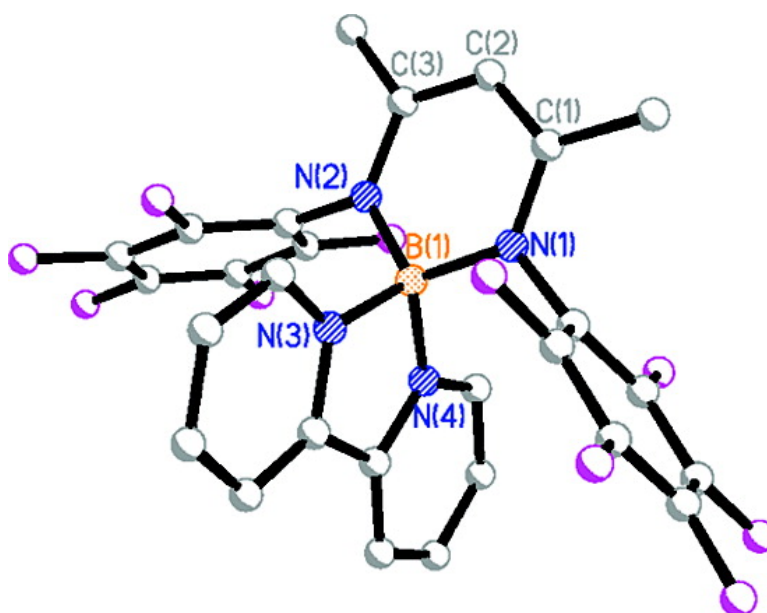


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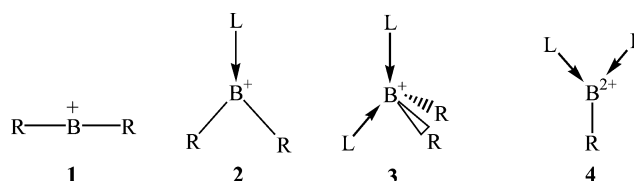
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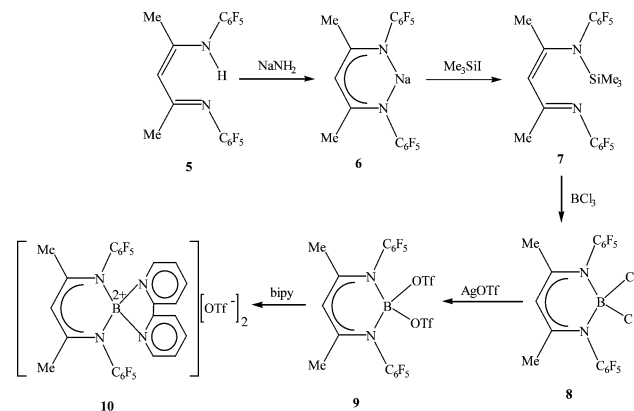
The characteristic acceptor property of boranes (BR_3) has spawned a wide variety of uses for such compounds, ranging from fluoride anion detectors¹ to reagents for the synthesis of pharmaceuticals and other valuable products.² In general, cationic boron compounds are expected to be significantly more potent acceptors than the corresponding neutral compounds, thus portending a new generation of catalysts and reagents with enhanced activities. At the present time, three types of boron monocations have been identified (Chart 1). Cations **1**, **2**, and **3** are typically referred to by the names borinium, borenium, and boronium, respectively.³ As expected on the basis of their low coordination number and the fact that the boron atom has only four valence electrons, borinium ions are highly reactive and usually studied in the gas phase. At the other extreme, boronium cations feature eight valence electrons and are therefore coordinatively saturated. Such cations can, however, be rendered catalytically active if one of the ancillary ligands is labile.⁴

