

# Synthesis and reactivity of $[N(C_6H_4Br)_3][B(C_6F_5)_4]$ : the X-ray crystal structure of $[Fe(C_5H_5)_2][B(C_6F_5)_4]$

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## Abstract

A new chemical oxidant  $[N(4-C_6H_4Br)_3][B(C_6F_5)_4]$ , was prepared and used to synthesize  $[Fe(C_5H_5)_2][B(C_6F_5)_4]$ . The crystal structure of  $[Fe(C_5H_5)_2][B(C_6F_5)_4]$  was determined.

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## 1. Introduction

Chemical oxidation has become quite popular in organometallic chemistry as a result of an increased desire to determine the species present in electron-transfer reactions [1]. One of the largest drawbacks to chemical oxidation is that undesired reactions can occur. The Magic Blue cation  $[N(4-C_6H_4Br)_3]^+$ , is a stable oxidant that typically does not lead to further reactions; however, the commercially available  $[N(4-C_6H_4Br)_3][SbCl_6]$  can suffer from complications due to the  $[SbCl_6]^-$  [1]. By using less reactive counter anions, these complications can be avoided [1].

There has been considerable growth in the use of bulky counter anions for electrochemical studies [2]. A variety of different anions have been investigated, including the tetrakis(pentafluorophenyl)borate ( $[B(C_6F_5)_4]^-$ ) anion which has been used in these labs [3]. Although signifi-

cantly more expensive,  $[B(C_6F_5)_4]^-$  provides many advantages over typical counter anions such as  $[PF_6]^-$  or  $[BF_4]^-$ . One of the most significant advantages is that  $[B(C_6F_5)_4]^-$  is relatively non-coordinating and can increase the solubility of highly charged cations [2e]. In addition  $[B(C_6F_5)_4]^-$  is less nucleophilic than other anions and is therefore, more likely to remain an innocent spectator in solution [2e].

There are a surprising limited number of methods for preparing compounds containing  $[B(C_6F_5)_4]^-$ , and none of those compounds are ideal chemical oxidants. The lithium salt is commercially available and can be used in metathesis reactions to prepare the tetrabutylammonium [2d] and silver salts [4]. Although the silver salt can serve as a chemical oxidant, oxidations using silver salts are unpredictable [1]. The trityl salt of  $[B(C_6F_5)_4]^-$  has also been synthesized [5]. While trityl salts can act as chemical oxidants, they more typically react as electrophiles [1]. Finally, tetrakis(pentafluorophenyl)boric acid has been prepared and is useful in preparing  $[B(C_6F_5)_4]^-$  salts of compounds that can be protonated [4].

Herein, we report the synthesis and characterization of two new chemical oxidants  $[N(4-C_6H_4Br)_3][B(C_6F_5)_4]$  (**1**), and  $[Fe(C_5H_5)_2][B(C_6F_5)_4]$  (**2**). In addition, the X-ray crystal structure of **2** was determined at three different temperatures.

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## 2. Results and discussion

Compound **1** was prepared in good yield by reacting  $[\text{Ag}][\text{B}(\text{C}_6\text{F}_5)_4]$  with  $\text{N}(4\text{-C}_6\text{H}_4\text{Br})_3$  in DCM in the presence of iodine. This preparation is a slight modification of the general method reported for other triarylaminium salts which are performed in ether [6]. Compound **1** is deep blue in color and is unstable in the presence of iodine in ether, forming a brown precipitate that was not characterized. Cyclic voltammetry was used to determine the oxidation potential of **1**, 0.68 V vs.  $\text{Fc}^{0/+}$  in DCM containing  $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$  as the supporting electrolyte. This value is similar to the oxidation potential of 0.70 V vs.  $\text{Fc}^{0/+}$  in DCM with  $[\text{NBu}_4][\text{PF}_6]$  as the supporting electrolyte [1]. The wave is reversible through all scan rates employed in this study.

Table 1  
Crystal data and structure analysis results

	$[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$
Empirical formula	$\text{C}_{34}\text{H}_{10}\text{BF}_{20}\text{Fe}$
Formula weight	865.08
Temperature (K)	100(2)
Wavelength Å	0.71073
Crystal system	Tetragonal
Space group	$P\bar{4}$
Unit cell dimensions	
<i>a</i> (Å)	19.4709(8)
<i>b</i> (Å)	19.4709(8)
<i>c</i> (Å)	8.0309(5)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume Å <sup>3</sup>	3044.6(3)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (mg/m <sup>3</sup> )	1.887
Absorption coefficient (mm <sup>-1</sup> )	0.647
<i>F</i> (000)	1700
Crystal size (mm <sup>3</sup> )	0.36 × 0.20 × 0.10
$\theta$ Range for data collection (°)	1.48–27.50
Data collected	
<i>h</i>	–25 to 24
<i>k</i>	–25 to 15
<i>l</i>	–10 to 10
Reflections collected	18602
Independent reflections	6940
[ <i>R</i> (int) = 0.0290]	
Completeness to $\theta = 27.50$ (%)	99.8
Absorption correction	SADABS/MULTI-SCAN
Maximum and minimum transmission	0.9381 and 0.8005
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	6940/0/506
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.013
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0332, <i>wR</i> <sub>2</sub> = 0.0808
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0380, <i>wR</i> <sub>2</sub> = 0.0836
Absolute structure parameter	0.00(8)
Largest difference peak and hole (e Å <sup>-3</sup> )	0.477 and –0.202

