Ionic Liquids | Hot Paper

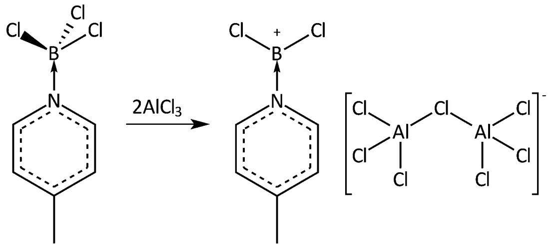
International Edition: DOI: 10.1002/anie.201508653
German Edition: DOI: 10.1002/ange.201508653

Lewis Superacidic Ionic Liquids with Tricoordinate Borenium Cations

Sesime Coffie, James M. Hogg, Lucie Cailler, Albert Ferrer-Ugalde, Richard W. Murphy, John D. Holbrey, Fergal Coleman, and Małgorzata Swadźba-Kwaśny**

***Abstract:** The first examples of ionic liquids based on borenium cations, $[BCl_2L]^+$, are reported. These compounds form highly Lewis acidic liquids under solvent-free conditions. Their acidity was quantified by determining the Gutmann acceptor number (AN). Extremely high ANs were recorded (up to AN = 182, $\delta_{31P} = 120$ ppm), demonstrating that these borenium ionic liquids are the strongest Lewis superacids reported to date, with the acidity enhanced by the ionic liquid environment.*

Borocations are important reagents in organic synthesis (e.g., for C−H borylation[1] or alkene hydroboration)[2] and as Lewis acidic components in frustrated Lewis pairs.[3] Their chemistry has been reviewed by Kölle and Nöth[4] and more recently by Piers et al.[5] and Ingleson.[6] A review on tricoordinate borenium cations, which are the focus of this work, has been published by De Vries and co-workers.[7] Borenium ions are very strong Lewis acids, with the electron deficiency of the vacant boron p orbital enhanced by the positive charge. The most important routes to generate borenium cations are hydride or halide abstraction reactions from tetracoordinate boron adducts, $[BX_3L]$, using an excess of abstracting agent (Scheme 1).[4–8]



Scheme 1. Formation and structure of a borenium cation with a $[Al_2Cl_7]^-$ counterion.

Many borenium complexes have been reported as oily materials.[4] Despite the increasing number of known crystal structures,[5,9,10] they are generally difficult to crystallize and are typically studied in solution by ^{11}B NMR spectroscopy. We hypothesized that these oily materials might in fact be ionic liquids. Studying them in this form may enable access to "naked" borenium cations in which the full Lewis acidity of the boron center could be harnessed without detrimental solvent effects. Ionic liquids are salts with low lattice energies and low melting points (arbitrarily below 100 °C) and can be generated by selecting ions with low symmetry and a low charge, which is preferably dispersed across multiple sites.[11] The borenium salt shown in Scheme 1 contains a large anion of low symmetry and a charge-dispersed cation, which is typical for ionic liquid formation. Continuing our efforts to develop strongly Lewis acidic systems from off-the-shelf reactants,[12–14] liquid borenium salts have been prepared, their speciation was determined, and their Lewis acidity measured.

Boron adducts, $[BCl_3L]$, with L-type ligands of differing donor characteristics were isolated as colorless powders. Aromatic N-donors [pyridine (py), 3-picoline (3pic), 4-picoline (4pic), and 1-methylimidazole (mim)] were selected as particularly suitable for the stabilization of borenium cations owing to their σ-donor properties.[15] For structural comparison, an adduct with an aliphatic base (trioctylphosphine, P_{888}) was prepared; the phosphine is a stronger donor to BCl_3 than the corresponding amine.[16] ^{11}B NMR spectra (see the Supporting Information, Figure S1, Table S1) were in agreement with the literature.[16,17]

Borenium ionic liquids were prepared by a solvent-free method, analogous to that used for chlorometalate ionic liquids.[18] All products were homogenous liquids, except for equimolar mixtures of $[BCl_3(mim)]$ and MCl_3, which resulted in white pastes. Aluminum(III) chloride and the $[BCl_3L]$ adducts were used in ratios of 1:1 or 2:1 because only two chloroaluminate(III) anions are found in homogeneous ionic liquids: $[AlCl_4]^-$ and $[Al_2Cl_7]^-$.[19,20] In contrast, higher chlorogallate(III) anion homologues are known,[20,21] so 1–3 equiv of gallium(III) chloride were used with respect to the $[BCl_3L]$ adducts.

