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Modelling fundamental arene-borane contacts: spontaneous formation of a dibromoborenium cation driven by interaction between a borane Lewis acid and an arene π system[†]

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Reaction of 2,6-dimesityl pyridine (L^{py}) with BBr₃ leads to the spontaneous formation of the trigonal dibromoborenium cation $[L^{py} \cdot BBr_2]^+$ via bromide ejection. Systematic structural and computational studies, and the reactivity displayed by a closely related *N*-heterocyclic carbene (NHC) donor, reveal the role played by arene–borane interactions in this chemistry. $[L^{py} \cdot BBr_2]^+$ features a structurally characterized (albeit weak) electrostatic interaction between the borane Lewis acid and flanking arene π systems.

The formation of arene π -complexes with potent electrophiles represents a key step in the mechanistic pathway ultimately leading to electrophilic aromatic substitution.¹ Despite this, and in contrast to the large number of complexes known with transition metals,² isolated arene adducts of p-block electrophiles are largely confined to those featuring low-valent posttransition elements.³ While η^6 -binding tends to predominate in such systems, a number of examples have been reported {featuring cations such as Cl⁺, and [SiR₃]⁺, or charge-neutral heavier Group 13 Lewis acids, ER₃ (E = Al, Ga or In)},⁴⁻⁷ which involve interaction with a single arene carbon, in a fashion reminiscent of classical Wheland intermediates.¹

The interactions of arenes with borane Lewis acids have obvious relevance to aromatic borylation chemistry (*e.g.* by BBr₃),⁸ and at a more general level to Lewis acid catalysis of electrophilic aromatic substitution.⁹ Despite this, unambiguous structural verification of such interactions remains elusive,¹⁰ with quantum chemical studies indicating that such binding events are likely to be relatively weak (*e.g.* 18.8 ± 11.2 kJ mol⁻¹ for BCl₃/benzene) and to involve interaction of the boron centre with a single arene carbon (at *ca.* 3.25 Å for BCl₃/benzene).^{9a,b} *Cationic* tri-coordinate boranes (*e.g.* borenium ions, [L·BX₂]⁺) offer the potential for stronger binding of Lewis basic

substrates than their neutral counterparts (based not least on electrostatic considerations),¹¹ and although less common,¹² have been exploited in their own right in the borylation of arenes,¹³ and as potent Lewis acid catalysts in organic synthesis.¹⁴ Among such systems, dihaloborenium species, $[L \cdot Bhal_2]^+$, offer particularly potent Lewis acid behaviour, but their potential for substrate binding has yet to be probed structurally; overwhelming electron deficiency and the lability of the B-hal bonds mean that reactivity studies have typically been carried out in situ.¹⁵ By contrast, in the current study we report a straightforward onestep procedure for the spontaneous formation of $[L \cdot BBr_2]^+$ from BBr₃ using a sterically loaded pyridine donor, together with the first crystallographic investigation of such a system. Moreover, systematic structural studies, and the reactivity displayed by a closely related NHC donor, reveal the role played by electrostatic arene-borane interactions in driving this transformation.

In contrast to its reactivity towards ECl_3 (E = Al, Ga), which generates the straightforward adducts L^{py}·ECl₃ (see Scheme 1 and ESI[†]), 2,6-Mes₂py (L^{py}) reacts with BBr₃ to generate [L^{py} BBr₂][BBr₄] in essentially quantitative yield (73% after recrystallization).^{16–18} The cationic component of this compound is characterized by downfield shifted ¹¹B NMR and pyridine ¹H NMR resonances ($\delta_{\rm B} = 42, \delta_{\rm H} = 7.86, 8.70$ ppm, *cf.* $\delta_{\rm B} = 38$ ppm for BBr₃, $\delta_{\rm H} = 7.24$, 7.83 ppm for L^{py}),¹⁶ and the formation of the tri-coordinate borenium species $[L^{py} \cdot BBr_2]^+$ was also confirmed crystallographically (Fig. 1). The related $[AlBr_4]^-$ salt has also been synthesized (see ESI⁺) and characterized by closely related spectroscopic and structural data. While the spontaneous loss of bromide to generate $[L^{py} BBr_2]^+$ (and $[BBr_4]^-$) in the presence of BBr₃ is unusual, it is noteworthy that an analogous step to generate the active borylation agent $[py \cdot BBr_2]^+$ has been proposed by Murakami in the N-directed functionalization of arenes.8

