Borenium cations derived from BODIPY dyes†

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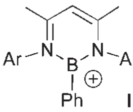
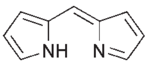
Fluoride abstraction from a BODIPY dye gives a well defined borenium ion which can be converted to a borenium hydride *via* treatment with DIBAL-H.

Cations of boron have been known for some time,[1] but are moving from the realm of chemical curiosities to applications in catalysis,[2] anion sensing[2,3] or as synthons for organoboron based materials. Classified according to the coordination number at boron, monocationic boron compounds become more reactive (and scarce) as the number of ligands decreases. Thus, while four coordinate boronium ions are relatively common, well characterized bis-ligated borinium ions are few in number.[4]

Tricoordinate borenium ions fall between these two classes and offer a balance between reactivity and accessibility. Recent examples have relied on incorporation of the borocation into a heterocyclic framework[5] or the use of large ligands[6] to provide electronically and/or sterically stabilized borenium ions. For example, use of a β-diketiminato ligand[7] provides the borenium ion **I**,[8,9] in which the C_3N_2B ring is aromatic and resistant to assuming boronium ion character through coordination of another ligand.



I



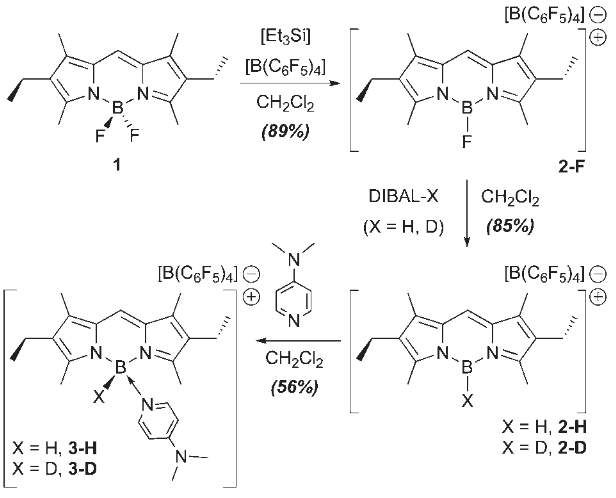
II

The dipyrrinato ligand framework[10] as in **II** is related to the β-diketiminato ligand,[7,11] and is familiar as the chromophore in the commercially important family of fluorescent F-BODIPY dyes.[12] Interest in methods for altering this basic structure so as to improve or modify its photophysical properties is high due to the many desirable characteristics of this dye family. One strategy has been replacement of the F^- donors with other ligands to make (F/X)- or X_2-BODIPY derivatives.[13] Additionally, water soluble examples are of interest particularly for use as fluorescent tags in biological applications.[8a] Since cationic boron compounds have the potential to serve in both of these areas, we have begun to explore the chemistry of BODIPY-based borenium cations.

Halide abstraction is a venerable method for the generation of cationic boron centers.[2] To effect abstraction of a fluoride ion from boron requires a potent reagent; for this we turned to the triethylsilylium ion,[14] partnered with the weakly coordinating perfluoroarylborate ion.[15] This reaction occurs smoothly, quickly and in excellent yield using the BODIPY derivative **1**[16] (Scheme 1), as indicated by formation of a dark purple solution.† The byproduct Et_3SiF provides a thermodynamic driving force and is easily removed from the filtered precipitate by evacuation; borenium ion **2-F** is isolated as purple crystals in 89% yield.

Although stable in a crystalline form (see below), **2-F** partially decomposes in CD_2Cl_2 solution over the course of 30–60 min, such that clean ^1H NMR spectra are difficult to obtain. The nature of this decomposition process is under investigation. In the ^{19}F NMR spectrum, taken at 203 K, a broad signal at −118.4 ppm is assigned to the B–F moiety. This is shifted downfield relative to the value of −147.4 ppm observed for **1**.[17]

X-Ray analysis of **2-F**‡ shows clearly its formulation as a borenium ion (Fig. 1). Because of the molecule's symmetry, the asymmetric unit consists of two borate anions, one cation lying about an inversion center (disordered over two sites) and two disordered half cations about inversion centers. Distances and angles in each molecule are similar although the disorder apparent renders measured distances somewhat uninformative. For example, the B–F distance of 1.414(5) Å is slightly longer than expected on the basis of the computed length of 1.328 Å (see below) and the average of 1.3915(3) Å observed in **1**.[18] Furthermore, the B–F distances in related four coordinate



Scheme 1 Synthetis of BODIPY derived borocations.

