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Fluoroaryl Boranes

Perfluoropentaphenylborole[**]

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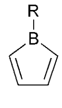
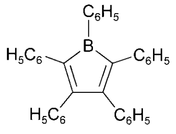
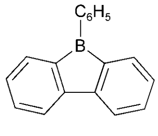
Boroles are unsaturated boron-containing pentacyclic molecules that have long been of interest due to their 4π, antiaromatic nature, isoelectronic with the elusive cyclopentadienyl cation.[1] The unsubstituted parent borole (**I**) has not been prepared, but it has been probed computationally;[2] isolation of boroles has relied on the preparation of pentasubstituted examples, such as the pentaphenyl derivative **II**,[3] or by incorporating the borole core into a more extensive polycyclic system, such as the 9-phenyl-9-borafluorene complex **III**.[4] While of fundamental interest for insights into concepts of aromaticity, boroles have found application as precursors to borrolides, dianionic cyclopentadienyl (Cp) mimics in transition-metal chemistry,[5] Diels–Alder acceptors,[6] and as core units in organic materials.[7]



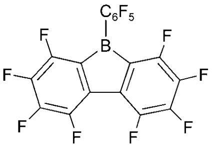
I



II



III

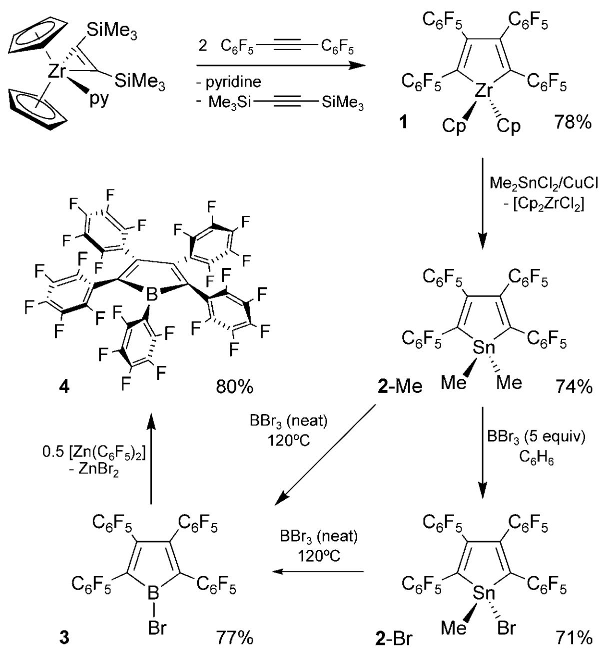


IV

Perfluoroaryl boranes constitute another important class of organoborane compounds.[8] For example, $B(C_6F_5)_3$ is a strong organometallic Lewis acid effective as a cocatalyst activator for various transition-metal-catalyzed transformations[9] and small-molecule activations.[10] The efficacy of these compounds stems largely from the enhanced Lewis acidity and hydrolytic stability conferred by the perfluorination of the aryl substituents. We have a long-standing interest in the chemistry of perfluoroaryl boranes, and have combined their properties with those of antiaromatic boroles by the preparation of perfluoro-9-phenyl-9-borafluorene (**IV**).[11] We have found enhanced Lewis acidity in **IV**, compared to $B(C_6F_5)_3$ and extended this concept to chelating diboranes as well.[12]

Although pentaphenylborole (**II**) was first synthesized in 1986, it was only recently that its structure was determined;[13] several related complexes were also recently reported and structurally characterized.[14] The high Lewis acidity of these rather sterically encumbered heterocycles was manifested in significant interactions observed in the solid state between the boron center and the π system of a phenyl group on a neighboring molecule. In all examples save **II** itself, localized bonding within the borole ring was observed. Apparent delocalized bonding in **II** was rationalized on the basis of observed solid-state interactions between a phenyl group and the boron center in adjacent molecules of **II**;[13] however in other instances, coordination of a Lewis base to boron results in more distinct electronic localization within the borole ring.

Our interest in both boroles and perfluoroaryl boranes prompted us to seek routes to the perfluorinated derivative of **II**. Given the utility of stannacyclic precursors in the synthesis of boroles, the route depicted in Scheme 1 was developed. However, the replacement of phenyl with pentafluorophenyl groups adds complications to these endeavours. For example, the stannacyclic precursor to **II** is prepared by quenching of a 1,4-dilithio-tetraphenylbutadiene reagent with Me_2SnCl_2; use of lithiated organofluorine reagents is hazardous due to the potential (explosive) loss of LiF. We therefore opted to construct the $\{C_4(C_6F_5)_4\}$ framework by reductive coupling of two equivalents of $(C_6F_5)CC(C_6F_5)$[15] at Zr^{II}. Various iterations of Negishi-type sources of $[Cp_2Zr^{II}]$[16] did not couple this alkyne efficiently, and the only effective zirconocene reagent for doing this proved to be Rosenthal's pyridine-stabilized bis-trimethylsilyl acetylene complex,[17] using a procedure developed by Tilley and co-workers.[18] In this way, zirconacycle **1** was prepared in good yield as a yellow crystalline solid that was characterized principally by



Scheme 1. Synthesis of perfluoropentaphenylborole (**4**).

