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Boron Complexes of Pyrrolyl Ligands

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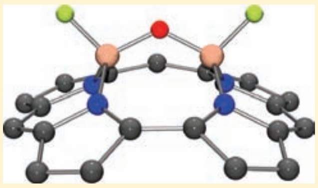
ABSTRACT: Complexes of boron with ligands containing pyrrolyl motifs are surveyed. The ligands range from simple pyrrolyl groups to dipyrroles and linear terpyrroles. Macrocyclic ligands include tripyrroles, which encompass subphthalocyanines, subporphyrins, subtriazaporphyrins, and subtribenzoporphyins, the familiar tetrapyrroles porphyrin and corrole but also N-confused and -fused porphyrins, and expanded porphyrins containing up to eight pyrroles. The role of boron in these compounds depends on the nature of the ligand. Boron acts as a Lewis acid center in simple boron pyrrolyl compounds, and as a structure-directing and templating agent in the cyclic terpyrroles and some of the expanded porphyrins. The difluoroboron dipyrrins are well-known as fluorescent dyes. Boron porphyrins and corroles are unusual in containing two coordinated boron atoms rather than the single coordinated atom usually occurring in these ligands, and the proximity of two boron atoms at close quarters in the ligand cavities gives rise to some unusual reaction and redox chemistry. The survey is organized by the number of pyrrole moieties occurring in the ligand and focuses on new and unique chemistry observed for the complexes.



INTRODUCTION

Our research group has for nearly 2 decades been exploring the chemistry of boron porphyrin and corrole complexes.[1,2] This chemistry has pushed the boundaries of traditional porphyrin and corrole chemistry, where coordination of a single element to the four nitrogen donors is the expected motif. In contrast, the macrocycles will accept two boron atoms, with each boron forming bonds to two adjacent nitrogen atoms. In porphyrins, this lowers the symmetry of the resulting complex from the idealized D_{4h} or C_{4v}, and the stereochemistry of the diboron coordination (in-plane, out-of-plane on the same face of the ligand, out-of-plane on opposite faces, etc.) has resulted in unprecedented coordination modes for the porphyrin ligand. The lower symmetry of the corrole ligand means there are different regiochemical possibilities as well as several stereochemical options for coordination of two boron atoms. Apart from these notable structural features, of more interest is the unusual chemistry that arises from the proximity of two boron atoms at very close quarters within the confines of the macrocyclic ring.

The features of this chemistry will be surveyed in this article. In addition, to put the chemistry into a wider perspective, the chemistry of boron with other pyrrole-based ligands ranging from simple boron pyrrolyl compounds to boron complexes of linear oligopyrroles and both contracted and expanded porphyrinoids will be briefly surveyed. The themes linking these topics will be the coordination preferences expressed by boron and the structural, chemical, and photophysical roles played by boron in these different environments.

Compounds containing boron coordinated to pyrrolyl ligands have significance in quite diverse areas: as fluorescent dyes for biomedical and light-harvesting applications, in unusal macrocycles in which boron has a critical structure-directing/templating role, and in unexpected chemistry arising from coordination of two boron atoms in close proximity within pyrrole-based macrocycles.

MONOPYRROLES: ENHANCED LEWIS ACIDITY AT BORON

Deprotonated pyrrole, essentially $(C_4H_4N)^-$, can behave as the anionic ligand (X^-) in simple BX_3 complexes. Tri-*N*-pyrrolylborane, $B(NC_4H_4)_3$, was first reported in the late 1960s, prepared either from the reaction of $H_3B\cdot NEt_3$ with pyrrole[3] or from BX_3 (X = F, Cl) with KNC_4H_4.[4] The use of pyrrole with $BH_3\cdot THF$ in tetrahydrofuran (THF) was subsequently shown to give improved yields.[5] Details of the B−N interaction in tri-*N*-pyrrolylborane have been studied by multinuclear NMR spectroscopy.[6,7] Like all BX_3 compounds, $B(NC_4H_4)_3$ is Lewis acidic at the electron-deficient boron atom; lone pairs on the *N*-pyrrolyl moieties can overlap with the empty p orbital at boron, resulting in partial B−N π bonding and reducing the Lewis acidity at boron. The pyrrole macrocycle is a Hückel aromatic π system but requires the lone pair of electrons on the pyrrole nitrogen atom to achieve the full complement of six π electrons. The B−N bonding in tri-*N*-pyrrolylborane thus involves a competition for the nitrogen lone pair between the electron-deficient boron atom and the heteroaromatic pyrrolyl group. Spectroscopic, chemical, and structural evidence all argue for reduced B−N (pp) π interactions and enhanced Lewis acidity at boron relative to simple aminoboranes.[5] For example, structural data for $B(NC_4H_4)_3$ and the 2,5-dimethylpyrrolyl derivative $B(2,5\text{-}Me_2NC_4H_2)_3$ have quite different torsion angles between the $B-N_3$ plane and the pyrrolyl ring planes (28° and 45°, respectively) but very similar average B−N bond lengths (1.445 and 1.443, Å, respectively) and ^{11}B NMR chemical shifts (δ 27.5 and 30.5, respectively). The larger torsion angle in the bulkier substituted compound most likely arises from steric effects and would inhibit B−N π bonding. The B−N bond length and ^{11}B NMR chemical shifts would be expected to be

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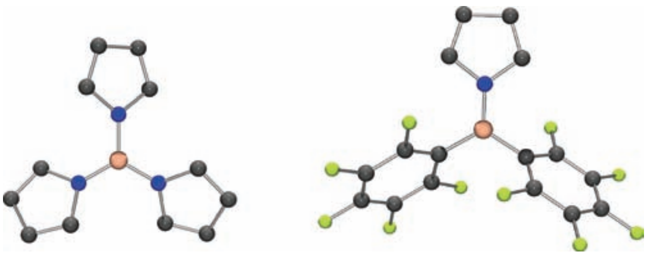


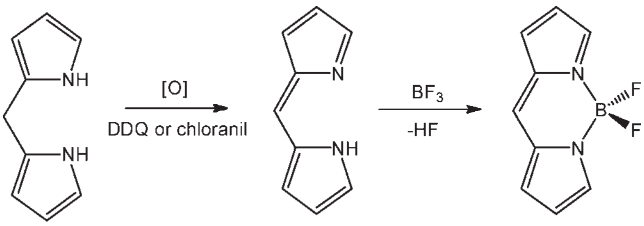
Figure 1. Molecular structures of $B(pyrrole)_3$ (left, torsion and angles between pyrrole and BN_3 plane 28°) and $B(pyrrole)(C_6F_5)_2$ (right, torsion angles between pyrrole and BNC_2 plane 1.6°).[5,9]

sensitive to the degree of π bonding, and the observation of only small differences between the two compounds suggests that this is not a significant component of the B−N bonding.[5]

The obvious comparisons for tripyrrolylboranes are the saturated triaminoborane compounds, for which a higher degree of B−N (pp) π bonding and reduced Lewis acidity at boron are observed. The most closely related of these is tri-*N*-pyrrolidinylborane, $B(NC_4H_8)_3$. Molecular structures of both $B(NC_4H_4)$[5] and $B(NC_4H_8)_3$[8] have been reported, but they show rather small differences in the average B−N bond lengths (1.445 and 1.438 Å, respectively), although the structure of the pyrrolidinyl compound features conformational disorder of the five-membered rings. The ^{11}B NMR shifts (δ 27.5 and 23.75, respectively)[5,8] are also quite similar. A more detailed comparison and analysis of the boron pyrrolyl and boron pyrrolidinyl B−N bonding derive from the spectroscopic data and low-temperature molecular structures determined for $(pyrrolyl)B(C_6F_5)_2$ and $(pyrrolidinyl)B(C_6F_5)_2$.[9,10] The ^{11}B chemical shifts (C_6D_6) for $B(C_6F_5)_3$, $(pyrrolyl)B(C_6F_5)_2$, and $(pyrrolidinyl)B(C_6F_5)_2$ are δ 60, 40.8, and 32.5, respectively, indicating that the pyrrolylborane is markedly more electrophilic than the pyrrolidinylborane.[10] Structural data for $(pyrrolyl)B(C_6F_5)_2$ and $(pyrrolidinyl)B(C_6F_5)_2$ show a longer B−N bond for the former [1.4094(9) Å] than the latter [1.3746(6) Å; Figure 1]. In both compounds, the C_6F_5 aryl rings are twisted 60−70° relative to the BNC_2 plane, while the pyrrolyl and pyrrolidinyl rings are almost coplanar (torsion angles 1.6° and 3.6°), allowing the possibility for B−N π bonding. However, topological analyses of the electron-density distributions are consistent with polarization of the B−N bond, and the electron-withdrawing C_6F_5 aryl groups lead to an increased positive charge at the boron atom in $(pyrrolyl)B(C_6F_5)_2$, whereas in $(pyrrolidinyl)B(C_6F_5)_2$, the shorter B−N bond correlates with a shift in the electron density from nitrogen to boron as a result of B−N π bonding and a decrease in the positive charge at boron.[9]

