Exploring structural and electronic effects in three isomers of tris{bis(trifluoromethyl)phenyl}borane: towards the combined electrochemical-frustrated Lewis pair activation of H₂

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Three structural isomers of tris(bis(trifluoromethyl)phenyl)borane have been studied as the acidic component of frustrated Lewis pairs. While the 3,5-substituted isomer is already known to heterolytically cleave H₂ to generate a bridging-hydride; ortho-substituents in the 2,4- and 2,5-isomers quench such reactivity through electron donation into the vacant boron π orbital and steric blocking of the boron centre; as shown by electrochemical, structural and computational studies. Electrochemical studies of the corresponding borohydrides identify that the two-electron oxidation of terminal-hydrides occurs at more positive potentials than observed for [HB(C₆F₅)₃]⁻, while the bridging-hydride oxidizes at a higher potential still, comparable to that of free H₂.

Introduction

Since the pioneering work of Stephan's group the field of frustrated Lewis pair (FLP) chemistry has grown rapidly. The archetypal FLP system combines the Lewis acid B(C₆F₅)₃ with a sterically demanding Lewis base such as P(ortho-C₆F₅)₃, to effect the heterolytic cleavage of H₂, resulting in the formation of the corresponding hydridic and protic products respectively.

FLPs have found applications as catalysts or mediators for a variety of reactions such as the metal-free hydrogenation of imines and nitrides, alkynes, silyl enol ethers and ketones. The activation of small molecules such as CO₂, and alkynes by FLPs has also found applications in the synthesis of heterocycles and other aromatic systems.

While much of the literature has focused on tris(pentafluorophenyl)borane, B(C₆F₅)₃ as the Lewis acid component in FLPs, other electron-deficient boranes have been used, including a range of halogenated triarylboranes, and borenium cations. Other examples of Lewis acids that have found use in FLPs include: the triaryl aluminium species, Al(C₆F₅)₃, which generates a bridging-hydride following cleavage of H₂; and the carbon based N-methylacridinium salts which activate H₂ even in the presence of H₂O. FLPs are not limited to the main group, with zirconocene–phosphane complexes pioneered by Wass and co-workers shown to act as intramolecular FLPs that exhibit unprecedented reactivity towards small molecules; similar chemistry has also been demonstrated with zirconocene-amines which act as hydrogenation catalysts with a wide range of substrates.

In 2014 we introduced the concept of “combined electrochemical-frustrated Lewis pairs” that couple the heterolytic cleavage of H₂ by a conventional FLP with in situ chemical-frustrated Lewis pairs to oxidise the resultant borohydride and subsequent regeneration of the parent borane. The combined electrochemical-FLP systems were shown to be electrocatalytic for the oxidation of H₂ (to form two protons and two electrons – a key reaction in many hydrogen-based energy technologies). These preliminary reports represent the first application of FLP chemistry other than to catalyse the hydrogenation of small molecules. For example, by combining the archetypal B(C₆F₅)₃/P(ortho-Bu)₃ FLP in the presence of H₂ whilst at the same time oxidizing the resultant [HB(C₆F₅)₃]⁻ intermediate formed, the potential for oxidation (the energetic driving force) of the borohydride at a glassy carbon electrode was found to be reduced by 0.61 V, in comparison to the direct oxidation of H₂ (observed at ca. +1.49 V vs. [FeCp₂]²⁺ under the same conditions), an energy saving equivalent to 117.7 kJ mol⁻¹.

Herein we report studies on three isomers of tris{bis(trifluoromethyl)phenyl}borane (Fig. 1) and their associated...
tris[bis(trifluoromethyl)phenyl]borohydrides. Electrochemical and computational investigations explain their varying ability to heterolytically cleave H₂ as part of a FLP and allow us to extend our studies into combined electrochemical-FLPs.