Structurally, $[L^{py} \cdot BBr_2]^+$ features a planar boron centre $\{\Sigma \text{ angles at } B(1) = 360.0(4), 360.0(5)^\circ$ for the $[BBr_4]^-$ and $[AlBr_4]^-$ salts, respectively} with the BBr₂ unit aligned essentially orthogonal to the plane of the pyridine donor [inter-plane torsion angle = 74.4, 87.2°, respectively]. While the B–N and B–Br distances are well precedented,¹⁹ the most unusual structural features of the $[L^{py} \cdot BBr_2]^+$ cation are the close contacts between the boron centre and the *ipso* carbons of both flanking

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Scheme 1 Syntheses of borenium and related derivatives of 2,6-dimesitylpyridine (counter-ions omitted for clarity). Key reagents and conditions; (i) BBr₃ (2.0 equiv.), hexanes, room temperature, 2 h, yield: 73% (of $[L^{Py}.BBr_2][BBr_4]$), or BBr₃ (1.0 equiv.), fluorobenzene, then AlBr₃ (1.0 equiv.), room temperature 12 h, yield: 57% (of $[L^{Py}.BBr_2][AlBr_4]$); (ii) BrBcat (1.0 equiv.), dichloromethane, then AlCl₃ (2.0 equiv.), room temperature, 12 h, yield: 68% (of $[L^{Py}.Bcat][AlCl_4]$); (iii) Li₂cat or H₂cat, fluorobenzene; (iv) ECl₃ (1.0 equiv.), fluorobenzene, room temperature, 24 h, yield: 79% (of $L^{Py}.AlCl_3$), 51% (of $L^{Py}.GaCl_3$).



Fig. 1 Molecular structures of the cationic components of (a) [L^{py}·BBr₂][BBr₄], (b) [L^{py}·Bcat][AlCl₄] and (c) [L^{NHC}·BBr₂][AlBr₄], and of (d) the adduct L^{NHC} ·BBr₃. H atoms and counter-ions omitted for clarity; thermal ellipsoids: 40% probability level. Closest contacts between boron and carbon atoms of the flanking rings shown by red dashed lines. Key distances [Å] and angles [°]: (for [L^{py}·BBr₂]⁺) B(1)-Br(2) 1.879(3), B(1)–N(4) 1.530(7), B(1)···C(8) 2.766(5), Br(2)– B(1)-Br(2A) 120.0(3), Br(2)-B(1)-N(4) 120.0(4); (for $[L^{py}\cdot Bcat]^+$) O(6)-B(14) 1.363(2), O(13)-B(14) 1.367(3), B(14)-N(15) 1.505(3), $B(14) \cdots C(17)$ 2.785(4), $B(14) \cdots C(30)$ 2.734(4); O(6)-B(14)-O(13)114.7(2), O(6)-B(14)-N(15) 122.2(2), O(13)-B(14)-N(15) 123.0(2); (for $[L^{\text{NHC}} \cdot BBr_2]^+$) Br(1)-B(2) 1.889(7), B(2)-Br(3) 1.874(6), B(2)-C(4) 1.604(7), B(2)···C(6) 2.798(8), B(2)···C(19) 2.786(7), Br(1)-B(2)-Br(3) 119.7(3), Br(1)-B(2)-C(4) 118.1(4), Br(3)-B(2)-C(4) 122.1(4); (for L^{NHC}·BBr₃) Br(1)-B(2) 2.042(3), B(2)-Br(3) 2.016(4), B(2)-Br(4) 2.015(4), B(2)-C(5) 1.668(5).

mesityl rings {2.766(5) and 2.754(5)/2.786(5) Å for the $[BBr_4]^-$ and $[AlBr_4]^-$ salts}, which are well within the sum of the respective van der Waals radii (3.93 Å). While these distances are much longer than those found in Al(C₆F₅)₃·(toluene) [2.342(6), 2.366(2) Å],^{6a} a complex described as being intermediate between an arene π -complex and a σ -complex (or Wheland intermediate), they are significantly shorter than the contacts calculated for benzene π -complexes of neutral boranes [*e.g.* 3.25 Å for BCl₃·(C₆H₆)].^{9a,b,20} That the boron centre in [L^{py}·BBr₂]⁺

retains a planar geometry reflects the presence of two such interactions involving opposite faces of the NBBr₂ unit. Interestingly, $[L^{py}.BBr_2]^+$ is unreactive towards the borylation of external arenes with the steric/electronic obstacle presented by the flanking rings presumably restricting access to the borenium centre.⁵⁶