Other simple pyrrolyl borane derivatives are, for example, hydridoboranes $H_2B(NC_4H_4)$,[11] alkylboranes $Et_2B(NC_4H_4)$,[12] and the neutral and doubly reduced diboranyl compounds $X(H_4C_4N)BB(NC_4H_4)X$ (X = NMe_2, mesityl)[13,14] and $[(Me_2N)(H_4C_4N)BB(NC_4H_4)(NMe_2)][Li(OEt_2)]_2$.[14] The molecular structure of the pyridine (py) adduct $(py)B(NC_4H_4)_3$ has been determined and has a B−N(py) bond of 1.633(2) Å and an average B−N(pyrrolyl) bond length of 1.54 Å.[15] Unfortunately, there are no simple adducts of the form $(py)B(amine)_3$ which with to compare this; however, other py adducts $(py)BX_3$ for X = C_6F_5, F, and Cl have comparable B−N(py) distances of 1.628(2), 1.603(av), and 1.593(1) Å, respectively.[16−18]

Scheme 1. Preparation of BF_2(dipyrrin) Compounds (Substituents Omitted from the Dipyrrin Ligands)



Overall, the structural and spectroscopic data for pyrrolylborane compounds give a picture of a markedly Lewis acidic boron center, and indeed the pyrrolyl substituent has been compared to the very electron-withdrawing C_6F_5 substituent that is featured in the borane $B(C_6F_5)_3$. This has been demonstrated chemically, for example, by the ready abstraction of a methyl group from Cp_3ZrCH_3 by $(pyrrolyl)B(C_6F_5)_2$ to give the ion pair $[Cp_3Zr]^+$-$[B(NC_4H_4)(C_6F_5)_2(CH_3)]^-$.[10] Given the current interest in $B(C_6F_5)_3$, which is one of only a few effective Lewis acids for the heterolytic activation of hydrogen by frustrated Lewis pairs,[19,20] it would be interesting to investigate whether the readily accessible $B(NC_4H_4)_3$ might also be active in such chemistry.

■ DIPYRROLES: FLUORESCENT DYES

Boron Dipyrrin Complexes. Boron complexes of dipyrroles have proven to be extremely significant primarily because of their pronounced photophysical properties, especially their luminescence. The benchmark compounds in this system are boron difluoride dipyrrins, which contain the monoanionic, conjugated dipyrrin ligands (also known as dipyrromethenes). These highly fluorescent compounds are known for their small Stokes shifts, high quantum yields, and sharp excitation and emission peaks. They have been widely used as fluorescent labels in biological systems (in which they are known as BODIPY dyes)[21,22] and as laser dyes (referred to in the literature by their systematic names 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes).[23,24] The boron dipyrrin compounds are generally prepared from the corresponding saturated dipyrrane (dipyrromethane) by oxidation (often with DDQ or chloranil), followed by complexation using $BF_3 \cdot OEt_2$ as the source of boron (Scheme 1).

The ability to prepare derivatives with a wide range of substituents on the pyrrolyl rings and at the central unsaturated carbon atom linking the two rings has resulted in an extensive array of derivatives tailored for particular applications, including incorporation into systems with extended π conjugation, donor/acceptor constructs, and supramolecular arrays. Recent reviews canvass dipyrrin synthetic routes and their complexation properties to a range of elements, including boron,[25,26] the photophysical properties of boron dipyrrin dyes,[27] and their rapidly developing uses in light-harvesting arrays and dye-sensitized solar cells.[28−31]

A characteristic of the (dipyrrin)BF_2 moiety is the planar C_9N_2B core containing tetrahedral boron, with the fluoro substituents lying above and below this plane. Among the extensive range of boron dipyrrin derivatives, almost all substitution occurs at the dipyrrin ligand, although there are some examples containing substituents other than fluoride at boron. There are a few compounds bearing *B*-alkyl groups,[32] and a rather larger number with aryl or alkynyl substituents at

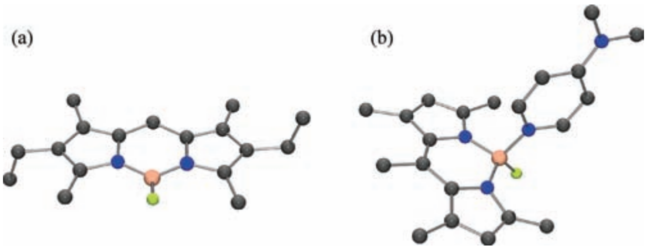


Figure 2. Molecular structures of borenium cations (a) $[(\text{dipyrrin})\text{BF}]^+$ and (b) $[(\text{dipyrrin})\text{BF}(\text{L})]^+$ [L = 4-(dimethylamino)pyridine].[44,45]

boron.[26,29,30] These compounds are generally prepared from the B−F precursors using Grignard or organolithium reagents. A very small number of recent reports considers BODIPY derivatives with alkoxide substituents, $(\text{dipyrrin})\text{B}(\text{OR})_2$. These either are intramolecular complexes with phenoxy groups appended to the dipyrrin[33,34] or are formed by substitution of fluoride using NaOMe/MeOH or AlCl_3/ROH. Interestingly, despite the existence of very strong B−F bonds, all substitution chemistry at boron appears to have been carried out beginning with the $(\text{dipyrrin})\text{BF}_2$ precursors, and the use of other boron halides to access boron dipyrrin compounds appears not to have been investigated.

Boron dipyrrins can be considered, simplistically, to contain an anionic pyrrolyl donor adjacent to a neutral imine-like pyrrole donor, although conjugation through the unsaturated framework means that coordination of dipyrrin to boron is symmetrical. In the search for new fluorescent BODIPY analogues, a number of boron pyrrolyl compounds have been prepared in which an alternative, unsaturated neutral donor is appended to the α position of the pyrrole ring, for example, pyridylpyrrolyl,[35,36] α-ketopyrrolyl,[37−39] and α-iminopyrrolyl[40] ligands. Aza-BODIPY compounds bear nitrogen rather than carbon at the meso position linking the two pyrrole rings.[41−43]

Very recent developments in boron dipyrrin chemistry investigated the formation of borenium ions in two simultaneously published reports.[44,45] Abstraction of the fluoride ion from $(\text{dipyrrin})\text{BF}_2$ is carried out using $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$[44] or $[\text{Me}_3\text{Si}][\text{OSO}_3\text{CF}_3]$,[45] giving the borenium ion as $[(\text{dipyrrin})\text{BF}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or $(\text{dipyrrin})\text{BF}(\text{OSO}_3\text{CF}_3)$. The fluoride in the former complex was substituted using diisobutylaluminum hydride to give the hydridoborenium ion $[(\text{dipyrrin})\text{BH}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, which can coordinate a substituted pyridine L [L = 4-(dimethylamino)pyridine] to give $[(\text{dipyrrin})\text{BH}(\text{L})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. Molecular structures of both $[(\text{dipyrrin})\text{BF}]^+$ and $[(\text{dipyrrin})\text{BH}]^+$ represent unusual examples of three-coordinate borocations (Figure 2a).[44] The triflato ligand in $(\text{dipyrrin})\text{BF}(\text{OSO}_3\text{CF}_3)$ could be displaced by L to give $[(\text{dipyrrin})\text{BF}(\text{L})]^+$. Both of these complexes were structurally characterized; they each contain four-coordinate boron (Figure 2b). The salt $[(\text{dipyrrin})\text{BF}(\text{L})]^+ [\text{OSO}_3\text{CF}_3]^-$ was very sensitive to the presence of fluoride ions, detected by a large increase in the fluorescence upon formation of the difluoride $(\text{dipyrrin})\text{BF}_2$.[45]

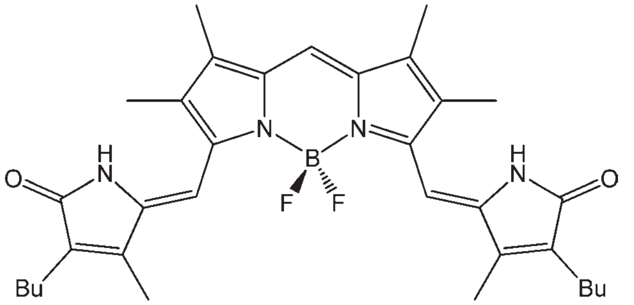


Figure 3. BF_2-tetrapyrrole complex.[48]

