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Synthesis and Characterization of Terpyridine-Supported Boron Cations: Evidence for Pentacoordination at Boron

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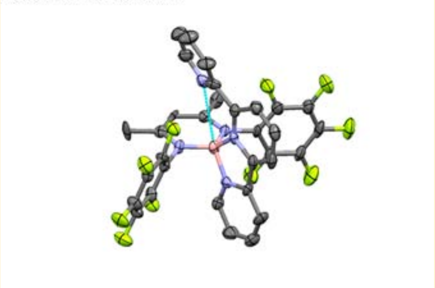
S *Supporting Information*

ABSTRACT: Hypervalent boron centers are proposed to be key intermediates in many stoichiometric and catalytic reactions. However, structurally characterized examples remain rare. We have isolated two new borocations with formal charges of 1+ and 2+. Because the dicationic complex displays evidence of pentacoordination at the boron center, we conclude that the interaction is predominantly electrostatic and is a result of the highly electrophilic dicationic boron atom.

To bond or not to bond...

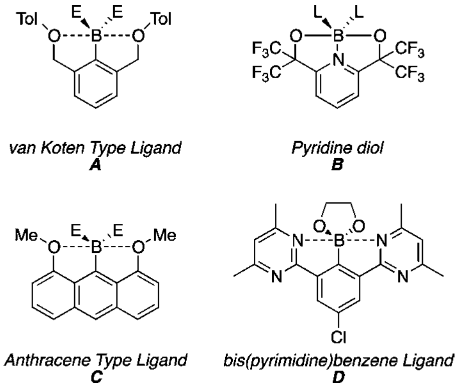


that is the coordination number

INTRODUCTION

Hypervalent pentacoordinate boron compounds have been postulated as transition states in S_N2-type reactions at a boron atom. For example, reaction of the $[BH_3CO]$ complex with NMe_3[1] and intramolecular bond switching at the boron atom in compounds bearing a van Koten type ligand (Chart 1, **A**) have been reported.[2] The earliest report of the isolation and characterization of a hypervalent boron compound was nearly 30 years ago (Chart 1, **B**),[3] but the complexes bearing tridentate pyridinediol ligand(s) were characterized using ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra in solution. X-ray analysis of these species has yet to be reported.

Chart 1. Common Ligand Motifs in Pentacoordinate Boron Systems



van Koten Type Ligand **A**

Pyridine diol **B**

Anthracene Type Ligand **C**

bis(pyrimidine)benzene Ligand **D**

However, by deployment of the sterically rigid 1,8-dimethoxy-9-anthracenyl ligand framework (Chart 1, **C**), Akiba and co-workers have successfully prepared, and structurally characterized, a raft of pentacoordinate boron[4] compounds. The geometry about the central boron atom in each case is a result of a variety of factors including the inflexible ligand backbone, the pendant donor atoms in the 1 and 8 positions, and the nature of the substituents at the boron atom. The structural diversity encountered prompted the use of the following terminology to more accurately depict the bonding situation at the boron center: loose pentacoordinate, tight pentacoordinate, and tetracoordinate.[4b] Yamamoto has recently extended this approach by utilizing the bis(pyrimidine)benzene ligand framework (Chart 1, **D**).[5]

Recently, we have described our efforts directed toward the preparation and characterization of polycationic boron species, where the formal charge residing at a central boron atom is greater than 1.[6,7] Such complexes would feature a highly electron-deficient boron center that would be expected to undergo facile reaction with nucleophilic species. However, as one may expect, the successful preparation and isolation of such polycationic systems requires judicious choice of ancillary ligands. To date, isolation of both di- and trications of boron has required coordinative saturation of the group 13 center. Such a requirement gives rise to highly inert systems.