The purpose of the present communication is to disclose the synthesis and characterization of the first example of a new class of boron cation, namely, a mononuclear boron dication (**4** in Chart 1). In selecting a supporting ligand, R, for the target dication, we opted for a β -diketiminato ancillary framework since such a coordination environment has proved to be effective for the stabilization of a wide range of p-, d-, and f-block fragments in a variety of oxidation states.⁵ The overall strategy for the synthesis of the targeted boron dication is outlined in Scheme 1. Deprotonation of the iminoamine **5** with NaNH_2 afforded the sodium derivative **6** which was isolated and characterized by ^1H and ^{19}F NMR spectroscopy. The structure of **6** is depicted with a bidentate ligand bonding mode by analogy with structurally characterized β -diketiminato lithium salts.⁷ Treatment of **6** with Me_3SiI produced **7** which was characterized by multinuclear NMR and high-resolution mass spectroscopy. In turn, the new boron dichloride **8** was prepared via the reaction of **7** with BCl_3 . Treatment of **8** with AgOTf resulted in the formation of the boron bis(triflate) **9**, which was also structurally characterized (Figure 1). The focal point of interest in the structure of **9** was to determine the extent, if any, of dicationic character. In terms of the range of boron–oxygen distances available from the Cambridge Structural Data Base, the $\text{B}(1)\text{--O}(1)$ bond distance for **9** of 1.496(5) Å is close to the mean B--O value of 1.440 Å. However, the $\text{B}(1)\text{--O}(4)$ bond distance (1.562(7) Å) is ~ 0.07 Å longer than the $\text{B}(1)\text{--O}(1)$ separation and thus suggestive of incipient ionization toward the monocation $[\text{LBOTf}]^+[\text{OTf}]^-$. Interestingly, when CD_3CN is added to **9**, the ^{11}B NMR resonance at δ 0.25 decays and a new peak at δ 21.2 emerges. Possibly, this is due to CD_3CN -promoted extrusion of one of the triflate anions. It was clear, however, that it would be necessary to employ a bidentate base to effect the removal of both triflate anions. Treatment of **9** with 2,2'-bipyridine (bipy) was found to be an appropriate method for the generation of the desired boron dication as its bis(triflate) salt (**10**). There are two very similar,

Chart 1



Scheme 1



but independent, cation–anion pairs in the asymmetric unit, and the structure of one of the cations is illustrated in Figure 2.

The closest boron–triflate oxygen distance is 3.772 Å, which exceeds the sum of van der Waals radii for B and O (3.5 Å). As in the cases of the β -diketiminato-substituted boron monocations $[\text{HC}(\text{CMe})_2(\text{NAr})_2\text{BPh}]^+$ (Ar = 2,6-*i*-Pr₂C₆H₃ (**11**);^{8a} C₆F₅ (**12**)^{8b}), the BN_2C_3 ring is planar within experimental error. The average N–C (1.358(8) Å) and C–C (1.381(5) Å) bond distances for **10** are identical to those for **11** (1.356(5) and 1.381(5) Å, respectively)

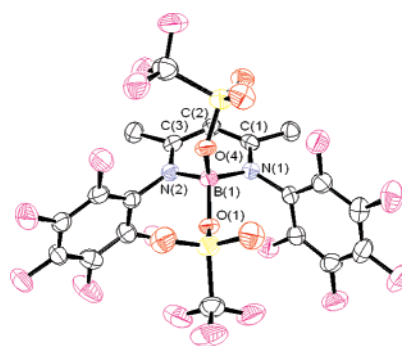


Figure 1. ORTEP view of the boron bis(triflate) **9** showing the atom numbering scheme. Selected bond distances (Å) and angles (°): $\text{B}(1)\text{--O}(1)$ 1.496(5), $\text{B}(1)\text{--O}(4)$ 1.562(7), $\text{B}(1)\text{--N}(1)$ 1.507(7), $\text{N}(1)\text{--C}(1)$ 1.345(6), $\text{C}(1)\text{--C}(2)$ 1.366(7), $\text{C}(2)\text{--C}(3)$ 1.385(7), $\text{N}(2)\text{--C}(3)$ 1.354(6), $\text{O}(1)\text{--B}(1)\text{--O}(4)$ 104.5(6), $\text{N}(1)\text{--B}(1)\text{--N}(2)$ 110.1(4), $\text{B}(1)\text{--N}(1)\text{--C}(1)$ 119.7(4), $\text{N}(1)\text{--C}(1)\text{--C}(2)$ 119.8(4), $\text{C}(1)\text{--C}(2)\text{--C}(3)$ 122.4(4), $\text{N}(2)\text{--C}(3)\text{--C}(2)$ 118.9(4), $\text{B}(1)\text{--N}(2)\text{--C}(3)$ 119.9(4).

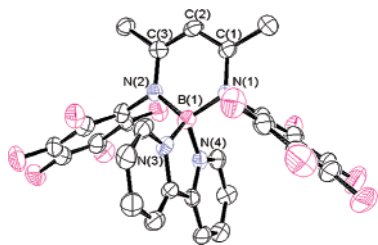


Figure 2. ORTEP view of the boron dication **10** showing the atom numbering scheme for one of the two independent dications in the asymmetric unit. Selected bond distances (Å) and angles (°): B(1)–N(3) 1.605(10), B(1)–N(4) 1.578(9), B(1)–N(1) 1.512(9), N(1)–C(1) 1.367(8), C(1)–C(2) 1.373(9), C(2)–C(3) 1.366(9), N(2)–C(3) 1.361(8), B(1)–N(2) 1.512(9), N(3)–B(1)–N(4) 95.5(5), N(1)–B(1)–N(2) 111.6(5), B–N(1)–C(1) 122.0(5), N(1)–C(1)–C(2) 120.6(6), C(1)–C(2)–C(3) 122.3(6), C(2)–C(3)–N(2) 121.2(6), C(3)–N(2)–B(1) 121.8(6).

