

A zwitterionic hydrocarbon-soluble borenium ion based on a β -diketiminato backbone

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A versatile synthetic route has been developed to access strongly Lewis acidic borenium cations (and heavier group 13 analogues) featuring a pendant weakly-coordinating borate function. The hydrocarbon-soluble borenium/borate zwitterion is more strongly Lewis acidic than $B(C_6F_5)_3$, despite featuring a pendant (non-fluorinated) aryl group and two flanking N-donors.

Borenium ions are representatives of a family of boron-centred cations of the type $[L_nBX_2]^+$ which feature a single L type ligand and a coordination number of three.¹ As such, the degree of electrophilicity at the boron atom is typically intermediate between that found in divalent (and much less common) borinium systems and formally saturated four-coordinate boronium ions (Figure 1).^{2,3}

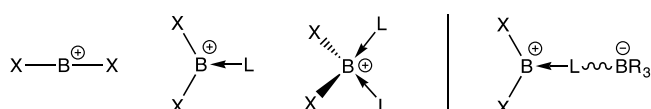
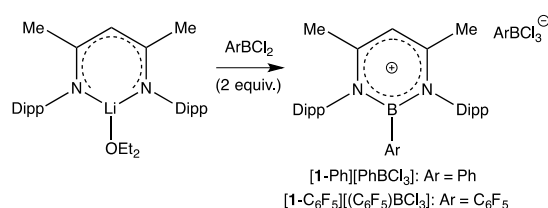


Figure 1 (left) Major classes of boron-centred monocation: borinium, borenium and boronium ions; (right) target borenium/borate zwitterion.

Understandably, the Lewis acidity of borenium cations underpins a significant proportion of their chemical utility – from initial reports of their exploitation in the electrophilic borylation of arenes stemming from the 1960s,⁴ through to highly topical recent applications as the boron-containing component in ‘frustrated Lewis pairs’ for E-H bond activation and catalysis.^{5,6} Recently, we have been interested in the modification of reactive cationic species by the incorporation of a weakly coordinating anion (WCA) backbone component.⁷

The resulting bi-functional systems have been shown to offer the benefits of enhanced solubility and modulated reactivity in apolar solvents,⁸ stemming from their zwitterionic nature. In this contribution we report on the application of this approach for the synthesis of strongly Lewis acidic borenium borates and their heavier group 13 analogues (Figure 1).

Reactions of $(\text{Nacnac})^{\text{Dipp}}\text{Li}(\text{OEt}_2)^9$ with two equivalents of an arylboron dichloride give straightforward access to the corresponding β -diketiminato stabilized borenium cation, as the respective aryltrichloroborate salt (Scheme 1). Thus, the phenyl and pentafluorophenyl cations $[1\text{-Ph}]^+$ and $[1\text{-C}_6\text{F}_5]^+$ can be isolated as the $[\text{PhBCl}_3]^-$ and $[(\text{C}_6\text{F}_5)\text{BCl}_3]^-$ salts in yields of 70 and 50%, respectively, and characterized by standard crystallographic, spectroscopic and analytical methods (see Figure 2 and ESI). While related cations have previously been reported by both Cowley¹⁰ and Driess,¹¹ the current approach for aryl-borenium systems bypasses the need for a second step utilizing an aluminium halide co-reagent.¹⁰



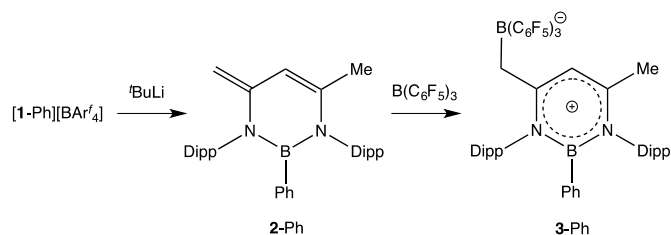
Scheme 1 Single step syntheses of β -diketiminato stabilized borenium cations $[1\text{-Ph}]^+$ and $[1\text{-C}_6\text{F}_5]^+$ as the respective aryltrichloroborate salts.