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^{19}F NMR spectroscopy, elemental analysis, and X-ray crystallography.[19]

While zirconacyclopentadienes are generally excellent substrates for the preparation of a variety of heterocycles through transmetallation reactions, the introduction of pentafluorophenyl groups renders the Zr–C bonds in **1** far less nucleophilic than nonfluorinated analogues, and as a consequence, normally facile transmetallation reactions are sluggish or do not occur at all. For example, **1** is unreactive towards Me_2SnCl_2, $PhBCl_2$, and BBr_3;[20] only HCl/THF results in cleavage of the Zr–C bonds. Fortunately, using a copper-mediated procedure reported by Takahashi and coworkers,[21] the target stannacycle **2** was obtainable in reasonably good yield, as shown in Scheme 1. When separated from the by-product $[Cp_2ZrCl_2]$, compound **2**-Me is isolated as an analytically pure crystalline white solid from hot toluene. The ^{19}F NMR spectrum shows two *ortho*/*meta*/*para* patterns for the inequivalent C_6F_5 groups, while the ^{1}H NMR spectrum shows the expected signal for the methyl groups accompanied by $^{117/119}$Sn satellites. Furthermore, its structure was also determined by X-ray crystallography.[18]

Conversion of stannacycle **2**-Me to a borole was nontrivial. Reactions with $ArBX_2$ reagents were ineffective even under forcing thermal conditions. Reaction with a moderate excess of BBr_3 in toluene resulted in exchange with one of the Sn–Me groups to yield **2**-Br, which could be isolated and characterized, underscoring the low reactivity of the $Sn{-}C_{sp^2}$ bonds in this fluorinated group. Only when compounds **2** were dissolved in neat BBr_3 and heated at 120 °C for 48 h could conversion to the bromoborole **3** be induced. Over this time, the reaction mixture gradually turned dark red, and upon removal of the BBr_3, **3** was obtained after recrystallization of the residue from hot toluene. The familiar pattern of resonances in the ^{19}F NMR spectrum for the $\{C_4(C_6F_5)_4\}$ remains but is shifted relative to those of **2**-Me, and the presence of boron in the compound is indicated by a resonance in the ^{11}B NMR spectrum at $\delta = 67$ ppm (CD_2Cl_2). However, **3** is highly moisture-sensitive, and attempts to grow crystals resulted in a determination of the structure of the boronic acid derived by its hydrolysis and cleavage of one B–C bond.[22] Thus, conversion to the title compound **4** by timely treatment with the C_6F_5 transfer agent $[Zn(C_6F_5)_2]$[23] proved most effective.[24]

Perfluoropentaphenylborole (**4**) is a dark purple solid with poor solubility in a wide variety of solvents. Nonetheless, with long acquisition times, the ^{19}F and ^{11}B NMR spectra can be acquired and are consistent with its formulation as drawn in Scheme 1. A new set of *ortho*/*meta*/*para* resonances for the $B{-}C_6F_5$ groups are present with half the intensity of those for the α and β C_6F_5 groups, and the ^{11}B signal at $\delta = 66$ ppm is fully consistent with that expected for a pentaaryl borole moiety.[7] X-ray quality crystals of **4** were obtained from hot toluene, in which **4** is sparingly soluble at room temperature; its molecular structure and crystal packing are shown in Figure 1.[25]

