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Planarized Triarylboranes: Stabilization by Structural Constraint and Their Plane-to-Bowl Conversion

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S Supporting Information

ABSTRACT: Triphenylborane and 9,10-diphenyl-9,10-dihydro-9,10-diboraanthracene, constrained to a planar arrangement with methylene tethers, were synthesized by intramolecular multi-fold Friedel−Crafts cyclization. These compounds were stable toward air, water, and amines, despite the absence of steric protection in the vertical direction with respect to the B atoms, and showed characteristic structural, electronic, and photophysical properties. In addition, upon treatment with a fluoride ion, these compounds underwent a plane-to-bowl conversion in a controlled manner.

Triarylborane represents an important electron-accepting building unit for π-conjugated materials.[1] A number of fascinating materials with the triarylborane substructure have been developed for various applications, such as organic light-emitting diodes, two-photon absorption materials, and anion sensors.[1] In the conventional molecular designs for these materials, a key issue is to sterically protect the boron moiety due to its inherent high reactivity. Most of the organoboron materials so far reported employed at least one or two bulky aryl groups on the B atom, such as mesityl,[1,2] triisopropylphenyl,[3] and supermesityl groups.[4] However, their steric bulkiness sometimes has a detrimental effect on the solid-state properties that rely on the intermolecular interaction, such as charge carrier transporting properties.

We now introduce a new idea for the stabilization of the tri-coordinated boron-containing π skeleton, which is "kinetic stabilization not by steric bulkiness, but by structural constraint". On the basis of this concept we designed two target compounds, a planarized triphenylborane **1** and its diboron homologue **2** (Figure 1). Although these compounds do not have any steric protection for the B atom in the vertical direction, they should be stabilized, because the rigidly fixed cyclic skeleton around the B atom would retard a decomposition process through the reaction with Lewis basic species, due to the destabilization of a tetra-coordinated intermediate and/or prevention of a C−B bond cleavage from the intermediate by the chelating effect. In addition, these compounds can be regarded as a boron congener for planarized trityl cations and triphenylamines, which are known to be a useful core for dyes[5a] or hole-transporting materials,[5b] respectively. In this regard, the planarized boranes should serve as useful two-dimensional π scaffolds with electron-accepting character. The planarized structure would enhance the π conjugation through the vacant p orbital of the B atom. Whereas a triphenylborane constrained with ethylene tethers was reported by Okada and Oda,[6] a completely planarized derivative is unprecedented. As a fundamental character of the planarized boranes, we are also interested in whether these compounds still maintain reactivity toward a strong Lewis base. If so, we can expect an additional possibility, such as a stimuli-responsive structural change. The addition of an external Lewis base would induce the coordination number change of the boron from tri-coordination to tetra-coordination,[7] resulting in a plane-to-bowl conversion accompanied by a significant electronic perturbation (Figure 1a).[8] We now report the efficient synthesis of these planarized triarylboranes and discuss the impacts of the planar constraint on their structures, electronic properties, and reactivity.

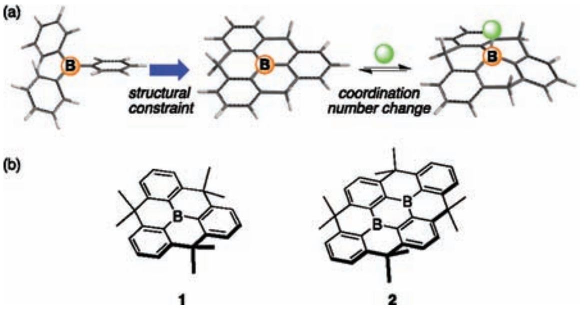

Figure 1. Molecular design. (a) Schematic representation of planarized triarylborane. (b) Planarized triphenylborane **1** and a diboron homologue **2**.