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† Electronic supplementary information (ESI) available: Synthetic procedures and X-ray data for **1**, **2-F**, and **2-H** as CIF files. CCDC reference numbers 689180, 687820 and 687821. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808739c

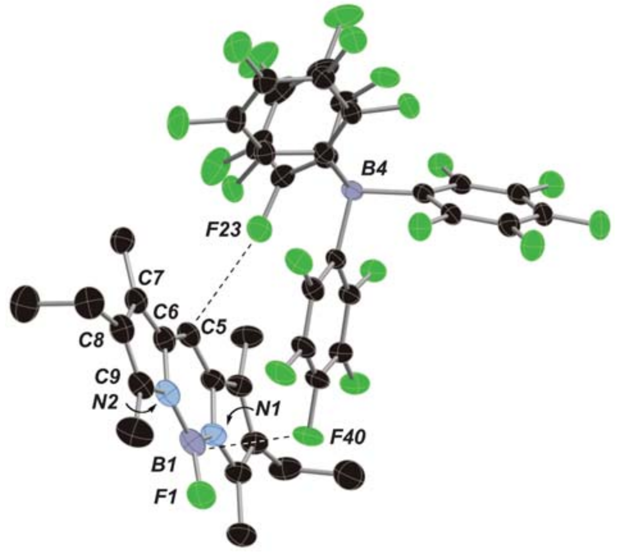

Fig. 1 Thermal ellipsoid diagram (50%) of **2-F**. Selected bond distances (Å): B(1)–F(1), 1.414(5); B(1)–N(1), 1.429(5); B(1)–N(2), 1.430(5); N(2)–C(6), 1.427(4); C(5)–C(6), 1.384(4); C(6)–C(7), 1.395(5); C(7)–C(8), 1.404(5); C(8)–C(9), 1.394(5); N(2)–C(9), 1.404(4). Selected non-bonded distances (Å): B(1)–F(40), 2.929; C(5)–F(23), 3.004. Selected bond angles (°): N(1)–B(1)–N(2), 116.9(3); N(1)–B(1)–F(1), 119.4(4); N(2)–B(1)–F(1), 123.5(3).

boronium ions are 1.370(3) and 1.385(5) Å.[3] Nonetheless, the constitution of the compound in terms of connectivity is clearly established. Overall, the dipyrrinato borenium cation is essentially planar; this includes the boron center, as indicated by the 359.8° sum of the angles around boron. The closest contact between the borenium cation and the $[B(C_6F_5)_4]$ anion is 2.93 Å (B(1)–F(40)).

The stabilization of a three coordinate borocation usually requires a bulky ligand set, so the isolation and structural characterization of **2-F** is significant and suggests that it may be a useful synthon for other borenium cations. We decided to attempt the preparation of an unprecedented borenium hydride cation, a borocation of fundamental interest. Treatment of **2-F** with silanes Et_3SiH or $PhSiH_3$, either with or without $B(C_6F_5)_3$ added as a catalyst,[19] gave promising results, but a clean product was not obtained *via* this route due to the length of time required for reaction (during which the aforementioned thermal decomposition of **2-F** complicated the chemistry). Ultimately, we found that treatment of freshly dissolved **2-F** with DIBAL-H resulted in immediate and complete conversion of purple **2-F** to deep blue **2-H**, presumably with loss of $(^iBu)_2AlF$[20] (Scheme 1). The ^{11}B NMR spectrum of this product shows a broad resonance centered around 24 ppm ($\omega_{1/2} \approx 500$ Hz) that narrows ($\omega_{1/2} \approx 330$ Hz) upon proton decoupling. The B–H moiety was not detected by ^1H NMR spectroscopy, but a broad signal centered at 7.4(1) ppm was observed in the ^2H NMR spectrum of **2-D** (prepared with DIBAL-D). IR spectroscopy of **2-H**/**2-D** was inconclusive. However, derivatization of **2-H** with one equivalent of DMAP yielded the boronium cation **3-H**, which exhibits a broad doublet at −1.6 ppm in the ^{11}B NMR spectrum ($^1J_{BH}$ = 96(2) Hz) that collapses to a singlet upon proton decoupling. Furthermore, a signal at 4.36 ppm in the $^1H\{^{11}B\}$ NMR spectrum emerges that is broadened into the baseline in the boron coupled spectrum. Compound **3-H** was also characterized by ESI mass spectrometry in positive ion mode (388.97, $[M]^+$).

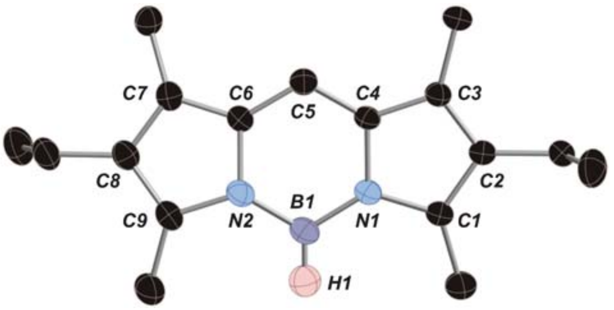

Fig. 2 Thermal ellipsoid diagram (50% probability) of the borenium cation **2-H** (anion omitted for clarity purposes). Selected bond distances (Å): B(1)–N(1), 1.404(4); B(1)–N(2), 1.402(4); N(1)–C(1), 1.412(4); N(1)–C(4), 1.411(3); C(1)–C(2), 1.411(4); C(2)–C(3), 1.388(4); C(3)–C(4), 1.408(4); C(4)–C(5), 1.385(4). Selected bond angle (°): N(1)–B(1)–N(2), 118.4(3).