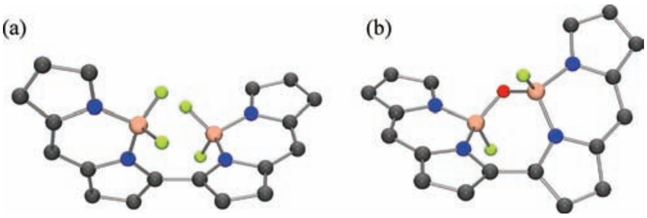


Figure 4. Molecular structures of (a) $(\text{BF}_2)_2$(2,2′-bidipyrrin) and (b) (B_2OF_2)(2,2′-bidipyrrin). The torsion angles between the two dipyrrin planes are 84.35°and 41.61°, respectively (peripheral substituents on the ligands are omitted for clarity).[50,51]

Boron Complexes of Linear Polypyrroles. Linear polypyrroles are intermediate between dipyrrins, which are not capable of forming a macrocyle, and cyclic polypyrroles, of which the smallest contains three pyrrole subunits.[2] The pyrroles may be connected directly by pyrrole $\text{C}_\alpha-\text{C}_\alpha$ bonds, in which case they are subunits of polypyrrole or are connected through unsaturated *meso*-carbon atoms as in the dipyrrins. Linear tetrapyrroles linked through single carbon atoms featured in heme catabolism, for example, biliverdin, and are also important in the synthesis of some cyclic tetrapyrrole ligands.[46]

A small number of studies of boron complexation to linear tetrapyrroles have been reported. Octaethyl-21*H*,24*H*-bilin-1,19-dione comprises four pyrrolic rings linked by unsaturated *meso*-carbon bridges; the central two rings are pyrroles, while the outer two are lactams bearing carbonyl groups α to the pyrrole-NH (Figure 3). This and similar compounds, all closely related to the naturally occurring pigment biliverdin, were treated with $\text{BF}_3\cdot\text{OEt}_2$.[47−49] In all instances, a fluorescent BF_2 complex of the central dipyrrin units formed. In one case, a nonfluorescent complex containing BF_2 coordinated to one pyrrolyl unit and the nitrogen of one of the terminal lactam rings was identified.

More recent reports have investigated boron complexation to 2,2′-bidipyrrins, "bis(BODIPY)", in which two dipyrrin units are directly linked through a $\text{C}_\alpha-\text{C}_\alpha$ bond. These ligands form binuclear bis(BF_2)-2,2′-bidipyrrin complexes in which each boron interacts with one dipyrrin moiety. The complexes are rather crowded, and the two BF_2(dipyrrin) units are twisted about the $\text{C}_\alpha-\text{C}_\alpha$ bond such that they lie almost orthogonal to each other and the boron atoms are tilted out of the dipyrrin planes (Figure 4a).[50,51] Simple BODIPY compounds are quite resistant to hydrolysis, but the bis(BF_2)-2,2′-bidipyrrins undergo hydrolysis to form an F−B−O−B−F unit, in which each boron is coordinated to one dipyrrin unit in a less strained arrangement than that of the precursor (Figure 4b).[50]

■ TRIPYRROLES: BORON AS A TEMPLATING AND STRUCTURE-DIRECTING AGENT

The best known tripyrrole macrocycle is subphthalocyanine (subPc), contracted relative of the phthalocyanine (Pc) rings (Figure 5a). Pc's technically do not contain pyrrole but rather isoindole groups linked through unsaturated nitrogen at the

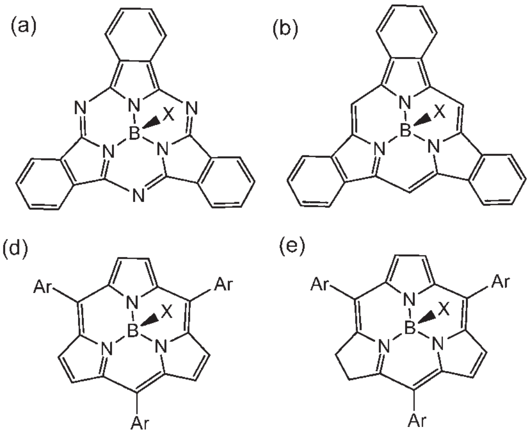


Figure 5. (a) Subphthalocyanine, (b) tribenzosubporphyrin, (c) triazasubporphyrin, (d) subporphyrin, (e) subchlorin, and (f) subbacteriochlorin.

meso position.[52] subPc's were first discovered in 1972 and exist only as their boron complexes,[53] formed in a template condensation reaction of phthalonitrile in the presence of a boron halide, typically BCl_3, BBr_3, or $PhBCl_2$. The subPc ligand is dianionic, and the boron complexes are formulated as (subPc)BX, where X is an anionic ligand (halide, phenyl, etc.). Other macrocycles in the tripyrrole family have been discovered only within the past decade and can each be viewed as contacted examples of their better known tetrapyrrole relatives. They include triazasubporphyrin (also known as subporphyrazine) and tribenzosubporphyrin (Figure 5b,c).[54−56]

The most recent and significant additions to this family are the subporphyrins (Figure 5d), which were first reported in 2007 when two independent reports described the syntheses of triarylsubporphyrins, prepared in low yields by the condensation of tripyrrolylborane or its py adduct with an arylaldehyde.[57−59] Very recently, the first examples of subchlorins and subbacteriochlorins have appeared (Figure 5e,f).[60,61] The tripyrrole family of macrocycles all share in common their formation templated by the presence of boron. The macrocycles exist only as boron complexes, and the free base ligands are unknown because attempts to remove the boron atom do not leave the macrocycles intact. This highlights the role of boron in these compounds as a templating and structure-directing agent.

Subporphyrins, triazasubporphyrins, and tribenzosubporphyrin are formally dianionic, share a 14-electron aromatic core, and comprise bowl-shaped structures in which the four-coordinate boron bears an axial anionic ligand, typically halide, OH, OR, or aryl, in addition to the three pyrrolic nitrogen donors (Figure 6). The depth of the bowl (measured as the distance between the central boron atom and the six β-pyrrole or indole carbon atoms) can vary depending on the class of macrocyle and the substituents on the periphery and on boron. For example, B(OH)(tribenzosubporphyrin) and B(OH)(triazasubporphyrin) have bowl depths of 1.76 and 1.41 Å, respectively.[54−56]

subPc's are well-known, and their unusual second-order nonlinear optical properties have attracted attention in materials chemistry for potential applications as inks, dyes, photosensitizers, and nonplanar aromatic materials.[62,63] For the triazasubporphyrins and tribenzosubporphyrins, apart from the initial reports of their syntheses, there are only a small number of studies on peripheral and axial substitution or theoretical studies.[64−68] In contrast, in the short period since subporphyrin complexes were first reported, there has been a surge of activity focusing on their syntheses including peripheral modification,[15,69−74] electronic properties,[59,75−77] theory,[67,78−80] and incorporation into extended architectures.[69,81−83] The subporphyrins show strong Soret-type absorptions at higher energies, intense green fluorescence, and marked substituent effects.[69]

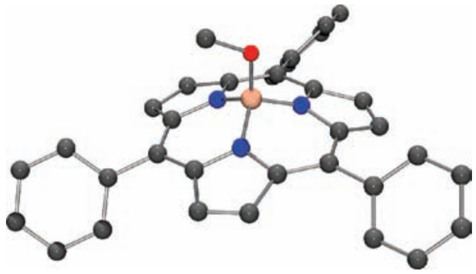
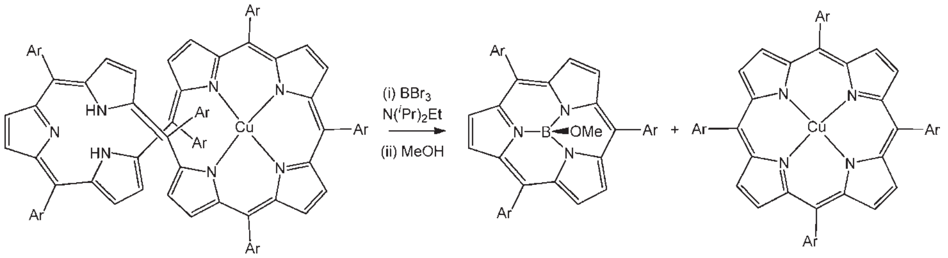


Figure 6. Molecular structure of B(OMe)(triphenylsubporphyrin).[59]