To explore the synthetic utility of **1**, the oxidation of ferrocene to give ferrocenium tetrakis(pentafluorophenyl)borate, **2**, was examined. The reaction proceeds efficiently giving **2** in high yield. The structure of **2** was determined at 100 K (Table 1) and the Cp rings of the ferrocenium cation are nearly eclipsed (Fig. 1). The eclipsed conformation of the Cp rings has been observed in the trigonal structure of  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{AsF}_6]$  [7] while the staggered form is seen in  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{PF}_6]$  [8]  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]$  [9] and the monoclinic structure of  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{AsF}_6]$  [7]. The average Fe–C distance in **2** is 0.005 Å longer than the corresponding distance in ferrocene while the Fe–centroid distance is 0.035 Å longer [10]; these distances are similar to other ferrocenium salts [8,11] (Table 2).

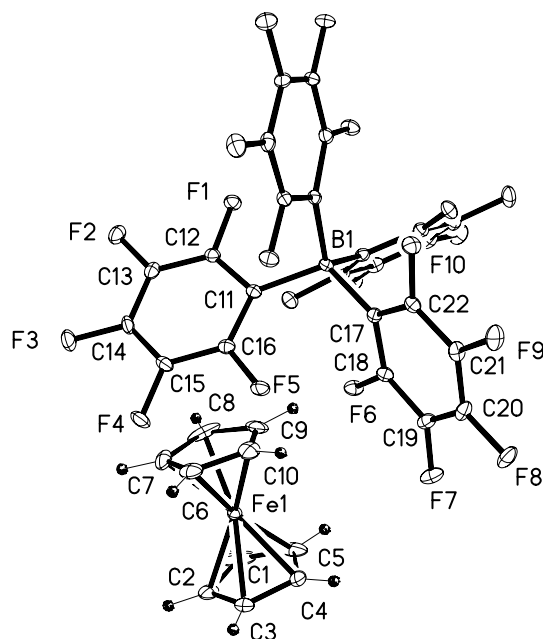


Fig. 1. ORTEP diagram of  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ . The thermal ellipsoids are drawn at the 30% level.

Table 2  
Selected bond angles (°) and lengths (Å) for  $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$

Bond lengths (Å)	
Fe–C <sub>Cp</sub> (avg.)	2.077
C <sub>Cp</sub> –C <sub>Cp</sub> (avg.)	1.392
B–C <sub>Ph</sub> (avg.)	1.653
C <sub>Ph</sub> –F (avg.)	1.348
C <sub>Ph</sub> –C <sub>Ph</sub> (avg.)	1.383
Fe–Cent. (avg.)	1.707
Bond angles (°)	
C <sub>Cp</sub> –C <sub>Cp</sub> –C <sub>Cp</sub> (avg.)	119.99
Cent.–Fe–Cent.	179.1
C <sub>Ph</sub> –B–C <sub>Ph</sub> (avg.)	110.4
C <sub>1</sub> –Cent.–Cent.–C <sub>8</sub>	8.9

Table 3  
Select hydrogen bonding angles (°) and lengths (Å) for [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

C–H...F	C–H	H...F	C...F	∠(CHF)
C(1)–H(1A)...F(14a)	1.00	2.37	3.321(3)	159.4
C(2)–H(2A)...F(5b)	1.00	2.46	3.015(3)	114.5
C(3)–H(3A)...F(17)	1.00	2.49	3.195(3)	127.2
C(5)–H(5A)...F(13c)	1.00	2.34	3.285(3)	157.5
C(7)–H(7A)...F(8b)	1.00	2.44	3.407(3)	162.5
C(8)–H(8A)...F(15a)	1.00	2.40	3.284(3)	146.8
C(10)–H(10A)...F(6)	1.00	2.32	3.132(3)	137.9

Intermolecular interactions similar to those associated with weak hydrogen bonding were noted between the hydrogen atoms and adjacent fluorine atoms (Table 3). Similar interactions have been noted in the structures of [Cp<sub>2</sub>Co][PF<sub>6</sub>], [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>] and [(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr][PF<sub>6</sub>] [7]. In the structure of **2** there are four C–H–F distances in the range of 2.3–2.4 Å. A similar number of C–H–F lengths in the same range have been observed for [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>] [9b]. While the structure of **2** displays similar C–H–F lengths [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> provides 20 fluorine atoms to interact with as opposed to the six in PF<sub>6</sub>; it may be the large number of fluorine atoms in **2** that are responsible for the short C–H–F distances.

### 3. Conclusion

A new chemical oxidant [N(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**1**), was prepared and characterized by electrochemistry and UV–Vis spectroscopy. The reaction of ferrocene with **1** produces [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**2**), which was characterized by UV–Vis spectroscopy and X-ray crystallography. The Cp rings of **2** are eclipsed and there appears to be hydrogen bonding between the Cp hydrogen atoms and the fluorine atoms of the anion, which may be due to the large number of fluorine atoms in [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>.