The structure of **2-H** was also confirmed *via* X-ray crystallography;‡ the molecular structure of the cation is shown in Fig. 2. **2-H** is isostructural to **2-F**, sharing similar structural features, including the contacts with the counteranion. Analogous disorder issues are also observed and the hydrogen bonded to B was not refined, but clearly there is no fluorine remaining in this position.

Borenium ions **2** are 12 π systems and therefore antiaromatic. A geometry optimization computation (B3LYP/6-311 + G**) was performed on both **2-F** and **2-H** (cations only) which reproduced the planar structure of the C_9N_2B framework. The frontier molecular orbitals (FMOs) obtained for both **2-F** and **2-H** are markedly different from those found for derivatives of neutral BF_2 compounds **1**.[21] Our computations indicate that the 12 π electrons are localized as two sets of aromatic 6 π electron rings on the flanking C_4N rings, while the LUMO is associated with the central ring on the N–B–N array and the *meso* carbon of the dipyrrinato ligand; a depiction of these orbitals for **2-H** is shown in Fig. 3. This picture is consistent with both Mulliken charge analysis and NICS(1) calculations.[22] In each of **2-F** and **2-H**, the N_2B units bear the bulk of the positive charge (+0.831 and +0.969, respectively). The NICS(1) values for the C_4N rings in **2-H** are −9.8, while the value for the central six-membered C_3N_2B ring is +0.7, consistent with the FMO shapes shown in Fig. 3. The values for **2-F** are −4.0 and +0.3 for the five and six membered rings, respectively.

That the LUMO is mostly associated with the boron center in compounds **2** is supported by preliminary reactivity studies. The borenium ions **2** readily take up Lewis bases (such as DMAP, see above). Indeed, Childs and co-workers' Lewis acidity[23] measurements on **2-F** (0.72) and **2-H** (0.78) suggest that the boron centers are more Lewis acidic than $TiCl_4$ (0.66) and comparable to BF_3 or $EtAlCl_2$ (0.77). Interestingly, compound **2-H** does not appear to engage in hydroboration reactivity; no reaction takes place upon treatment with phenylacetylene.

In summary, we have prepared and characterized two examples of three coordinate borenium ions in which one of the boron substituents is either a fluoride or a hydride moiety. We are currently exploring the photophysical properties of

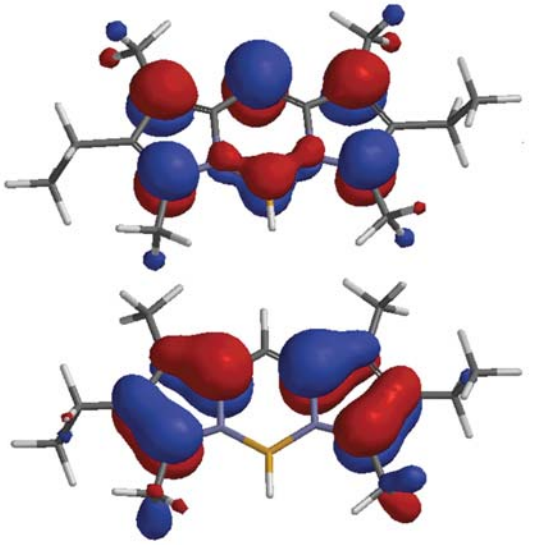

Fig. 3 HOMO (bottom) and LUMO (top) of borenium cation **2-H**.

these compounds, whose visible colors are markedly different than the neutral BODIPY complex from which they are derived. Furthermore, we are evaluating their potential as Lewis acids, particularly towards protic Lewis bases such as water and alcohols, and as synthons for novel unsymmetrically substituted BODIPY type dyes.[24]

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Notes and references

[‡] Crystal data for **2-F** $C_{41}H_{23}B_2F_{21}N_2$, M = 964.24, T = 173(2) K, space group $P\bar{1}$, triclinic, a = 11.156(2), b = 14.767(2), c = 24.693(4) Å, α = 92.013(7), β = 94.606(10), γ = 101.549(11)°, V = 3967.2(11) Å^3, Z = 4, D_c = 1.614 g cm^{-3}, μ(Mo-K$_\alpha$) = 0.163 mm^{-1}, 32 528 reflections measured, 17 599 unique (R_{int} = 0.0285) which were used in all calculations. The final R and $wR(F^2)$ were 0.0594 and 0.1397, respectively.
Crystal data for **2-H**: $C_{41}H_{24}B_2F_{20}N_2$, M = 946.24, T = 123(2) K, space group $P\bar{1}$, triclinic, a = 11.085(2), b = 14.768(3), c = 24.420(6) Å, α = 92.761(10), β = 95.149(14), γ = 100.781(12)°, V = 3902.6(14) Å^3, Z = 4, D_c = 1.610 g cm^{-3}, μ(Mo-K$_\alpha$) = 0.161 mm^{-1}, 26 433 reflections measured, 14 169 unique (R_{int} = 0.0292) which were used in all calculations. The final R and $wR(F^2)$ were 0.0485 and 0.1104, respectively. CCDC 687820 for **2-F** and 687821 for **2-H**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b808739c

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