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A dialkylborenium ion *via* reaction of *N*-heterocyclic carbene–organoboranes with Brønsted acids—synthesis and DOSY NMR studies†‡

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A dialkylborenium ion stabilized by an *N*-heterocyclic carbene has been prepared for the first time by reaction of IMes·9-BBN-H with triflic acid. The ion-separated nature of the borenium ion was confirmed by ^{1}H and ^{19}F diffusion ordered NMR spectroscopy.

The intrinsic electron-deficiency of trivalent boron has led to a variety of organoboron-based compounds finding use as Lewis acids in organic synthesis.[1] Cationic, divalent boron derivatives have a much higher Lewis acidity than their neutral counterparts, attracting interest in the two-, three- and four- co-ordinate boron cations termed borinium- **1**, borenium- **2** and boronium ions **3**, respectively (Fig. 1).[2]

The extremely high reactivity of borinium ions **1** towards even solvents and counter-ions often precludes their study in all but the gas phase and their utility in organic synthesis is clearly limited. However, there is scope for further studies, and applications, of the more stable borenium- and boronium ions **2** and **3**. The use of borocations in organic synthesis is currently limited to the oxazaborolodinium cations reported by Corey *et al.*,[3] and a catalyst for propylene oxide polymerization reported by Wei and Atwood.[4] The Corey "Lewis superacids" are exceptionally potent, rendering unreactive Diels–Alder substrates reactive at very low temperatures. Borocations are not only of general interest, but also significant as a source of new, powerful Lewis acids for organic synthesis.

Many of the borenium ions reported to date possess heteroatom substituents; the lone pairs on these atoms conferring some extra stability on the highly electron deficient boron.[5] However, borenium ions bearing hydrido-, alkyl- or

Fig. 1 Borocations: borinium-, borenium- and boronium ions.

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aryl substituents are markedly less stable (though there can be a stabilizing π-contribution from aryl substituents), and this is reflected in their relative scarcity in the literature.[6]

In recent years, *N*-heterocyclic carbenes (NHCs) have been widely used as ligands for a variety of transition metal-mediated processes.[7] In contrast, applications of NHC–main group complexes have begun to appear only recently,[8] and the NHC–main group area in general has received relatively little attention.[9]

We have an interest in developing main group–NHC complexes for use in a variety of organic processes, and in particular the application of NHC–boron complexes in organic synthesis, including the use of chiral NHC–boranes and –diorganoboranes in the asymmetric reduction of ketones.[10] The electron-rich nature and steric bulk of some of the common NHCs should make them ideal for stabilization of the highly electrophilic dialkyl boro-cations and we therefore initiated a programme of research based on NHC-stabilized borocations. Although some early reports hinted at the potential of NHCs in stabilizing diaminoborenium ions,[11] this general class of species has been largely overlooked until Matsumoto and Gabbaï recent report on an NHC-stabilized diaryl borenium ion.[12] We hereby disclose our preliminary findings on the synthesis of an NHC-stabilized *dialkyl* borenium ion, generated from an NHC–diorganoborane complex by reaction with Brønsted acids.

Strategies reported to date for the synthesis of borenium ions include: (a) halide abstraction from tetra-co-ordinate *ate* complexes;[2,12] (b) displacement of anionic leaving groups from boron by a neutral ligand;[2] (c) conversion of a formally neutral *N*-substituent to a positively charged species by protonation, or co-ordination of a Lewis acid;[2] and (d) hydride abstraction using the trityl cation with a non-co-ordinating counter-ion.[2] Distinct from these four approaches is the borenium ion formation reported by Fox *et al.*, employing protic cleavage of a carborane B–B bond.[13]

The hydride abstraction method described above is attractive, since it allows the synthesis of borenium ions from *ate* complexes of a wide-range of diorganoboranes, which are, in turn, either commercially available or readily prepared using hydroboration chemistry. We envisioned the possibility of forming NHC-stabilized borenium ions **5** from the NHC–organoboron *ate* complexes **4**, *via* hydride abstraction by acid-induced cleavage of the B–H bond (Scheme 1).
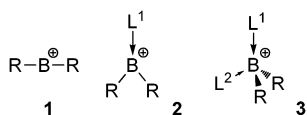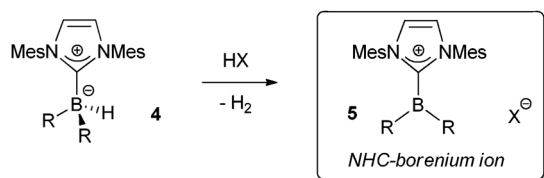
**Scheme 1** Proposed Brønsted acid-mediated borenium ion synthesis.

We investigated the feasibility of this B–H protonolysis route by first studying the reaction of NHC–boranes with Brønsted acids.

