·$OEt_2$ (0.009 mL, 0.075 mmol, 2 equiv). The reaction mixture was stirred for 30 min at RT, and the solvent was removed under reduced pressure. The crude product was purified via column chromatography ($SiO_2$, $CH_2Cl_2$/*n*-hexane 1:1). The pure product was eluted in the second band as a blue/green fraction. Yield, 7 mg, 22%. $^1$H NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = −1.07 (br s, 1H, NH), −0.96 (br s, 1H, NH), 8.20 (d, 1H, CH, $^3J$ = 4.73 Hz), 8.34 (d, 1H, CH, $^3J$ = 4.73 Hz), 8.39 (d, 1H, CH, $^3J$ = 4.73 Hz), 8.53 (d, 1H, CH, $^3J$ = 4.73 Hz), 8.58 (d, 1H, CH, $^3J$ = 4.73 Hz), 8.88 (d, 1H, CH, $^3J$ = 4.73 Hz), 9.06 (d, 1H, CH, $^3J$ = 4.73 Hz), 9.26 ppm (d, 1H, CH, $^3J$ = 4.73 Hz). $^{19}$F{$^1$H} NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = −135.42 (d, 1F, $CF^{ortho}$, $^3J$ = 23.26 Hz), −137.07 (d, 1F, $CF^{ortho}$, $^3J$ = 23.26 Hz), −137.22 (d, 1F, BF, $^2J$ = 23.41 Hz), −137.71 (d, 1F, $CF^{ortho}$, $^3J$ = 23.26 Hz), −138.67 (d, 1F, $CF^{ortho}$, $^3J$ = 23.26 Hz), −139.15 (d, 1F, $CF^{ortho}$, $^3J$ = 23.26 Hz), −139.56 (d, 1F, $CF^{ortho}$, $^3J$ = 23.26 Hz), −150.71 (t, 1F, $CF^{para}$, $^3J$ = 23.26 Hz), −151.44 (t, 1F, $CF^{para}$, $^3J$ = 23.26 Hz), −151.71 (t, 1F, $CF^{para}$, $^3J$ = 23.26 Hz), −155.48 (br d, 1F, BF, $^2J$ = 112.41 Hz), −160.64 (t, 1F, $CF^{meta}$, $^3J$ = 23.26 Hz), −160.75 (t, 1F, $CF^{meta}$, $^3J$ = 23.26 Hz), −160.83 (t, 1F, $CF^{meta}$, $^3J$ = 23.26 Hz), −161.19 (t, 1F, $CF^{meta}$, $^3J$ = 23.26 Hz), −161.36 (t, 1F, $CF^{meta}$, $^3J$ = 23.26 Hz), −161.92 ppm (t, 1F, $CF^{meta}$, $^3J$ = 23.26 Hz). $^{11}$B{$^1$H} NMR ($CDCl_3$, 25 °C, 400 MHz): $\delta$ = −8.8 ppm (br s). $^{13}$C NMR ($CDCl_3$, 25 °C, 100 MHz): $\delta$ = 93.28, 93.80, 104.07, 108.97, 118.99, 119.09, 120.39, 120.65, 121.15, 122.41, 123.31, 124.25, 126.49, 127.20, 128.01, 132.29, 132.93, 133.86, 134.50, 134.57, 135.46, 136.84, 137.88, 138.14, 138.58, 142.01, 142.65, 144.78, 145.78, 146.26, 146.69. UV−vis ($\lambda_{max}$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$), $CH_2Cl_2$): 423 (267 789), 555 (18 635), 580 (21 808), 617 (16 267). HRMS (ESI+): Calcd for $C_{37}H_{10}BF_{17}N_4Na$: 876.0626, found 867.0585.

**$BF_2$(HNCH$_3$-T(4-$CH_3$−P)C).** $BF_3$·$Et_2O$ (0.149 mL, 1.21 mmol) was added dropwise via syringe to a solution of $H_2NCH_3$-T(4-$CH_3$−P)C (88.0 mg, 0.151 mmol) in dry $CH_2Cl_2$ (10 mL), under nitrogen. NEt($^i$Pr)$_2$ (0.421 mL, 2.42 mmol) was added dropwise, and the bright green solution was stirred at RT for 1 h. The solvent was removed in vacuo, and then the product was purified by column chromatography ($SiO_2$, $CH_2Cl_2$/*n*-hexane 1:4). Yield: 40 mg, 42.0%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ −2.91 (s, 3H, $NCH_3$), 0.45 (s, 3H, N*H*), 2.58 (s, 3H, $C_6H_4CH_3$), 2.62 (s, 6H, 2 × $C_6H_4CH_3$), 7.19−7.20 (d, 1H, $J$ = 4.16 Hz, *βH*), 7.45−7.47 (d, 2H, $J$ = 7.7 Hz, $C_6H_4CH_3$), 7.49−7.51 (d, 2H, $J$ = 7.6 Hz, $C_6H_4CH_3$), 7.58−7.60 (d, 2H, $J$ = 8.00 Hz, $C_6H_4CH_3$), 7.65−7.66 (d, 1H, $J$ = 4.0 Hz, *βH*), 7.72−7.73 (d, 1H, $J$ = 4.4 Hz, *βH*), 7.82−7.84 (d, 2H, $J$ = 7.6 Hz, $C_6H_4CH_3$), 7.97−7.99 (d, 2H, $J$ = 6.8 Hz, $C_6H_4CH_3$), 8.07−8.09 (d, 1H, $J$ = 4.8 Hz, *βH*), 8.15−8.17 (d, 2H, $J$ = 8.0 Hz, $C_6H_4CH_3$), 8.19−8.21 (m, 2H, 2 × *βH*), 8.53−8.54 (d, 1H, $J$ = 4.8 Hz, *βH*), 8.58−8.59 (d, 1H, $J$ = 4.0 Hz, *βH*). $^{19}$F NMR (376.45 MHz, $CDCl_3$): $\delta$ −162.1−(−161.7) (m, 1F, $BF_2$), −136.1−(−135.7) (m, 1F, $BF_2$).