A major resonance in the ^{11}B NMR spectra was observed at 30–50 ppm (Figure 1; Table S1). The shift depended on the $[BCl_3L]$ to MCl_3 stoichiometry, but not on the metal (Al or Ga); the signals were shifted upfield for systems with 1:1 stoichiometry compared to those with 1:2 stoichiometry (Figure S2). This revealed incomplete halide abstraction using 1 equiv of MCl_3, and complete ionization with 2 or 3 equiv of MCl_3, which is in agreement with solution studies.[8,10] For $[BCl_3L]/2\,MCl_3$ systems, the main feature was a broad peak at 44 ± 4 ppm, which corresponds to formation of tricoordinate $[BCl_2L]^+$ cations.[5,7] A shoulder at 45 ± 1 ppm indicates the presence of BCl_3 and consequently partial transfer of the ligand to the Al or Ga centers.[10,22] Similarly, the main resonance at 36 ± 1 ppm

---

[*] S. Coffie, J. M. Hogg, L. Cailler, Dr. A. Ferrer-Ugalde, R. W. Murphy, Dr. J. D. Holbrey, Dr. F. Coleman, Dr. M. Swadźba-Kwaśny
The QUILL Research Centre
The School of Chemistry and Chemical Engineering
The Queen's University of Belfast
Belfast, BT9 5AG (UK)
E-mail: f.coleman@qub.ac.uk
m.swadzba-kwasny@qub.ac.uk

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201508653.

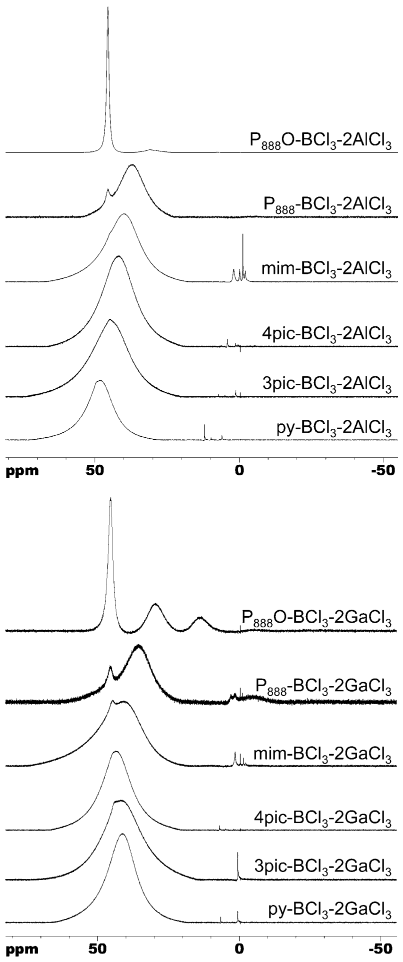


Figure 1. ^{11}B NMR spectra (128.37 MHz, 27 °C, neat liquid with $[D_6]$DMSO lock) of borenium ionic liquids with the general formula $[BCl_3L]/2\,MCl_3$, where M = Al (top) and Ga (bottom).

and the shoulder at approximately 45.5 ppm for the $[(P_{888})BCl_3]/2\,MCl_3$ systems are consistent with $[BCl_2(P_{888})]^+$[23] and BCl_3.

Partial ligand transfer onto a metal center was confirmed by ^{27}Al NMR spectroscopy (Figure S3, Table S2). For N-donors, the main resonance was observed at approximately 106 ppm, which corresponds to the equilibrated tetracoordinate complexes $[AlCl_4]^-$, $[Al_2Cl_7]^-$, and $[AlCl_3L]$,[24–26] with a shoulder at 75 ± 1 ppm, which is due to the pentacoordinate complex $[AlCl_3L_2]$ and/or the cationic complex $[AlCl_2L_2]^+$.[25,27] The ^{27}Al NMR spectrum of $[(P_{888})BCl_3]/2\,AlCl_3$ showed a broad feature with two maxima at 66 and 114 ppm, consistent with species analogous to those identified for the N-donors.[12,28]

The crystal structure of $[BCl_2(py)][AlCl_4]$, isolated here as an ionic liquid, has been previously reported.[10] This indicates that some systems described in this work may in fact be supercooled liquids.[29] It is also likely that dynamic equilibria with components other than $[BCl_2L]^+$ and $[MCl_4]^-$ (metal complexes, BCl_3) hinder crystallization.