Herein we report the synthesis and characterization of two new borocations, $[\{(Me_3Si)_2N\}B(Br)(terpy)][Br]$ (**1**) and $[(\beta\text{-diketiminate})B(terpy)][OTf]_2$ (**2**) (terpy = 2,2′:6′,2″-terpyridine; OTf = trifluoromethanesulfonate; β-diketiminate = 2,3,4,5,6-pentafluoro-*N*-[1-methyl-3-[(2,3,4,5,6-pentafluorophenyl)amino]-2-buten-1-ylidene]benzeneamine). We chose terpy because of our previous success in supporting group 13 cations with this ligand.[8] Dicationic complex **2**

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displays evidence of a pentacoordinate boron center. This interaction is unique in the context of pentacoordinate boron systems in that there is no rigidly enforced binding pocket to “promote” a fifth coordinative interaction at boron.

■ EXPERIMENTAL SECTION

Chemicals and Instrumentation. All reagents were purchased from commercial sources and used without further purification unless otherwise noted. CH_3CN and CH_2Cl_2 were distilled from CaH_2. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a glovebox. ^1H and ^{13}C NMR were recorded on a 400 MHz spectrometer with Me_4Si or solvent resonance as the internal standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectrometry (HRMS) was performed on an electron ionization time-of-flight mass spectrometer.

X-ray diffraction data for compounds **1** and **2** were obtained on a Bruker SMART Apex II CCD diffractometer. All data were collected at room temperature using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Structures were solved by direct methods and refined by full-matrix least squares against F^2 (*SHELXTL*[9]). All hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. CCDC 938603 and 938604 (**1** and **2**, respectively) contain the supplementary crystallographic data for this paper (see the Supporting Information). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

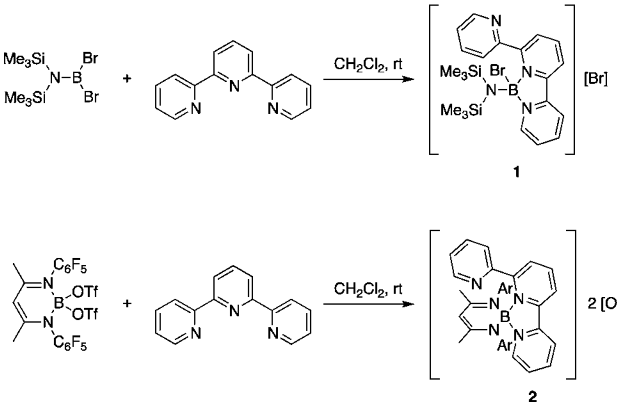
Preparation of 1. Solid terpy (0.015 g, 0.07 mmol) was added to a solution of $[(Me_3Si)_2N]BBr_2$[10] (0.023 g, 0.07 mmol) in 10 mL of methylene chloride at ambient temperature. After the reaction mixture had been stirred for 24 h, the solvent was removed under vacuum, resulting in a pale-yellow powder. Crystals suitable for single-crystal X-ray diffraction study were obtained by recrystallization of this powder from a 50:50 methylene chloride/hexane solvent mixture. Yield: 0.032 g (80%). HRMS (CI^+, CH_4). Calcd for $C_{21}H_{29}BBrN_4Si_2$: m/z 483.1307. Found: m/z 483.1169. ^1H NMR (CD_2Cl_2): δ −0.26 (s, 9H, CH_3), 0.13 (s, 9H, CH_3), 7.55−7.58 (m, 1H, 6,5″-CH), 7.84 (dd, J = 4.1 and 7.8 Hz, 2H, 2,3′-6,3″-CH), 7.94 (dt, J = 1.8 and 7.8 Hz, 1H, 6,4″-CH), 8.19 (at, J = 7.3 Hz, 1H, 2,6′-CH), 8.76 (d, J = 5.0 Hz, 1H, 6,6″-CH), 8.81−8.87 (m, 3H, 4-2,4′-2,5′-CH), 10.26 (d, J = 7.8 Hz, 2H, 3,5-CH). ^{11}B NMR (CD_2Cl_2): δ 5.0 (sharp, s). ^{13}C NMR (CD_2Cl_2): δ 4.76 (CH_3), 6.40 (CH_3), 125.87 (6,5″-CH), 126.25, 126.65, 126.83, 129.89 (2,6′-CH), 133.28, 137.48 (6,4″-CH), 142.38, 143.69, 144.03, 146.98, 147.60, 149.85 (6,6″-CH), 151.63, 156.42.

