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Synthesis and Reactivity of *N,N'*-1,4-diazabutadiene Derived Borocations

James R. Lawson, Lewis C. Wilkins, Manon André, Emma C. Richards, Mohammed N. Ali, James A. Platts and R. L. Melen*

A series of borocations have been synthesised from the addition of haloboranes to synthetically accessible *N,N'-1,4*-diazabutadiene precursors, which are derived from commercially available anilines. The synthesis and structural studies of the borocations is described.

The revival of main group mediated transformations in recent decades has led to the re-emergence of borocation chemistry,[1] which has shown great promise in a variety of chemical reactions, such as metal free FLP catalysed hydrogenation,[2] 1,n-carboration reactions[3] as well as 1,2-haloborations[4] and 1,2-hydroborations[5] *inter alia*.[6] Borocations, which feature a cationic boron centre and thus act as boron electrophiles, are traditionally classified by their coordination number: two-coordinate boriniums, three-coordinate boreniums, and four-coordinate boroniums. Due to the fact that boriniums are often highly unstable, thereby requiring extensive steric or electronic stabilisation,[7] and boroniums often possess low Lewis acidity as a result of the saturated coordination sphere at boron, boreniums represent an attractive target of investigation, occupying a middle ground between stability and reactivity (Lewis acidity).[1c] Therefore, it is of great synthetic importance to investigate new routes to uniquely tuneable boreniums, and to probe their reactivity. To date, many of the reported procedures to generate borocations utilise coordinating carbene,[8, 2b] amine[9] or phosphine[3b] groups to gain the necessary stability to form the borocation through halide or hydride abstraction (Scheme 1), however, the scaffold from which these stabilising ligands are built upon are mainly substituted aromatic motifs such as pyridyl,[4] quinolinyl[10] or catechol[11] units. This in turn restricts the tailoring of steric and electronic properties due to the accessibility to suitably functionalise these aromatic precursors. To combat this limitation, we have shown herein that a series of readily synthesised *N,N'*-1,4-diazabutadienes have led to a series of novel functional borocations with particular control over the steric properties surrounding the
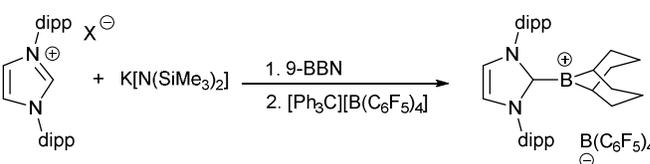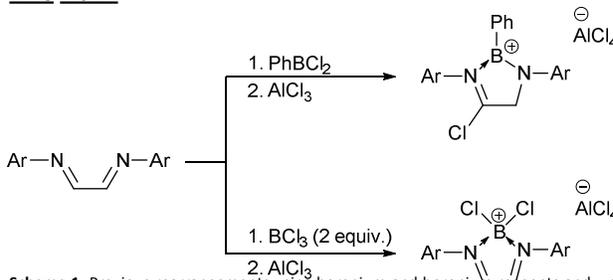
electron deficient boron centre.

Previous work:

Halide abstraction (boronium)
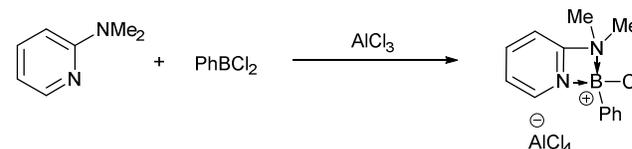
Hydride abstraction (borenium)

This work:

Scheme 1. Previous rearrangements using borenium and boronium reagents and work covered herein.

Initially, the diimine precursors (**1a**-**h**, Scheme 2) were targeted for synthesis through the condensation reaction between various anilines and glyoxal using an established literature protocol.[12] As reported, it was shown that increasing steric bulk in the *ortho* position of the aniline led to more challenging reaction conditions. **1f** required heating at reflux for 3 days, and was isolated in a low yield (23%), and **1h** could not be formed even after 1 week heating at reflux. In initial studies, diimine **1a** was reacted with dichlorophenylborane (PhBCl$_2$) in a 1:1 molar ratio and monitored *via in situ* multinuclear NMR spectroscopy.