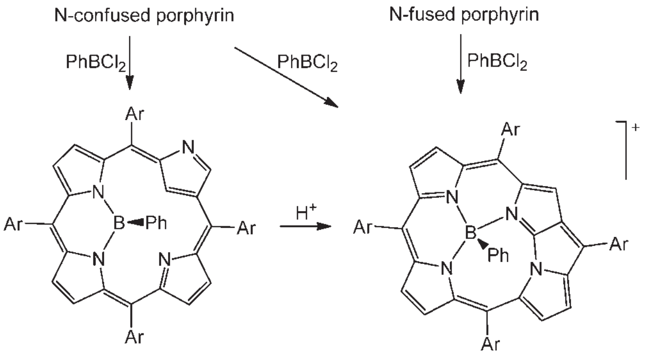
The structure-directing role of boron has been further demonstrated by an unusual and unexpected route for the formation of subporphyrins by extrusion of a boron tripyrrolyl unit from an expanded porphyrin system. [32]Heptaphyrin(1.1.1.1.1.1.1) is a 32-electron expanded porphyrin containing seven pyrroles linked by seven *meso*-carbon atoms bearing pentafluorophenyl groups. It can be metalated by zinc or copper, and the resulting complexes show that the metal binds in a tetrapyrrolic, porphyrin-like site. The ligand appears in a twisted arrangement in which the remaining three pyrroles form a loop reminiscent of a subporphyrin. Further treatment of these complexes with excess BCl_3 or BBr_3 resulted in fragmentation of the heptaphyrin to form the metalloporphyrin, together with the boron subporphyrin, although in measurable yields only for the case of copper (Scheme 2).[69,84] Similar chemistry was observed for the *meso*-CF_3-substituted heptaphyrin, yielding copper porphyrin and boron subporphyrin, with the latter exhibiting the most blue-shifted Soret-like band yet observed for a subporphyrin complex.[85]

Ring contraction processes mediated by boron are also evident in the chemistry of N-confused porphyrins. These porphyrin isomers were first identified in 1994 and contain one inverted pyrrole ring such that the nitrogen atom occurs on the periphery and a CH group in the center of the ring.[86,87] N-fused porphyrin is a formally two-electron-reduced macrocycle in which the ring is contracted through fusing of two adjacent pyrroles.[88,89] Both

Scheme 2. Extrusion of B(OMe)(subporphyrin) and Cu(porphyrin) from Cu[32]heptaphyrin(1.1.1.1.1.1.1) (Ar = C_6F_5)[69]



Scheme 3. Boron N-Confused and -Fused Porphyrin Complexes[90]



rings form complexes with boron when $PhBCl_2$ is used as the boron source. In the N-confused porphyrin complex, boron interacts with only two of the three available nitrogen atoms, while the N-fused porphyrin complex is coordinated to three. The complexes can be prepared directly, or, alternatively, the former can be converted to the latter by protonation (Scheme 3).[90]

■ TETRAPYRROLES: BINUCLEATING LIGANDS AND UNEXPECTED REDOX CHEMISTRY

Porphyrin and Corrole as Binucleating Ligands. The "traditional" conditions for formation of a metalloporphyrin complex are the reaction of a suitable metal salt with the free-base porphyrin, often in the presence of a base to assist with deprotonation of the porphyrin. These are the conditions that we employed to prepare the first examples of boron porphyrins and corroles using boron trihalides. While successful, these reactions featured concomitant partial hydrolysis at boron. Although chromatographic workups were typically employed, even carrying out the reactions under anhydrous conditions and direct isolation of the products without chromatography still resulted in products containing B−O−B linkages. The reactions of $BF_3\cdot OEt_2$ with H_2TPP and H_3TTC both gave products containing an F−B−O−B−F moiety, $B_2OF_2(TTP)$ and $[B_2OF_2(TTC)]^-$, although with different stereochemistry (Figure 7a,b).[91−95] The reaction of $BCl_3\cdot MeCN$ with H_2TTP resulted in hydrolysis of all of the B−Cl bonds to give $B_2O_2(BCl_3)_2(TTP)$, which contains an unusual example of a B_2O_2 four-membered ring within the porphyrin core and additional BCl_3 Lewis acid acceptors coordinated to the bridging oxygen atoms (Figure 7c).[96] Upon chromatography, this complex underwent further reaction to form $B_2O(OH)_2(TTP)$ or, if alcohols were added during the workup, $B_2O(OR)_2(TTP)$.[94] These are structural analogues of $B_2OF_2(TTP)$. Finally, under conditions where only very limited partial hydrolysis was possible, the cationic complex $[B_2O(TTP)]^{2+}$ formed (Figure 7d).[94]

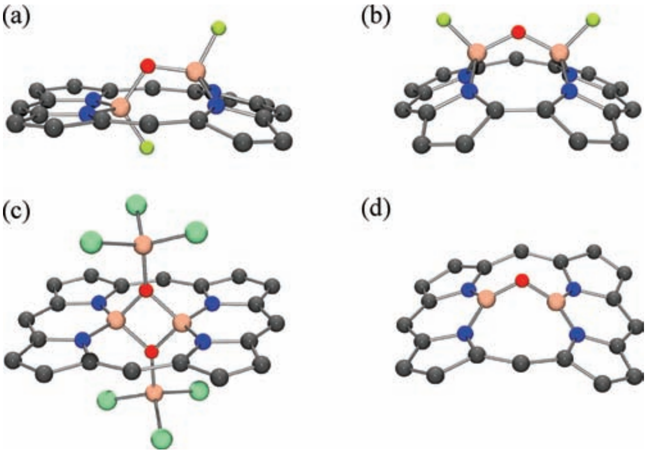


Figure 7. Molecular structures of boron porphyrins and corroles: (a) $B_2OF_2(OEP)$,[93] (b) $[B_2OF_2(TTC)]^-$,[95] (c) $B_2O_2(BCl_3)_2$(T-*p*-ClPP),[96] and (d) $[B_2O$(T-*p*-ClPP)$]^{2+}$[94] (peripheral substituents on the ligands removed for clarity).

These early results were instructive about the possibilities for coordination of boron to a porphyrin or corrole. First, the diboron motif was conserved in all of the examples, despite their quite different structures. In the porphyrin complexes, the stereochemical arrangements of the two boron atoms, in or out of the porphyrin plane, appear to be quite flexible, as is the porphyrin or corrole ligand, which can be planar, stepped, or domed depending on the arrangement of the boron atoms (Figure 7). In addition, the porphyrin undergoes a marked in-plane tetragonal distortion, denoted Δ(N···N), defined by the nonbonded N···N distances parallel to the B···B axis, which are over 1 Å longer than those perpendicular to the B···B axis, a marked departure from the usual square arrangement of the four nitrogen atoms (Figure 8). Tetragonal distortions have been induced by appending sterically bulky groups to the periphery of free-base porphyrins, but the differences in the N···N distances are around 0.5 Å.[97,98] Adjacent nitrogen atoms within the corrole macrocyle can be described as dipyrrin-like (where two pyrrole rings are linked through a *meso*-carbon atom) or bipyrrole-like (where the two pyrrole rings are directly linked by a $C_\alpha−C_\alpha$ bond). Two boron atoms could conceivably occupy bipyrrole/dipyrrin sites, or two dipyrrin sites, and it is this latter arrangement that is observed (Figure 9). Finally, the very closely related porphyrin and corrole complexes $B_2OF_2(TTP)$ and

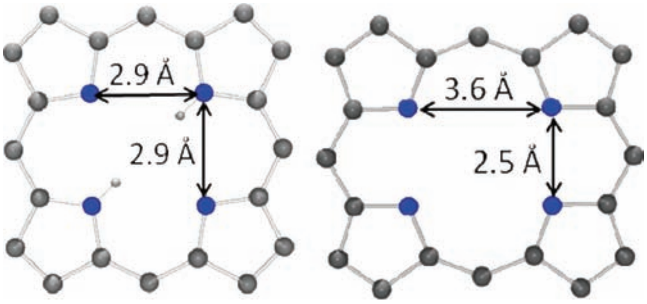


Figure 8. Nonbonded N···N distances in free-base porphyrin (left) and $B_2O_2(BCl_3)_2(H_2T$-*p*-ClPP) (right; only the porphyrin ligand is shown).[96]

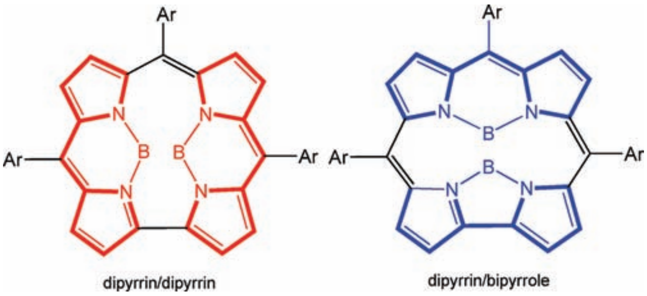


Figure 9. Dipyrrin/dipyrrin (left) and dipyrrin/bipyrrole (right) regiosiomers.

