

Synthesis and Structure of a Ferrocenylboron Dication

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Treatment of the borane Br_2BFc (Fc = ferrocenyl) with the Lewis base 4-methylpyridine and $\text{Na}[\text{BAR}^f_4]$ [$\text{Ar}^f = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$] afforded the boron dication $[\text{FcB}(\text{NC}_5\text{H}_4\text{-4-Me})_3][\text{BAR}^f_4]_2$. This compound is a rare example of a structurally characterized boron dication.

Cationic boron compounds have attracted considerable interest in recent years¹ because of their potential as catalysts in polymerization² and Diels–Alder³ reactions or as initiators in the dehydrogenation of ammonia–borane.⁴ Three types of cationic boron derivatives are established, known as boronium $[\text{R}_2\text{BL}_2]^+$, borenium $[\text{R}_2\text{BL}]^+$, and borinium $[\text{R}_2\text{B}]^+$ ions.^{1b} In these compounds, boron has a formal oxidation state of III+ and is bound to two substituents R with a varying number (0–2) of Lewis bases L. Boron dications of the type $[\text{L}_3\text{BR}]^{2+}$ and trications $[\text{L}_4\text{B}]^{3+}$ have been known for years;⁵ however, molecular structures are rarely known, and only a handful of examples have been reported recently. Cowley and co-workers reported the β -diketiminato dication **1**,⁶ in which the boron atom is surrounded by four nitrogen atoms. The group of Himmel synthesized the unusual dimeric boron dication **2**, in which the boron centers have the formal oxidation state of II+ (Figure 1).⁷

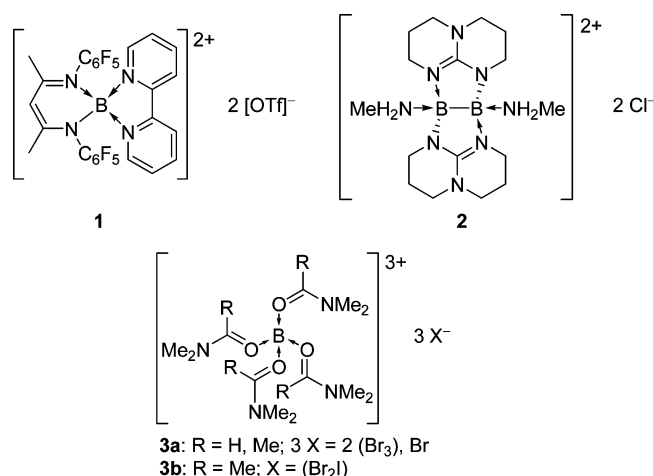


Figure 1. Different structurally characterized boron di- and trications.

Two boron trications, **3a** and **3b**, with four oxygen donor ligands coordinated to the boron atom were published by Danan et al.⁸ Herein we report the synthesis of $[\text{FcB}(\text{NC}_5\text{H}_4\text{-4-Me})_3][\text{BAR}^f_4]_2$ [**4**; Fc = ferrocenyl, $\text{Ar}^f = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$], the second example of a structurally characterized mononuclear boron(III) dication, however, the first without chelating ligands. This compound was prepared by treating Br_2BFc with 4-methylpyridine and $\text{Na}[\text{BAR}^f_4]$ in a molar ratio of 1:3:2. The reaction was performed in CH_2Cl_2 or CDCl_3 with heating at 45 or 65 °C, respectively, for 10 days. During this time, orange crystals precipitated and were separated and recrystallized from CH_2Cl_2 /hexane at -35 °C in order to remove NaBr. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the isolated product shows a sharp singlet at $\delta -7.6$ ppm for the $[\text{BAR}^f_4]$ anion and a broad signal at $\delta 8.2$ ppm for the boron dication, which is comparable to **1** ($\delta 6.4$ ppm)⁶ and other boronium cations.^{1b,5b} In the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, corresponding signals have been observed for the ferrocenyl group, the 4-methylpyridine ligand, and the $[\text{BAR}^f_4]$ anions (Figure 2).