With this straightforward synthetic approach in hand we then targeted the synthesis of related zwitterionic systems featuring a backbone-appended (weakly-coordinating) borate anion. Given the propensity of the backbone methyl groups of β -diketiminato ligands to undergo deprotonation,^{11–14} the strategy employed involved reaction with a potent base, and subsequent quenching with the strongly electrophilic tris(pentafluorophenyl)borane. Thus, following anion exchange with $\text{Na}[\text{BAR}^f_4]$ $\{\text{Ar}^f = \text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5}\}$ to remove the B-Cl

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containing counter-ion, the reaction of $[1\text{-Ph}]^+$ with $t\text{BuLi}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ can be shown to generate (sequentially) the charge neutral diamidoborane intermediate (Nacnac') $^{\text{Dipp}}\text{BPh}$ (**2-Ph**) and the backbone-functionalized zwitterion **3-Ph** (Scheme 2).^{††}



Scheme 2 Synthesis of the zwitterionic borenium borate **3-Ph** from $[1\text{-Ph}][\text{BARf}_4]$ via sequential deprotonation/electrophilic quenching with $\text{B}(\text{C}_6\text{F}_5)_3$.

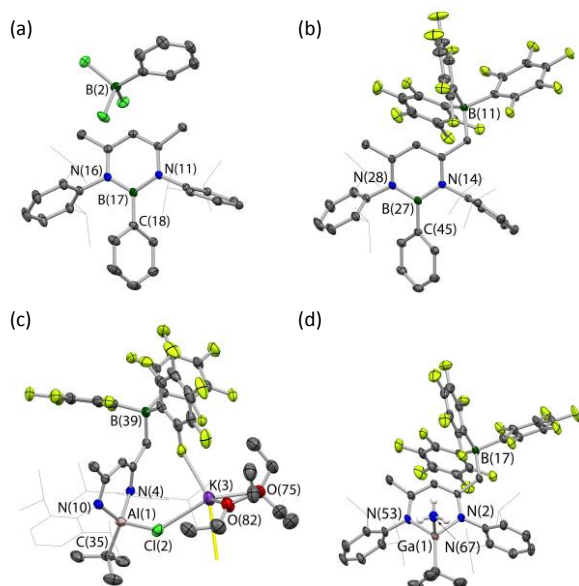


Figure 2 Molecular structures of (a) $[1\text{-Ph}][\text{PhBCl}_3]$, (b) **3-Ph**, (c) $[\text{K}(\text{OEt}_2)_2][6\text{-tBu-Cl}]$ and (d) 7-tBu-NH_3 as determined by X-ray crystallography. Hydrogen atoms have been omitted and selected substituents shown in wireframe format for clarity; thermal ellipsoids have been depicted at the 40% probability level. Key bond lengths (Å) and angles ($^\circ$): (for $[1\text{-Ph}][\text{PhBCl}_3]$): B-C 1.569(3), B-N 1.449(2), 1.459(2), C-N 1.358(2), 1.360(2), N-B-N 114.9(1), N-B-C 122.2(1), 122.9(1); (for **3-Ph**): B-C 1.579(2), B-N 1.457(2), 1.457(2), C-N 1.361(2), 1.363(2), N-B-N 114.6(1), N-B-C 121.8(1), 123.7(1); (for $[\text{K}(\text{OEt}_2)_2][6\text{-tBu-Cl}]$): Al-N 1.896(3), 1.898(4), Al-C 2.011(6), Al-Cl 2.181(2), K-Cl 3.063(2); (for 7-tBu-NH_3): Ga-N 1.932(4), 1.934(5), Ga-C 1.990(5), Ga-NH₃ 2.082(5), N-Ga- γ C 81.2(2).