Our synthetic strategy to construct the planarized borane **1** was to conduct a two-fold intramolecular Friedel−Crafts cyclization in a simultaneous fashion using a di(2-propenyl)-substituted triarylborane **4** as the key precursor (Scheme 1a). This route has already proven effective for the synthesis of constrained triphenylphosphines and -arsines, as reported by Hellwinkel and co-workers, in which they conducted the proton-promoted cyclization.[9] Compound **4** was prepared by the reaction of a bromoborane **3** with 2,6-di(2-propenyl)-phenyllithium in toluene in 80% yield. For the cyclization of **4**, the choice of Lewis acid was crucial. All of our initial attempts using various proton acids as well as Lewis acids, such as $AlCl_3$, $FeCl_3$, $BF_3 \cdot OEt_2$, and $TiCl_4$, only gave complex mixtures. Alternatively, we focused on metal triflates as the Lewis acid.

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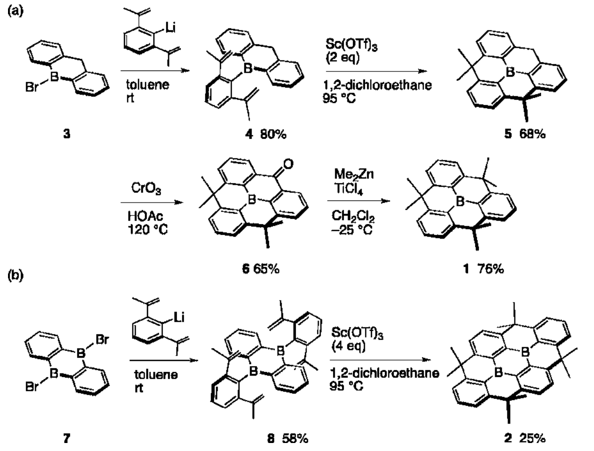
Scheme 1. Intramolecular Multi-fold Friedel−Crafts Cyclization



Whereas the use of $Sn(OTf)_2$ and $Bi(OTf)_3$ gave similar results, $Sc(OTf)_3$ could cleanly promote the cyclization. Thus, treatment of **4** with 2 equiv of $Sc(OTf)_3$ in 1,2-dichloroethane at 95 °C gave a planar triarylborane **5** in 68% yield. The use of a catalytic amount (0.5 equiv) of $Sc(OTf)_3$ also gave the product, but the yield decreased to 40% (see Supporting Information (SI)). To synthesize the all-methylated D_{3h}-symmetry product **1**, the methylene bridge in **5** was further functionalized. Thus, oxidation of **5** with CrO_3 in refluxing acetic acid produced a carbonyl-bridged planar borane **6** in 65% yield without decomposition despite the harsh conditions. Treatment of **6** with Me_2Zn in the presence of $TiCl_4$ successfully gave the D_{3h} product **1** in 76% yield.

This synthetic strategy was also applicable to the synthesis of a more extended π-conjugated compound **2** that has two B atoms. Thus, treatment of a tetra(2-propenyl)-substituted **8**, which was prepared from **7**,[10] with 4 equiv of $Sc(OTf)_3$ promoted the four-fold intramolecular Friedel−Crafts cyclization to produce the planarized dihydro-dibora-anthracene à dihydro-diboraanthracene **2** in 25% yield (Scheme 1b).

Compounds **1** and **2** were unambiguously characterized by NMR spectroscopy, mass spectrometry, and X-ray crystallography (*vide infra*). As expected, both compounds are quite stable against air and water and could be purified by silica gel column chromatography in an open atmosphere. This high stability is in stark contrast to that of Ph_3B, which is easily decomposed on silica gel. These compounds also have a high thermal stability. The decomposition temperature with a 5% weight loss (T_{d5}) of **2** was 353 °C (see SI).