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†Electronic Supplementary Information (ESI) available describing experimental procedures, NMR spectra and crystal data. See DOI: 10.1039/x0xx00000x

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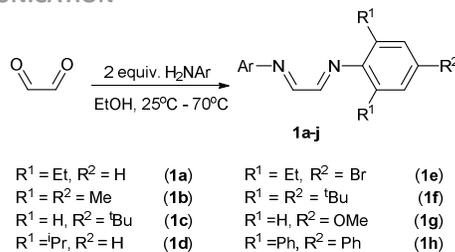
Scheme 2. 1,4-Diazabutadiene synthesis. Ar = Corresponding aniline derivative.

The ^{11}B NMR spectrum showed complete consumption of the PhBCl$_2$ signal at δ = 54.5 ppm within 10 minutes, with a new singlet resonance at δ = 24.4 ppm suggestive of a diazaborole intermediate (**2a**, Scheme 3).[13] **2a** could be characterised by NMR spectroscopy and showed the addition of a chloride ion to the backbone of the starting material. Subsequent addition of 1 equivalent of AlCl$_3$ to the *in situ* generated intermediate **2a** resulted in conversion of the intermediate to the new compound **3a**. Analysis of the ^{11}B NMR spectrum showed a single new peak at δ = 34.4 ppm while ^{27}Al NMR spectrum showed a single peak at δ = 103.92 ppm, which is synonymous with the formation of AlCl$_4^-$.[4] The product **3a** was subsequently crystallised from a CH$_2$Cl$_2$/hexane mixture at -40 °C, garnering red/brown coloured crystals in 91% yield. Subsequent analysis by single crystal X-ray diffraction revealed that **3a** was a borenium cation which crystallised in the *P-1* space group, consisting of the intramolecularly chelated N–B–N heterocycle (Figure 1). The solid-state structure of **3a** confirms the hybridisation of each nitrogen atom with C^1–N^1 being in line with typical imine C–N double bond distances (1.296(2) Å) whilst C^2–N^2 displays more single bond character (1.462(2) Å). The bond lengths between boron and each nitrogen also show disparity with the B–N^1 distance lying at 1.529(3) Å, typical of N–B dative bonds, and B–N^2 at 1.383(3) Å, with all experimental bond lengths being consistent with the calculated structures (Table 1).[14] This slight contraction of the B–N^2 bond, coupled with the high planarity of the structure (RMS = 0.01075 Å) despite the presence of two adjacent sp^3 centres, indicates donation of the lone pair on N^2 into the vacant *p*-orbital at boron. This may lead to a slight quenching of the Lewis acidity of the borocation, but it is postulated that these boreniums will be reactive enough to undergo reactions with small molecules (H$_2$, CO etc.)[15] and π-nucleophiles (alkynes, arenes etc.)[16] similar to that reported previously.
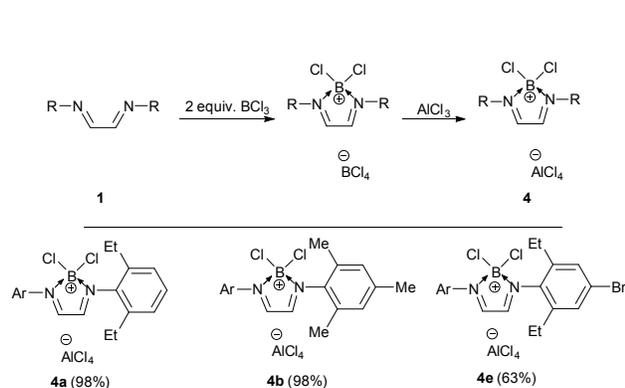
Table 1. Selected experimental and calculated bond lengths (Å).