$[B_2OF_2(TTC)]^-$ have quite different stereochemistries, transoid for the porphyrin and cisoid for the corrole (Figure 7a,b). Density functional theory (DFT) geometry optimizations indicate that for the porphyrin complex the transoid geometry is 16 kcal mol^{-1} more stable than the cisoid, while for the corrole complex, the reverse is true, with the cisoid geometry being 19.5 kcal mol^{-1} more stable.[92,94,95]

Boron complexes that do not contain B−O−B links could be prepared by utilizing lithiated porphyrins $Li_2(TTP)$ prepared under strictly anhydrous conditions,[99,100] allowing us to prepare the diborylporphyrins $(BF_2)_2(TTP)$ and $(BCl_2)_2(TTP)$ beginning with BF_3 and BCl_3, respectively.[101,102] DFT optimizations of both diboryl structures were consistent with their spectroscopic data and showed that the most likely geometries for the complexes are transoid arrangements with the two boron atoms displaced to opposite sides of the porphyrin plane.[102] These compounds were extremely hydrolytically sensitive and, upon exposure to even trace moisture, formed products containing B−O−B groups, $B_2OF_2(TTP)$ or $B_2O_2(BCl_3)_2(TTP)$.

The very facile hydrolysis observed in formation of the B−O−B porphyrins appears to be a phenomenon connected with the close proximity of the two boron atoms. The BODIPY complexes BF_2(dipyrrin) are quite inert to hydrolysis, and forcing conditions are required to break the strong B−F bonds to form boron-substituted BODIPY analogues.[103] Even within expanded porphyrins, for example, the hexapyrrole $(BF_2)_2$(amethyrin) complex, exposure to a 10% aqueous NaOH solution at reflux in CH_2Cl_2 did not induce hydrolysis of the B−F bond.[93] This difference in reactivity can be justified by investigating the steric demands on the porphyrin in the diboryl complexes $(BX_2)_2(TTP)$, for which the in-plane Δ(N···N) distortion is greater than 1.25 Å and there is also a significant out-of-plane distortion. Formation of the B−O−B link relaxes both distortions somewhat [for $B_2OF_2(TTP)$ Δ(N···N) = 1.06 Å] and presumably reduces the steric strain, providing a driving force for hydrolysis of even the very strong B−F bonds.

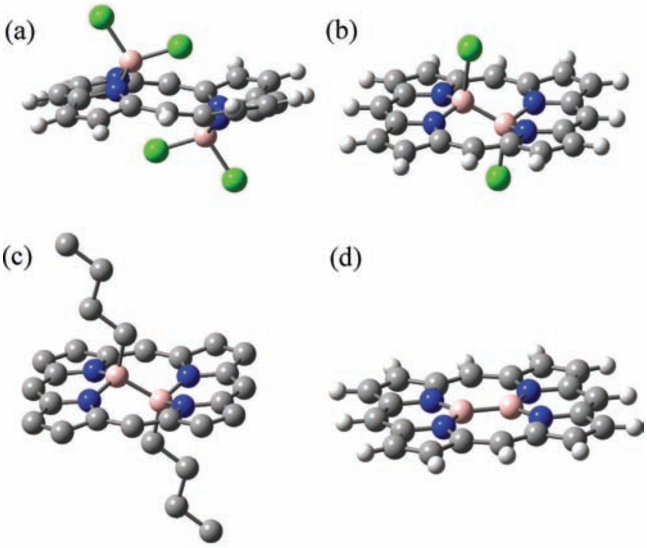


Figure 10. Optimized structures of (a) $(BCl_2)_2$(porphine),[102] (b) $(BCl)_2$(porphine),[102] (c) $(B^nBu)_2$(porphine),[2] and (d) B_2(porphine)[102] [B3LYP/6-311G(d,p)]. Reproduced with permission from ref102. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission from ref 2. Copyright 2008 Royal Society of Chemistry.

Redox Chemistry: Diboranylporphyrin and Isophlorin. The pronounced tetragonal elongation of the porphyrin ligand in the diboryl complexes $(BX_2)_2(TTP)$ suggested that a B−B-bonded moiety should be able to be comfortably accommodated in the porphyrin plane (Figure 10a). The diborane B_2Cl_4 as the boron source[104,105] with $Li_2(TTP)$ as the porphyrin precursor gave the diboranylporphyrin $(BCl)_2(TTP)$, and halide exchange with SbF_3 gave the analogue $(BF)_2(TTP)$ (Figure 10b).[101] The reaction of $(BCl)_2(TTP)$ with ^{n}BuLi gave the butyl-substituted product $(B^nBu)_2(TTP)$, which was characterized by X-ray crystallography (Figure 10c), confirming the transoid arrangement and the presence of a B−B single bond [1.769(7) Å], in good agreement with the B−B bond lengths calculated from the DFT optimizations for $(BX)_2$(Por) (1.737 and 1.790 Å for X = Cl and ^{n}Bu)[101,102] and typical of B−B single-bond distances.[106] A further derivative of $(BCl)_2(TTP)$ was produced by halide abstraction using the bulky anion $Na[B(Ar_F)_4]$, forming the diboranyl dication $[B_2(TTP)]^{2+}$ as the $[B(Ar_F)_4]^-$ salt [Ar_F = 3,5-$C_6H_3(CF_3)_2$].[102]

The diboranyl complexes $(BCl)_2(TTP)$ and $[B_2(TTP)]^{2+}$ can be formally conceived of as the products of two-electron reduction of the diboryl complex $(BCl_2)_2(TTP)$, and indeed this chemistry was realized experimentally using a $NaK_{2.8}$ alloy to reduce the diboryl complex to the diboranyl complex. Further reduction of $[B_2(TTP)]^{2+}$ to the neutral $B_2(TTP)$ could be effected by magnesium anthracenide (Figure 10d). The two diboranyls $[B_2(TTP)]^{2+}$ and $B_2(TTP)$ are different only by two electrons, but the key question is the location of the two electrons in the reduced product, potentially either on the B_2 moiety (formally reduced to B^I) or on the redox-active porphyrin ligand. Their structures (as determined by DFT optimizations of the unsubstituted porphine analogues) and spectroscopic signatures are quite different. The optimized structures of both complexes show trigonal-planar boron atoms residing within the porphyrin plane but with different symmetries, D_{2h} for $[B_2(Por)]^{2+}$ and C_{2h} for $B_2(Por)$. The B−B bond lengths are very similar [1.737, 1.70, and 1.73 Å for $(BCl)_2(Por)$, $[B_2(Por)]^{2+}$, and $B_2(Por)$, respectively], but the lower symmetry (C_{2h}) $B_2(Por)$ complex shows marked alternation of the B−N and B−B bond lengths (Figure 10d). Even more striking differences are observed in the ^1H NMR data. For $[B_2(TTP)]^{2+}$, the H_β protons on the pyrrole rings resonate at δ 9.16, a typical value not just for boron porphyrins but, in fact, for all diamagnetic tetraarylporphyrin complexes. In contrast, H_β for $B_2(TTP)$ occur at δ 1.05 and 0.51, exhibiting marked paratropic shifts, and the other ligand resonances for $B_2(TTP)$ also show significantly different chemical shifts relative to $[B_2(TTP)]^{2+}$. These data indicate that some chemical phenomenon is disrupting the normal 18π-electron aromatic character associated with diamagnetic porphyrin complexes.

The question of aromaticity in porphyrinoid systems is currently a hot topic that is being investigated on several fronts. Expanded porphyrins (containing more than four pyrrole subunits) have allowed both Hückel (two-sided) and Möbius (twisted, single-sided) aromatic and antiaromatic systems to be explored.[107,108] For 18π-electron porphyrin (Por^{2-}) systems,[108] either oxidation to the neutral 16π-electron macrocycle (Por)[109,110] or reduction to the 20π-electron isophlorin (Por^{4-})[111−114] is a departure from Hückel aromaticity, and a number of such examples have been reported in recent years. The porphyrin examples are particularly prevalent for main-group elements. In group 14, the silicon complex $Si(TPP)(THF)_2$ does not contain silicon(II) within a TPP^{2-} ligand, as might be deduced from the formula, but is, in fact, a silicon(IV) compound containing a reduced ligand in which the porphyrin has been reduced to TPP^{4-}.[111] Similar phenomena are observed for the heavier group 14 congeners. Ge(TPP) is an aromatic germanium(II) compound, but its py adduct $Ge(TPP)(py)_2$ contains germanium(IV) and TPP^{4-}, and the same is true of the Pc compounds $SiPc(Py)_2$ and $GePc(Py)_2$, which contain silicon(IV) or germanium(IV) and Pc^{4-}.[112−114] The compounds containing the 20π-electron-reduced macrocycles show strong paratropic ring currents and alternating short and long C−C bonds in the structurally characterized complexes $Si(TPP)(THF)_2$ and $Ge(TPP)(py)_2$,[111,113] all evidence consistent with antiaromaticity in the reduced isophlorin ligand. A transition-metal example of this phenomenon is provided by the reduction of Zn(TPP) to $[Zn(TPP)]^{2-}$, in which porphyrin is reduced and the complex shows similar paratropic shifts in the ^1H NMR spectrum.[115] The free-base isophlorin H_4L [L^{4-} = reduced form of β-tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin] along with its *N*-methyl derivatives H_2Me_2L and Me_4L have also been recently reported. The crystal structure of H_4L shows clear evidence of C−C bond-length alternation.[116]

Against this background of paratropic shifts observed for porphyrins reduced to the 4-isophlorin oxidation state, it is apparent that the reduced diboron porphyrin $B_2(TTP)$ provides a further example of this phenomenon. The chemical shifts of the H_β protons (δ 1.05 and 0.51) are directly comparable to those observed for $Si(TPP)(py)_2$, $Ge(TPP)(py)_2$, and $[Zn(TTP)]^{2-}$ (δ 1.29, 0.59, and −0.9, respectively). These data, together with the bond alternation apparent in the DFT-optimized structure, indicate that the diboron porphyrin is a further example of a reduced isophlorin compound (Figure 11).[102] The chemistry of the diboryl and diboranylporphyrins is summarized in Scheme 4.