IMes·BH$_3$ **6**[9e] and IMes·9-BBN-H **7**[10] were prepared in excellent yields by the reaction of IMes with BH$_3$·SMe$_2$ and 9-BBN-H, respectively. The tetra-co-ordinate *ate* nature of these air-stable complexes **6** and **7** was confirmed by their ^{11}B NMR chemical shifts, displaying a sharp quartet at −38.3 ppm, and a doublet at −16.6 ppm, respectively.

In agreement with the observations of Lacôte and Curran *et al.* in NHC–boranes employing the DIPP ligand system,[8f] reaction of IMes·BH$_3$ **6** with both HCl and TsOH proceeded smoothly, with the evolution of hydrogen, to yield new NHC–borane complexes **8** and **9** in high yield (Scheme 2). Treatment of IMes·BH$_3$ **6** with triflic acid provided the monotriflate complex IMes·BH$_2$OTf **10**. Chloro- and tosyl complexes **8** and **9** are air-stable solids, whereas triflate complex **10** was found to be air-sensitive. This complex was not isolated, but was formed quantitatively as demonstrated by ^{11}B NMR analysis.

The [11]B chemical shift and multiplicity of **8–10** suggested that all three complexes exist as tetra-co-ordinate boronates and not borenium ions; no ligand system is known which stabilizes the elusive dihydridoborenium ion.[5a,6c] We reasoned that instead, a dialkylborane complex might be induced to expel triflate and form a borenium ion, due to both the increased steric congestion and inductive electronic stabilization, compared to the corresponding dihydrido complex.[14] Thus, treatment of IMes·9-BBN-H **7** with triflic acid cleanly produced the corresponding IMes·9-BBN OTf **11** (Scheme 3). In contrast to **10**, the ^{11}B NMR chemical shift of **11** (+81.4 ppm in CD$_2$Cl$_2$) and width at half-height (715.8 Hz) suggested a three co-ordinate boron and a dissociated triflate counter-ion, *i.e.* a borenium ion.

For reference, 9-BBN-OTf exhibits an ^{11}B NMR chemical shift of +66 ppm (in hexanes),[15] and the two previously-reported 9-BBN-based borenium ions, the 2,6-lutidine-[6a]
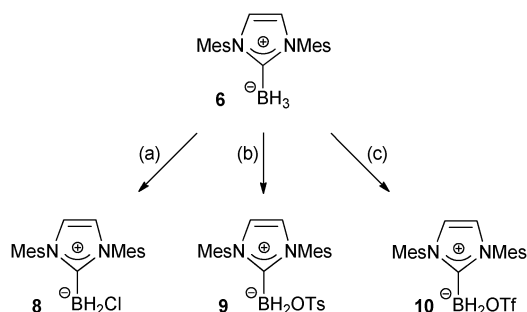
Scheme 2 Reaction conditions: (a) 2 M HCl in Et$_2$O, CH$_2$Cl$_2$, rt, 1 h, 100%; (b) TsOH, CHCl$_3$, rt, 1 h, 85%; (c) TfOH, CH$_2$Cl$_2$, −40 °C, 0.5 h.
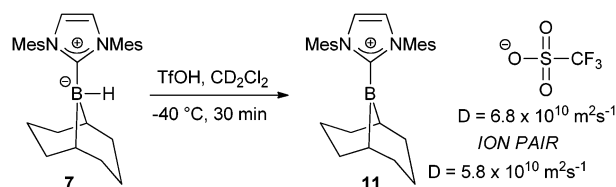
Scheme 3 Formation of an NHC-stabilized dialkylborenium ion.

and triethylamine[16] complexes of the 9-BBN borenium ion, are reported as having an [11]B chemical shift of +59.2 and +85.1 ppm, respectively. The large, positive ^{11}B NMR chemical shift of **11** is good evidence for a dissociated triflate and a genuine, NHC-stabilized dialkylborenium ion. Furthermore, the magnitude of the chemical shift suggests that the NHC offers little in the way of π-stabilisation, given how similar the value is to that reported by Vedejs *et al.* for the corresponding triethylamine complex.[16]

