**Novel H₂ activation by a Tris[3,5-bis(trifluoromethyl)phenyl]borane Frustrated Lewis Pair**

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Tris[3,5-bis(trifluoromethyl)phenyl]borane (1, BArF₁₈), has been synthesised on a practical scale for the first time. According to the Gutmann-Beckett method it is a more powerful Lewis acid than B(C₆F₅)₃. It forms a ‘frustrated Lewis pair’ with 2,2,6,6-tetramethylpiperidine which cleaves H₂ to form a salt containing the novel anion [µ-H(BArF₁₈)]⁻.

In recent years the concept and reactivity of “frustrated Lewis pairs” (FLPs) continues to develop apace. Within these systems, dative bond formation is restricted by steric encumbrance about the donor and acceptor atoms which leads to ‘unquenched’ reactivity. This enables the activation of small molecules such as CO₂, and importantly the heterolytic cleavage of H₂, which has led to application for the metal-free hydrogenation of polar organic substrates (e.g. nitriles and imines), and even the weak oxidant CO₂. Typically, FLPs consist of an electrophilic borane (most commonly B(C₆F₅)₃ or derivatives thereof), whose Lewis acidity is promoted by electron-withdrawing substituents, in combination with a hindered phosphine or amine e.g. iBu₃P or 2,2,6,6-tetramethylpiperidine (TMP).

![Diagram of Tris[3,5-bis(trifluoromethyl)phenyl]borane](image)

Figure 1. Commonly used fluorinated aryl borates and their ‘parent’ Lewis acid boranes.

Tetraaryl borate anions [B(C₆F₅)₃]⁻ and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, [BARF₂₄]⁻, (Figure 1) have widely gained use as weakly-coordinating counterions for reactive cationic metal centres (e.g. in homogeneous olefin polymerisation). Their high stability in acidic and oxidative conditions is attributed to the electron-withdrawing properties of their F-substituents (which lower aromatic π-basicity and hence susceptibility towards electrophilic B-C bond cleavage), and the strength of their C-F bonds. Remarkably, in view of the rich chemistry developed for B(C₆F₅)₃ (which can be viewed as the Lewis acid ‘parent’ of [B(C₆F₅)₃]⁻) only one report exists for the synthesis of the analogous tris[3,5-bis(trifluoromethyl)phenyl]borane (BARF₁₈), resulting from decomposition of the [BARF₂₄]⁻ anion by the electrophilic platinum complex trans-{(Ph₃P)₂Pt(Me)(OEt₂)}⁺. Only X-ray crystallographic data was reported, and no subsequent reactivity studies have been conducted.

In continuation of our interest in FLP-H₂ activation chemistry, we herein report a practical synthesis of BArF₁₈ and communicate preliminary findings of its Lewis acidic properties and differing reactivity with H₂ in an FLP system, relative to B(C₆F₅)₃.

Na[BARF₂₄] is synthesised via reaction of excess [3,5-bis(trifluoromethyl)phenyl]MgX (X = Cl, Br) with NaBF₄ or BF₃·OEt₂, we reasoned that BArF₁₈ should be an intermediate en route to the borate anion and decided to employ a rigid stoichiometry. Accordingly, the Grignard was generated via metal-halogen exchange of PrMgCl and 1-bromo-3,5-bis(trifluoromethyl)benzene in THF, which was subsequently reacted in situ with BF₃·OEt₂ (3:1) (Scheme 1). Facile work-up followed by high vacuum sublimation (80°C, 1 x 10⁻⁶ mbar) afforded tris[3,5-bis(trifluoromethyl)phenyl]borane (1, BArF₁₈) in good yield (65-70%, 2-5 gram scale) as a free-flowing white powder (Scheme 1). The reaction solvent appeared to be important; Grignard formation can also be conducted in Et₂O, yet metathesis with BF₃·OEt₂ led to formation of [BARF₂₄]⁻, as shown by ¹¹B NMR spectroscopy. It is thought the use of THF may retard the competitive addition of a fourth Grignard equivalent by coordinating to 1 as it is formed in solution; indeed the sublimation step is required to remove THF from the moderately labile adduct 1-THF, which is the actual product extracted immediately after the Grignard step, as evinced by ¹H, ¹³C and ¹¹B NMR spectroscopy. I is practically insoluble in aliphatic hydrocarbons, moderately so in aromatic solvents and displays optimum solubility in CH₂Cl₂ or CHCl₃; this property contrasts with B(C₆F₅)₃ (soluble in most common non-donor media).
solid-state for 1; a distance of 2.63 Å is found in the reported crystal structure [sum of vdW radii, r_H(F) + r_H(H) = 2.67 Å], which would obviously be lacking for B(C_6F_5)_3. 14–16

