

Diarylborenium Cations: Synthesis, Structure, and Electrochemistry

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Summary: Mes_2BF and $\text{Ar}^{\text{N}}_2\text{BF}$ ($\text{Ar}^{\text{N}} = 4-(\text{Me}_2\text{N})-2,6-\text{Me}_2-\text{C}_6\text{H}_2$) react with trimethylsilyltriflate and *p*-dimethylaminopyridine in chlorobenzene to afford the corresponding borenium salts $[\text{Mes}_2\text{B-DMAP}]^+ \text{OTf}^-$ ($[1]^+ \text{OTf}^-$) and $[\text{Ar}^{\text{N}}_2\text{B-DMAP}]^+ \text{OTf}^-$ ($[2]^+ \text{OTf}^-$), which have been fully characterized.

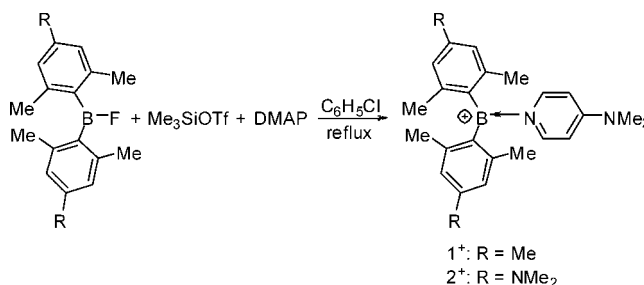
Introduction

Cationic boron derivatives continue to attract a great deal of attention because of their instability and reactivity.^{1–6} Diphenylborenium cations of general formula $[\text{Ph}_2\text{B-L}]^+$ (L = neutral ligand) provide a good example of such species, which had long been proposed but whose definitive characterization in solution has only recently been achieved.^{7–11} Despite these recent successes, diphenylborenium cations have not been structurally characterized. Furthermore, the acridine-9-boratrafluorenyl cation is the only structurally characterized example of a diarylborenium cation.¹² The difficulties encountered in the isolation of such cations can be correlated to the unsaturation of the boron center and the weak π -donating ability of the aryl groups. In an effort to overcome these limitations, we have probed the use of more sterically protecting aryl substituents featuring *o*-methyl groups. We have also probed the stabilizing effects that can be provided by remote amino-substituents appended to the aryl groups of diarylborenium cations.¹³

Results and Discussion

The reaction of Mes_2BF with trimethylsilyl triflate (Me_3SiOTf) and *p*-dimethylaminopyridine (DMAP) in refluxing chlorobenzene affords after 24 h $[\text{Mes}_2\text{B-DMAP}]^+ \text{OTf}^-$

Scheme 1



($[1]^+ \text{OTf}^-$) (Scheme 1).¹⁴ In an effort to determine the effect of remote amino-substituents on the stability of such borenium ions, we also synthesized $\text{Ar}^{\text{N}}_2\text{BF}$ ($\text{Ar}^{\text{N}} = 4-(\text{Me}_2\text{N})-2,6-\text{Me}_2-\text{C}_6\text{H}_2$) and converted it into $[\text{Ar}^{\text{N}}_2\text{B-DMAP}]^+ \text{OTf}^-$ ($[2]^+ \text{OTf}^-$) by following the method used for $[1]^+ \text{OTf}^-$. The formation of $[1]^+ \text{OTf}^-$ and $[2]^+ \text{OTf}^-$ was confirmed by ^1H NMR, which showed the presence of one DMAP ligand bound to the boron center. The ^1H NMR spectra of $[1]^+ \text{OTf}^-$ and $[2]^+ \text{OTf}^-$ are also different from those of $[\text{Mes}_2\text{BF-DMAP}]$ and $[\text{Ar}^{\text{N}}_2\text{BF-DMAP}]$, respectively, which could be generated in situ by simple mixing of the diarylboron fluoride with DMAP. Of special note, the ^1H NMR resonance of the Me_2N group of DMAP is shifted downfield by 0.36 ppm on going from $[\text{Mes}_2\text{BF-DMAP}]$ to $[1]^+ \text{OTf}^-$ and 0.31 ppm on going from $[\text{Ar}^{\text{N}}_2\text{BF-DMAP}]$ to $[2]^+ \text{OTf}^-$. These observations are in agreement with an ionic formulation for $[1]^+ \text{OTf}^-$ and $[2]^+ \text{OTf}^-$. This was confirmed by the detection of a ^{11}B NMR signal at 64 ppm for $[1]^+ \text{OTf}^-$ and 62 ppm for $[2]^+ \text{OTf}^-$. These chemical shifts are comparable to the value reported for $[(\text{C}_6\text{H}_5)_2\text{B}(\text{Py})]^+$ (58.2 ppm) which also features a tricoordinate boron atom.¹¹ While $[1]^+ \text{OTf}^-$ is isolated as colorless crystals, $[2]^+ \text{OTf}^-$ is an orange solid.