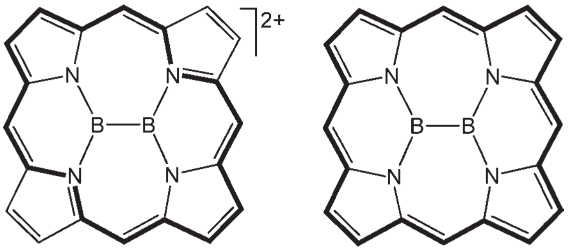
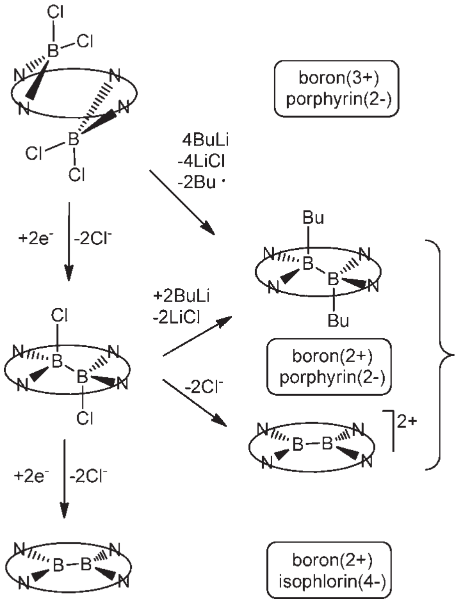


Figure 11. Diboranylporphyrin, 18π electrons (left); diboranyl isophlorin, 18π electrons (right). Conjugation pathways are shown in bold.

Scheme 4. Chemistry of Diboryl- and Diboranylporphyrins

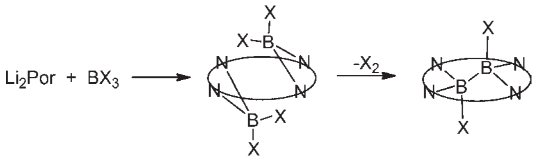


Redox Chemistry: Spontaneous Reductive Coupling. The reduction of the diboryl $(BCl_2)_2(TTP)$ to the diboranyl $(BCl)_2(TTP)$, followed by chloride substitution using ^nBuLi to form $(B^nBu)_2(TTP)$, was described above. Unexpectedly, the reaction of the diboryl $(BCl_2)_2(TTP)$ with ^nBuLi resulted in both reduction and substitution in a single step, giving the same product, $(B^nBu)_2(TTP)$.[101,102] Further analysis of this spontaneous reductive coupling reaction showed it to be a feature of diboron porphyrin chemistry that arises from the close proximity of two boron atoms confined within the porphyrin core. The reaction of BF_3 or BCl_3 with Li_2TTP gave the diboryl complexes $(BF_2)_2(TTP)$ or $(BCl_2)_2(TTP)$, respectively, as described above. However, in extending this chemistry to the heavier boron halides, further unexpected spontaneous reductive coupling reactions were observed. The reaction of Li_2TTP with BBr_3 gave a mixture of the diboryl and diboranyl products, while its reaction with BI_3 gave only the reduced diboranyl product $(BI)_2(TTP)$ (Scheme 5).[102]

An exploration of the driving force for these unusual reactions was carried out using DFT to calculate the optimized geometries of reactants, intermediates, and products and the thermochemistry.[102] The optimized geometries of the series of diboryl complexes (or presumed diboryl intermediate in the iodide case)

$(BX_2)_2(Por)$ showed that for each of them the porphyrin ligand was severely distorted through both out-of-plane and in-plane tetragonal elongation and that these distortions did not increase markedly as the halide was varied from F to I. However, increasing distortion was apparent in the boryl groups, with a narrowing of the X−B−X angle and a lengthening of the outer B−X bond apparent down the series F, Cl, Br, and I. Our hypothesis was that the driving force for the reductive coupling derived from the sterically crowded environment arising from the two boron atoms coordinated within the tight confines of the macrocyle and the presence of bromide, iodide, or butyl groups able to reductively eliminate. This was tested by carrying out thermochemical calculations on the reductive coupling reactions for both the diborylporphyrins and the corresponding boryl dipyrrin complexes. In the dipyrrin analogues, the coupling reaction is chemically identical, but the two dipyrrin units (each essentially "half" a porphyrin) are not constrained with a macrocycle and thus the steric strain is relieved. The results are shown graphically in Figure 12a,b and demonstrate that, for the diborylporphyrin, coupling reactions Δ*H* and Δ*G* are positive for F and Cl but negative for Br and I, indicating that the reactions are exothermic and spontaneous for the latter pair but not the former pair, just as observed experimentally. For all of the boryldipyrrin reactions, however, Δ*H* and Δ*G* are positive for all four halides, indicating that the reaction is not favored for any member of the series and reinforcing the hypothesis that the sterically strained environment within the diborylporphyrins drives the spontaneous coupling reactions.[102]

Scheme 5. Reactions of Boron Halides (X = F, Cl, Br, I) with Li_2Por^a



[a] $(BX_2)_2(TTP)$ is the product for X = F and Cl, while $(BX)_2(TTP)$ only occurs for X = Br and I.

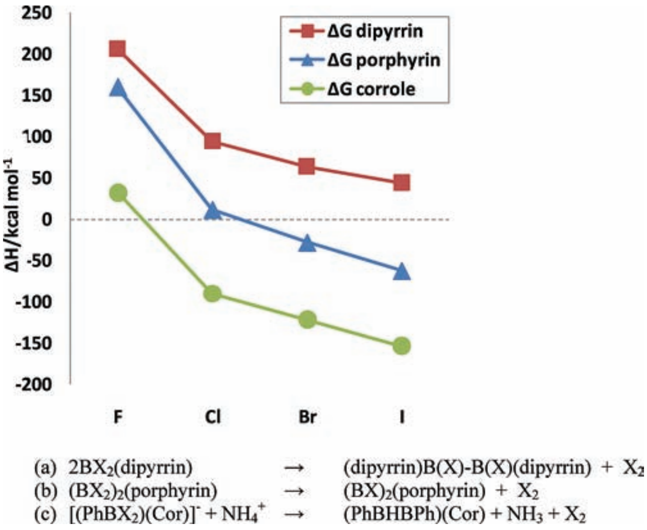
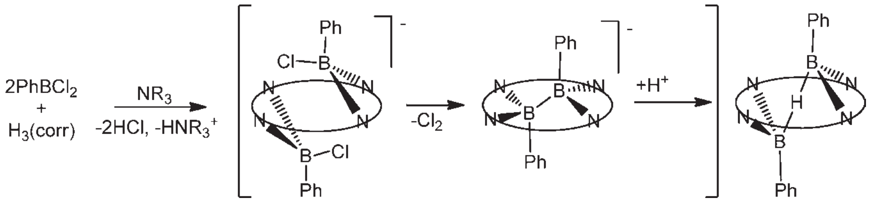


Figure 12. Plot of Δ*G*/kcal mol^{-1} calculated (DFT) for reductive coupling reactions of (a) dipyrrin, (b) porphyrin, and (c) corrole for X = F, Cl, Br, I.[102,117]