Single crystals of the planar boranes **1** and **2** were obtained by recrystallization from CH_2Cl_2/hexane solutions. X-ray structural analysis confirmed that both compounds indeed have nearly planar structures (Figure 2a). The central B atoms have an ideal trigonal planar geometry with the sum of the three C_{ipso}−B−C_{ipso} angles of 360.0° for both **1** and **2**. The dihedral angles between the phenyl groups on the B atom are 0.0−0.15° and 0.0−2.6° for **1** and **2**, respectively. All the methylene-bridge carbon atoms sit in the same plane with the boron planes. Noteworthy is that the B−C_{ipso} bond distances (1.519(2)−1.520(2) Å) of **1** are much shorter than those of normal triarylboranes, such as Ph_3B (1.571−1.589 Å)[11a] and trimesitylborane (Mes_3B, 1.573−1.580 Å).[11b,c] The B−C_{ipso} bonds (1.520(2)−1.532(2) Å) in **2** are also shorter than those of other 9,10-dihydro-9,10-diboraanthracene derivatives (1.554−1.589 Å) in the literature.[12] The short B−C_{ipso} bond distances (1.506(3)−1.528(3) Å) were also observed in the intermediate product **6**. These data suggest that this is a common feature of the planarized triarylboranes with methylene bridges. In the packing structure, no special intermolecular interaction was observed in both **1** and **2**, presumably due to steric hindrance of the peripheral methyl groups at the bridge moieties. However, in the case of **6** with a carbonyl bridge, this compound forms a face-to-face dimeric π-stacked structure with a distance of 3.46 Å (see SI).

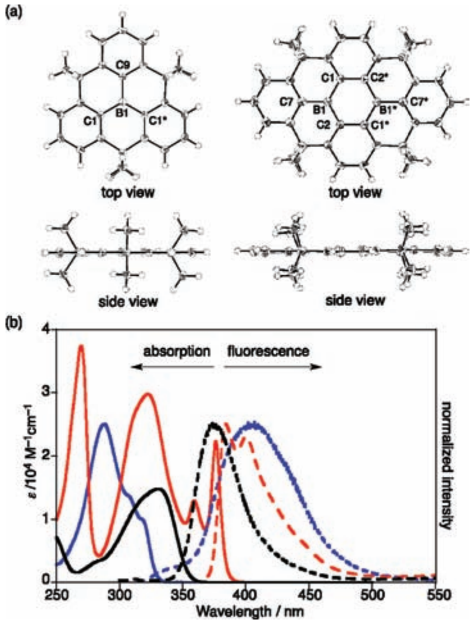


Figure 2. Crystal structures and photophysical properties of planarized triphenylboranes. (a) ORTEP drawings of **1** (left) and **2** (right) (50% probability for thermal ellipsoids). (b) UV−vis absorption (solid lines) and fluorescence spectra (dashed lines) for **1** (blue), **2** (red), and Mes_3B (black) in THF.

The photophysical properties of the planarized boranes **1** and **2** were investigated (Figure 2b). Their data are summarized in Table 1, together with data for Mes_3B,[13] for comparison. In the UV−vis absorption spectra in THF, **1** showed the strongest absorption band at λ_{max} = 289 nm, with two shoulder bands at 310 and 320 nm. Notably, this longest λ_{max} is slightly shorter than the λ_{max} of Mes_3B, despite the highly coplanar structure of **1**. On the other hand, the diboron homologue **2** showed its λ_{max}

Table 1. Photophysical and Electrochemical Data

	absorption[a]		fluorescence[a]		reduction potential
compd	λ_{abs} [nm]	log ε	λ_{em} [nm]	Φ_F	$E_{1/2}$[V][b]
1	289	4.40	407	0.10	−2.59 (−2.69)
	310(sh)	4.11			
	320(sh)	3.97			
2	377	4.35	384	0.10	−2.04 (−2.09)
			400		−2.56 (−2.61)
Mes_3B	332	4.17	374	0.08	−2.57 (−2.63)[c]

[a] In THF. [b] In THF with $Bu_4N^+PF_6^-$ (0.1 M) at a scan rate of 100 mVs^{-1}. Potentials vs ferrocene/ferrocenium. Peak reduction potential (E_{pc}) in parentheses. [c] Reported in ref 13.