Bearing in mind that the only structurally characterized diarylborenium salt features a fused 9-boratrafluorenyl moiety,¹² we undertook the characterization of $[1]^+ \text{OTf}^-$ and $[2]^+ \text{OTf}^-$ by X-ray analysis. Both salts crystallize in the $P\bar{1}$ space group with two molecules in the unit cell. Both structures are very similar (Figure 1). The boron center of $[1]^+ \text{OTf}^-$ and $[2]^+ \text{OTf}^-$ is trigonal planar as indicated by the sum of the bond angles, which is equal to 360° in both cases. The B(1)–C(8) (1.560(3) Å in $[1]^+$, 1.550(4) Å in $[2]^+$) and B(1)–C(18) bonds (1.570(3) Å in $[1]^+$, 1.532(4) Å in $[2]^+$) connecting the aryl ligand to the boron centers are significantly shorter than the $\text{C}_{\text{Mes}}-\text{B}$ bonds measured in Mes_2BPh (1.579(2) Å),¹⁵ suggesting increased π -donation to the electron-deficient boron center. The average

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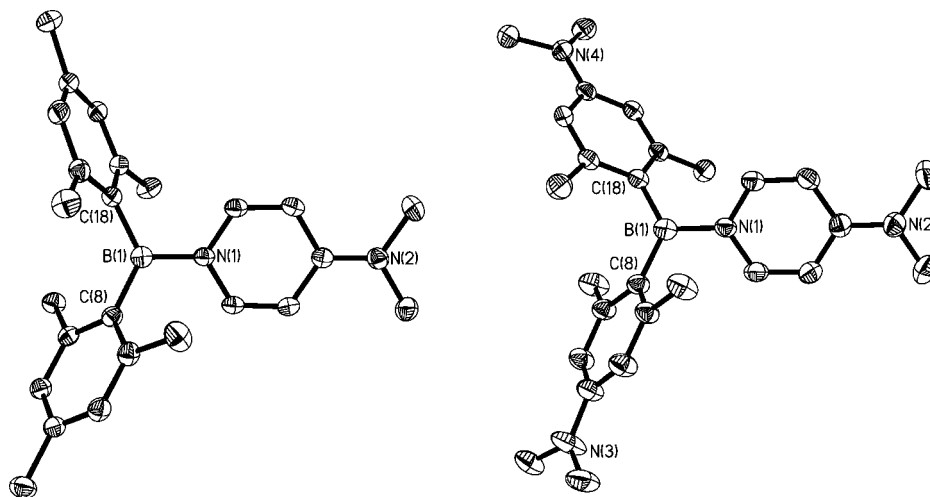


Figure 1. Crystal structure of $[1]^+$ and $[2]^+$ with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Pertinent metrical parameters can be found in the text.

dihedral angles θ formed between the boron trigonal plane and the plane containing the Mes ligand in $[1]^+$ and the Ar^{N} ligand in $[2]^+$ are respectively 58.1° and 48.3° . The slight shortening of the B(1)–C(8) and B(1)–C(18) bonds as well as the smaller θ angle observed for $[2]^+$ may be correlated to the stronger π -donating ability of the Ar^{N} ligand, a conclusion supported by the planarity of the N(3) and N(4) atoms ($\Sigma(\text{C–N–C}) = 359.8^\circ$ (N(3)) and 358.2° (N(4))). The B(1)–N(1) bonds connecting the DMAP ligand to the boron centers ($1.480(3)\text{Å}$ in $[1]^+$, $1.501(4)\text{Å}$ in $[2]^+$) in both structures are shorter than the value computed for $[(\text{C}_6\text{H}_5)_2\text{B}(\text{Py})]^+$ (1.552Å).¹¹ They are also shorter than the B–N_{DMAP} bond observed in $\text{Ar}^*\text{P}=\text{B}(\text{DMAP})\text{Tmp}$ ($\text{Ar}^* = \text{C}_6\text{H}_3\text{–}2,6\text{–}(\text{C}_6\text{H}_2\text{–}2,4,6\text{–iPr}_3)_2$; $\text{Tmp} = 2,2,6,6\text{-tetramethylpiperidine}$) and are in fact comparable to traditional B–N single bonds.^{16,17} The electron deficiency of the cationic boron center as well as the strong σ -donor character of the DMAP ligand are most certainly responsible for this feature.