Related synthetic studies show that the corresponding Bcat derivative $[L^{py}\cdot\text{Bcat}]^+$ (cat = $O_2C_6H_4$ -1,2) can be generated from BrBcat and L^{py} by the use of stronger aluminium-containing Lewis acids (see ESI† and Fig. 1). Structurally, this cation also features a trigonal boron centre [Σ angles at B(14) = 359.9(2)°] and short B···C_{ipso} contacts [2.734(4) and 2.785(4) Å]. A related feature common to these borenium cations is a marked bending of the flanking arene rings towards the boron centre. Thus, in $[L^{py}\cdot\text{BBr}_2]^+$ and $[L^{py}\cdot\text{Bcat}]^+$, the 'bite' angles defined by the centroid of the central pyridine ring and those of the flanking mesityl substituents (Fig. 2) are 109.8/112.9 and 114.4°, respectively, compared to 126.1 and 126.9° for the simple AlCl₃/GaCl₃ adducts (which feature no short intramolecular contacts).

Reasoning that the stronger σ -donor capabilities of the N-heterocyclic carbene (NHC) class of ligand (coupled with the similar steric profiles of the L^{py} and L^{NHC} systems)²¹ should lead to enhanced stabilization of the cationic borenium system $[L^{\text{NHC}} \cdot BBr_2]^+$, the analogous reactivity of L^{NHC} with BBr3 was also examined. Somewhat counter-intuitively, the 1:2 reaction in fluorobenzene leads to the formation of the simple adduct L^{NHC}·BBr₃: addition of the stronger Lewis acid AlBr₃, however, generates the borenium ion [L^{NHC}·BBr₂]⁺ (as the [AlBr₄]⁻ salt). Structural studies indicate that the inter-arene 'bite' angle is somewhat wider in charge neutral adducts of this NHC than in their L^{py} counterparts [e.g. 137.5, 133.4, 133.0° for adducts of BBr₃, AlCl₃ and GaCl₃, respectively (see ESI[†])]. However, consistent with the general notion of arene stabilization of dibromoborenium systems, [L^{NHC}·BBr₂]⁺ features a markedly narrowed 'bite' angle of 120.2° [cf. 137.5° for L^{NHC}·BBr₃] and B···C_{ipso} contacts of 2.786(7) and 2.798(8) Å.

In order to differentiate between steric and electronic factors underpinning these structural changes, and to quantify the energy changes associated with the observed bending of the L^{py} ligand on borenium ion formation, Density Functional Theory (DFT) calculations were carried out at the BLYP(tzp) level using the ADF2010 software package and taking the crystallographically determined geometries of the L^{py} fragment in 'free' L^{py} or $[L^{py} \cdot BBr_2]^+$ as the starting geometry (see ESI†). These reveal that the energetic penalties associated with distorting L^{py} or L^{NHC} from its minimum energy geometry to that found in $[L \cdot BBr_2]^+$ are 23.3 and 21.7 kJ mol⁻¹, respectively;‡ such data presumably give an indirect estimate of the 'binding energy' associated with the arene borane interaction in these



Fig. 2 Definitions of the inter-arene 'bite' angle for L^{py} and L^{NHC} ligands.



Fig. 3 HOMO of the L^{py} ligand.

systems. Moreover, analyses of the electronic structures of both L^{py} and L^{NHC} show that for both ligands, orbitals featuring a significant contribution from the π system of the flanking mesityl rings are found at energies close to the HOMO-LUMO gap (-5.23 and -5.22 eV for L^{py} and L^{NHC}, respectively). Somewhat surprisingly, for L^{py}, this orbital is the HOMO itself (Fig. 3) with the deeper lying HOMO-4 (at -5.48 eV) being of N-based lone pair character. As such, the availability of energetically high-lying regions of electron density at the flanking rings is demonstrated. That said, the relatively long $B \cdots C$ contacts measured for all of the borenium systems reported here and the lack of significant pyramidalization at the *ipso* carbon imply that the interaction of the arene π system with the cationic boron centre is a predominantly electrostatic one.¹⁸ Consistent with this notion, the $[(L^{py})H]^+$ cation also features a 'bite' angle (ca. 111°) somewhat narrower than that found in the free ligand L^{py}.¹⁸

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