Results and discussion

Synthesis and characterization

The synthesis of tris[3,5-bis(trifluoromethyl)phenyl]borane 1 has been previously reported, and whilst a synthetic route to tris[2,4-bis(trifluoromethyl)phenyl]borane 2 has been reported by Cornet et al., their method led to a mixture of products requiring the isolation of 2 in low yield by fractional sublimations. The commercial availability of 2,4-bis(trifluoromethyl)bromobenzene and 2,5-bis(trifluoromethyl)bromobenzene allows us to report an improved synthetic route to 2 and also the synthesis of the novel tris[2,5-bis(trifluoromethyl)phenyl]borane 3.

Boranes 2 and 3 were synthesized by lithium–halogen exchange of BrC₆H₃(CF₃)₂ with nBuLi at −77 °C generating the aryllithium species LiC₆H₃(CF₃)₂. Treatment of this with a third of an equivalent of BCl₃, followed by warming to room temperature, subsequent removal of the volatiles and purification by sublimation or recrystallization allowed for the isolation of pure 2 and 3, in 90 and 77% yields respectively. It should be noted that applying the same synthetic route for the synthesis of 1, leads to a mixture of products with [Li(OEt₂)ₙ][B{3,5-(CF₃)₂C₆H₃}₄] as the major component.

The crystallography molecular structure of B{2,5-(CF₃)₂C₆H₃}₃ (hydrogen atoms removed for clarity).

Fig. 2 The crystallographic molecular structure of B(2,5-(CF₃)₂C₆H₃)₃ (hydrogen atoms removed for clarity).
H₂ activation observable by NMR spectroscopy over a minimum period of 48 hours.

Direct synthesis of authentic terminal-hydride species [HB-(C₆H₅(CF₃)₂)₃]⁻ proved to be possible for all three isomers 1–3 by direct reaction of the borane with sodium triethylborohydride in toluene solution, resulting in near quantitative conversion to the corresponding borohydrides. NMR spectra of the terminal-hydride species Na[1-H]–Na[3-H] show doublets in the ¹¹B spectra (δ_B: -9.1, -15.3, -14.2 and J_BH: 88, 93, 84 Hz respectively) and broad 1 : 1 : 1 : 1 quartets in the proton spectra (δ_H: +3.66, +4.06, +3.06 respectively). Additionally, for Na[2-H] and Na[3-H] clear evidence of through-space coupling between the hydride and ortho-CF₃ groups is observed in the ¹⁹F spectra (J_FH: 6.8, 7.6 Hz respectively); further, in the case of Na[3-H] this coupling is also observable in the proton spectrum with the hydride signal observable as a 1 : 1 : 1 : 1 quartet of broad 1 : 3 : 3 : 1 quartets (Fig. 3).

Synthesis of Na[2-H] and Na[3-H] allows for the confirmation that the inability of the 2,3/P(tBu)₃ FLPs to cleave H₂ is not due to unfavourable thermodynamics, but due to the significant kinetic barrier resulting from the steric and electronic effects of the ortho-CF₃ groups. Reaction with authentic [(tBu)₃PH]Cl results in rapid metathesis (indicated by precipitation of NaCl) and formation of the salts [(tBu)₃PH][2-H] and [(tBu)₃PH][3-H]. NMR spectra of which, show no liberation of H₂, regeneration of free borane/phosphine, or any other evidence of reaction over a 66 hour period.

Electrochemical studies

Cyclic voltammetric studies of 1–3 were performed in the non-coordinating solvent CH₂Cl₂ using [(tBuN)B(C₆F₅)₃] as the added electrolyte at a glassy carbon electrode (GCE). In all three cases a one-electron, reduction process is observed with quasi-reversible (moderately fast) electron transfer kinetics. However for 1 (Fig. 4a) the process appears to be chemically irreversible (but not electrochemically irreversible) at scan rates up to 2.0 V s⁻¹ due to fast chemical follow-up kinetics of the rate of electron transfer, while for both 2 (Fig. 4b) and 3 (Fig. 4c) an associated oxidation wave is observed indicating that the radical anions 2⁻ and 3⁻ are sufficiently stable on the electrochemical timescale for their subsequent (re-)oxidation to be observable.