In an attempt to better understand the properties of $[1]^+$ and $[2]^+$, we have studied their electrochemistry. As indicated by cyclic voltammetry, both $[1]^+$ and $[2]^+$ undergo an irreversible reduction at $E_{\text{peak}} -2.03$ and -2.30 V (vs Fc/Fc^+), respectively (Figure 2). Because of their increased electron deficiency, the reduction potentials of $[1]^+$ and $[2]^+$ are more positive than that of neutral boranes, such as Mes_3B , which is reduced at -2.73 V (vs Fc/Fc^+). It is also important to note that the reduction potential of $[1]^+$ is substantially more positive than that of $[2]^+$ once again indicating the greater donating ability of the Ar^{N} ligand. The redox behavior of these derivatives is different from that of neutral boranes which typically display a reversible one-electron reduction wave corresponding to the formation of stable radical anion.¹⁸ Hence, these results indicate that the radical $[\text{Mes}_2\text{B–DMAP}]^\bullet$ and $[\text{Ar}^{\text{N}}_2\text{B–DMAP}]^\bullet$ are not stable. It also suggests that radicals such as $[\text{Mes}_2\text{B–pyridine}]^\bullet$ whose generation has been attempted¹⁹ might be too unstable to actually observe in solution.²⁰

A geometry optimization of $[1]^+$ and $[2]^+$ with DFT methods (B3LYP, 6-31G*) affords structures that closely match those

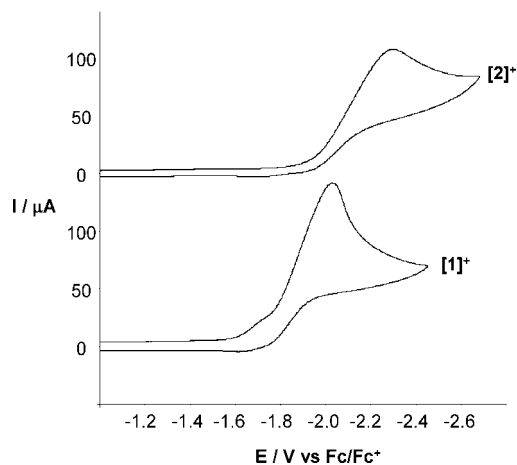


Figure 2. Cyclic voltammograms of $[1]^+$ and $[2]^+$ in CH_2Cl_2 with a glassy-carbon working electrode ($0.1\text{ M } n\text{Bu}_4\text{NPF}_6$) at scan rate of 300 mV s^{-1} .

observed experimentally. In both cases, the LUMO is localized on the boron atom and DMAP ligand (Figure 3). An evaluation of the orbital energies by using the PCM solvation model^{21,22} (solvent = CH_2Cl_2) indicates that the LUMO of $[1]^+$ is 0.37 eV lower than that of $[2]^+$. This energy difference is close to the results of our electrochemical measurements ($\Delta E_{\text{peak}(\text{red})} = 0.27\text{ V}$).

Experimental Section

General Considerations. Trimethylsilyl triflate (Me_3SiOTf) was purchased from TCI America and used without purification. *p*-Dimethylaminopyridine (DMAP) was purchased from Lancaster and used without purification. 4-Bromo-3,5-tetramethylaniline was synthesized by following a published procedure.²³ Chlorobenzene was dried over P_2O_5 under N_2 atmosphere and distilled prior to

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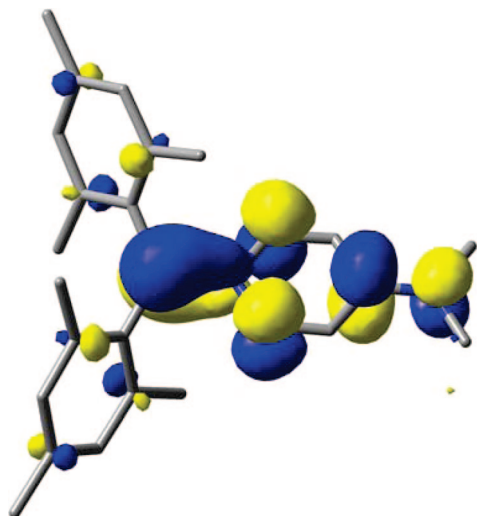