Preparation of 2. Solid terpy (0.015 g, 0.07 mmol) was added to a solution of (β-diketiminate)$B(OTf)_2$[6a] (0.050 g, 0.07 mmol) in 10 mL of methylene chloride at ambient temperature. After the reaction mixture had been stirred for 48 h, the resulting pale-yellow precipitate was isolated by filtration. Crystals suitable for single-crystal X-ray diffraction study were obtained by recrystallization of this powder from a 50:45:5 methylene chloride/hexane/acetonitrile solvent mixture. Yield: 0.055 g (85%). Mp: 180 °C (dec). MS (CI^+, CH_4): m/z 672 ($[M^{2+} - H^+]^+$). HRMS (CI^+, CH_4). Calcd for $C_{32}H_{17}BF_{10}N_5$: m/z 672.1417. Found: m/z 672.1420. ^1H NMR (CD_3CN): δ 2.17 (s, 6H, $CH3$), 6.45 (s, 1H, γ-CH), 7.72 (m, 1H, 6,4″-CH), 8.15−8.29 (m, 3H, 2,4′-2,5′-6,5″-CH), 8.61−8.65 (m, 2H, 3,5-CH), 8.73−8.83 (m, 3H, 4-2,6′-6,6″-CH), 8.95−9.05 (m, 2H, 2,3′-6,3″-CH). ^{11}B NMR (CD_3CN): δ 7.43 (sharp, s). ^{19}F NMR (CD_3CN): δ −79.71 (s, 6F, OTf), −142.36 to −142.80 (m, *o*-F, 4F), −151.25 (t, *p*-F, 2F, $^3J_{FF}$ = 21.4 Hz), −159.04 to −159.78 (m, *m*-F, 4F).

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Monocation 1 and Dication 2. As summarized in Scheme 1, we chose a simple bond heterolysis approach to generate the new borocations. Thus, the treatment of either $[(Me_3Si)_2N]BBr_2$[10] or (β-diketiminate)$B(OTf)_2$,[6a] methylene chloride solutions, with terpy affords monocation **1** or dication **2**, respectively. Both **1** and **2** are obtained in good yield, 80 and 85%, respectively, as pale-yellow solids. Satisfactory spectroscopic data were acquired for both **1** and **2**. The ^{11}B NMR spectra exhibit intense singlet resonances at δ 5.0 (**1**) and 7.43 (**2**), the values of which are typical for a tetracoordinate boron atom.[11] However, it is difficult to assess pentacoordination based strictly on ^{11}B NMR data. The bipyridine analogue of **2** was recently reported by us[6a] and showed a distorted tetrahedral geometry (tetracoordinate) at boron, with a ^{11}B NMR resonance at δ 6.44. Yamamoto and co-workers reported a pentacoordinate boron compound with a broad ^{11}B NMR resonance at δ 16,[5] whereas Lee and Martin reported a pentacoordinate boron with a ^{11}B NMR resonance at δ −20.[3] It is conceivable that the structure of **2** could be fluxional at high temperatures, with N3 and N5 swapping roles. Hence, we recorded ^{11}B NMR spectra over a wide temperature range (−40 to +70 °C) and found no change in the ^{11}B NMR resonance (spectra available in the SI). Given the lack of structural information afforded us by solution NMR studies, we considered it of paramount importance to obtain a molecular structure of complexes **1** and **2** to address the nature of the coordination number at boron.

Scheme 1. Synthesis of Monocation 1 and dication 2



Crystals suitable for single-crystal X-ray diffraction were obtained for both complexes. In the determination of the crystal structure for compound **1**, the disordered electron density, assumed to be solvent, was removed using the *SQUEEZE* routine in *PLATON*. Unfortunately, despite repeated efforts, no crystal of **1** gave satisfactory diffraction at higher angles. The molecular structure of **1** displays a distorted tetrahedral geometry at the cationic boron center; bond distances and angles are in the typical range for B−N and B−Br bonds. Significantly, the distance between the non-coordinated nitrogen atom and the boron center is 3.937 Å, and the torsion angle between N3 and N4 is 100.2(15)°. These values clearly indicate the absence of any interaction between N4 and the boron center. In contrast, the molecular structure of **2** reveals evidence for pentacoordination at boron. **2** crystallized in the $P\bar{1}$ space group, and the unit cell contains two crystallographically independent structures (bonds and angles for both structures are given in Figure 1).