One other boron halide that was investigated as the boron source for porphyrin and corrole complexes was $PhBCl_2$. In its reaction with H_2TTP, the result was a partially hydrolyzed complex, PhBOB(OH)(TTP), which has the same asymmetric XBOBX′ arrangement as the benchmark fluoroboron complex $B_2OF_2(TTP)$.[94] To our surprise, the reaction of the same reagent $PhBCl_2$ with H_3TTC and N^iPr_2Et gave a different and unexpected product, $Ph_2B_2H(TTC)$, which contains a Ph−B−H−B−Ph moiety in which the two boron atoms are linked through a hydride bridge.[117] The presence of the hydride was unequivocally established through its location and refinement in two molecular structures and observation of a resonance at δ −6.3 in the ^1H NMR spectrum. Formation of this product from $PhBCl_2$ and H_3TTC requires a formal 2-electron reduction and we proposed that this was a further example of spontaneous reductive coupling, proceeding according to the sequence shown in Scheme 6. The reductive coupling step inside the brackets has precedence from the boron porphyrin chemistry, and the final protonation step has models in the chemistry of the polyhedral boranes. The elimination of chlorine shown in the coupling step is, of course, chemically unlikely and is required to satisfy the stoichiometry. The reaction may, in fact, proceed via chlorine atom abstraction by solvent.[117]

The plausibility of this reaction was tested by DFT thermochemical calculations for the reaction in Figure 12c, and these gave positive values of Δ*H* and Δ*G* for X = F but negative values for X = Cl, Br, and I.[117] In the porphyrin system, coupling was not favored for X = Cl, but in corrole chemistry, we proposed that the smaller corrole macrocycle combined with the bulkier phenyl substituents might increase the steric strain such that coupling of the chloroboryl becomes favorable. To test these results experimentally, the reaction of H_3TTC with $PhBBr_2$ should give the same product as $PhBCl_2$ but the reaction with $PhBF_2$ should give a different product that does not require chemical reduction in order to form. This is exactly what was observed, with $PhBBr_2$ giving $Ph_2B_2H(TTC)$ and $PhBF_2$ producing (PhBF)(BPh)-(TPC), a new structural type containing one four-coordinate boron and one three-coordinate boron. Two distinct sets of phenyl resonances are observed in the ^1H NMR spectrum and two quite different resonances (δ +29.4 and −5.9) in the ^{11}B NMR spectrum.[117]

Scheme 6. Proposed Route for Formation of $Ph_2B_2H(TTC)$ via a Reductive Coupling Reaction[117]



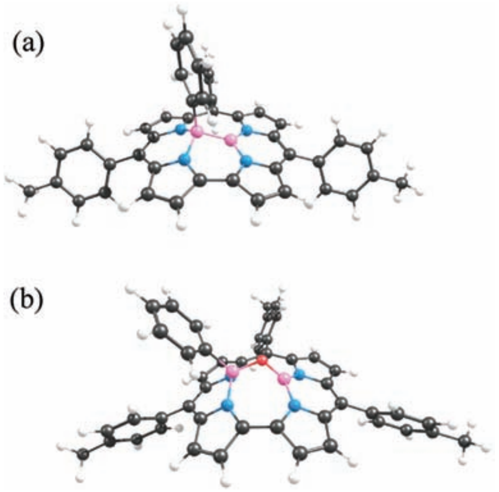


Figure 13. Optimized geometries (DZP/BP86-D) of (a) (PhBB)(TTC) and (b) (PhBOB)(TTC).[121]

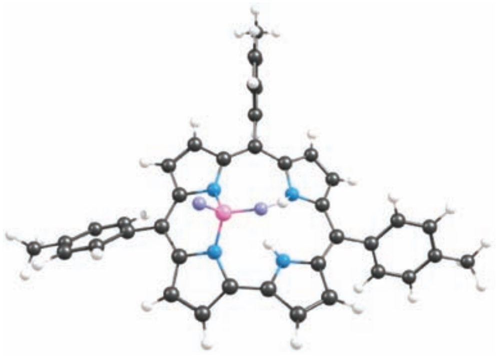


Figure 14. Optimised geometry (DZP/BP86-D) of $(BF_2)(H_2TTC)$.[119,121]

The bridging hydride complex $Ph_2B_2H(TTC)$ undergoes further redox chemistry, and mild solid-state pyrolysis (130 °C, 6 h) results in elimination of benzene and formation of PhBB(TTC), which, on the basis of analytical and NMR spectroscopic results confirmed by a DFT optimization, contains a PhBB group coordinated to the corrole (Figure 13a). The ^1H NMR spectrum contains just one set of phenyl resonances, while two resonances (δ +29.96 and −21.65) appear in the ^{11}B NMR spectrum.[118] Preliminary results indicate that both $Ph_2B_2H(TTC)$ and PhBB(TTC) undergo hydrolysis and/or oxidation to form a further new type of corrole complex, PhBOB(TTC) (Figure 13b), containing three- and four-coordinate boron linked through a B−O−B bridge (^{11}B NMR: δ +30 and −7). The spectroscopic data and DFT optimizations are consistent with cisoid stereochemistry for both PhBB(TTC) and PhBOB(TTC).[118−120]

Monoboron Corrole Complexes. A distinguishing feature of the boron porphyrin and corrole chemistry is the behavior of the macrocycles as binucleating ligands, a marked departure from their usual chemistry. This is despite the severe steric crowding manifest in some of the complexes by the pronounced elongation of the porphyrin and the enhanced reactivity toward reductive coupling and hydrolysis reactions. We never observed evidence for monoboron porphyrin complexes but we have been successful in isolating monoboron corrole complexes bearing a single boryl group and two internal corrole hydrogen atoms. $BF_2(H_2TTC)$ is prepared under the same conditions as the diboron complex $[B_2OF_2(TTC)]^-$ but using a reduced amount of $BF_3 \cdot OEt_2$.[118] The two internal NH protons occur at δ −0.99 and −0.87 in the ^1H NMR spectrum, which also shows that all three peripheral tolyl groups are chemically different indicating that the BF_2 group coordinates in the lower symmetry dipyrrin site. The regiochemistry, out-of-plane stereochemistry and the presence of one B−F$\cdots$H−N(corrole) hydrogen bond were confirmed by DFT optimization (Figure 14).[95] A monoboron corrole was the only possible product formed when the N-methyl corrole H_2(N-21-MeTTC) was used and the product has very similar characteristics to $BF_2(H_2TTC)$.[95,118] Further examples of monoboron corroles could be prepared by using $PhBCl_2$ and $PhBF_2$ as reagents with H_3TTC, giving $PhB(OH)(H_2TTC)$ and $PhBF(H_2TTC)$, respectively. All complexes show evidence for internal hydrogen bonding.[118−120] The combination of the single dipyrrin-like boron coordination and the internal NH hydrogens offer intriguing possibilities for sensing applications.

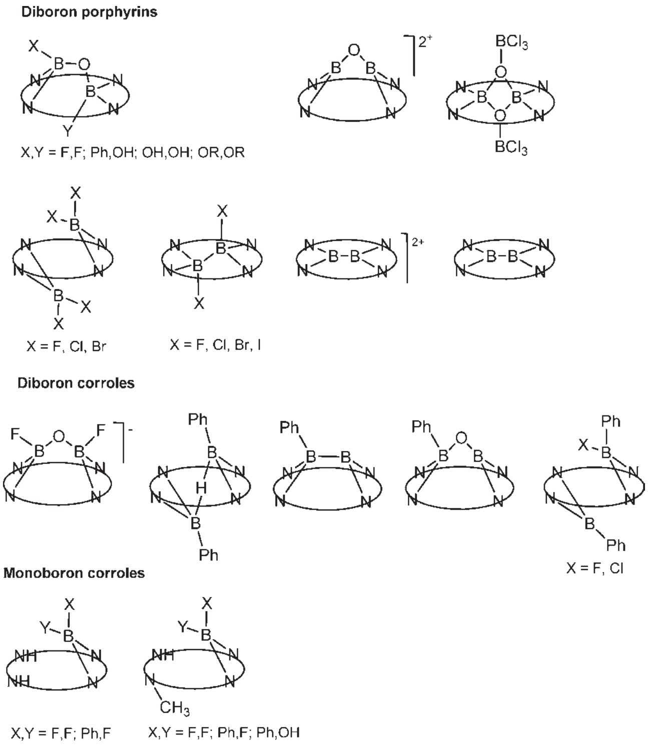


Figure 15. Summary of the structural types observed for boron porphyrins and corroles.

