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Lewis superacidic ionic liquids with tricoordinate borenium cations

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Abstract: The first examples of ionic liquids based on borenium cations, [BCl3L]3, are reported. These compounds form solvent-free highly Lewis acidic liquids. Acidity was quantified using the Gutmann Acceptor Number (AN) method with extremely high ANs recorded (up to AN = 182, δ_{AN} = 120 ppm) demonstrating that these borenium ionic liquids are the strongest Lewis superacids reported to date.

Borocations are important reagents in organic synthesis (viz. C–H borylations[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] Chemistry of tricoordinate borenium cations, which are the focus of this work, have been reviewed by De Vries et al.[7] Boronium 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 from tetracoordinate boron adducts, [BX3L], using an excess of abstracting agent (Figure 1).[4,5,7,10]

Many boronium complexes have been reported as ‘oily materials’. [4] Despite the increasing number of known crystal structures,[5,8,9] they are generally difficult to crystallize, and are typically studied in solution, using $^{11}$B NMR spectroscopy. We hypothesised that these ‘oily materials’ might be in fact ionic liquids. Studying them in this form may enable access to ‘naked’ borenium cations in which the full Lewis acidity of the boron centre 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 with 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, exemplars for ionic liquid formation. Continuing our effort to develop strongly Lewis acidic systems from off-the-shelf reactants,[12-14] liquid borenium salts have been prepared, their speciation determined and Lewis acidity measured.

Supporting information for this article is given via a link at the end of the document.

Scheme 1. The formation and structure of a borenium cation with [AlCl3] anion

Boron adducts, [BCl3L], with L-type ligands of differing donor characteristics were isolated as colourless powders. Aromatic N-donors (pyridine, py; 3-picoline, 3pic; 4-picoline, 4pic; and 1-methylimidazole, mim) were selected as particularly suitable for the stabilisation of borenium cations, due to their δ-donor properties.[15] For structural comparison, an adduct with an aliphatic base (triethylphosphine, P888) was prepared; the phosphine is a stronger donor to BCl3 than the corresponding amine.[16] $^{11}$B NMR spectra (Figure 1-SI, Table 1-SI) were in agreement with the literature.[16,17]

Borenium ionic liquids were prepared via a solventless procedure, analogous to that used for chlorometallolate ionic liquids.[18] All products were homogenous liquids, except for equimolar mixtures of [BCl3(mim)] and MCls, which formed white pastes. Aluminium(III) chloride was used in 1 or 2 mol ratio with respect to [BCl3L] adducts, because only two chlorometallate(III) anions exist in homogeneous ionic liquids: [AlCl4] and [Al2Cl7] .[19,20] In contrast, higher chlorogallate(III) anion homologues are known,[20,21] so gallium(III) chloride was used in 1-3 mol ratio.

A major peak in the $^{11}$B NMR spectra was observed at 30-50 ppm (Table 1-SI). The shift depended on [BCl3L] to MCl5 stoichiometry, but not on the metal (Al or Ga), with the signals shifted upfield for systems with 1:1 stoichiometry compared to those with 1:2 (Figure 2-SI). This revealed incomplete halide abstraction using 1 mol eq. of MCl5, and complete ionisation with 2 or 3 mol eq. of MCl5, in agreement with solution studies.[16,10] For L-BCl3,2MCl5 systems, the main feature was a broad peak at 44±4 ppm, corresponding to formation of tricoordinate [BCl3L] cations.[5,7] A shoulder at 45±1 ppm indicates the presence of BCl3, and consequently partial exchange of the ligand to Al or Ga centres.[10,22] Similarly, the main signal at 36±1 ppm and shoulder ca. 45.5 ppm for P888-BCl3,2MCl5 systems is consistent with [BCl3(P888)] and BCl3.
Acid has oxide (tepo) is used as a Gutmann Acceptor Number (AN) in the crystallisation.

\[ \text{AN} = 0, \text{SbCl}_5 \text{ in 1,2-dichloroethane has AN} = 100, \text{and acids with AN} > 100 \text{ are considered Lewis superacids.} \]

