COMMUNICATION

Formation of *N*-heterocyclic, donor-stabilized borenium ions†

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Cationic and zwitterionic boryl bromide species and a borenium–boryl bromide cation have been synthesised which represent new N-donor stabilised cationic boron compounds with β-diketiminate ligands. The unexpected borenium–boryl bromide results from a head-to-tail dimerisation of the corresponding zwitterionic boryl bromide accompanied by proton migration. The electronic nature of these new species was studied by DFT calculations.

Boryl cations (borenium ions) are very reactive and highly electrophilic species that play a key role in boron chemistry.[1] Since the first crystallographic characterization of diammoniate of diborane by Parry and co-workers,[2] the structural chemistry of boryl cations has attracted much interest over many years because of their related electronic features of analogous group 14 cations in terms of orbital occupancy, electron count, and net charge.[3] On the other hand, β-diketiminato ligands L are valuable ligands for the donor–acceptor stabilisation of various chemical elements in different coordination modes and oxidation states.[4] In particular, stable *N*-heterocyclic carbene analogues, *i.e.* silicon(II),[5] germanium(II),[6] aluminium(I),[7] gallium(I),[8] indium(I)[9] and thallium(I)[10] species were stabilized by using the mono-anionic, bidentate β-diketiminato ligand L (Scheme 1). Furthermore, cationic boron species have also been synthesized using a β-diketiminato ligand or BODIPY derivatives (BODIPY = dipyrromethene boron).[3a,f,g,m] Recently, we have reported the intriguing reactivities of zwitterionic *N*-heterocyclic silylene **I**[5] and germylene **II**[6] with a modified, *dianionic* β-diketiminato L′ (Scheme 1).[11] Accordingly, we have reported the synthesis and structure of

aromatic 6π-electron stabilised silylidenium ions through addition of electrophiles at the terminal anionic methylene moiety of **I**.[11a]

The peculiar reactivity of **I** and **II** prompted us to synthesize a boron analogue L′BX, which is expected to show a unique reactivity. Herein we wish to report the successful synthesis and structural characterisation of the *N*-heterocyclic boryl bromide L′BBr **2** *via* the N-donor stabilised borenium ion **1** [LBBr]⁺[BBr₄]⁻, and of the related species [LBBr]⁺[OSO₂CF₃]⁻ **3** and the head-to-tail dimer [LB-L′BBr] + Br⁻ **4**. Because compound **2** exhibits a zwitterionic nature akin to **I**, it is susceptible to protonation and dimerization, affording the 6π-electron, N-donor stabilised borenium ion in **3** and the unexpected ylidic boron cation in **4**, respectively.

The reaction of LLi with two molar equiv. of tribromoborane, BBr₃, in toluene at −78 °C yielded the N-donor supported borenium salt [LBBr]⁺[BBr₄]⁻ **1** (Scheme 2). Parallel to our efforts, very recently, Cui and co-workers have reported the synthesis of L′BBr **2** using an alternative protocol, however, they were not able to determine the molecular structure by X-ray crystallography.[12] The boryl bromide **2** can be prepared by reductive deprotonation of borenium ion **1** with lithium naphthalenide (Scheme 2).

Yellow crystals of **2** were obtained from a concentrated pentane solution. As shown in Fig. 1, the X-ray diffraction analysis revealed that the six-membered C₃N₂B ring is essentially planar. The B–Br [1.932(8) Å] and B–N [1.412(9) Å and 1.417(9) Å] bond lengths of **2** are within reported ranges of the related heteronuclear bonds.[13] The endo- and exocyclic C–C distances [C1–C2 1.401(9) Å, C2–C3 1.417(9) Å, C3–C4 1.379(9) Å and C4–C5 1.444(9) Å] revealed a 1,3-butadiene-like

Scheme 1 Ligand L and L′, zwitterionic silylene **I** and germylene **II**.

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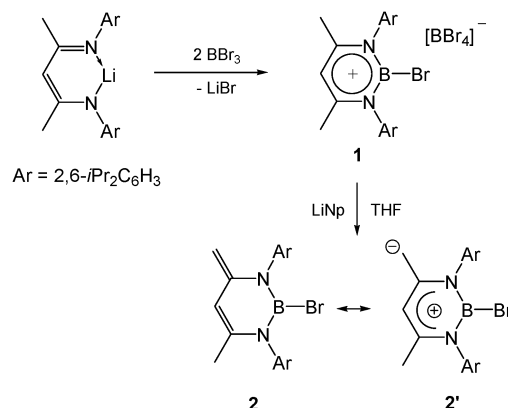*Tel: + 49 (0)30-314-29731*
† Electronic supplementary information (ESI) available: Experimental details of syntheses and X-ray structure determination. See DOI: 10.1039/c1cc11789k