Boron Porphyrin and Corrole Structural Types. In structural and coordination chemistry terms, one of the surprises arising from the chemistry of porphyrin and corrole ligands with boron is the rich array of structural types observed for ligands more commonly associated with a single coordinated atom in a square-planar N_4 array. The structural types observed for the boron porphyrins and corroles are shown in Figure 15. In the diboron corroles, the two boron atoms are invariably located in two opposite dipyrrin sites; in monoboron corroles, the boron is located in the lower-symmetry dipyrrin site adjacent to the bipyrrole moiety. Porphyrin and corrole have a close relationship; they differ in the lower symmetry and smaller ring size for corrole and the 3− (corrole) versus 2− (porphyrin) formal charge on the deprotonated ligand. Despite the similarities, there

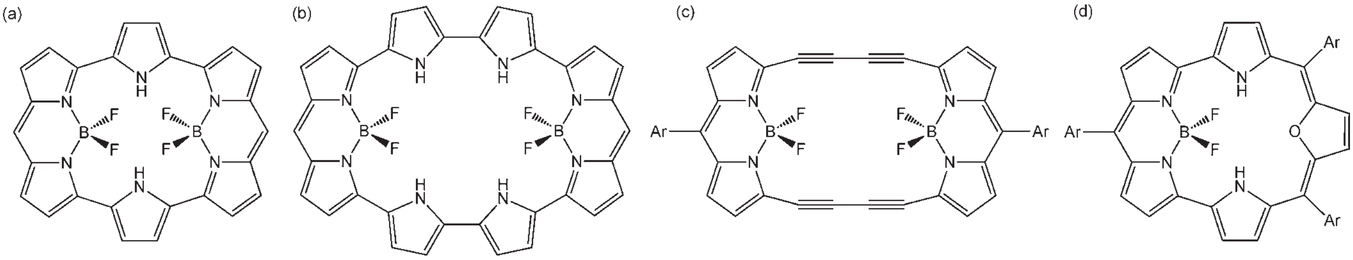
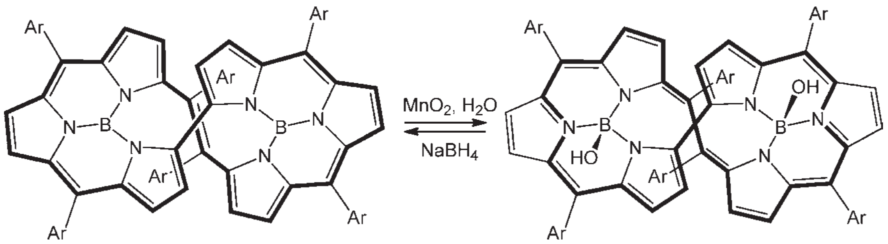


Figure 16. (a) $(BF_2)_2$(amethyrin);[93] (b) $(BF_2)_2$([32]octaphyrin);[93] (c) BF_2(dipyrrin) units linked by conjugated alkynyl groups;[127] (d) (BF_2)-oxasmaragdyrin.[128]

Scheme 7. Redox Interconversion in Diboron Hexaphyrin(2.1.1.0.1.1) between the 30π-Electron, Aromatic Complex Containing Trigonal Boron (Left) and the 28π-Electron, Antiaromatic Complex Containing Tetrahedral Boron (Right)[130]



is very little overlap in the structural types of complexes observed for the two ligand classes. All of these structural types have been demonstrated to be energy minima through comparison of the various regio- and stereochemical possibilities by DFT. Several have been confirmed by X-ray crystallography, and in each case, the DFT-optimized structure (derived without using the molecular structure coordinates) is in good agreement with the experimentally observed structure. Only the more symmetrical complexes have been amenable to growing crystals suitable for X-ray crystallography.

■ EXPANDED POLYPYRROLE MACROCYCLES: EXTENDED Π SYSTEMS AND AROMATICITY

Macrocycles containing more than four pyrrole units are dubbed expanded porphyrins, and these have proved to be a rich area of research, especially over the last 2 decades. They are important in a number of arenas: as polynucleating ligands for more than one metal, as sensors, as ion receptors, and for optical effects arising from the extended π systems.[122−124] Very recently, interest has been stimulated by the observation of unusual Hückel and Möbius aromatic and antiaromatic systems.[107] Little of this chemistry intersects with boron, although there are some interesting examples that reinforce the same themes already encountered for boron pyrrole chemistry.

Mono- and diboron complexes of hexapyrrole amethyrin(1.0.0.1.0.0) and [32]octaphyrin(1.0.0.0.1.0.0.0)[125,126] were prepared by reaction with $BF_2 \cdot OEt_2$.[93] The ligands each contain two dipyrrin-like sites in which pyrroles are linked through a *meso*-carbon, and the remaining pyrroles are linked directly by $C_\alpha - C_\alpha$ bonds. The complexes exclusively contain BF_2 units in the dipyrrin sites, showing again clear preferences for boron coordination in these rather than bipyrrole sites (Figure 16a,b). Both the mono- and diboron complexes essentially behave as BODIPY derivatives with none of the unusual propensity for hydrolysis or redox reactions observed in the boron porphyrin and corrole complexes, reinforcing the principle that it is steric crowding in the boron porphyrins and corroles that stimulates the unusual chemistry. Other BODIPY-like expanded porphyrins were prepared by coupling reactions to give BF_2(dipyrrin) units linked by conjugated alkynyl groups (Figure 16c).[127] Oxasmaragdyrin is a core-modified expanded porphyrin containing four pyrroles and one furan, and it too coordinates a single BF_2 group in the only dipyrrin-like site contained within the macrocycle (Figure 16d).[128]

The structure-directing role of boron in forming subporphyrin-type macrocycles was described earlier, along with examples of extrusion of boron subporphyrins from heptaphyrin. These reactions are thought to be induced by transannular π interactions at the hinge positions.[84,85] Uncomplexed pentafluorophenylheptaphyrin(1.1.1.1.1.1.1) is subject to N-fusion reactions, leading to singly, doubly, and quadruply N-fused heptaphyrins. In the quadruply N-fused macrocycle, two of the *meso*-aryl groups have fused across two adjacent pyrroles, producing new N−C(aryl) bonds. Four of the pyrrole groups are twisted into a cyclophane-like unit, leaving the unfused pyrroles in a subporphyrin-like loop, which is able to complex boron.[129] The heptaphyrin systems contain seven pyrroles, well-disposed to form a tetrapyrrole (either as a transition-metal complex or in the quadruply N-fused arrangement) and a boron tripyrrole. The related hexaphyrin(1.1.1.1.1.1), as might be expected, can form two linked boron tripyrroles and a new transannular pyrrole $C_\alpha - C_\alpha$ bond.[130] When the boron instertion protocol is changed, a second diboron complex is formed in which a skeletal rearrangement to hexaphyrin(2.1.1.0.1.1) is reached. Another feature of expanded porphyrins is that they can often exist in several oxidation states, with two-electron changes linked by a variation in the protonation of the pyrrole nitrogen atoms. The new diboron hexaphyrin(2.1.1.0.1.1) also exhibits this phenomenon, reminiscent of the observation of diboron porphyrin and isophlorin complexes in the porphyrin system.[102] Two boron complexes, the 30π-electron, aromatic B_2[30]hexaphyrin(2.1.1.0.1.1) containing trigonal-planar boron and the 28π-electron, anyiaromatic B_2[28]hexaphyrin(2.1.1.0.1.1) containing tetrahedral boron, can be reversibly interchanged by MnO_2 oxidation or $NaBH_4$ reduction (Scheme 7).[130]

SUMMARY

This survey illustrates that, although the complexes discussed have in common ligands containing pyrrolyl moieties, the role played by boron varies considerably with the number and architecture of the pyrrole units in those ligands. Simple boron pyrrolyl complexes are stronger Lewis acids than their aminoboron counterparts; the electrons in the aromatic pyrrolyl unit are less available for B−N π bonding. The difluoroboron dipyrrins are very well-known compounds, with important applications resulting from their strong fluorescence, but modifications at boron are relatively unexplored. Boron porphyrins and corroles show rich and unexpected chemistry, much of it arising from complexation of two boron atoms within the confined space of these tetrapyrrole macrocycles. Although each boron in these complexes coordinates to two nitrogen atoms in a dipyrrin-like site, pronounced fluorescence is not a feature of these compounds. A key difference is the planar six-membered ring that occurs in boron dipyrrins, whereas in most examples of boron porphyrins and corroles, the boron atoms reside out of this plane and these geometrical differences presumably affect the optical properties, an area of research that is currently being initiated. Cyclic tripyrrole ligands feature boron in a structure-directing and templating role, and this is also observed in some examples of twisted expanded porphyrin where boron can coordinate in a terpyrrolic loop of the larger ligand. Both of these complexes and boron porphyrins show redox chemistry involving the ligand. Overall, this survey shows a rich and unique chemistry for boron, particularly when it is featured in ligands that are more familiar as transition-metal complexes. Intriguing applications that arise from the special features of boron pyrrolyl chemistry can be anticipated as this area of chemistry matures.

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(91) Abbreviations: H_2TTP, 5,10,15—20-tetra-*p*-tolylporphyrin; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin; H_2T-*p*-ClPP, 5,10,15—20-tetra-*p*-chlorophenylporphyrin; H_2TTC, 5,10,15-tri-*p*-tolylcorrole; H_2Por, unspecified porphyrin; H_3Cor, unspecified corrole.

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