Remarkably, despite the cationic three-coordinate nature of the boron centre in $[1\text{-Ph}]^+$, the use of the highly encumbered $t\text{BuLi}$ ensures that conversion of $[1\text{-Ph}][\text{BARf}_4]$ to **2-Ph** can be achieved in ca. 95% yield via attack at the backbone Me group (as determined by *in situ* multi-nuclear NMR measurements). Moreover, although **2-Ph** is a pale yellow oil, it can be obtained in spectroscopically pure form by extraction from the reaction mixture into toluene. Particularly diagnostic are the ^1H NMR signals for the exocyclic $\text{C}=\text{CH}_2$ group (at $\delta_{\text{H}} = 3.31, 3.98$ ppm),^{11–13} the backbone methyl signal (at $\delta_{\text{H}} = 1.49$ ppm) integrating to three protons, and the reduction in symmetry (compared to precursor $[1\text{-Ph}]^+$) revealed by a doubling in the

number of Dipp CH_3 and CH resonances. The ^{11}B NMR resonance for **2-Ph** ($\delta_{\text{B}} = 31.3$ ppm) is shifted to slightly higher field compared to those measured for both $[1\text{-Ph}]^+$ and **3-Ph** ($\delta_{\text{B}} = 33.7, 32.9$ ppm, *vide infra*).

The target compound **3-Ph** can be isolated as a colourless crystalline material in 44% yield, and characterized by spectroscopic/analytical and crystallographic methods (Figure 2). In addition to the ^{11}B signal associated with the three-coordinate borenium centre, a further signal at $\delta_{\text{B}} = -14.4$ ppm (together with a ^{19}F NMR spectrum featuring a small chemical shift difference between the *meta* and *para* Fs of the C_6F_5 substituents; $\Delta\delta_{\text{m,p}} = 4.8$ ppm), is consistent with the presence of a four-coordinate borate function.⁷ These inferences are borne out crystallographically (Figure 2), with the solid state structure confirming the presence of a backbone appended $\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3^-$ group, and a three-coordinate borenium centre (for which the N-B-N and N-B-C angles sum to 360° within error). In a broader context, the structural metrics for the heterocyclic component of **3-Ph** are very similar to those measured for the corresponding unit in the $[1\text{-Ph}][\text{PhBCl}_3]$ ion pair.

Having successfully synthesized the target zwitterionic borenium system we set out to probe its Lewis acidity through a combination of computational and experimental approaches. Optimization of the structure of **3-Ph** using Density Functional Theory (see ESI for details) provides excellent agreement with the metrics determined crystallographically, and allows assessment of the key (virtual) molecular orbitals. The LUMO (-3.64 eV; Figure 3) is localized principally on the β -diketiminato fragment, but has very little contribution from the boron centre, being mainly $\text{C}=\text{N}$ π^* in character. The LUMO+1 (-2.84 eV) by contrast, is centred on the BPh fragment and features a significant contribution (27%) from the boron $2p_z$ orbital. Quantitative comparison with other Lewis acids was carried out using the modified version of the Gutmann method reported by Adamczyk-Woźniak *et al.*¹⁵ Thus, using Et_3PO as the Lewis basic probe, an acceptor number (AN) of 79.6 can be calculated for **3-Ph**, based on the chemical shift ($\delta_{\text{P}} = +77.0$ ppm) measured for the phosphine oxide in the presence of two equivalents of the borenium/borate zwitterion. The corresponding values obtained for $\text{B}(\text{C}_6\text{F}_5)_3$ and BPh_3 using the same method are 78.2 and 65.6, respectively, implying that **3-Ph** is comparable (or even more potent) in its Lewis acidity compared with tris(pentafluorophenyl)borane.¹⁵

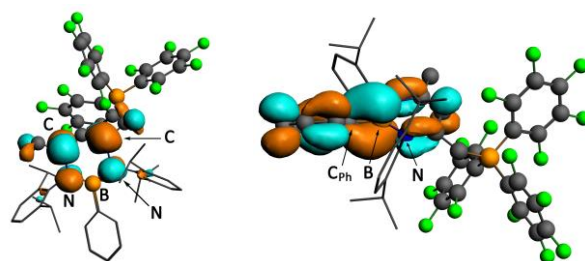
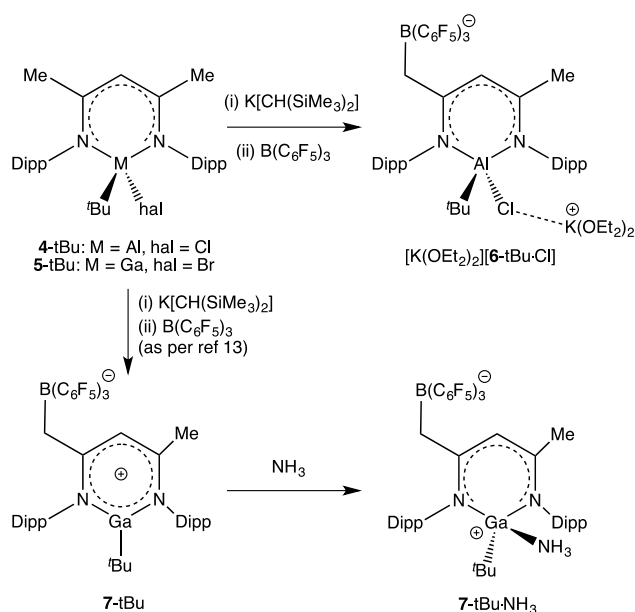