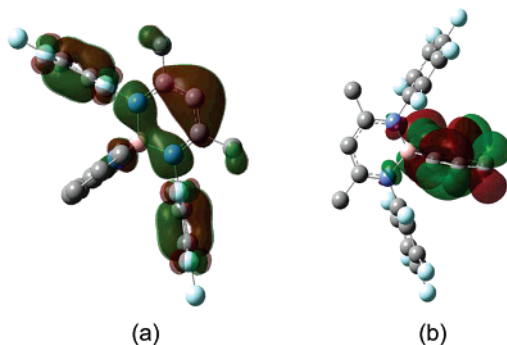


Figure 3. HOMO (a) and LUMO (b) for **10**.

and **12** (1.361(10) and 1.377(11) Å, respectively) within experimental error. The bipy ligand is attached to the boron center in a bidentate fashion such that the bipy and BN_2C_3 planes are approximately orthogonal. As a consequence of the tetrahedral boron geometry in **10**, the average B–N bond distance for the BN_2C_3 ring (1.514(9) Å) is longer than that for the trigonal planar boron atom of **11** (1.450(5) Å) or **12** (1.441(9) Å). However, the average N–B–N bond angle for **10** (111.2 (6)°) is comparable to those for **11** (114.6(3)°) and **12** (113.7(1)°). The ^{11}B chemical shift for **10** (δ 6.44) falls in the range observed for boronium cations.^{3b}

Further insight into the electronic structure of the boron dication **10** was gained from DFT calculations that were carried out at the B3LYP level of theory using the 6-31G* basis set. The input coordinates for the geometry optimization of the bipy-coordinated dication were generated from the X-ray crystallographic data. The HOMO is located primarily on the C_6F_5 substituents and the $\text{C}_3\text{N}_2\text{B}$ ring (Figure 3). Regarding the latter, the ring π -character comprises π -allylic N–B–N and C–C–C fragments separated by a nodal plane that passes through the two N–C bonds. The LUMO, which is of π^* -character, is located primarily on the bipy rings, and the HOMO–LUMO gap is 85.3 kcal/mol. The computed charge at the boron center is +1.3 (cf. that for **9** is +0.9). This partial quenching of positive charge by a donor ligand is also a feature of boronium (**2**) and boronium (**3**) monocations.^{3b} DFT calculations also provide an indication of the potentially high reactivity of the hypothetical uncoordinated boron dication, **13**. Removal of the bipy ligand and

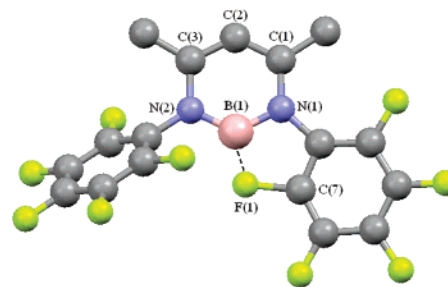


Figure 4. Optimized structure of the model boron dication, **13**. Computed bond distances (Å) and angles (°): B(1)–N(1) 1.418, B(1)–N(2) 1.393, B(1)–F(1) 1.507, F(1)–C(7) 1.536, N(1)–C(1) 1.401, N(2)–C(3) 1.404, C(1)–C(2) 1.402, C(2)–C(3) 1.404, N(1)–B(1)–N(2) 127.1, B(1)–N(1)–C(1) 116.9, N(1)–C(1)–C(2) 116.1, C(1)–C(2)–C(3) 126.5, C(2)–C(3)–N(2) 117.9, B(1)–N(2)–C(3) 115.4.

generation of the free boron dication result in a structure in which one of the fluorine atoms of a C_6F_5 group interacts with the highly electron-deficient B^{2+} center (Figure 4).

This interaction is accomplished by rotation of one of the C_6F_5 rings such that it is approximately coplanar with the BN_2C_3 ring. The computed $\text{B}\cdots\text{F}$ and C–F distances are 1.507 and 1.536 Å, respectively. For comparison, the mean B–F and C–F bond distances from the Cambridge Structural Data Base are 1.362 and 1.335 Å, respectively. In turn, this $\text{B}\cdots\text{F}\cdots\text{C}$ interaction has the effect of reducing the strongly electrophilic nature of the B^{2+} center.

In conclusion, we have prepared and structurally characterized the first example of a boron dication. The β -diketiminato-supported dication $[\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\text{B}]^{2+}$ was stabilized by 2,2'-bipyridine coordination and isolated as the bis(triflate) salt. DFT calculations on the model uncoordinated dication reveal that it would be highly electrophilic.

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Supporting Information Available: Experimental procedures, spectroscopic data, X-ray crystallographic data for **9** and **10** (CIF), and details of the DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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