### 4. Experimental

Ferrocene was purchased from Strem and sublimed prior to use. Silver nitrate and tris(4-bromophenyl)amine were purchased from Aldrich and used without additional purification. Lithium tetrakis(pentafluorophenyl)borate diethyl etherate (Li[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) was purchased from Boulder Scientific. Li[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was used to prepare [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], according to literature preparation [2d].

All solvents were purified by standard methods under an atmosphere of nitrogen. Diethyl ether was distilled over potassium benzophenone ketyl while hexanes and dichloromethane (DCM) were refluxed over CaH<sub>2</sub> and then distilled. HPLC grade DCM from Aldrich was

distilled from CaH<sub>2</sub> under argon before use in electrochemical experiments. UV–Visible spectra were obtained on a Varian Carey 300B UV–Vis spectrometer and are reported as λ<sub>max</sub> (nm) (ε, M<sup>−1</sup> cm<sup>−1</sup>).

#### 4.1. Synthesis

##### 4.1.1. [Ag][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]

Was prepared according to the literature procedure [4].

##### 4.1.2. [N(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**1**)

In the dark [Ag][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.23 g, 0.29 mmol) and tris(4-bromophenyl)amine (0.16 g, 0.32 mmol) were dissolved in 15.0 mL of DCM, and this solution was allowed to stir for 10 min. In a separate flask, 1.5 mL of hexanes were added to I<sub>2</sub> (0.019 g, 0.074 mmol), and this solution was added to the DCM solution. The reaction quickly turned from colorless to deep blue. This mixture was allowed to stir for 30 min to ensure complete reaction. The solution was then filtered via filter cannula into a flask, and hexanes (40.0 mL) were added giving a fine blue precipitate. The flask was placed in the freezer for 30 min, and then the solution was filtered, leaving behind a blue solid, **1** (0.25 g, 0.21 mmol, 66%). The solid was dried in vacuo to ensure complete dryness and stored in the freezer until use. *Anal.* Calcd. for C<sub>42</sub>H<sub>12</sub>BBR<sub>3</sub>F<sub>20</sub>N · 3/4CH<sub>2</sub>Cl<sub>2</sub>: C, 41.92; H, 1.07; N, 1.14. Found: C, 42.00; H, 1.37; N, 0.95%. UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>): 729 nm (~25,000).

##### 4.1.3. [Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**2**)

A solution of ferrocene (0.0074 g, 0.040 mmol) in 2.0 mL of DCM was added dropwise to a solution of **1** (0.0419 g, 0.036 mmol) in 2.0 mL of DCM. Upon mixing, the solution turned blue–green. The reaction was allowed to stir for 10 min. It was then reduced to approximately 2 mL in vacuo and layered with 10.0 mL of ether. The flask was placed in a freezer overnight, and red–violet crystals of **2** formed. The crystals were collected and dried under vacuum yielding 0.044 g (90%) of **2**. X-ray quality crystals were obtained using this method, however those crystals were not dried in vacuo. *Anal.* Calcd. for C<sub>34</sub>H<sub>10</sub>BFeF<sub>20</sub> · 1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 45.66; H, 1.22. Found: C, 45.75; H, 1.13%.

#### 4.2. Electrochemistry

Cyclic voltammetric studies were done with a Princeton Applied Research 263-A potentiostat. The electrochemical data were obtained and analyzed by Power Suite. The solution of the analyte was 1.0 mM in 10.0 mL of DCM and contained 0.1 M [NBu<sub>4</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as the supporting electrolyte. The solution was purged with argon and stirred prior to study. A blanket of argon was kept over the solution for all

experiments. Scans were made at rates of 50, 100, 500, and 1000 mV/s. The 1.5 mm glassy carbon working electrode was polished with a 1- $\mu\text{m}$  diamond paste, rinsed with acetone, and then polished with 1/4  $\mu\text{m}$  diamond paste. Prior to use, the working electrode was rinsed with acetone and then DCM. A platinum wire counter electrode was used along with a non-aqueous silver/silver chloride reference electrode. The potential was referenced to the ferrocene/ferrocenium couple.

#### 4.3. X-ray crystallography

A purple crystal of **2** was cut from a block of crystals and mounted on a glass fiber with Paratone-N oil. X-ray data were collected on a Siemens/Bruker P4/CCD – Apex system at 100 K in a stream of nitrogen gas. Diffraction data indicated a tetragonal crystal system, and the solution statistics indicated *P4* space group. The structure was solved by direct methods, and all non-hydrogen atoms were refined as anisotropic by least-squares Fourier analyses. All hydrogen atoms were placed in calculated positions and their  $U_{\text{iso}}$  were set to 1.2 times that of the carrier atoms. Data were corrected for absorption using SADABS. All programs used in the structural solution and refinement are part of the SHELXL package and are available from Bruker AXS, Inc. (Madison, Wisconsin).

#### 5. Supplementary material

Crystallographic data (CIF files) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 230042. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www.ccdc.cam.ac.uk>).

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