Figure 2 DFT calculated LUMO and LUMO+1 for **3-Ph** (at -3.64 and -2.84 eV, respectively).

With a view to extending this comparison, and also to probing the scope/limitations of our synthetic approach for the synthesis of borate-functionalized group 13 zwitterions, we have also targeted closely related aluminium and gallium systems (Scheme 3).



Scheme 3 Extension of the synthetic approach to aluminium- and gallium-based systems.

In both cases, the use of a more sterically imposing M-bound *tert*-butyl group was found to be necessary to prevent side-reactions at the backbone deprotonation stage resulting from attack at the metal centre by either the $\text{K}[\text{CH}(\text{SiMe}_3)_2]$ base or (inter-molecularly) by the exocyclic CH_2 group generated in this step. By employing this modification in the corresponding aluminium system, incorporation of the backbone borate WCA can be achieved in good yield via the deprotonation/electrophilic quench methodology. However, in this case, the product isolated is the KCl inclusion complex $[\text{K}(\text{OEt}_2)_2][6\text{-tBu-Cl}]$, which has been characterized by standard spectroscopic/analytical techniques, and its structure in the solid state confirmed by X-ray crystallography (Scheme 3 and Figure 2). Notably, these structural studies reveal an Al-Cl bond that is only marginally elongated compared to that found in the precursor 4-tBu [2.181(2) vs. 2.168(1) Å];¹³ comparison with the spontaneous ejection of halide observed in the formation of both 3-Ph and 7-tBu (vide infra) is consistent with the highly halophilic nature of the aluminium centre in $[\text{K}(\text{OEt}_2)_2][6\text{-tBu-Cl}]$.⁵

In the case of gallium, however, application of a comparable approach allowed the desired (halide-free) zwitterionic species 7-tBu to be isolated in moderate (ca. 30%) overall yield from 5-tBu (Scheme 3).¹⁶ By employing the same Gutmann approach used for 3-Ph, an AN of 69.6 could then be calculated (based on a ³¹P NMR shift of +71.5 ppm for the adduct 7-tBu-OPeT₃) - consistent with reduced Lewis acidity compared to boron-centred 3-Ph.¹⁷ Although the structure of this adduct could not be determined crystallographically, that

of the corresponding ammonia adduct 7-tBu-NH₃ could be obtained (Figure 2), thereby confirming coordination of the external base at the group 13 centre, with the Ga-NH₃ vector being inclined essentially perpendicular to the β-diketiminato plane [$\angle\text{N-Ga-}\gamma\text{C} = 81.2(2)^\circ$].

In conclusion, we present a simple procedure for the synthesis of a hydrocarbon-soluble zwitterionic borenium species, incorporating a weakly-coordinating pendant borate function. A Gutmann-type assay of Lewis acidity reveals that the effect of the positive charge within the heterocycle component is profound, with 3-Ph displaying comparable (or even slightly enhanced) Lewis acidity to $\text{B}(\text{C}_6\text{F}_5)_3$, despite featuring a pendant (non-fluorinated) phenyl group and two flanking N-donors. This synthetic approach is also applicable to related species featuring a three-coordinate gallium centre, with attempts to synthesize the aluminium analogue being frustrated by the greater intrinsic Lewis acidity of the putative three-coordinate aluminium cation, and consequent retention of chloride.¹⁷