The Gutmann Acceptor Number (AN) was quantified by \( ^{31} \text{P} \) NMR spectroscopy (Figure 2, Table 2). \( ^{31} \text{P} \) NMR chemical shifts measured for 1 % tepo solutions, \( \delta_{^{31} \text{P} \text{ 1\%tepo}} \), were also reported. All the AN values fall within the Lewis superacidity region, \( \text{AN} = 120-182 \). Al-containing systems gave two primary \( ^{31} \text{P} \) signals (Figure 2, bottom). The more upfield signal (\( \delta_{^{31} \text{P} \text{ 1\%tepo}} = 84 \pm 2 \) ppm; \( \text{AN} = 96 \pm 2 \)) was consistent with tepo coordinating to the Al centre. \( ^{31} \text{P} \) NMR signals from tepo (used in 1 % solution) were obscured by signals from the \( \text{P}_{\text{tepo}} \) ligand.

AN values were calculated based on the signal originating from \([\text{BCl}_3\text{L(tepo)}]^+\) (Table 2). \( ^{31} \text{P} \) NMR chemical shifts measured for 1 % tepo solutions, \( \delta_{^{31} \text{P} \text{ 1\%tepo}} \), were also reported. All the AN values fall within the Lewis superacidity region, \( \text{AN} = 120-182 \). Al-containing systems gave two primary \( ^{31} \text{P} \) signals (Figure 2, bottom). The more upfield signal (\( \delta_{^{31} \text{P} \text{ 1\%tepo}} = 84 \pm 2 \) ppm; \( \text{AN} = 96 \pm 2 \)) was consistent with tepo coordinating to the Al centre. \( ^{31} \text{P} \) NMR signals from tepo (used in 1 % solution) were obscured by signals from the \( \text{P}_{\text{tepo}} \) ligand.

The crystal structure of \([\text{BCl}_3\text{L(tepo)}]^-\), isolated here as an ionic liquid, has been reported. This indicates that some systems described in this work may be in fact supercooled liquids. It is also likely that dynamic equilibria with other than \([\text{BCl}_3\text{L}]^+\) and \([\text{MCl}_n]^+\) components (metal complexes, \( \text{BCl}_3 \)) hinder the crystallisation.

Lewis acidity of borenium ionic liquids was quantified by the Gutmann Acceptor Number (AN), where triethylphosphate oxide (tepo) is used as a \( ^{31} \text{P} \) NMR probe. In AN scale, hexane has AN = 0, \( \text{SbCl}_5 \) in 1,2-dichloroethane has AN = 100, and acids with AN > 100 are considered Lewis superacids.

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In L-\( \text{BCl}_3-n\text{GaCl}_3 \) systems (\( n = 1 \) or 2) only one main signal was detected, consistent with tepo coordinated to a borenium cation (Figure 2, top). With three moles of \( \text{GaCl}_3 \), a second signal appeared (\( \delta_{^{31} \text{P} \text{ 1\%tepo}} = 93 \pm 1 \) ppm; \( \text{AN} = 118 \pm 1 \)), at a slightly higher value than that reported for chlorogallate(III) ionic liquids with \([\text{Ga}_3\text{Cl}_3]^+\) anion (\( \text{AN} = 107 \)).\( ^{[18]} \)
Comparing the AN values (Figure 3), for systems with pyridine-based donors (py, 3pic, 4pic), the same pattern was observed, with acidity dependent both on the molar ratio of MCl₃ and on the metal (Al or Ga). In contrast, all ionic liquids based on 1-methylimidazole (the strongest base, Table 1) had the same acidity, AN = 174±1. Apparently, for the strongest donor, a ‘naked’ [BCl₃(mim)]⁺ cation is formed, as reflected in the constant, high, AN values. In contrast, borenium cations with weaker donors (py, 3pic, 4pic) interacted strongly with the anions resulting in anion-dependent AN values, with the least coordinating anion, [Ga₃Cl₁₁]⁻, affording the highest acidity. This distinction is unexpected, taking into consideration apparently full halide abstraction in all L-BCl₃-2MCl₃ systems, inferred from ¹¹B NMR spectra.