at 377 nm, which is red-shifted by 28 nm compared to that of 9,10-dimesityl-9,10-diboraanthracene (349 nm).[12c] The red-shifted absorption maximum for **2** compared to **1** demonstrates the effective expansion of π conjugation through the two boron moieties in **2**. In contrast, in the fluorescence spectra, while the monoboron compound **1** showed a bluish purple emission with the maximum at 407 nm, the diboron homologue **2** showed a fluorescence at 384 nm, which is 23 nm shorter than **1**. The Stokes shift for the diboron compound **2** was 484 cm^{-1}, which is reasonably small for its rigid skeleton. Instead, the significant shift ($\Delta\lambda$ = 6680 cm^{-1}) of the emission band of **1** from the absorption band is unusual for its rigid structure. Although the origin of this emission spectrum is unclear at this stage, this should be one of the features of this skeleton, since the propeller-shaped Mes_3B only shows an intense emission band at 374 nm with a reasonable Stokes shift of 3380 cm^{-1}.

To study the effect of the planar constraint on the electronic structure, we conducted cyclic voltammetry (CV) measurements in THF. As envisioned, the planarized borane **1** showed reversible redox waves, indicative of sufficient stability even in the reduced state under the measurement conditions, despite the absence of steric protection over the boron moiety. Its reduction potential ($E_{1/2}$) was −2.59 V (E_{pc} = −2.69 V) vs the ferrocene/ferrocenium ion couple (Fc/Fc^+), which is slightly more negative than that of triphenylborane (E_{pc} = −2.57 V) and comparable to that of Mes_3B ($E_{1/2}$ = −2.57 V).[13] This comparison demonstrates that planarization of the triphenylborane skeleton does not contribute significantly to decreasing the LUMO level, despite its coplanar structure. In the CV of the π-expanded diboron **2**, two reversible reduction waves were observed at $E_{1/2}$ = −2.04 and −2.64 V. Interestingly, **6** with one carbonyl bridge showed an irreversible reduction wave at the more positively shifted potential of E_{pc} = −1.82 V, indicative of electronic tunability by structural modification at the bridge moiety (see SI).

A question we had here was why the planarization of the triphenylborane skeleton is not particularly effective to increase the electron affinity. This is likely due to the effect of π donation from the ipso-carbon atoms to the B atom via p−π conjugation, which may also contribute to the short B−C_{ipso} bonds observed in the crystal structure as well as the high chemical stability. Natural bond orbital analysis for **1** (B3LYP/6-31G(d)) suggested that in the planar-constrained triarylboranes, not only the p−π* interaction but also the p−π interaction between B and ipso-carbon atoms effectively occur to a greater extent than for conventional triarylboranes. These electronic effects result in the moderate increment of electron-accepting ability in **1**. The π-donating effect from the ipso-carbon atoms was also experimentally demonstrated by the ^{11}B NMR spectrum. Thus, **1** features a broad signal at a higher magnetic field (48.6 ppm) compared to those of the nonplanarized triarylboranes (Ph_3B, 67.4 ppm;[14a] Mes_3B, 79.0 ppm[14b]).

The shortened B−C_{ipso} bond distances observed in the crystal structures of **1** and **2** suggest that the rigidity of the triarylborane skeletons is enhanced by the planar constraint with the methylene tethers. This rigid structure would retard reactions of the boron center with certain nucleophiles that result in the formation of a tetrahedral tetra-coordinated species. Indeed, **1** was inert even toward highly Lewis basic amines, such as DBU or DABCO. The ^1H NMR spectra of **1** did not show any change upon the addition of an excess of these amines. However, we found that this compound can still react with a fluoride ion to form a fluoroborate complex $\mathbf{1}\cdot F^-$. Thus, treatment of **1** with 1 equiv of $[Me_3SiF_2]^-\cdot[S(NMe_2)_3]^+$ (TASF) in THF immediately formed a fluoroborate salt of $\mathbf{1}\cdot F^-$ with $S(NMe_2)_3^+$ as a white precipitate, which was isolated in 77% yield by filtration (Figure 3a). As expected for a tetra-coordinated B atom, in the ^{11}B NMR spectrum, $\mathbf{1}\cdot F^-$ showed a sharpened signal at the higher magnetic field of −4.2 ppm ($h_{1/2}$ = 510 Hz) compared to that of **1** (48.6 ppm, $h_{1/2}$ = 1000 Hz). The ^{19}F NMR spectrum features a broad signal at −176.4 ppm, which is comparable to the chemical shifts observed for other dimesitylfluoroborates.[1f] To determine the binding constant, we conducted a UV titration experiment. The binding constant (K) of **1** in THF toward a fluoride ion was determined to be 7.0 × 10^5 M^{-1} by a standard curve-fitting method with a 1:1 binding isotherm, which is comparable to that of Mes_3B (3.3 × 10^5 M^{-1}).[15,16] This result demonstrates that **1** still has a significant Lewis acidity despite the planar constraint.