The Lewis acidity of the borenium ionic liquids was quantified by determining the Gutmann acceptor number (AN),[30] for which triethylphosphine oxide (tepo) was used as a ^{31}P NMR probe. AN values scale from 0 (hexane) to 100 ($SbCl_5$ in 1,2-dichloroethane), and acids with AN > 100 are considered to be Lewis superacids. The method has been well established for determining the Lewis acidity of both borenium cations[7,22] and ionic liquids.[18,20]

Unambiguous results could only be obtained for systems with N-donors because the ^{31}P NMR resonances of tepo (1–3 mol %) were obscured by signals from the P_{888} ligand. Aluminum-containing systems gave two primary ^{31}P signals (Figure 2, bottom). The more upfield peaks [$\delta_{31P} = 84 \pm 2$ ppm, AN = 96 ± 2 (1 mol % tepo)] were consistent with tepo in chloroaluminate(III) ionic liquids with $[Al_2Cl_7]^-$ anions.[31] The downfield resonances [$\delta_{31P} = 94.5$–117.2 ppm, AN = 120–174 (1 mol % tepo)] correspond to tepo coordinated to the borenium cation. For $[BCl_3L]/n\,GaCl_3$ systems ($n = 1$ or 2), one main resonance was detected, which is consistent with tepo coordinated to a borenium cation (Figure 2, top). With three equiv of $GaCl_3$, a second resonance appeared [$\delta_{31P} = 93 \pm 1$ ppm, AN = 118 ± 1 (1 mol % tepo)] with a slightly higher AN value than that reported for chlorogallate(III) ionic liquids with $[Ga_3Cl_{10}]^-$ anions (AN = 107).[18]

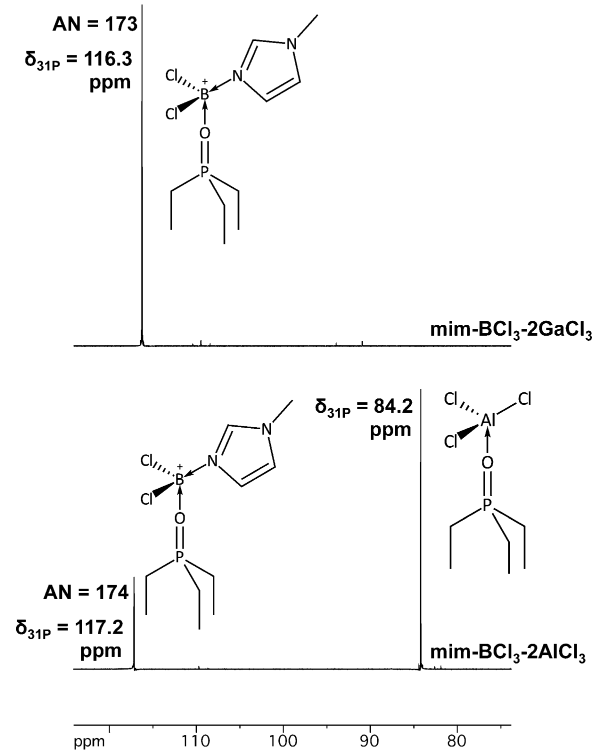


Figure 2. ^{31}P NMR spectra (161.96 MHz, 27 °C, neat liquid with $[D_6]$DMSO lock) of solutions of the borenium ionic liquids with the general formula $[(mim)BCl_3]/2\,MCl_3$ with 1 mol % tepo.