Bond	3a Exp.	3a Calc.	3d Exp.	3d Calc.
C^1–N^1	1.296(2)	1.299	1.296(4)	1.302
C^2–N^2	1.462(2)	1.453	1.454(4)	1.457
B–N^1	1.529(3)	1.559	1.530(4)	1.551
B–N^2	1.383(3)	1.408	1.401(5)	1.407
C^1–C^2	1.484(3)	1.489	1.468(5)	1.488

Calculations carried out using B3LYP/6-31G(d,p) level of theory.[17]
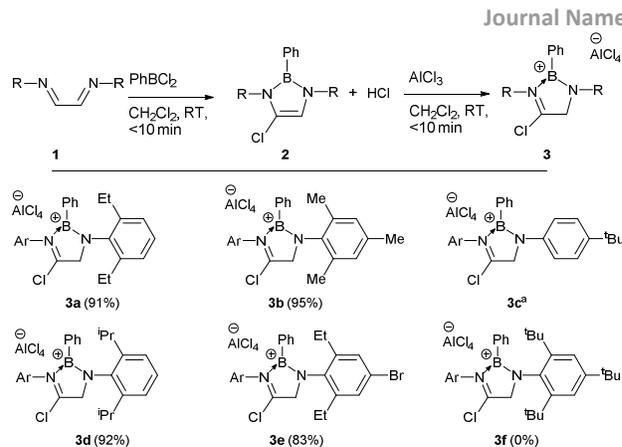
Scheme 3. Reaction between diazabutadienes **1** with PhBCl$_2$/AlCl$_3$ to give **3a-f**. Ar = corresponding aniline derivative. ^{a}Multiple products observed *via in situ* NMR spectroscopy.

Due to the favourable outcomes of this initial trial, our attentions then turned to the other diimines bearing various other functionality in the *ortho-* and/or *para*-position (Scheme 3). **1b**-**g** were reacted sequentially with PhBCl$_2$ then AlCl$_3$ with **3d** being isolated as single crystals and its structure subsequently being confirmed crystallographically. It was observed that, for successful borenium ion formation, diimines featuring a 2,6-substitution pattern of the phenyl rings bound to nitrogen were required. It is postulated that this steric bulk is required in the *ortho* positions to protect the reactive boron centre as it was seen that diimines that did not feature this substitution pattern (e.g. **1c** and **1g**) did not react cleanly as observed by *in situ* NMR spectroscopic analysis. Conversely, in the case of **1f** no reactivity was observed with PhBCl$_2$ even at elevated temperatures presumably due to excessive steric bulk from the ^{t}butyl groups.
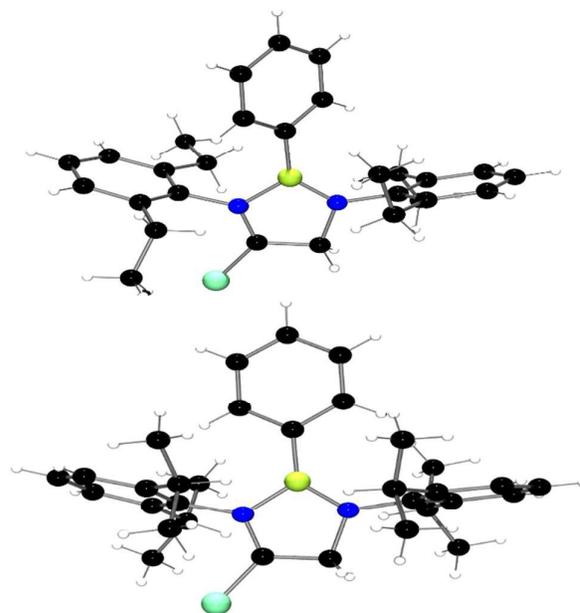
Figure 1. Solid-state structure of **3a** (top) and **3d** (bottom). C: black, N: blue, H: white, B: yellow-green, Cl: aquamarine. AlCl$_4^-$ counterion omitted for clarity.

Scheme 4. Reaction between diazabutadienes **1** and BCl$_3$/AlCl$_3$.