I has been fully characterised by 1H, 13C, 19F and 11B NMR spectroscopy; the latter shift (δ = 68.1 ppm; CD_2Cl_2) lends support for a three-coordinate geometry in the solution-phase and is noticeably deshielded in comparison with that found for B(C_6F_5)_3 (δ = 61.2 ppm; CD_2Cl_2). Whilst B(C_6F_5)_3 has been shown to be inert in pure oxygen at room temperature, 11 admission of dry O_2 to a CD_2Cl_2 solution of I led to rapid decomposition (numerous uncharacterisable resonances in the 1H, 13F and 11B NMR spectra). Despite strongly electron-withdrawing CF_3 groups in I (rationalised to contribute to the observed oxidative stability of the [BArF_2]_4 anion), it is possible that the ortho-F substituents in B(C_6F_5)_3 are more important in suppressing reaction with O_2; the absence of this structural feature in I might then lead to the heightened reactivity observed for this trigonal borane in this case. Interestingly, H_2O reversibly forms the dative complex I·OH_2, the donor can be removed under vacuum or through addition of 3Å molecular sieves in CH_2Cl_2 solution, in contrast with the tightly bound analogue (C_6F_5)_3B·OH_2. 12

Table 1. 31P and 1H NMR spectral data derived for Lewis acidity measurements of I and B(C_6F_5)_3.

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>Et_3PO</th>
<th>trans-Crotonaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>31P NMR</td>
<td>δ (ppm)</td>
</tr>
<tr>
<td>None</td>
<td>50.7</td>
<td>6.85</td>
</tr>
<tr>
<td>B(C_6F_5)_3</td>
<td>77.3</td>
<td>7.93</td>
</tr>
<tr>
<td>1</td>
<td>78.9</td>
<td>7.52</td>
</tr>
</tbody>
</table>

* CD_2Cl_2 at room temperature.  
† δ = [Et_3PO(coordinated) – H(BArF_2)_2] (1.376(6) Å).  
‡ δ = [H_2(coordinated) – H(CD_2Cl_2)].

In order to better understand the reactivity of I, Lewis acidity assessments were performed by employing the Gutmann-Beckett (Et_3PO probe; 31P NMR) and Childs (trans-crotonaldehyde; 1H NMR of H_2 resonance) methods; both rely on respective chemical shift differences (Δδ) upon complexation of the probe to the Lewis acid, which is proportional to the Lewis acid strength of the acceptor site. 13 The results, compared with data acquired for B(C_6F_5)_3, are tabulated in Table 1. It can be seen that I displays a Lewis acidity ca. 6% greater than that for B(C_6F_5)_3, which contrasts markedly with a ca. 38% reduction observed employing the Childs. A linear correlation is usually documented between methods, 14 although an increasing number of boron systems oppose this observation. 15 Notably, Britvsek et al. reported a non-linear trend for the series B(C_6F_5)_3·(OCD_2Cl_2) (x = 1–3), where preference for Et_3PO binding over crotonaldehyde is observed as x increases. 16 This was rationalised using Pearson’s HSAB principle where the covalent (softer) C=O bond is a preferable donor to B(C_6F_5)_3 compared with the more ionic (harder) P=O bond, favoured by B(OCD_2Cl_2).

Since Lewis acidity is a composite of both steric and electronic factors at the acceptor site, it would be useful to compare the steric profile of I with B(C_6F_5)_3; however, to date no solid-state structure of the latter has been reported. Fortunately the pyridine adducts, C_6H_5N·A (A = I, B(C_6F_5)_3), have been crystallographically characterised for both boranes in which both have virtually identical B–N bond lengths (1.63 Å, within e.s.u.), permitting valid comparison. 16 Excision of the pyridine ligand enabled a comparison of the relative free volume from the B centre, at a given radius, for the remaining pyramidalised borane fragments. The results show that I is less hindered in the 2–4 Å region (i.e. that occupied by the pyridine molecule), as anticipated from the smaller size of the ortho-H in I relative to the ortho-H in B(C_6F_5)_3; in conjunction with the 11B NMR spectroscopic data (an electronic probe at the B atom), this supports the Gutmann-Beckett assignment that I is more Lewis acidic than B(C_6F_5)_3.