The AN values were calculated based on the signal that is due to $[BCl_2L(tepo)]^+$ (Table 1). The ^{31}P NMR chemical shifts determined for solutions with 1 mol % tepo are also given. All of the AN values fall within the Lewis superacidity region (AN = 120–182). For systems with pyridine-based donors (py, 3pic, 4pic), the acidity depended both on the molar ratio of

Table 1: AN values for all $[BCl_3L]/n\,MCl_3$ systems based on N-donors that were homogenous liquids along with the δ_{31P} resonances (in ppm) measured for solutions of these liquids containing 1 mol% tepo (referenced to $\delta_{31P,\,H_3PO_4\,(85\,\%)} = 0.0$ ppm).

	$AlCl_3$		$2\,AlCl_3$		$GaCl_3$		$2\,GaCl_3$		$3\,GaCl_3$	
L (pK_a)	AN	δ_{31P}	AN	δ_{31P}	AN	δ_{31P}	AN	δ_{31P}	AN	δ_{31P}
py (5.12)	120	94.5	162	109.6	121	94.7	134	99.9	180	119.2
3pic (5.63)	124	95.5	170	113.2	121	95.5	135	99.6	182	119.8
4pic (5.85)	124	96.2	170	112.5	121	94.5	140	101.7	181	119.9
mim (6.82)	–	–	174	117.2	–	–	173	116.3	175	117.4

MCl_3 and the borenium species and on the metal (Al or Ga). In contrast, all ionic liquids based on 1-methylimidazole (the strongest base; see Table 1) had the same acidity (AN = 174 ± 1; Figure 3). Apparently, for this strong donor, a "naked" $[BCl_2(mim)]^+$ cation was formed, as reflected by the constantly high AN values. In contrast, borenium cations with weaker donors (py, 3pic, 4pic) interacted strongly with the anions, which resulted in anion-dependent AN values, and the least coordinating anion, $[Ga_3Cl_{10}]^-$, afforded the highest acidity. This distinction was unexpected considering that all of the $[BCl_3L]/2\,MCl_3$ systems appeared to show full halide abstraction by ^{11}B NMR spectroscopy.

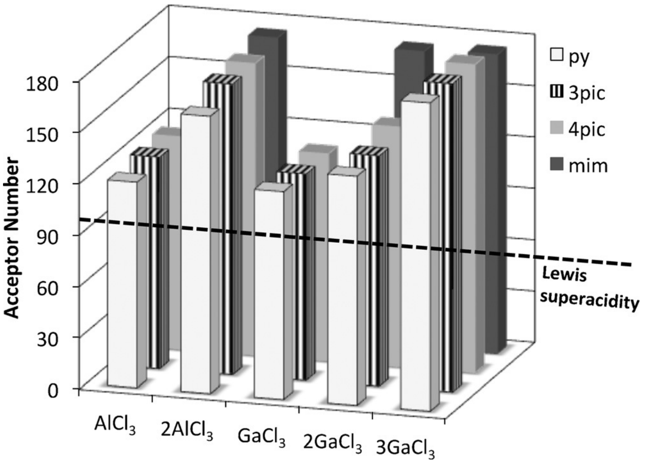


Figure 3. AN values for borenium cations, determined for the $[BCl_3L]/n\,MCl_3$ systems.

The ionic liquids containing borenium cations, $[BCl_2L]^+$, were found to be the strongest Lewis acids reported to date, with AN values of up to 182. These values are much higher than those determined for the corresponding solutions, for example, AN = 80–85 for $[B(C_6F_5)_2L]^+$ in CD_2Cl_2 and $\delta_{31P} = 106.9$ ppm in C_6D_6 for the $[(cat)B]^+$ cation (cat = catecholato).[22,32] To confirm that the increase in acidity was due to the ionic environment and not the structure of particular cations, we compared the AN values of a neat ionic liquid, $[(3pic)BCl_3]/2\,AlCl_3$, and its solutions in dichloromethane (DCM) and acetonitrile (MeCN). To prepare the solutions, equal volumes of the ionic liquid and the dry solvent were used. The acidities measured for $[(3pic)BCl_3]/2\,AlCl_3$ in solution were much lower than those recorded under neat conditions ($AN_{DCM} = 123$ and $AN_{MeCN} = 125$ vs. $AN_{neat} = 170$). The difference in the ^{31}P NMR chemical shifts, $\Delta\delta \approx 16$ ppm, was too large to arise solely from changing the solvent. Interestingly, ^{11}B NMR spectra of the solutions revealed that the cation retained its tricoordinate structure in DCM, but was tetracoordinate in MeCN (e.g., a "masked" borenium cation).[6] Nevertheless, the use of either solvent led to similar reductions in acidity, suggesting that the decrease in electrophilicity arises from solvation rather than coordination.