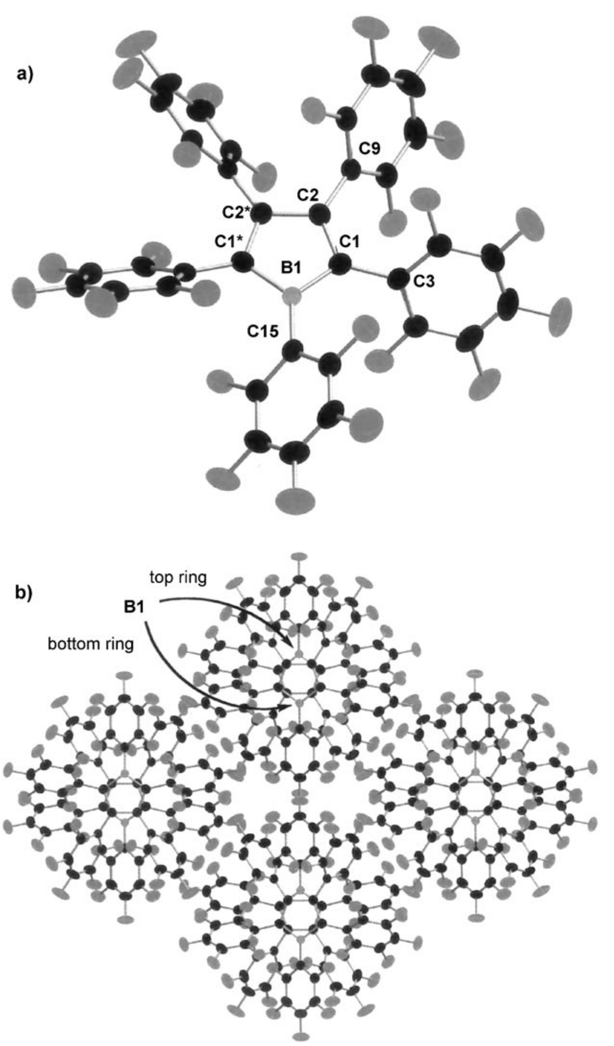

Figure 1. Thermal ellipsoid (50%) diagrams of the molecular structure of **4** (top) and the packing motif (bottom). Selected bond lengths [Å] and angles [°]: B1–C1 1.522(3), C1–C2 1.435(4), C2–C2* 1.456(5), B1–C15 1.508(5), C1–C3 1.492(3), C2–C9 1.482(3); C1-B1-C1* 105.8(3), C1-B1-C15 127.11(15), B1-C1-C2 107.3(2), C1-C2-C2* 109.80(13).

The central ring of **4** is essentially planar, and the molecule lies on a twofold axis of symmetry aligned with the B1–C15 vector and bisecting C2–C2*. As in the nonfluorinated derivative **II**, the C_6F_5 groups are arrayed in a propeller-like arrangement; unlike **II**, however, there are no close contacts between B1 and adjacent aromatic groups and the molecules are stacked in staggered conformation as dimers with interdigitated propellers as shown in Figure 1 b. These disks are packed in a cubic pattern, with intermolecular F–F contacts under 3 Å.

The metrical parameters for **4** are more similar to those found for unfluorinated **II** than they are to those obtained for derivatives of **II** where the B–Ar group is different from C_6H_5. In other words, the bond lengths found for **4** are indicative of electronic delocalization within the BC_4 ring, rather than the alternation of single and double bonds expected on the basis of the antiaromaticity of the ring. Whereas Braunschweig, Frenking et al. addressed this issue as being a consequence of intermolecular B–phenyl interactions,[13] these are not present here, nor did Yamaguchi and co-workers see this effect in related compounds, even though such intermolecular interactions were observed to be present.[14] In the case of **4**, it seems likely that the "delocalization" as indicated by the bond lengths is rather a consequence of five-fold disorder in this highly symmetric molecule. Thus, the structural parameters (i.e., intraring bond lengths) observed here are not a reliable indication of the extent of delocalization in **4**.

This notion is supported by the computed structure of **4** (singlet) as determined using the Gaussian G03 program suite[26] at the UB3LYP level using the 6-31G* basis set. Starting from an input file derived from the crystallographic pdb file, the optimized structure features the localized bonding expected for the 4π antiaromatic borole heterocycle.[3,14] Thus, while the general structural features are maintained, the B1−C1 and C2−C2* bonds elongate to 1.585 and 1.525 Å, respectively, and the C1−C2 distance contracts to 1.356 Å in the computed structure. These parameters are in line with those found in Yamaguchi and co-workers' less symmetrical pentaaryl boroles.[14] The triplet structure of **4** was also optimized and found to be higher in energy than the singlet by 16.9 $\mathrm{kcal\,mol^{-1}}$, somewhat larger than the singlet–triplet gaps of 15.4–15.9 $\mathrm{kcal\,mol^{-1}}$ found for the nonfluorinated compounds.