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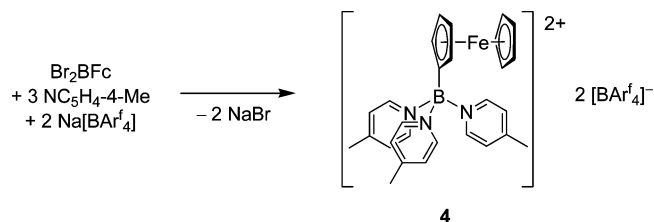


Figure 2. Synthesis of the boron dication **4**.

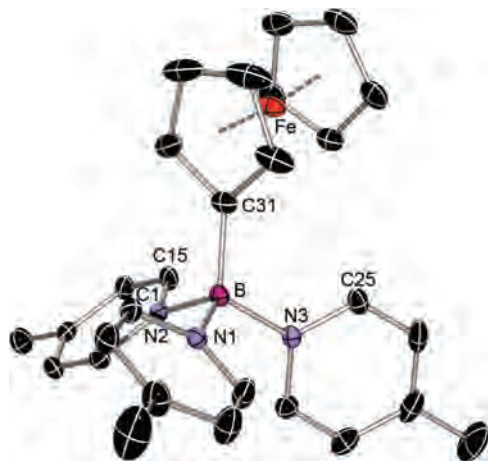


Figure 3. Molecular structure of **4**. The two $[\text{BARf}_4]^-$ counterions and hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability. Selected bond lengths [Å] and angles [deg]: B–N1 1.595(4), B–N2 1.586(4), B–N3 1.591(4), B–C31 1.584(4), C31–B–N3–C25 15.1(4), C31–B–N1–C1 54.3(3), C31–B–N2–C15 58.5(3).

As expected, three resonances can be detected in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for the ferrocenyl group [^1H NMR δ 4.69 (m, $\text{C}_5\text{H}_4\text{B}$), 3.71 (m, $\text{C}_5\text{H}_4\text{B}$), 4.05 (s, C_5H_5) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR δ 74.6 (s, $\text{C}_5\text{H}_4\text{B}$), 74.5 (s, $\text{C}_5\text{H}_4\text{B}$), 70.8 (s, C_5H_5) ppm; C^{ipso} of $\text{C}_5\text{H}_4\text{B}$ is not located] and signals for 4-methylpyridine [^1H NMR δ 8.18 (d, $^3J_{\text{H-H}} = 7$ Hz), 7.80 (d, $^3J_{\text{H-H}} = 7$ Hz), 2.66 (s, Me) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR δ 164.6 (s, C^{para}), 144.0 (s, C^{ortho}), 130.0 (s, C^{meta}), 22.8 (s, Me) ppm], which show chemical shifts similar to those of $[\text{B}(\text{NC}_5\text{H}_4\text{-4-Me})_4]\text{Br}_3$ in D_2O [^1H NMR δ 8.60 (br s), 8.19 (d, $^3J_{\text{H-H}} = 7$ Hz), 2.85 (s, Me) ppm]^{5d} or *trans*- $[(\text{C}_3\text{P})_2\text{Pt}(\text{Br})\{\text{B}(\text{NC}_5\text{H}_4\text{-4-Me})\text{Fc}\}][\text{BARf}_4]^-$ [$^{13}\text{C}\{^1\text{H}\}$ NMR δ 163.5 (s, C^{para}), C^{ortho} was not located, 127.6 (br s, C^{meta}), 22.8 (s, Me) ppm].