Figure 3. DFT optimized geometry of $[1]^+$ with an overlay of the LUMO (isovalue = 0.03, H-atoms omitted).

use. Air-sensitive compounds were handled under N_2 atmosphere, using standard Schlenk and glovebox techniques. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). NMR spectra were recorded on a Varian Unity Inova 400 FT NMR spectrometer (399.59 MHz for 1H , 375.95 MHz for ^{19}F , 128.2 MHz for ^{11}B , 100.5 MHz for ^{13}C). Chemical shifts δ are given in ppm, and are referenced against external Me_4Si (1H , ^{13}C), $BF_3 \cdot Et_2O$ (^{11}B), and $CFCl_3$ (^{19}F).

Synthesis of Ar^N_2BF ($Ar^N = 4-(Me_2N)-2,6-Me_2-C_6H_2$). 4-Bromo-3,5-tetramethylaniline (10 g, 0.04 mol) was allowed to react with excess Mg powder in THF (30 mL) at reflux for 5 h. Once the reaction mixture was cooled to room temperature, the THF solution was filtered and then slowly added into an Et_2O solution of $BF_3 \cdot OEt_2$ (2.7 mL, 0.02 mol) at $-78^\circ C$. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvents were then removed under reduced pressure and the solid residue was extracted with hexane (3×50 mL). The combined hexane fractions were dried under vacuum to afford a yellow solid. This solid was washed with hexane (5 mL) to afford Ar^N_2BF in moderate yield (3.8 g, 53%). This compound was used without further purification for the synthesis of $[2]^+OTf^-$ (vide infra). 1H NMR ($CDCl_3$, 399.59 MHz): δ 2.39 (d, 12H, *o*-Me), 3.06 (s, 12H, Ar^N-NMe_2), 6.46 (s, 4H, Ar^N-CH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 23.2 (*o*-Me), 40.0 (Ar^N-NMe_2), 111.3, 125.6, 144.4, 151.6. ^{19}F NMR ($CDCl_3$, 375.95 MHz): δ -23.4. ^{11}B NMR ($CDCl_3$, 128.2 MHz): δ 52.

Synthesis of $[1]^+OTf^-$. Dimesitylboron fluoride (0.60 g, 2.2 mmol), DMAP (0.23 g, 1.9 mmol), and Me_3SiOTf (0.34 mL, 1.9 mmol) were dissolved in 5 mL of chlorobenzene and heated at reflux overnight to give a colorless solution. Upon cooling, compound $[1]^+OTf^-$ precipitated and was isolated as a white solid by filtration. It was washed with Et_2O (10 mL) and dried under reduced pressure (0.78 g, 80% yield). Single crystals were obtained by slow cooling a hot chlorobenzene solution of $[1]^+OTf^-$ to $-40^\circ C$. 1H NMR ($CDCl_3$, 299.91 MHz): δ 2.01 (s, 12H, *o*-Me), 2.30 (s, 6H, *p*-Me), 3.43 (s, 6H, DMAP- NMe_2), 6.87 (s, 4H, Mes-CH), 7.00 (d, 2H, $^3J_{H-H} = 7.8$ Hz, DMAP-CH), 7.87 (d, 2H, $^3J_{H-H} = 7.8$ Hz, DMAP-CH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 21.3 (*o*-Me), 22.5 (*p*-Me), 41.3 (DMAP- NMe_2), 109.2, 122.3, 129.3, 133.2, 142.2, 143.9, 158.1. ^{11}B NMR ($CDCl_3$, 128.2 MHz): δ 64. Anal. Calcd for $C_{26}H_{32}BF_3N_2O_3S$: C, 60.01; H, 6.20. Found: C, 59.36; H, 6.16.

The sample could be further purified by an additional recrystallization from hot chlorobenzene. Anal. Calcd for $C_{26}H_{32}BF_3N_2O_3S$: C, 60.01; H, 6.20. Found: C, 60.16 H, 6.19.