The UV/Vis spectrum of **4**[18] is similar to that of **II**, but it exhibits a blue-shifted $\lambda_{\max}$ of 530 nm ($\varepsilon = 422(5)\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) for the low-energy band giving rise to the characteristic deep colors of pentaaryl borole derivatives.[3b] This is expected on the basis of a larger HOMO–LUMO gap as a consequence of perfluorination. This perturbation should also result in higher Lewis acidity, and indeed **4** is exceptionally water-sensitive. Thus, the UV spectrum had to be acquired in a 1 mm pathlength cell in order to maintain concentrations above 10^{-3} M; more dilute solutions were observed to discolor rapidly due to reaction with adventitious water. Analysis of the products of reaction with stoichiometric water indicates that a ring B−C bond in **4** is readily hydrolyzed, presumably subsequent to coordination of water to the highly Lewis acidic boron center.

This Lewis acidity is demonstrated in a competition experiment wherein one equivalent of **4**, one equivalent of $B(C_6F_5)_3$, and one equivalent of CH_3CN are mixed together. No reaction is observed between **4** and $B(C_6F_5)_3$, and when the acetonitrile equivalent is added, the adduct **4**·$NCCH_3$ is formed exclusively (as determined by ^{19}F and ^{1}H NMR spectroscopy) with no trace of the known $H_3CCN{\rightarrow}B(C_6F_5)_3$ adduct observable within the limits of NMR spectroscopy.

In summary, we have developed a route to the fully fluorinated analogue of the antiaromatic pentaphenylborole system **II**. The challenges associated with carrying out chemistry on perfluorinated compounds necessitated forcing conditions to incorporate the boron center into the borole ring, but the compound can be prepared in reasonable yields. Like **II**, the molecular structure determination suggests delocalization about the C_4B ring, but we attribute this to crystallographic disorder rather than true delocalization. Computations indicate that localized bonding, as expected for an antiaromatic ring of this type, is operative. Due to both perfluorination and antiaromaticity, compound **4** is highly Lewis acidic and water-sensitive. We are continuing to explore its reactivity, including its propensity to undergo Diels–Alder reactions.[6]

Experimental Section

Synthesis of **4**: In an argon atmosphere, **3** (0.51 g, 0.63 mmol) and $[Zn(C_6F_5)_2]$ (0.13 g, 0.32 mmol) were mixed in toluene (15 mL). The mixture was stirred and heated at 80 °C overnight. The clear red liquid was decanted. The purple solid was washed with toluene (3 × 3 mL), dried in vacuum, and redissolved in C_6F_6 (50 mL). The purple solution was filtered and the solvent was removed in vacuum to give a purple powder. Purple crystals suitable for X-ray analysis were obtained by slowly cooling the hot toluene solution to room temperature. Yield: 0.45 g (80 %). ^{11}B{^{1}H} NMR (CD_2Cl_2, 128 MHz): $\delta = 66$ ppm (br). ^{19}F{^{1}H} NMR (CD_2Cl_2, 376 MHz): $\delta = -124.6$ (m, 2F, o-BC_6F_5), -137.6 (m, 4F, o-CC_6F_5), -139.3 (m, 4F, o-CC_6F_5), -141.8 (t, 1F, p-BC_6F_5), -149.2 (t, 2F, p-CC_6F_5), -153.6 (t, 2F, p-CC_6F_5), -159.2 (m, 2F, m-BC_6F_5), -159.6 (m, 4F, m-CC_6F_5), -161.3 ppm (m, 4F, m-CC_6F_5). Samples for elemental analysis were obtained by recrystallization from C_6F_6, which by ^{19}F NMR spectroscopy is incorporated into the crystal lattice in a 1:1 ratio with **4**. Elemental analysis (%) calcd for $C_{34}H_3BF_{25}\cdot 1\,C_6F_6$: C 44.48; found: C 44.71.

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[19] Full experimental details and characterization data for compounds **1–3** can be found in the Supporting Information.

[20] Compound **1** is unreactive towards stoichiometric quantities of BBr_3 in refluxing toluene, and converts to multiple species in neat BBr_3.

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[25] Crystal data for **4**: $C_{34}BF_{25}$, $M_w = 894.15$, monoclinic, $C2/c$, $a = 22.399(14)$, $b = 13.725(10)$, $c = 11.298(6)$ Å, $\alpha = 90$, $\beta = 115.79(3)$, $\gamma = 90°$, $V = 3127(3)$ Å^3, $Z = 4$, $\rho = 1.899$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 173(2)$ K, 5694 measured reflection, 3562 unique ($R_{int} = 0.0279$), min/max transmission = 0.9501 and 0.9872, $R1(I > 2\sigma) = 0.0487$, $wR2 = 0.0960$, GoF = 1.056, no. of parameters = 274, final difference map within +0.346 and −0.224 e Å^3. CCDC 711029 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[26] See Supporting Information for full citation for Gaussian 03.