Single crystals of compound **4** (Figure 3) were analyzed by X-ray diffraction and confirmed the constitution assigned on the basis of spectroscopic data.¹⁰

Compound **4** crystallizes in the triclinic space group $P\bar{1}$ and shows dications, which are fully separated from the counteranions. The boron atom in the dication is coordinated tetrahedrally by the ferrocenyl moiety and three molecules of 4-methylpyridine, the latter of which are twisted propeller-like [C31–B–N3–C25 15.1(4)°, C31–B–N1–C1 54.3(3)°, and C31–B–N2–C15 58.5(3)°]. The B–N distances [1.595(4), 1.586(4), and 1.591(4) Å] are comparable to those in **1** [bipyridine: 1.605(10) and 1.578(9) Å]⁶ and **2**

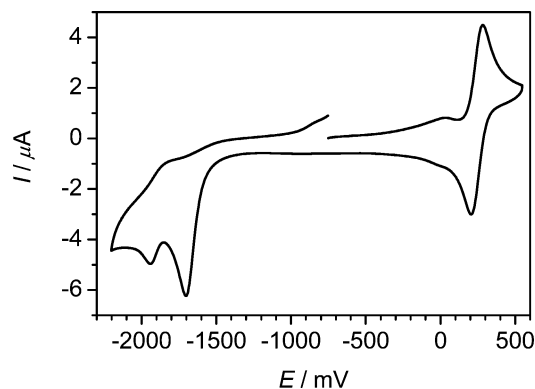


Figure 4. Cyclic voltammogram of **4** (0.4 mM) recorded at a platinum disk electrode in dichloromethane/tetrabutylammonium perchlorate (0.2 M) and referenced against Fc/Fc^+ . Scan rate: $\nu = 0.2 \text{ V s}^{-1}$.

[1.539(4)–1.606(4) Å],⁷ thus indicating corresponding single bonds. Likewise, the B–C bond length [1.584(4) Å] is in line with a typical B–C single bond.¹¹

Related monocationic compounds were prepared by Wagner and co-workers.¹² The UV–vis spectrum of **4** in dichloromethane shows a λ_{max} value of 432 nm, which is comparable to those of ferrocene ($\lambda_{\text{max}} = 440$ nm) and $[\text{FcBMe}(\text{NC}_5\text{H}_4\text{-4-Me})_2]\text{Br}$ ($\lambda_{\text{max}} = 448$ nm; acetonitrile).^{12a}

Cyclic voltammetric (CV) measurements of compound **4** in dichloromethane (0.4 mM) with tetrabutylammonium perchlorate as the supporting electrolyte (0.2 M) revealed one reversible oxidation at $E_{1/2} = +240$ mV vs Fc/Fc^+ and two irreversible reductions at $E_{\text{pc}}^1 = -1700$ mV and $E_{\text{pc}}^2 = -1940$ mV (Figure 4). Reduction of **4** to the monocation under thin-layer conditions leads to a loss of the oxidation signal due to decomposition of **4**. The reversibility of the oxidation process is proven by (i) the ratio of the anodic and cathodic peak currents $i_{\text{pa}}/i_{\text{pc}}$, which is equal to 1.05 for different scan rates ranging from 0.02 to 1 V s^{-1} , (ii) the peak separation of anodic and cathodic waves, which is

- (10) The crystal data of **4** were collected on a Bruker X8Apex diffractometer with a CCD area detector and multilayer mirror-monochromated $\text{Mo K}\alpha$ radiation. The structure was solved using direct methods, refined with the *SHELX* software package (G. Sheldrick, University of Göttingen, 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystal data for **4**: $\text{C}_{92}\text{H}_{54}\text{B}_3\text{F}_{48}\text{FeN}_3$, $M_r = 2201.66$, orange block, $0.210 \times 0.205 \times 0.200$, triclinic space group $P\bar{1}$, $a = 13.1283(4)$ Å, $b = 13.4927(4)$ Å, $c = 26.7028(8)$ Å, $\alpha = 86.4180(10)^\circ$, $\beta = 84.8160(10)^\circ$, $\gamma = 78.3220(10)^\circ$, $V = 4608.4(2)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.587 \text{ g cm}^{-3}$, $\mu = 0.310 \text{ mm}^{-1}$, $F(000) = 2200$, $T = 100(2)$ K, $R_1 = 0.0611$, $wR_2 = 0.1319$, 17 959 independent reflections [$2\theta \leq 52.04^\circ$] and 1385 parameters. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 687804. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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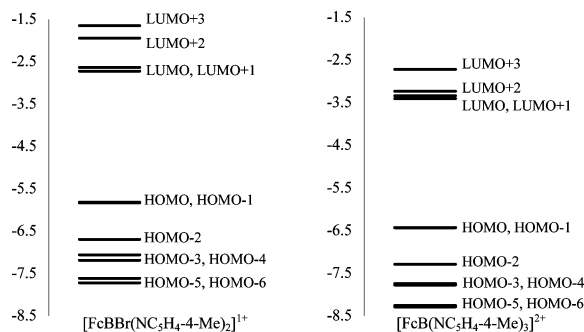