In conclusion, ionic liquids containing borenium cations, [BCl₃L]⁺, were demonstrated to be the strongest Lewis acids reported to date, with Acceptor Number values up to 182. Their Lewis acidity appears to be much higher than that from corresponding solution studies, e.g. AN = 80-85 found for [B(C₆F₅)₃]⁻ in CD₂Cl₂, or δ₁₁P = 106.9 ppm recorded for the [CatBr]⁺ cation (cat = catecholate).22,31 offering the exciting prospect harnessing the full acidity of these ‘naked’ borenium cations in the ionic liquid state.

### Table 1. AN values for all L-BCl₃-nMCl₃ systems based on N-donors, which were homogenous liquids, along with δ₁₁P signals measured for 1% solution of tepo in these liquids (referred to δ₁₁P(NPO₄₅₅) = 0 ppm).

<table>
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<th>L (pKₐ)</th>
<th>AN</th>
<th>δ₁₁P</th>
<th>AN</th>
<th>δ₁₁P</th>
<th>AN</th>
<th>δ₁₁P</th>
<th>AN</th>
<th>δ₁₁P</th>
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<td>94.5</td>
<td>162</td>
<td>109.6</td>
<td>121</td>
<td>94.7</td>
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<td>99.9</td>
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<tr>
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<td>95.5</td>
<td>170</td>
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<td>121</td>
<td>95.5</td>
<td>135</td>
<td>99.6</td>
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<tr>
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<td>124</td>
<td>96.2</td>
<td>170</td>
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<td>94.5</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>174</td>
<td>117.2</td>
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<td>-</td>
<td>173</td>
<td>116.3</td>
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</tbody>
</table>

### Experimental Section

Triocylphosphine was provided by Cytec, all other reactants were purchased from Sigma-Aldrich. Solvents, and bases were dried over molecular sieves (3 Å) and stored under argon. Triocylphosphine oxide was dried (70 °C, 2 days, 10⁻² mbar) and stored in glovebox. Metal halides (anhydrous, in glass ampoules) and triocylphosphine were used as received. Boron trichloride adducts were prepared using an argon Schlenk line, by drop-wise addition of a base (0.9 mol eq.) to the vigorously stirred mixture of boron trichloride (1 M solution in heptane, 1.0 eq.) and DCM, at -78 °C. After reaction (-78 °C, 30 min, 600 rpm), excess reactants and solvents were removed under reduced pressure, and the adduct dried under high vacuum (60 °C, 10⁻² bar, overnight).

Complexes of pyridine and picolines were recrystallised from a mixture of dry dichloromethane and hexane. Boronium ionic liquids were synthesized in a nitrogen-filled glovebox. Metal(III) chloride (1, 2 or 3 mol eq.) was added slowly to the boron trichloride adduct (1 mol eq.), and left to react until homogenous mixture was obtained, or no further change was observed (30-50 °C, 10 min - 2 h, 600 rpm). NMR spectroscopy. Boron trichloride adducts were measured as solutions in d-chloroform, the ionic liquids as neat liquids, with sealed capillaries of d₇-DMSO as an external lock. ¹¹B, ²⁷Al and ³¹P NMR spectra were recorded using a Bruker AvanceIII 400 MHz spectrometer. Background from the borosilicate tube was removed for ¹¹B NMR spectra using iNMR (Mestrelab Research). To determine Acceptor Number, three solutions of triethylphosphine oxide (tepo) in an ionic liquid were prepared; at concentrations of ca. 1, 2 and 3%. ³¹P NMR spectra were recorded neat, with d₇-DMSO as an external lock, and referenced to H₃PO₄, 85% (δ₁₁P(NPO₄₅₅) = 0 ppm). The ³¹P NMR chemical shift at infinite dilution of tepo, δᵦₑᵢᵦ, was determined by extrapolation from ³¹P NMR chemical shifts at three different tepo concentrations and normalised to the chemical shift of tepo in hexane at infinite dilution (δᵦₑᵢᵦ(nhex) = 0 ppm). The AN values for all samples were calculated from: AN = 2.348 δᵦₑᵦ.

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**Keywords:** Lewis superacids • borenium cations • ionic liquids • group 13 • acceptor number
Borenium Lewis superacids:
Solventless synthesis of ionic liquids based on borenium cations and chlorometallate anions afforded a new class of liquid Lewis superacids, with acceptor numbers up to 182. The Lewis acidity was enhanced by the absence of a solvent, allowed by the ionic liquid environment.