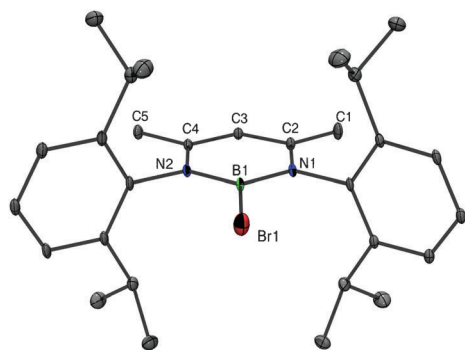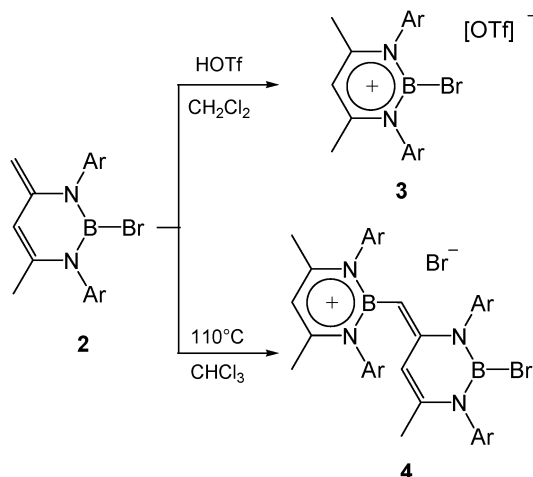**Scheme 2** Synthesis of **1** and **2**. LiNp = LiC₁₀H₈.

Fig. 1 Molecular structure of **2**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Br1–B1 1.932(8), B1–N1 1.412(9), B1–N2 1.417(9), C1–C2 1.401(9), C2–C3 1.427(9), C3–C4 1.379(9), C4–C5 1.444(9), C2–N1 1.411(8), C4–N2 1.413(8), N2–B1–N1 121.8(6), N2–B1–Br1 119.2(5), N1–B1–Br1 119.0(5).

structure, which is consistent with those of silylene **I** and germylene **II**.[5,6]

Because of the iso(valence)electronic structure of compound **2** with silylene **I** and germylene **II**, we have investigated its reactivity towards electrophiles. Indeed, reaction of boryl bromide **2** with trifluoromethanesulfonic acid in dichloromethane at ambient temperature furnishes the corresponding N-donor stabilised borenium salt $[L'BBr]^+[OSO_2CF_3]^-$ **3** as a separated ion pair (Scheme 3). The composition and constitution of **3** was proven by HRMS and NMR spectroscopy (^1H, ^{13}C, and ^{11}B). The ^1H, ^{13}C, and ^{11}B NMR chemical shifts for the borenium moiety in **1** and **3** are practically almost identical and independent of the counter anions (BBr_4^- and $OSO_2CF_3^-$), indicating that **1** and **3** contain least coordinating ions even in solution. The ^1H NMR chemical shift of the γ-H proton of the C_3N_2B ring in **3** ($\delta = 7.95$ ppm) suggests the presence of aromatic 6π-electron stabilisation. Furthermore, the ^{11}B NMR of boron cation **3** exhibits a singlet resonance ($\delta = 29.8$ ppm) that is slightly downfield from that of the precursor **2** ($\delta = 27.2$ ppm). Indeed, the calculated NICS values for compound **3** [NICS(1) = −4.3, NICS(0) = −2.5] revealed negative values, indicating aromatic character of the
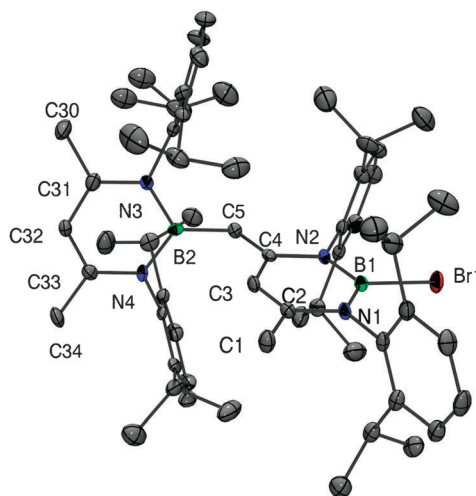

Fig. 2 Molecular structure of **4**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms and the Br atom as a counter anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–Br1 1.945(5), B1–N1 1.399(6), B1–N2 1.421(6), C1–C2 1.495(6), C2–C3 1.348(6), C3–C4 1.430(6), C4–C5 1.349(5), B2–C5 1.538(6), B2–N3 1.450(6), B2–N4 1.467(6), C33–C34 1.505(6), C32–C33 1.359(6), C31–C32 1.357(6), C30–C31 1.509(6), N1–B1–N2 121.5(4), N1–B1–Br1 118.8(4), N2–B1–Br1 119.7(4), N3–B2–N4 113.7(4), N3–B2–C5 123.5(4), N4–B2–C5 122.6(4).

borenium subunit in **3**. This is contrary to the situation of compound **2** [NICS(1) = +1.3, NICS(0) = +2.4].