Scheme 2. Generation of 2 from heterolytic activation of H_2 by I and TMP.

Addition of I to 2,2,6,6-tetramethylpiperidine (TMP) in CD_2Cl_2 (1:1) demonstrated the formation of an FLP, as evidenced by unchanged resonances in the 1H, 19F and 11B NMR spectra relative to the species in isolation. Subsequent admission of H_2 (1 atm) led to the rapid precipitation of a white solid, and 1H NMR spectroscopy revealed exactly half of the initial TMP remained in solution, whereas 11B NMR showed complete consumption of I, indicating complete sequestration of the borane. Elemental analysis of the solid was consistent with the molecular formula unit (I)_2(TMP)(H_2) (2, Scheme 2). 1 Remarks, H_2 activation occurs even in Et_2O, and led to the generation of large single crystals suitable for study by X-Ray diffraction, which solved as the novel [TMP][µ-H(BArF_2)]·Et_2O (2·Et_2O; Figure 2). The anion geometry approximates to D_3 symmetry, and the bridging borohydride unit is virtually linear (B–H–B = 176.3°). The B–H bond lengths (1.40 and 1.42 Å) are similar to those for seen in L[µ-H(BArF_2)]·Et_2O (1.376(6) Å). 17 yet distinct from [TMP][H–B(C_6F_5)_3] (1.18 (2) Å), 18 the longer bonds reflect the electron-deficient B–H–B interactions relative to terminal B–H. The aryl rings adopt an almost staggered conformation (torsion angles 58.7–61.5°). The [TMP] cation shows H-bonding to an Et_2O molecule with N–O and H–O separations of 2.869(4) and 1.97 Å respectively, the N–H···O angle being ca. 178°. Evidently the ammonium ion binds to the neutral O atom in preference to the charged borohydride anion. This is the first example of H_2 cleavage by an FLP to produce a bridging borohydride salt.
The facile synthesis of tris[3,5-bis(trifluoromethyl)phenyl]borane (1) has been achieved on a multi-gram scale. Gutmann-Beckett

Conclusions

The facile synthesis of tris[3,5-bis(trifluoromethyl)phenyl]borane (1) has been achieved on a multi-gram scale. Gutmann-Beckett
(CD$_2$Cl$_2$, 376 MHz); $\delta$ ≈ -63.4 (s, CF$_3$). $^{13}$B NMR (CD$_2$Cl$_2$, 128 MHz); $\delta$ 68.1 (s, br). HRMS (ES, m/z): for BC$_6$F$_{13}$: Calc’d: 650.0510. Found: 650.0510. IR (KBr, cm$^{-1}$): 1615 (m), 1607 (m), 1385 (m), 1283 (s), 1227 (m), 1169 (s), 1127 (s), 909 (m), 844 (w), 720 (m), 708 (w), 683 (m), 657 (m). Anal. Calcd. for C$_{57}$H$_{39}$B$_2$F$_{36}$N: C 47.43; H 2.72; N 0.97.

Data for 2: $^{1}H$ NMR (CD$_2$Cl$_2$, 400 MHz, 353 K); $\delta$ 7.84 (s, 6H, para- H). $\delta$ 7.73 (s, 12H, ortho-H). $\delta$ 4.00 (br, 2H, NH). 1.57 (m, 2H, CH$_2$). 1.46 (m, 4H, CH$_2$). 1.23 (s, 12H, CH$_2$). IR (KBr, cm$^{-1}$): 3274 (m), 3234 (m), 3093 (m), 2938 (m), 1616 (m), 1577 (w), 1459 (w), 1365 (s), 1279 (s), 1165 (s), 1126 (s), 900 (s), 841 (m), 710 (s), 682 (s), 649 (s). Anal. Calcd. for C$_{48}$H$_{19}$B$_2$F$_{36}$: C 44.34; H 1.40; N 0.00.

References


9 It has been advised that metal-halogen exchange should be used for Grignard formation from halogeno(trifluoromethyl)benzenes, instead of direct synthesis using Mg, since the latter protocol has led to explosions (presumably due to Mg insertion into C-F bonds), especially in large scale syntheses. See N. A. Yakelis, and R. G. Bergman, Organometallics, 2005, 24, 3579-3581 and references contained therein.


20 The kinetics of EtO dissociation from 1-OEt$_2$ using $^1$H or $^3$F NMR spectroscopy were unobtainable due to the insolubility of uncoordinated I, precluding quantitative data at temperatures low enough to resolve exchange.