Definitive evidence of the borenium ion nature of **11** can be derived from diffusion ordered NMR spectroscopy (DOSY NMR)—measuring the diffusion co-efficients of the NHC–boron moiety and the triflate, respectively. Significantly different diffusion co-efficients for the cationic and anionic components would confirm the ion-paired, borenium character of **11**. Such studies are well-known in transition metal chemistry, thanks to the pioneering work of Pregosin,[17] but to the best of our knowledge, this technique has not yet been employed in determining ion-pairing in borocation chemistry. Instead, in the cases where there is an absence of X-ray crystallographic data, ^{11}B NMR chemical shifts have been relied on to determine the nature of borocation species. The diffusion co-efficient of the NHC–boron moiety was measured by a ^{1}H NMR DOSY experiment and ^{19}F DOSY was used to obtain the triflate diffusion co-efficient, in CD$_2$Cl$_2$ solution. Fluorobenzene was used as an inert internal standard in both experiments to ensure consistency between the ^{1}H and ^{19}F experiments. The NHC–9-BBN moiety of **11** was found to have a diffusion co-efficient of 5.8×10^{10} m^2 s^{-1} whilst the triflate's diffusion co-efficient was 6.8×10^{10} m^2 s^{-1}.[15] The ratio of the cation and anion diffusion co-efficients is reflective of the amount of ion-pairing in the system, with a ratio of 1 being the theoretical value for the covalently bound anion and cation (*i.e.* 100% ion-pairing),[18] values of 0.98–1.00 suggest complexes that are close to complete ion pairing, and ratios of <0.96 are indicative of a separated ion pair.[18] Using this approach, the ratio of diffusion co-efficients for the cation and anion in borenium salt **11** is 0.85, unquestionably in the realm of a separated ion pair.[19] Hence these DOSY NMR measurements provide compelling evidence for a separated ion pair, indicating *the first N-heterocyclic carbene-stabilized dialkylborenium ion*.

The composition of complex **11** was also confirmed by an independent synthetic method. Addition of IMes to a commercially available solution of 9-BBN-OTf in hexanes produced a single species by ^{11}B NMR with an identical chemical shift to **11**. Given the thermal instability of even *N*- or *O*-stabilized borenium ions, we were surprised at the remarkable stability of NHC–dialkylborenium complex **11**: a sample of **11** (CD$_2$Cl$_2$ solution under N$_2$) showed no signs of decomposition after storage for two weeks at room temperature, providing clear evidence for the thermodynamic

stability conferred by the NHC ligand, as well as the kinetic shielding provided by the bulky mesityl groups.

Thus, we have prepared the first example of a dialkylborenium ion stabilized by an NHC, *via* a novel route employing triflic acid to effect protolytic cleavage of the B–H bond of an NHC–diorganoborane complex. The remarkable stability of this system augers well for their application as Lewis acids in a range of organic transformations; such studies are underway in our laboratory and will be reported on in due course.

Notes and references

1 *Science of Synthesis Organometallics: Boron Compounds, in vol. 6*, ed. D. E. Kaufmann and D. S. Matteson, Georg ThiemeVerlag, Stuttgart, New York, 2004.

2 For a review of borocations, see: W. E. Piers, S. A. Bourke and K. D. Conroy, *Angew. Chem., Int. Ed.*, 2005, **44**, 5016.

3 (*a*) Y. Hayashi, J. J. Rohde and E. J. Corey, *J. Am. Chem. Soc.*, 1996, **118**, 5502; (*b*) E. Canales and E. J. Corey, *J. Am. Chem. Soc.*, 2007, **129**, 12686 and references therein.

4 P. Wei and D. A. Atwood, *Inorg. Chem.*, 1998, **37**, 4934.

5 For recent examples, see: (*a*) T. S. De Vries and E. Vedejs, *Organometallics*, 2007, **26**, 3079; (*b*) M. A. Dureen, A. Lough, T. M. Gilbert and D. W. Stephan, *Chem. Commun.*, 2008, 4303; (*c*) C. Bonnier, W. E. Piers, M. Parvez and T. S. Sorensen, *Chem. Commun.*, 2008, 4593; (*d*) A. Del Grosso, R. G. Pritchard, C. A. Muryn and M. J. Ingleson, *Organometallics*, 2010, **29**, 241; (*e*) A. J. V. Marwitz, J. T. Jenkins, L. N. Zakharov and S.-H. Liu, *Angew. Chem., Int. Ed.*, 2010, **49**, 7444; (*f*) A. Del Grosso, P. J. Singleton, C. A. Muryn and M. J. Ingleson, *Angew. Chem., Int. Ed.*, 2011, **50**, 2102.

6 (*a*) C. K. Narula and H. Nöth, *Inorg. Chem.*, 1985, **24**, 2532; (*b*) P. Jutzi, B. Krato, M. Hursthouse and A. J. Howes, *Chem. Ber.*, 1987, **120**, 1091; (*c*) E. Vedejs, T. Nguyen, D. R. Powell and M. R. Schrimpf, *Chem. Commun.*, 1996, 2721; (*d*) I. Ghesner, W. E. Piers, M. Parvez and R. McDonald, *Chem. Commun.*, 2005, 2480; (*e*) M. K. Uddin, Y. Nagano, R. Fujiyama, S.-I. Kiyooka, M. Fujio and Y. Tsuno, *Tetrahedron Lett.*, 2005, **46**, 627; (*f*) C.-W. Chiu and F. Gabbaï, *Organometallics*, 2008, **27**, 1657; (*g*) T. S. De Vries, A. Prokofjevs, J. N. Harvey and E. Vedejs, *J. Am. Chem. Soc.*, 2009, **131**, 14679.