The distances between the noncoordinated nitrogen atom and boron are 2.991(10) and 2.943(10) Å (respectively for the two crystallographically independent structures), approximately

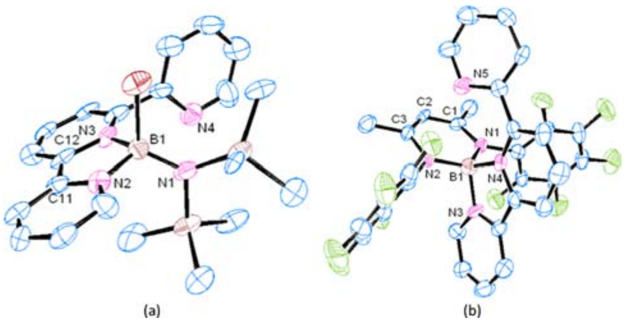


Figure 1. (a) ORTEP view of the cation of **1**. Thermal ellipsoids are shown at 40%. Hydrogen atoms and the bromide counterion have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): B1−N1 1.474(19), B1−N2 1.571(19), B1−N3 1.665(19), B1−Br1 2.051(17); N1−B1−Br1 117.3(10), N1−B1−N2 117.2(12), N1−B1−N3 115.8(12), N2−B1−Br1 103.5(9), N2−B1−N3 97.6(10), N3−B1−Br1 102.6(9). (b) ORTEP view of the cation of **2**. Thermal ellipsoids are shown at 40%. Hydrogen atoms and the triflate counterions have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): B1−N1 1.511(12), B1−N2 1.503(11), B1−N3 1.592(12), B1−N4 1.631(11); N1−B1−N2 111.4(7), N1−B1−N3 109.9(7), N1−B1−N4 114.2(6), N2−B1−N3 108.0(6), N2−B1−N4 116.4(7), N3−B1−N4 95.5(6).[13]

a full 1 Å shorter than those in **1**, and both fall well within the sum of the van der Waals radii for boron and nitrogen (3.55 Å).[12] Perhaps more tellingly, the N4−N5 torsion angles are a mere 24.0(12) and 30.0(11)° for the two independent structures [cf. 100.2(15)° in **1**], and the noncoordinated nitrogen atom now points directly toward the dicationic boron center. Examination of a packing diagram of **2** does not indicate any significant contribution from nonbonding interactions that could account for the orientation of the third terpy ring. Thus, we attribute this pentacoordination to the increased Lewis acidity of the dicationic boron center in **2**.

Density Functional Theory (DFT) Calculations. To gain additional insight into the electronic structure of monocation **1** and dication **2**, calculations were carried out at the DFT level by means of the functional B3LYP[14] and the 6-311G*[15] basis set. The Stuttgart effective core potential with its respective basis set was added to bromine.[16] All geometric parameters were kept relaxed during the optimization procedure. Further frequency calculation showed that the optimized structures of the monocationic (**1**) and dicationic (**2**) systems corresponded to minima. All calculations were carried out using the *Gaussian* suite of programs.[17] In each case, the fractional coordinates from the X-ray crystal structure were used as input data.

In general, there is very good agreement between the theoretical and experimental values. For example, the computed B1−N1 and B1−N3 bond distances of 1.452 and 1.634 Å compare well with the experimental values of 1.474 and 1.665 Å, respectively, in **1**. Similarly, the calculated B1−N1 and B1−N3 bond distances of 1.519 and 1.613 Å are very similar to the experimental values of 1.530 and 1.579 Å, respectively, found in **2** (average of both crystallographically distinct structures in the unit cell). Moreover, and perhaps most importantly, the pentacoordinate interaction is accurately reproduced by the DFT calculation (Figure 2). The calculated distance from B1−N5 in dication **2** is 3.055 Å, which compares very well with the experimental value of 2.991(10) Å.