$^{11}$B NMR (128.38 MHz, $CDCl_3$): $\delta$ −6.97. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.42, 29.40, 106.26, 109.31, 112.56, 116.69, 119.29, 125.05, 125.35, 126.49, 127.59, 127.75, 128.13, 128.41, 129.04, 129.45, 128.89, 130.87, 133.09, 133.65, 134.18, 134.62, 135.43, 135.97, 137.20, 137.95, 138.36, 138.54, 139.34, 139.42, 145.36, 147.24, 148.34. Elemental analysis: calcd for $C_{41}H_{33}BF_2N_4$: C, 78.10; H, 5.28; N, 8.89. Found: C, 77.13−77.18; H, 5.42−5.37; N, 8.74−8.67%. HRMS (FAB+): calcd for $C_{41}H_{33}{}^{11}BF_2N_4$: 630.276 63, found: 630.277 28. UV−vis ($\lambda_{max}$/nm, $CH_2Cl_2$): 416, 449, 592, 626, 674 nm.

**X-ray Structure Determination of [($BF_2$)$_2$($Br_8$T(4-F−P)C)][HNEt$^i$Pr$_2$].** A dichroic red-blue needle of dimensions 0.22 × 0.06 × 0.04 $mm^3$ was mounted in the 100(2) K nitrogen cold stream provided by an Oxford Cryostream low-temperature apparatus on the goniometer head of a Bruker D85 diffractometer equipped with an Apex II CCD detector on Beamline 11.3.1 at the Advanced Light Source in Berkeley, CA. Diffraction data were collected using synchrotron radiation monochromated with silicon(111) to a wavelength of 0.774 90(1) Å. A full sphere of data, to $2\theta$ = 67°, was collected using 0.3° $\omega$ scans. A multiscan absorption correction was applied using the program *SADABS 2008/1*. The data consist of 36 643 reflections collected, of which 15 054 were unique [$R$(int) = 0.044] and 11 378 were observed [$I > 2\sigma(I)$]. The space group was determined, and the structure was solved by intrinsic phasing (*SHELXT*) and refined by full-matrix least-squares on $F^2$ (*SHELXL-97*) using 618 parameters and 130 restraints. The hydrogen atoms on the carbon atoms were generated geometrically and refined as riding atoms with C−H = 0.95−0.99 Å, $U_{iso}$(H) = 1.2$U_{eq}$(C) for aromatic carbon atoms and $U_{iso}$(H) = 1.5$U_{eq}$(C) for $CH_3$ groups. There is one disordered phenyl ring on the corrole and a disordered bis(isopropyl)-ethylamine. Both were treated using a split-site disorder model and restrained. The maximum and minimum peaks in the final difference Fourier map were 4.26 and −2.17e Å$^{-3}$. The largest difference peak is adjacent to a bromine atom position. Crystal data: $C_{37}H_{12}B_2Br_8F_7N_4$·$C_8H_{19}N$·$CH_2Cl_2$, $M_w$ = 1520.57, triclinic, $P\bar{1}$, $a$ = 10.016(2) Å, $b$ = 11.514(2) Å, $c$ = 23.409(5) Å, $\alpha$ = 85.850(3)°, $\beta$ = 79.514(3)°, $\gamma$ = 72.240(3)°, $V$ = 2527.5(9)Å$^3$, $T$ = 100(2) K, $Z$ = 2, $R1$ [$I > 2\sigma(I)$] = 0.064, $wR2$ (all data) = 0.175, GOF (on $F^2$) = 1.04.

## ■ ASSOCIATED CONTENT

### Supporting Information

X-ray crystallographic data (CIF) for [($BF_2$)$_2$($Br_8$T(4-F−P)C)][HNEt$^i$Pr$_2$]. $^1$H NMR spectra for boron corrole complexes. Optimized coordinates for DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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(26) Abbreviations. Cor = trianions of 5,10,15-triphenylcorrole (TPC), 5,10,15-tris(4-methylphenyl)corrole (T(4-$CH_3$-P)C), 5,10,15-tris(4-trifluoromethylphenyl)corrole (T(4-$CF_3$-P)C), 5,10,15-tris(pentafluorophenyl)corrole (TPFPC), 10-(4-methoxyphenyl)-5,15-dimesitylcorrole ($Mes_2$(4-MeOP)C), 2,3,7,8,12,13,17,18-octabromo-5,10,15-tris(4-fluorophenyl)corrole ($Br_8$T(4-F-P)C).
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