In summary, these preliminary findings provide first evidence that the full acidity of these "naked" borenium cations can be harnessed when they are employed as ionic liquids, rather than in solution.

Experimental Section

Trioctylphosphine was provided by Cytec, other reactants were purchased from Sigma–Aldrich. Solvents and bases were dried over 3 Å molecular sieves and stored under argon. Trioctylphosphine oxide was dried (70 °C, 2 days, 10^{-2} mbar) and stored in a glovebox. Metal halides (anhydrous, in glass ampoules) and trioctylphosphine were used as received. Boron trichloride adducts were prepared using an argon Schlenk line, by dropwise addition of a base (0.9 equiv) to a vigorously stirred mixture of boron trichloride (1 M solution in heptane, 1.0 equiv) and DCM at −78 °C. After the reaction (−78 °C, 30 min, 600 rpm), excess reactants and solvents were removed under reduced pressure, and the adduct was dried under high vacuum (60 °C, 10^{-2} bar, overnight). Complexes of pyridine and 3- and 4-picoline were recrystallized from a mixture of dry dichloromethane and hexane. Borenium ionic liquids were synthesized in a nitrogen-filled glovebox. A metal(III) chloride (1, 2, or 3 equiv) was added slowly to the boron trichloride adduct (1 equiv) and left to react until a homogenous mixture was obtained or no further change was observed (30–50 °C, 10 min–24 h, 600 rpm).

NMR spectroscopy: Boron trichloride adducts were analyzed as solutions in $CDCl_3$ and the ionic liquids as neat liquids, with sealed capillaries of $[D_6]$DMSO as an external lock. ^{11}B, ^{27}Al, and ^{31}P NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometer. The background signals from the borosilicate tube were removed from the ^{11}B NMR spectra using iNMR (Mestrelab Research).

To determine the acceptor number, three solutions of tepo in an ionic liquid were prepared, at concentrations of about 1, 2, and 3 mol%. ^{31}P NMR spectra were recorded under neat conditions with $[D_6]$DMSO as an external lock and referenced to H_3PO_4 (85%; $\delta_{H_3PO_4,\,85\,\%} = 0$ ppm). The ^{31}P NMR chemical shift at infinite tepo dilution, δ_{inf}, was determined by extrapolation from the ^{31}P NMR chemical shifts at the three different tepo concentrations and normalized to the chemical shift of tepo in hexane at infinite dilution ($\delta_{inf,hex} = 0$ ppm). The AN values for all samples were calculated according to: $AN = 2.348 \times \delta_{inf}$.

Acknowledgements

QUILL and its Industrial Advisory Board are acknowledged for financial support. M.S.-K. thanks the QUB Research Fellowship Scheme for funding. Cytec Industries Inc. are acknowledged for kindly providing phosphine ligands.

Keywords: borenium cations · boron · Group 13 elements · ionic liquids · Lewis acids

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 14970–14973
Angew. Chem. **2015**, *127*, 15183–15186