Figure 2. Solid-state structure of **4a**. C: black, N: blue, H: white, B: yellow-green, Al: grey, Cl: aquamarine.

In addition to utilising PhBCl$_2$, the neutral borane BCl$_3$ was also reacted with **1a** (Scheme 4). In an equimolar reaction between the two, a mixture of products was observed by multinuclear NMR spectroscopy. However, when two equivalents of BCl$_3$ was used, a single product was formed as shown by *in situ* monitoring of the ^{11}B NMR spectrum (see Supporting Information). The ^{1}H NMR spectrum indicated that both backbone protons remained (unlike reactions with PhBCl$_2$), although with a greater downfield chemical shift (δ = 9.43 ppm) compared to the initial diimine (δ = 8.14 ppm). Additionally, the ^{11}B spectrum shows a single sharp resonance at δ = 10.6 ppm, indicating a 4-coordinate boron species, in keeping with boronium formation.[18] Upon addition of AlCl$_3$ to this initial product, no notable change was observed in the ^{1}H NMR spectrum, however the ^{11}B NMR spectrum showed reformation of BCl$_3$, in addition to the previous resonance (δ = 10.6 ppm) which was consistent with the spectrum prior to AlCl$_3$ addition. The ^{27}Al spectrum showed a resonance at 103.98 ppm, indicating AlCl$_4^-$ formation, and that a pseudo-counterion exchange process had occurred to yield the borocation tetrachloroaluminate species. Recrystallisation of the sample from a CH$_2$Cl$_2$/hexane solution at -40 °C yielded deep red crystals which were identified to be the boronium species **3a** featuring the aforementioned AlCl$_4^-$ counterion (Figure 2) produced in 98% yield. Clean reactivity was observed with **1a**, **1b**, and **1e**, however addition of **1d** resulted in the formation of multiple products presumably due to the increased steric bulk of the isopropyl groups. The equimolar reaction between BCl$_3$ and **1b** was re-examined, to see if the two equivalents of borane are necessary in the first step. The reaction was repeated, but this time equimolar AlCl$_3$ was subsequently added to the reaction mixture. Analysis by NMR spectroscopy of the reaction mixture still showed a mixture of products in both ^{1}H and ^{11}B NMR spectra, and although resonances that may correspond to **4b** are visible they are an extremely minor product. The ^{27}Al NMR spectra of the mixture showed a single resonance at 104.2 ppm, indicating possible AlCl$_4^-$ formation, but the broadness of the peak suggests it is not the sole aluminium species present.
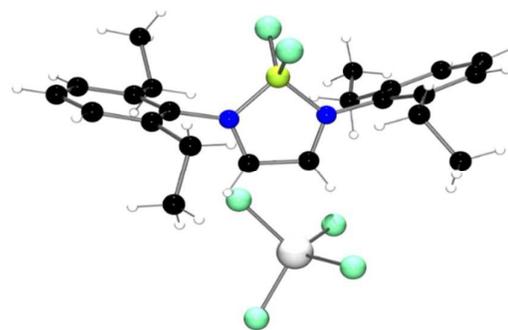
Finally, a brief study was conducted to probe the proclivity for these borenium and boronium cations to undergo their respective carboboration and haloboration reactions, as well as activation of small molecules such as H$_2$.[2-5] In the first instance **3a** was added to 2-hexyne in 1:1 molar ratio in a bid to promote either a 1,1- or 1,2-carboboration reaction, as has been observed with similar systems. *In situ* multinuclear NMR spectroscopy indicated that a mixture of products had formed, including a new resonance in the ^{11}B NMR spectra at ~30 ppm, however attempts to isolate the major product from this mixture has proven unsuccessful. Attempts at H$_2$ activation (5 atm H$_2$) using the borocation **3a** in CDCl$_3$ and toluene proved unsuccessful, as no cleavage of molecular H$_2$ was observed by ^{11}B NMR spectroscopy. Furthermore, addition of a phosphine to form an FLP (Scheme 5) was also unsuccessful, as the use of a strongly basic phosphine (P^{t}Bu$_3$) resulted in abstraction of one of the backbone protons of **3a**, reforming the intermediate **2a** along with [H-P^{t}Bu$_3$][AlCl$_4$] (see Supporting Information). Even the combination of the less basic phosphine, tris(o-tolyl)phoshine, yielded the same product. This deprotonation was clearly observed through multinuclear NMR spectroscopy, of particular note was the P-H environment confirmed in the ^{1}H and ^{31}P NMR spectra, which presented as a doublet in each with the typical $^1J_{HP}$ coupling constant of ~500 Hz.[19]
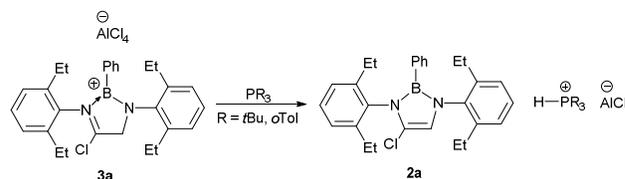
Scheme 5. Addition of a phosphine to **3a**.