The most telling feature revealed in the optimized structures of **1** and **2** is the orientation of the third terpy ring (Figure 2). DFT optimization occurs in the gas phase, and freed of any solid-state packing effects, the noncoordinated ring in **1** rotates even farther away from the congested *mono*cationic boron center. This is most readily assessed by a comparison of the torsion angle between N2 and N4, which is 141.2° in the DFT-optimized structure and only 100.2(15)° in the X-ray structure. However, in the optimized structure of **2**, the noncoordinated ring remains in an orientation that allows for close approach of the nitrogen to the *di*cationic boron center. The calculated torsion angle between N4 and N5 is 33.0° [cf. the experimental values of 24.0(12) and 30.0(11)°]. These results support our assertion that the pentacoordination observed in **2** is not the result of crystal-packing effects.

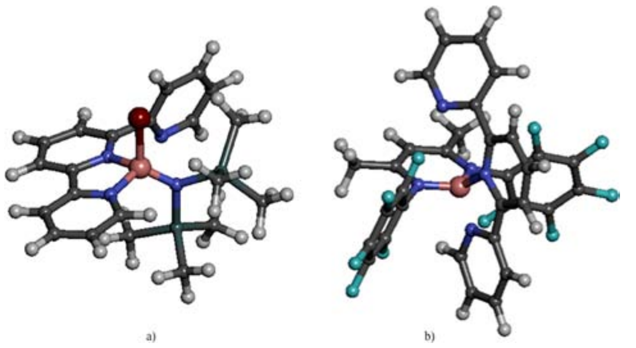


Figure 2. (a) Optimized geometry of monocation **1**, as calculated by B3LYP/6-411G*. (b) Optimized geometry of dication **2**, as calculated by B3LYP/6-411G*.

An assessment of the atomic charges at the boron centers in **1** and **2**, using natural population analysis, resulted in charges of ∼0.9 and ∼1.2, respectively. Although these values are somewhat “quenched” from the formal assignments of 1+ and 2+,[6b] we believe it is the higher residual charge (electrophilicity) at the “dicationic” boron center of **2** that gives rise to pentacoordination.

To further examine the bonding in **2**, the chemical bonds were analyzed by natural bond analysis.[18] As a criterion for the assignment of covalent bond character, a covalent bond occupation was chosen for which a threshold of 1.50 was obtained. Using this criterion, no covalent bonds were found between the central boron atom and “pentacoordinate” nitrogen atom. Thus, we must conclude that the interaction of N5 with the central boron atom in **2** is purely electrostatic. In an effort to estimate the stabilization afforded by the introduction of a fifth coordinative interaction at the boron center of dication **2**, we carried out a calculation in which the dihedral angle of N4−N5 was fixed at 180° (no interaction of N5 with B1) and the rest of the structure was allowed to relax. It was found that the tetracoordinate structure was 8.05 kcal/mol *less stable* (uncorrected for zero-point energy) than the experimentally observed pentacoordinate structure. This value places it at the upper limits of typical hydrogen-bond strengths, yet significantly lower than a truly electrostatic Lewis acid−Lewis base adduct formation.[19]

■ CONCLUSIONS

In summary, we have isolated and structurally characterized two novel borocations, a monocation and a dication both supported by a terpy ligand. Structurally characterized boron dications are extremely rare; only a handful have been reported.[6] In the case of the dication **2**, we have found evidence of a hypervalent (pentacoordinate) interaction at the boron center. Using DFT calculations, we have demonstrated that pentacoordination is not the result of crystal-packing forces and stabilization afforded by the fifth coordination interaction is ca. 8 kcal/mol. We postulate that this interaction arises because of the extreme electrophilicity of the dicationic boron center.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, general information, ^{11}B NMR spectra, computational results, and references. 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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■ DEDICATION

Dedicated to Professor Alan H. Cowley for his many years of service to inorganic and main-group chemistry.

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