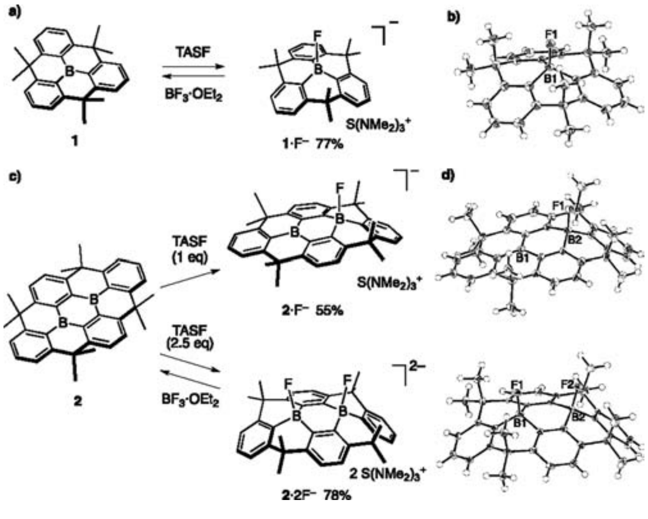


Figure 3. Plane-to-bowl conversion by fluoride ion coordination in **1** and **2**. (a) Reaction of **1** with a fluoride ion to form $\mathbf{1}\cdot F^-/S(NMe_2)_3^+$. (b) Crystal structure of $\mathbf{1}\cdot F^-/S(NMe_2)_3^+$. (c) Reactions of diborane **2** with 1 equiv or an excess of fluoride ion to produce $\mathbf{2}\cdot F^-/S(NMe_2)_3^+$ or $\mathbf{2}\cdot 2F^-/2S(NMe_2)_3^+$, respectively. (d) Crystal structures of $\mathbf{2}\cdot F^-/S(NMe_2)_3^+$ and $\mathbf{2}\cdot 2F^-/2S(NMe_2)_3^+$. In the ORTEP drawings in (b) and (d), the thermal ellipsoids are drawn at the 50% probability level, and the countercations are omitted for clarity.

The X-ray crystal structural analysis revealed that the fluoroborate complex $\mathbf{1}\cdot F^-$ has a bowl-shaped structure (Figure 3b). Thus, the coordination number change of the boron center from tri-coordination to tetra-coordination results in a plane-to-bowl conversion. The depth of the resulting bowl structure, defined by the distance between the B atom and the plane that consists of three C_{para} atoms, is 1.65 Å. The countercation $S(NMe_2)_3^+$ sits on the concave side of the bowl structure. This complex has several notable structural features. First, the B atom indeed takes a tetra-coordinate tetrahedral geometry with the sum of the C_{ipso}−B−C_{ipso} angles of 326.7°. The C_{ipso}−B bond distances (1.603(3)−1.610(3) Å) in $\mathbf{1}\cdot F^-$ are elongated by ~0.07−0.09 Å compared to those (1.519(2)−1.532(2) Å) in **1**. The B−F bond length of 1.494(2) Å is slightly longer than those of the known fluoroborates, such as $(9\text{-anthryl})_3BF^-/K^+[2.2.2]$cryptand (1.466 Å)[7] and Mes_2PhBF^-/nBu_4N^+ (1.481 Å).[1f] Second, the boracyclohexadiene ring takes a boat conformation. This structural flexibility likely allows the boron center to take the tetra-coordinated geometry. Third, in this boat conformation, the F atom and one H atom of the axial methyl group are in close proximity. Its distance is in the range of 2.28(2)−2.32(2) Å, which is substantially shorter than the sum of van der Waals radii (r_{vdw} = 1.5 Å for F, 1.2 Å for H), indicative of the formation of C−H···F−B H-bonds.[17]