In order to assess the Lewis acidity of the borenium cations, an attempt was made to utilise the Gutmann-Beckett method.[20] To samples of **3a**, **3b**, **3d** and **3e** triethylphosphine oxide (Et$_3$PO) was added, and the NMR spectra analysed. In each case, the borenium had reverted to its corresponding adduct **2**, as observed by ^{1}H and ^{11}B NMR spectra. We postulate that the phosphine oxide forms an adduct with AlCl$_3$, releasing a chloride which subsequently reforms **2** and HCl.

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Addition of triphenylphosphine oxide (Ph_3PO) to borenium compounds **3** showed similar results reforming **2** with the ^{27}Al and ^{31}P spectra giving new resonances at ~91 ppm and ~46 ppm, respectively. To support this theory, the NMR spectra of a solution of Ph_3PO and $AlCl_3$ in $CDCl_3$ were obtained, which showed very similar resonances in the ^{27}Al and ^{31}P NMR spectra (see ESI). Attempts to use Childs method[21] met with similar results, with reformation of **2** by NMR spectroscopy.

To overcome the limitations of these experimental methods a study of Lewis acidity of **3** was carried out computationally. Calculations[22] to determine the fluoride ion affinity (FIA) of the boreniums were carried out at the BP86/SVP [23] level using Gaussian09.[17] Atomic coordinates of **3a** and **3d** were extracted from the relevant crystal structures and fully geometry optimised without symmetry constraint, with harmonic frequency calculation confirming the resulting structures as true minima. These were manually adapted to **3b** and **3e**, which were also fully optimised at the same level. Fluoride was added to all four borenium cations, and the resulting structures re-optimised and confirmed as minima. FIA was calculated as the gas phase energy difference between each borenium and its fluoride adduct, corrected for zero-point and thermal energy as well as for BSSE, the latter using a counterpoise procedure.[24] The FIA values of the boreniums were 605 (**3a**), 603 (**3b**), 598 (**3d**) and 622 (**3e**) kJmol^{-1}. Whilst the FIA of all four boreniums was shown to be very similar, the bromo-compound (**3e**) showed the greatest FIA and all borenium compounds have a significantly higher FIA than BF_3 (334 kJmol^{-1}).[22]

Conclusions

We have shown that a new range of borocations can be readily synthesised in good yields from commercially ubiquitous boranes and readily synthesised diimines. With the utilisation of borocations in main group mediated transformations becoming more prevalent, novel methodologies for synthesis have heightened importance. With the methodology to produce this family of borocations now at our disposal, we hope to further fine tune these into useful borenium reagents, and expand our reactivity studies beyond this initial investigation to truly gauge their utility as cationic Lewis acid reagents.

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Synthesis and Reactivity of *N,N'*-1,4-diazabutadiene Derived Borocations

A new route to generate borocations has been established. By utilising readily synthesised diimines derived from commercially available materials, a new family of borenium- and boronium-cations can be synthesised from haloboranes.