Figure 5. Energy diagram [eV] for the frontier orbitals of $[\text{FcBBr}(\text{NC}_5\text{H}_4\text{-4-Me})_2]^+$ (left) and $[\text{FcB}(\text{NC}_5\text{H}_4\text{-4-Me})_3]^{2+}$ (right). B3LYP/SVP results.

between 60 and 80 mV for various scan rates, and (iii) the linear dependency of $v^{1/2}$ vs i_{pa} in the aforementioned range of scan rates. Moreover, the oxidation process is fully reversible under thin-layer conditions. Compared to the tetracoordinated boronium monocation $[\text{FcBMe}(2,2'\text{-bipy})]^+$ (bipy = 2,2'-bipyridine) reported by Wagner et al.,^{12a} the ferrocene-based oxidation of the boron dication **4** is shifted by about 260 mV to higher potentials.

This is in accordance with the observed trend of increasing oxidation potentials for the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox process in going from a monoanionic species $[\text{Fc}_2\text{BMe}_2]^-$ (−430 mV)¹³ to a neutral compound $[\text{FcBMe}_2(\text{NC}_5\text{H}_4\text{-4-Me})]$ (−330 mV)¹⁴ and to a monocationic compound $[\text{FcBMe}_2(\text{NC}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NC}_3\text{H}_7)]^+$ (−250 mV).¹⁴ However, the type of borane substituent also has a great impact on the oxidation potentials, as can be inferred from the strongly differing potentials of the monocationic compounds $[\text{FcBMe}_2(\text{NC}_5\text{H}_4\text{-4-C}_5\text{H}_4\text{NC}_3\text{H}_7)]^+$ (−250 mV) and $[\text{FcBMe}(2,2'\text{-bipy})]^+$ (−20 mV).

Quantum-Chemical Calculations. Structure optimizations for $[\text{FcB}(\text{NC}_5\text{H}_4\text{-4-Me})_3]^{2+}$ and for the monocation $[\text{FcBBr}(\text{NC}_5\text{H}_4\text{-4-Me})_2]^+$ have been performed in a polarizable continuum solvent model (COSMO)¹⁵ for dichloromethane ($\epsilon = 8.93$) with the *Turbomole 5.10* program package¹⁶ at the B3LYP/SVP density functional theory (DFT) level.¹⁷ The optimized B–C and B–N bond lengths deviate by less than 0.02 Å from the crystal structure. Figure 5 shows frontier orbital diagrams for the two cations.

The highest occupied molecular orbital energy of the dication **4** is at −6.43 eV, 0.81 eV lower than that for the monocation $[\text{FcBBr}(\text{NC}_5\text{H}_4\text{-4-Me})_2]^+$, indicating a higher oxidation energy for the dication. Quantitative agreement with differences in oxidation potentials at this level is not to be expected. Qualitatively, the shift of the potential in **4** to

higher values due to the dipositive charge is reproduced. The highest occupied molecular orbital–lowest unoccupied molecular orbital gaps of the two cations differ very little however (3.10 eV for the monocation and 3.02 eV for **4**).