Notes and references

‡ **Synthesis of 3-Ph from [1-Ph][BAR₄]:** [1-Ph][BAR₄] (0.490 g, 0.36 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. ^tBuLi (0.38 mL of a 1.9 M solution in pentane, 0.72 mmol) was added dropwise and the solution instantly turned pale brown. The reaction mixture was allowed to warm to room temperature and stirred overnight. Volatiles were removed *in vacuo* and the residue extracted into toluene and filtered onto solid $\text{B}(\text{C}_6\text{F}_5)_3$ (0.180 g, 0.36 mmol) to yield a pale yellow solution. After stirring at room temperature for 3 h, the reaction mixture was concentrated to the point of incipient crystallization; storage at -30 °C yielded the product as colourless crystals. Yield: 0.160 g, 44%. **Spectroscopic data:** ¹H NMR (400 MHz, benzene-d₆, 298 K): δ_{H} 0.56 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 0.58 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 0.85 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.41 (6H, d, ³J_{HH} = 6.8 Hz, CH₃ of Dipp ⁱPr), 1.61 (CH₃ of β-diketiminato backbone), 2.08 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 2.58 (2H, sept, ³J_{HH} = 6.8 Hz, CH of Dipp ⁱPr), 3.23 (2H, s, CH₂B), 6.40 (2H, d, ³J_{HH} = 8.0 Hz, *o*-CH of Ph), 6.48 (1H, t, ³J_{HH} = 8.0 Hz, *p*-CH of Dipp), 6.61 (1H, t, ³J_{HH} = 8.0 Hz, *p*-CH of Dipp), 6.74 (2H, d, ³J_{HH} = 8.0 Hz, *m*-CH of Dipp), 6.91 (2H, d, ³J_{HH} = 8.0 Hz, *m*-CH of Dipp), 7.05 (m, 3H, *m*-CH and *p*-CH of Ph), 7.60 (s, 1H, γ -CH). ¹³C{¹H} NMR (126 MHz, benzene-d₆, 298 K): δ_{C} 22.2 (CH₃ of β-diketiminato backbone), 22.9, 23.9, 24.1, 24.7 (CH₃ of Dipp ⁱPr), 26.8 (CH₂B), 29.4, 29.5 (CH of Dipp ⁱPr), 115.4 (γ -CH), 125.8, 126.2, 127.3, 128.9, 129.7, 130.5, 131.0, 131.3, 135.5 (*ipso*-C, *m*-C and *p*-C of Dipp and ArC of Ph), 143.7, 144.1 (*o*-C of Dipp), 137.2 (dm, ¹J_{CF} = 250 Hz, *m*-CF), 139.0 (dm, ¹J_{CF} = 244 Hz, *p*-CF), 148.9 (dm, ¹J_{CF} = 250 Hz, *o*-CF), 167.6, 186.9 (NC). ¹⁹F NMR (376 MHz, benzene-d₆, 298 K): δ_{F} -131.4 (br s, *o*-CF), -160.1 (br s, *m*-CF), -164.9 (br s, *p*-CF). ¹¹B{¹H} NMR (128 MHz, benzene-d₆, 298 K): δ_{B} -14.4 (-B(C₆F₅)₃), 32.9 (-BPh). Elemental microanalysis: calc. for C₅₃H₄₅N₂B₂F₁₅: C 62.62% H 4.46% N 2.76%; meas. C 62.45% H 4.06% N 2.57%.

† The corresponding chemistry with [1-C₆F₅]⁺ proceeds less cleanly, presumably as a result of the more reactive nature of the BAR unit in the presence of ^tBuLi (*cf.* [1-Ph]⁺).

§ Attempts to sequester the metal-bound chloride in such systems were only successful through the use of polar donor solvents (such as thf),^{12c} in which case the very strong intrinsic Lewis acidity of the aluminium centre within the cationic heterocycle leads to coordination of a thf molecule, and retention of the four-coordinate metal geometry. Thus, for

example, the structure of (Nacnac^{BCF})^{Dipp}Al(thf)Me has been shown by X-ray crystallography to feature a four-coordinate thf-ligated aluminium centre (see ESI).

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