---

[1] A. Del Grosso, P. J. Singleton, C. A. Muryn, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2011**, *50*, 2102–2106; *Angew. Chem.* **2011**, *123*, 2150–2154.
[2] A. Prokofjevs, A. Boussonnière, L. Li, H. Bonin, E. Lacôte, D. P. Curran, E. Vedejs, *J. Am. Chem. Soc.* **2012**, *134*, 12281–12288.
[3] D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541.
[4] P. Kölle, H. Noth, *Chem. Rev.* **1985**, *85*, 399–418.
[5] W. E. Piers, S. C. Bourke, K. D. Conroy, *Angew. Chem. Int. Ed.* **2005**, *44*, 5016–5036; *Angew. Chem.* **2005**, *117*, 5142–5163.
[6] M. J. Ingleson, *Top. Organomet. Chem.* **2015**, *49*, 39–71.
[7] T. S. De Vries, A. Prokofjevs, E. Vedejs, *Chem. Rev.* **2012**, *112*, 4246–4282.
[8] G. E. Ryschkewitsch, J. W. Wiggins, *J. Am. Chem. Soc.* **1970**, *92*, 1790–1791.
[9] A. Del Grosso, M. D. Helm, S. A. Solomon, D. Caras-Quintero, M. J. Ingleson, *Chem. Commun.* **2011**, *47*, 12459–12461.
[10] A. Del Grosso, E. R. Clark, N. Montoute, M. J. Ingleson, *Chem. Commun.* **2012**, *48*, 7589–7591.
[11] I. Krossing, J. M. Slattery, C. Daguenet, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427–13434.
[12] F. Coleman, G. Srinivasan, M. Swadźba-Kwaśny, *Angew. Chem. Int. Ed.* **2013**, *52*, 12582–12586; *Angew. Chem.* **2013**, *125*, 12814–12818.
[13] J. Hogg, F. M. Coleman, A. F. Ugalde, M. P. Atkins, M. Swadzba-Kwasny, *Green Chem.* **2015**, *17*, 1831–1841.
[14] K. Matuszek, A. Chrobok, J. M. Hogg, F. Coleman, M. Swadźba-Kwaśny, *Green Chem.* **2015**, *17*, 4255–4262.
[15] W. F. Schneider, C. K. Narula, H. Noeth, *Inorg. Chem.* **1991**, *30*, 3919–3927.
[16] D. E. Young, G. E. McAchran, S. G. Shore, *J. Am. Chem. Soc.* **1966**, *88*, 4390–4396.
[17] P. N. Gates, E. J. McLauchlan, E. F. Mooney, *Spectrochim. Acta* **1965**, *21*, 1445–1448.
[18] J. Estager, A. A. Oliferenko, K. R. Seddon, M. Swadźba-Kwaśny, *Dalton Trans.* **2010**, *39*, 11375–11382.
[19] H. A. Øye, M. Jagtoyen, T. Oksefjell, J. S. Wilkes, *Mater. Sci. Forum* **1991**, *73*, 183–190.
[20] J. Estager, J. D. Holbrey, M. Swadźba-Kwaśny, *Chem. Soc. Rev.* **2014**, *43*, 847.
[21] C. Hardacre, R. W. Murphy, K. R. Seddon, G. Srinivasan, M. Swadźba-Kwaśny, *Aust. J. Chem.* **2010**, *63*, 845–848.
[22] A. Del Grosso, R. G. Pritchard, C. A. Muryn, M. J. Ingleson, *Organometallics* **2010**, *29*, 241–249.
[23] T. S. De Vries, E. Vedejs, *Organometallics* **2007**, *26*, 3079–3081.
[24] S. Takahashi, M.-L. Saboungi, R. J. Klingler, M. J. Chen, J. W. Rathke, *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 3591–3595.
[25] D. A. Atwood, *Coord. Chem. Rev.* **1998**, *176*, 407–430.
[26] A. Dimitrov, D. Heidemann, E. Kemnitz, *Inorg. Chem.* **2006**, *45*, 10807–10814.
[27] K. Yoshii, X. Jiang, X. G. Sun, T. Tsuda, N. Mehio, S. Dai, *Electrochim. Acta* **2015**, *160*, 82–88.
[28] *Multinuclear NMR* (Ed.: J. Mason), Plenum Press, New York, **1987**.
[29] J. D. Holbrey, K. R. Seddon, *J. Chem. Soc. Dalton Trans.* **1999**, 2133–2140.
[30] V. Gutmann, *Electrochim. Acta* **1976**, *21*, 661–670.
[31] T. A. Zawodzinski, Jr., R. A. Osteryoung, *Inorg. Chem.* **1989**, *28*, 1710–1715.
[32] I. B. Sivaev, V. I. Bregadze, *Coord. Chem. Rev.* **2014**, *270–271*, 75–88.

Received: August 15, 2015
Revised: October 2, 2015