Synthesis of $[2]^+OTf^-$. Ar^N_2BF (0.28 g, 0.85 mmol), DMAP (0.08 g, 0.65 mmol), and Me_3SiOTf (0.11 mL, 0.61 mmol) were dissolved in 5 mL of chlorobenzene and heated at reflux overnight to give an orange solution. After cooling to room temperature, addition of Et_2O (20 mL) resulted in the precipitation of $[2]^+OTf^-$ as an orange solid that was isolated by filtration. It was washed with Et_2O (10 mL) and dried under reduced pressure (0.24 g, 69% yield). Single crystals were obtained by vapor diffusion of Et_2O into a $CHCl_3$ solution of the $[2]^+OTf^-$. 1H NMR ($CDCl_3$, 399.59 MHz): δ 1.94 (s, 12H, *o*-Me), 2.98 (s, 12H, Ar^N-NMe_2), 3.36 (s, 6H, DMAP- NMe_2), 6.32 (s, 4H, Ar^N-CH), 6.91 (d, 2H, $^3J_{H-H} = 8.0$ Hz, DMAP-CH), 7.89 (d, 2H, $^3J_{H-H} = 8.0$ Hz, DMAP-CH). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 23.4 (*o*-Me), 39.8 (Ar^N-NMe_2), 40.9 (DMAP- NMe_2), 108.5, 111.7, 144.3, 152.4, 157.9. ^{11}B NMR ($CDCl_3$, 128.2 MHz): δ 62. Anal. Calcd for $C_{28}H_{38}BF_3N_4O_3S$: C, 58.13; H, 6.62. Found: C, 57.60; H, 6.56.

Electrochemistry. Electrochemical experiments were performed with an electrochemical analyzer from CH Instruments (Model 610A) with a glassy carbon working electrode and a platinum auxiliary electrode. The reference electrode was built from a silver wire inserted into a small glass tube fitted with a porous vycor frit at the tip and filled with a THF solution containing (*n*-Bu) $_4$ NPF $_6$ (0.1 M) and $AgNO_3$ (0.005 M). All three electrodes were immersed in a CH_2Cl_2 solution (5 mL) containing (*n*-Bu) $_4$ NPF $_6$ (0.1 M) as a support electrolyte and the analyte (7.7 mM for $[1]^+OTf^-$, 7.3 mM for $[2]^+OTf^-$). The electrolyte was dried under vacuum prior to use. In all cases, ferrocene was used as an internal standard, and all reduction potentials are reported with respect to the $E_{1/2}$ of the Fc/Fc^+ redox couple.

Crystallography. The crystallographic measurements were performed by using a Bruker APEX2 diffractometer, with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Specimens of suitable size and quality were selected and mounted onto glass fiber with apiezon grease. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 with use of the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. A summary of the pertinent crystallographic data follows:

Crystal data for $[1]^+OTf^-$: $C_{26}H_{32}BF_3N_2O_3S$, $M_r = 520.41$, $T = 140$ K, space group $P\bar{1}$, triclinic, $a = 8.2944(8)$ Å, $b = 10.4347(10)$ Å, $c = 16.1597(15)$ Å, $\alpha = 104.6880(10)^\circ$, $\beta = 96.8560(10)^\circ$, $\gamma = 100.4320(10)^\circ$, $V = 1310.3(2)$ Å 3 , $Z = 2$, $D_c = 1.319$ g cm $^{-3}$, $\mu(Mo K\alpha) = 0.175$ mm $^{-1}$, 15106 reflections measured, 6033 unique ($R_{int} = 0.0306$), $R_1 = 0.0575$, $wR_2 = 0.1185$.

Crystal data for $[2]^+OTf^- \cdot (OEt_2)_{0.5}$: $C_{30}H_{43}BF_3N_4O_{3.5}S$, $M_r = 615.55$, $T = 140$ K, space group $P\bar{1}$, triclinic, $a = 8.110(3)$ Å, $b = 13.043(4)$ Å, $c = 15.489(5)$ Å, $\alpha = 85.454(3)^\circ$, $\beta = 78.149(3)^\circ$, $\gamma = 83.434(4)^\circ$, $V = 1590.4(9)$ Å 3 , $Z = 2$, $D_c = 1.285$ g cm $^{-3}$, $\mu(Mo K\alpha) = 0.158$ mm $^{-1}$, 11305 reflections measured, 5861 unique ($R_{int} = 0.0295$), $R_1 = 0.0841$, $wR_2 = 0.1276$.

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Supporting Information Available: Computational details and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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