In conclusion, we prepared and fully characterized the second mononuclear boron dication $[\text{FcB}(\text{NC}_5\text{H}_4\text{-4-Me})_3]^{2+}$, in which the boron atom is bound to a ferrocenyl group and three 4-methylpyridine molecules. CV and DFT methods revealed an increased oxidation potential of the title compound in comparison with corresponding monocationic ferrocene species.

Experimental Part. 4: A red solution of $\text{Br}_2\text{BFc}^{18}$ (0.020 g, 0.056 mmol) in CDCl_3 (0.6 mL) was treated with 4-methylpyridine (0.020 g, 0.215 mmol) and $\text{Na}[\text{BAr}^f_4]$ (0.100 g, 0.112 mmol). The mixture turned orange and was heated at 65 °C over a period of 10 days. During that time, red-orange crystals formed, which were separated, dissolved in CH_2Cl_2 , and separated from NaBr by filtration. Layering with hexane (0.2 mL) and cooling to −35 °C yielded crystals of pure **4** (0.060 g, 50%).

¹H NMR (500 MHz, CD_2Cl_2 , 24 °C): δ 8.18 (d, $^3J_{\text{H-H}} = 7$ Hz, 6H, $\text{NC}_5\text{H}_4\text{-4-Me}$), 7.80 (d, $^3J_{\text{H-H}} = 7$ Hz, 6H, $\text{NC}_5\text{H}_4\text{-4-Me}$), 7.72 (m, 16H, BAr^f_4), 7.55 (br s, 8H, BAr^f_4), 4.69 (m, 2H, $\text{C}_5\text{H}_4\text{B}$), 3.71 (m, 2H, $\text{C}_5\text{H}_4\text{B}$), 4.05 (s, 5H, C_5H_5), 2.66 (s, 9H, Me, $\text{NC}_5\text{H}_4\text{-4-Me}$). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2 , 24 °C): δ 164.6 (s, C^{para} , $\text{NC}_5\text{H}_4\text{-4-Me}$), 162.1 (q, $^1J_{\text{C-B}} = 50$ Hz, C^{ipso} , BAr^f_4), 144.0 (s, C^{ortho} , $\text{NC}_5\text{H}_4\text{-4-Me}$), 135.2 (br s, C^{ortho} , BAr^f_4), 130.0 (s, C^{meta} , $\text{NC}_5\text{H}_4\text{-4-Me}$), 129.2 (qq, $^2J_{\text{C-F}} = 31$ Hz, $^3J_{\text{C-B}} = 3$ Hz, C^{meta} , BAr^f_4), 125.0 (q, $^1J_{\text{C-F}} = 272$ Hz, CF_3 , BAr^f_4), 117.9 (sep, $^3J_{\text{C-F}} = 4$ Hz, C^{para} , BAr^f_4), 74.6 (s, $\text{C}_5\text{H}_4\text{B}$), 74.5 (s, $\text{C}_5\text{H}_4\text{B}$), 70.8 (s, C_5H_5), 22.8 (s, Me, $\text{NC}_5\text{H}_4\text{-4-Me}$), C^{ipso} of $\text{C}_5\text{H}_4\text{B}$ is not located. ¹¹B{¹H} NMR (160 MHz, CD_2Cl_2 , 24 °C): δ 8.2 (br s), −7.6 (s, BAr^f_4). Anal. Calcd for $\text{C}_{92}\text{H}_{54}\text{N}_3\text{B}_3\text{F}_4\text{Fe}$: C, 50.19; H, 2.47; N, 1.91. Found: C, 50.01; H, 2.48; N, 2.20.

CV. A BAS CV-50 W electrochemical workstation was used together with a three-electrode setup consisting of a platinum-disk working electrode (2 mm in diameter), an Ag/AgCl pseudoreference electrode, and a platinum-wire counter electrode. Measurements were performed in dichloromethane (Baker, HPLC grade, predried over molecular sieve 3 Å and distilled over CaH_2) with tetrabutylammonium perchlorate (0.2 M) as the supporting electrolyte. For thin-layer conditions, the working electrode was placed onto a mobile glass hemisphere.¹⁹

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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