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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, [BCl₃]⁺, 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₋₋ = 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] 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 from tetracoordinate boron adducts, [BX₄]⁻, using an excess of abstracting agent (Figure 1).[4,5,7,10]

Many borenium 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 ¹¹B 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 reagents,[12-14] liquid borenium salts have been prepared, their speciation determined and Lewis acidity measured.

Boron adducts, [BCl₃]⁻, 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 σ-donor properties.[15] For structural comparison, an adduct with an aliphatic base (triethylphosphine, P₃Et) was prepared; the phosphine is a stronger donor to BCl₃ than the corresponding amine.[16] ¹¹B 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 chlorometallate ionic liquids.[18] All products were homogenous liquids, except for equimolar mixtures of [BCl₃(mim)] and MCl₃, which formed white pastes. Aluminium(III) chloride was used in 1 or 2 mol ratio with respect to [BCl₃(L)] 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,[21,22] so gallium(III) chloride was used in 1-3 mol ratio.

A major peak in the ¹¹B NMR spectra was observed at 30-50 ppm (Table 1-SI). The shift depended on [BCl₃(L)] to MCl₃ 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 MCl₃, and complete ionisation with 2 or 3 mol eq. of MCl₃, in agreement with solution studies.[9,10] For L-BCl₃·2MCl₃ systems, the main feature was a broad peak at 44±4 ppm, corresponding to formation of tricoordinate [BCl₃(L)]⁺ 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.[9,20] Similarly, the main signal at 36±1 ppm and shoulder ca. 45.5 ppm for P₃Et·BCl₃·2MCl₃ systems is consistent with [BCl₃(P₃Et)]⁺[22] and BCl₃.
Acid oxide (tepo) is used as a Gutmann Acceptor (AN) number in the crystallization. The BCl₃-2AlCl₃ liquids used in this work may be in fact supercooled ionic donor systems described in this work. It is also likely that dynamic equilibria with other than [AlCl₃]⁻⁺⁺⁺ components (metal complexes, BCl₃) hinder the crystallisation.

Lewis acidity of borenium ionic liquids was quantified by the Gutmann Acceptor Number (AN), where triethylphosphine oxide (tepo) is used as a 31P NMR probe. In AN scale, hexane has AN = 0, SbCl₅ in 1,2-dichloroethane has AN = 100, and acids with AN > 100 are considered Lewis superacids. The method is well established in Lewis acidity studies of both borenium cations and of ionic liquids. Unambiguous results could only be obtained for systems with N-donors, because the 31P NMR signals from tepo (used in 1-3% quantity) were obscured by signals from the P₆₆₆ ligand.

AN values were calculated based on the signal originating from [BCl₃]L(tepo)]⁺⁺ (Table 2). 31P NMR chemical shifts measured for 1% tepo solutions, δ31P 1%tepo, were also reported. All the AN values fall within the Lewis superacidity region, AN = 120-182. Al-containing systems gave two primary 31P signals (Figure 2, bottom). The more upfield signals (δ31P 1%tepo = 84±2 ppm; AN = 96±2) were consistent with tepo coordinating to the Al centre. The downfield signals (δ31P 1%tepo = 94.5-117.2 ppm; AN = 120-174) correspond to tepo coordinating to the borenium cation. In L-BCl₃-nGaCl₃ 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 GaCl₃, a second signal appeared (δ31P 1%tepo = 93±1 ppm; AN = 118±1), at a slightly higher value than that reported for chlorogallate(III) ionic liquids with [Ga₃Cl₆]⁻ anion (AN = 107). The AN values were calculated based on the signal originating from [BCl₃]L(tepo)]⁺⁺ (Table 2). 31P NMR chemical shifts measured for 1% tepo solutions, δ31P 1%tepo, were also reported. All the AN values fall within the Lewis superacidity region, AN = 120-182. Al-containing systems gave two primary 31P signals (Figure 2, bottom). The more upfield signals (δ31P 1%tepo = 84±2 ppm; AN = 96±2) were consistent with tepo coordinating to the Al centre. The downfield signals (δ31P 1%tepo = 94.5-117.2 ppm; AN = 120-174) correspond to tepo coordinating to the borenium cation. In L-BCl₃-nGaCl₃ 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 GaCl₃, a second signal appeared (δ31P 1%tepo = 93±1 ppm; AN = 118±1), at a slightly higher value than that reported for chlorogallate(III) ionic liquids with [Ga₃Cl₆]⁻ anion (AN = 107).

Partial ligand transfer onto a metal centre was confirmed with 27Al NMR spectroscopy (Figure 3-S1, Table 2-S1). For N-donors, the main signal at ca. 106 ppm was found, corresponding to equilibrated tetracoordinate complexes: [AlCl₃]⁻⁺, [AlCl₄]⁻, and [AlCl₆]⁻ with a shoulder at 75±1 ppm, originating from a pentacoordinate complex, [AlCl₆]⁻, and/or cationic complex, [AlCl₄]⁻. 27Al NMR spectrum of P₆₆₆-BCl₃-2AlCl₃ gave a broad feature with two maxima at 66 and 114 ppm, consistent with species analogous to those identified for N-donors.

The crystal structure of [BCl₃(py)][AlCl₆], 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 [BCl₃]⁺⁺⁺⁺ and [MCl₆]⁻ components (metal complexes, BCl₃) hinder the crystallisation.

Lewis acidity of borenium ionic liquids was quantified by the Gutmann Acceptor Number (AN), where triethylphosphine oxide (tepo) is used as a 31P NMR probe. In AN scale, hexane has AN = 0, SbCl₅ in 1,2-dichloroethane has AN = 100, and acids with AN > 100 are considered Lewis superacids.
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, [Ga₃Cl₆]⁻, affording the highest acidity. This distinction is unexpected, taking into consideration apparently full halide abstraction in all L-BCl₃·2MCl₃ systems, inferred from ³¹P 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)₂]⁺ in CD₂Cl₂, or δ₁₃P = 106.9 ppm recorded for the [CatB]⁺ cation (cat = catecholate).[22,31] offering the exciting prospect harnessing the full acidity of these ‘naked’ borenium cations in the ionic liquid state.

### Experimental Section

Trioctylphosphine 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. Trioctylphosphine oxide was dried (70°C, 2 days, 10⁻² mbar) and stored in glovebox. Metal halides (anhydrous, in glass ampoules) and trioctylphosphine 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 mol eq.) and DCM, at -78°C. After reaction (-78°C, 30 min, 600 rpm), excess reagents and solvents were removed under reduced pressure, and the adduct dried under high vacuum (60°C, 10⁻³ bar, overnight). Complexes of pyridine and picolines were recrystallised from a mixture of dry dichloromethane and hexane. **Borenium ionic liquids** were synthesised in a nitrogen-filled glovebox. Metal(III) chloride (1, 2 or 3 mol eq.) was added slowly to the borenium 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 - 24 h, 600 rpm). NMR spectroscopy. Borenium trichloride adducts were prepared as solutions in d-chlorofrom, the ionic liquids as neat liquids, with sealed capillaries of d₂-DMSO as an external lock. ¹⁷B, ²⁷Al and ³¹P NMR spectra were recorded using a Bruker AvanceII 400 MHz spectrometer. Background from the borosilicate tube was removed for ¹⁷B 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 d₂-DMSO as an external lock, and referenced to H₂PO₄, 85% (δ₁₃P₀₉₂ 85% = 0 ppm). The ³¹P NMR chemical shift at infinite dilution of tepo, δₓ, 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 (δₓ,∞ = 0 ppm). The AN values for all samples were calculated from: AN = 2.348 δₓ.

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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.