Surprisingly, boryl bromide **2** underwent a slow but clean dimerization at 110 °C to give compound **4** in 89% yield (Scheme 2). The structure of **4** was established by NMR spectroscopy and a single crystal X-ray diffraction analysis as shown in Fig. 2. The structure of **4** consists of two six-membered BN_2C_3 rings, featuring nearly planar geometry. Both BN_2C_3 rings are arranged almost perpendicular to each other. The B–Br bond length in **4** [1.945(5) Å] is similar to that in **2** [1.932(8) Å]. The alternating lengths of the endo- and exocyclic C–C bonds of **4** [C1–C2 1.495(6), C2–C3 1.348(6), C3–C4 1.430(6), C4–C5 1.349(5)] suggest little π-conjugation as observed for compound **2**. The B1–N1 and B1–N2 distances [B1–N1 1.399(6) and B1–N2 1.421(6)] are shorter than those of the B2–N3 and B2–N4 bonds [B2–N3 1.450(6) and B2–N4 1.467(6)], indicating a stronger π interaction of the nitrogen lone pair with the cationic boron centre (B2).

Although the reaction mechanism is unclear, a possible stepwise path for the dimerisation of **2** to **4** can be envisaged (Scheme 4). We assume that the betaine-like resonance structure of compound **2** promotes this reaction. The initial

Scheme 3 Synthesis of **3** and **4**.
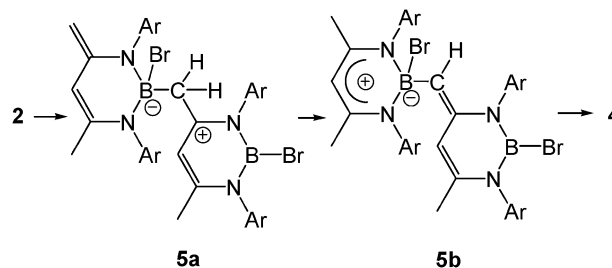
Scheme 4 Proposed mechanism for the formation of **4**.

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step is a nucleophilic attack at the boron atom to give intermediate **5a**. The next step is the migration of a proton to the methylene carbon atom of the backbone to give intermediate **5b**. The tetracoordinate boron centre of intermediate **5b** is unfavourable and affords the ion separated isomer **4** with a tricoordinate cationic boron centre and π donor stabilisation by the adjacent nitrogen lone pairs.

In the ^{11}B NMR of **4**, two broad signals are observed at δ 27.3 and 29.6 ppm, respectively. These chemical shifts are in good agreement with the values of boryl bromide **2** (27.2 ppm) and borenium-like cation **3** (29.6 ppm), respectively. The ^{1}H NMR spectrum of **4** reveals two characteristic singlets at 4.84 and 9.33 ppm, corresponding to the γ-H atoms of the BN_2C_3 rings (4.84 ppm for the boryl bromide moiety and 9.33 ppm for the cationic boron moiety), respectively. This significant downfield shifted signal of the γ-H on C32 (cationic moiety) of compound **4** as compared to that on C3 atom (boryl bromide moiety) can be explained by the aromatic character of the cationic BN_2C_3 ring. Indeed, these trends are also supported by NICS values [boryl bromide moiety: NICS(1) = +0.2, NICS(0) = +1.4; boryl cation unit: NICS(1) = −4.3, NICS(0) = −2.7 ppm]. Apparently, the boryl bromide unit BN_2C_3 bears a negative net charge, while the cationic BN_2C_3 ring has a positive one [NPA charges in borylbromide unit: B1 +0.82, N (mean) −0.69, C (mean) 0.05 vs. boron cation unit: B2 +1.04, N −0.60, C (mean) +0.12]. Furthermore, the HOMO's show the presence of π-orbital interaction within the butadiene moiety of the BN_2C_3 ring in the boryl bromide moiety (Fig. 3). On the other hand, the LUMO is located on the BN_2C_3 ring of the cationic unit. These computed results indicate that compound **4** consists of a borenium-like subunit (electron acceptor) and a boryl bromide subunit (electron donor).

In summary, reaction of the β-diketiminato ligand LLi with BBr_3 furnished the N-donor stabilised borenium salt **1**. Its reduction with lithium naphthalenide furnishes the boryl bromide **2**. Reactivity studies of **2** provide evidence for its zwitterionic character, resulting in the formation of the cationic borenium-like salts **3** and **4**. The compounds **1**, **3** and **4** exhibit some aromatic character. The borenium-like species **1**, **3** and **4** could be promising precursors for elusive N-heterocyclic borylene and borylene–transition metal complexes. Respective investigations are in progress.
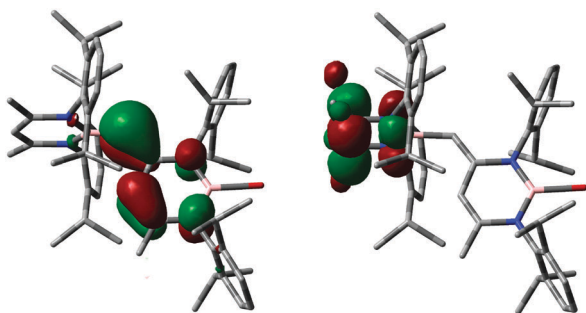

Fig. 3 Frontier orbitals of compound **4**. (a) KS-HOMO −0.181 eV, right and (b) KS-LUMO −0.271 eV, left. Hydrogen atoms are omitted for clarity.

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