7 (*a*) N-*Heterocyclic Carbenes in Synthesis*, ed. S. P. Nolan, Wiley-VCH, Weinheim, 2006; (*b*) *Topics in Organometallic Chemistry*, ed. F. Glorius, Springer, Berlin, Heidelberg, 2007, vol. 21.

8 (*a*) S. H. Ueng, M. M. Brahmi, É. Derat, L. Fensterbank, E. Lacôte, M. Malacria and D. P. Curran, *J. Am. Chem. Soc.*, 2008, **130**, 10082; (*b*) K. S. Lee, A. R. Zhugralin and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2009, **131**, 7253; (*c*) Q. Chu, M. M. Brahmi, A. Solovyev, S. Ueng, D. P. Curran, M. Malacria, L. Fensterbank and E. Lacôte, *Chem.–Eur. J.*, 2009, **15**, 12937; (*d*) S. Ueng, A. Solovyev, X. Yuan, S. J. Geib, L. Fensterbank, E. Lacôte, M. Malacria, M. Newcomb, J. C. Walton and D. P. Curran, *J. Am. Chem. Soc.*, 2009, **131**, 11256; (*e*) J. Monot, A. Solovyev, H. Bonin-Dubarle, É. Derat, D. P. Curran, M. Robert, L. Fensterbank, E. Lacôte and M. Malacria, *Angew. Chem., Int. Ed.*, 2010, **49**, 9166; (*f*) A. Solovyev, Q. Chu, S. J. Geib, L. Fensterbank, M. Malacria, E. Lacôte and D. P. Curran, *J. Am. Chem. Soc.*, 2010, **132**, 15072.

9 (*a*) N. Kuhn, G. Henkel, T. Kratz, J. Kreutzberg, J. Boese and A. H. Maulitz, *Chem. Ber.*, 1993, **126**, 2041; (*b*) D. Enders, K. Breuer, J. Runsink and J. H. Teles, *Liebigs Ann.*, 1996, 2019; (*c*) A. J. Arduengo, F. Davidson, R. Krafczyk, W. J. Marshall and R. Schmutzler, *Monatsh. Chem.*, 2000, **131**, 251; (*d*) X. Zheng and G. E. Herberich, *Organometallics*, 2000, **19**, 3751; (*e*) T. Ramnial, H. Jong, I. D. McKenzie, M. Jennings and J. A. C. Clyburne, *Chem. Commun.*, 2003, 1722; (*f*) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xe, R. B. King, H. F. Schaeffer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2007, **129**, 12414; (*g*) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones and M. Tamm, *Angew. Chem., Int. Ed.*, 2008, **47**, 7428; (*h*) P. A. Chase and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2008, **47**, 7433.

10 D. M. Lindsay and D. McArthur, *Chem. Commun.*, 2010, **46**, 2474.

11 (*a*) L. Weber, E. Dobbert, H.-G. Stammler, B. Neumann, R. Boese and D. Bläser, *Chem. Ber.*, 1997, **130**, 705; (*b*) A. Wacker, H. Pritzkow and W. Siebert, *Eur. J. Inorg. Chem.*, 1998, 789.

12 T. Matsumoto and F. Gabbaï, *Organometallics*, 2009, **28**, 4252.

13 M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, I. S. Neretin and K. Wade, *Chem. Commun.*, 1999, 1649.

14 Triflate is covalently bound in IMes·InMe$_2$OTf; see: J. H. Cotgreave, D. Colclough, G. Kociok-Köhn, G. Ruggiero, C. G. Frost and A. S. Weller, *Dalton Trans.*, 2004, 1519.

15 See ESI†.

16 A. Prokofjevs, J. W. Kampf and E. Vedejs, *Angew. Chem., Int. Ed.*, 2011, **50**, 2098.

17 For reviews, see: (*a*) M. Valentini, H. Rüegger and P. S. Pregosin, *Helv. Chim. Acta*, 2001, **84**, 2833; (*b*) P. S. Pregosin, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2006, **49**, 261.

18 See, for example, A. Moreno, P. S. Pregosin, L. F. Veiros, A. Albinati and S. Rizzato, *Chem.–Eur. J.*, 2008, **14**, 5617.

19 For reference, the corresponding ratio for ^{1}H and ^{19}F in fluorobenzene was 0.99. See ESI†.