Similarly, diborane **2** also reacted smoothly with the fluoride ions to form the corresponding fluoroborates. Thus, treatment with 1 equiv of TASF produced the corresponding monofluoroborate $\mathbf{2}\cdot F^-$, which was isolated in 55% yield. Notably, treatment of **2** with an excess of TASF (2.5 equiv) selectively gave a *cis* isomer of difluoroborate $\mathbf{2}\cdot 2F^-$ in 78% yield (Figure 3c). In the ^1H NMR spectrum of the reaction mixture, the formation of a *trans* isomer was not observed at all (see SI). To elucidate the origin of this high selectivity, we conducted DFT calculations at the B3LYP/6-31+G(d,p) level of theory. According to the results, the *cis* isomer is more stable than the *trans* isomer by 6.7 kcal/mol. This thermodynamic stability of the *cis* isomer is presumably responsible for the *cis* selectivity.

The structures of these fluoroborates were also confirmed by X-ray crystal structural analysis (Figure 3d). In the structure of $\mathbf{2}\cdot F^-$, while one B atom maintains the planar geometry ($\sum C_{ipso}-B-C_{ipso} = 359.6°$), the other B atom changes to the tetrahedral geometry ($\sum C_{ipso}-B-C_{ipso} = 330.9°$). In the structure of *cis*-$\mathbf{2}\cdot 2F^-$, the combination of two tetrahedral fluoroborate units ($\sum C_{ipso}-B-C_{ipso} = 329.4°$ and 329.1°) results in the formation of a larger and deeper bowl structure than in the monofluoroborate $\mathbf{1}\cdot F^-$. The depth of the bowl structure in *cis*-$\mathbf{2}\cdot 2F^-$ is 2.49 Å, which is much deeper than that in $\mathbf{1}\cdot F^-$ (1.65 Å). This large and deep bowl structure with a dianionic electron-donating character suggests the potential use of this system as a host for a specific guest molecule with an electron-accepting character. In this regard, the reversibility of the plane-to-bowl conversion should render this molecular system more attractive. In fact, the ^1H NMR experiments showed that $\mathbf{1}\cdot F^-/S(NMe_2)_3^+$ and $\mathbf{2}\cdot 2F^-/2S(NMe_2)_3^+$ can revert to the original neutral boranes **1** and **2** upon the addition of a stronger Lewis acid, such as $BF_3\cdot OEt_2$ (see SI).

In summary, we have succeeded in the synthesis of the planarized triarylboranes **1** and **2**. The most notable feature for these molecular systems is their high chemical stability, despite the absence of steric protection in the vertical direction with respect to the B atoms, demonstrating the efficacy of the concept of "kinetic stabilization by structural constraint". It should also be noted that, despite their inertness, the planarized boranes still maintain a Lewis acidity and undergo a plane-to-bowl conversion upon treatment with a fluoride ion. This unique structural change, induced by chemical stimulus, can be solely attributed to the presence of the electron-deficient B atom embedded in the 2D π scaffold, setting it apart from the conventional carbon-based 2D π scaffolds. The formation of a large and deep bowl structure, as well as the reversibility of the plane-to-bowl conversion, further enhances the attractiveness of the present molecular system. To pursue the multifaceted potentials of the present 2D π scaffolds, further studies on the synthesis of more complex systems employing the planarized triarylborane scaffold are now in progress in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, theoretical calculations, and X-ray structural analysis (PDF, CIF). 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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