Based on our previous experience from an electrochemical study of B(C₆F₅)₃, we performed digital simulations of the...
Table 1  Mechanistic parameters obtained by digital simulation of voltammetric data for the one-electron reductions of 1–3

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$E^0$ vs. [FeCp]$_2$ $^{(0/1)}$/V</th>
<th>$k_c$/cm$^2$/s$^{-1}$</th>
<th>$k_a$/cm$^2$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BArF$<em>{18}^–$ − e$–$ − BArF$</em>{18}^–$</td>
<td>$–1.61 \pm 0.01$</td>
<td>0.419</td>
<td>4.56 × 10$^{-3}$</td>
</tr>
<tr>
<td>BArF$_{18}^–$ − $\rightarrow$ ‘decomposition’</td>
<td>$–1.79 \pm 0.01$</td>
<td>0.498</td>
<td>2.61 × 10$^{-2}$</td>
</tr>
<tr>
<td>$D(BArF_{18}) = D(BArF_{18}^–)$/cm$^2$/s$^{-1}$</td>
<td>$–1.85 \pm 0.01$</td>
<td>0.468</td>
<td>2.22 × 10$^{-2}$</td>
</tr>
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*Diffusion constants (D) obtained via $^1$H and $^{19}$F DOSY NMR spectroscopy. $^b$ $k_c$ values are modelled as a pseudo first-order process.

Experimental voltammetric data modelled using an EC-mechanism (i.e. a reversible, homogeneous electron transfer step followed by an irreversible, homogeneous chemical step which generates electro-inactive products. Other postulated mechanisms produced a poor fit to the data). These digital simulations allowed us to extract pertinent mechanistic parameters such as the formal redox potentials and charge transfer coefficients ($E^0$ and $a$, respectively) and kinetic parameters for the electron transfer ($k_c$) and follow-on chemical step ($k_a$) as shown in Table 1.

The formal reduction potentials ($E^0$) suggest that 1 is the most electrophilic of the three boranes, while 3 is the least. While the difference in electrophilicity between 2 and 3 is consistent with a simplified view of the inductive electron-withdrawing effects of the different meta- and para-(CF$_3$)$_2$ groups positions based on Hammett parameters ($\sigma_{meta}(CF_3) = 0.43$ vs. $\sigma_{para}(CF_3) = 0.54$) the relative electrophilicity of 1 cannot be similarly rationalized. This is in part because simple Hammett parameters for ortho-(CF$_3$)$_2$ substituents do not satisfactorily account for any additional steric and/or electronic effects.

We can rationalize the reduced electrophilicity of 2 and 3 in comparison to 1 by considering the electronic effect of having ortho-CF$_3$ groups present in 2 and 3. As noted above, the crystal structures of 2 and 3 show the ortho-(CF$_3$)$_2$ groups are positioned at sufficiently close distances above the central BC$_3$ plane such that donation from the lone pairs on the fluorine atoms into the vacant boron p$_c$ orbital on boron could occur; such donation of electron density would be expected to reduce the electrophilicity of the boron centre, as is observed experimentally by our electrochemical measurements and indicated in electronic structure DFT calculations (vide infra).

Furthermore, the steric shielding of the boron centre by the ortho-(CF$_3$)$_2$ groups in 2 and 3 is qualitatively evident from the observation of more reversible redox processes in the cyclic voltammetric data. Quantitatively this is shown in the values of the rate constants ($k_f$) obtained from voltammetric digital simulation for the radical anion decomposition step, which is assumed to proceed in a similar fashion as was previously ascertained for the analogous [B(C$_6$F$_5$)$_3$]$^{3–}$ intermediate via reaction between solvent molecules and the boron centre in the reduced radical anion intermediates, 1$^{3–}$, 2$^{3–}$, or 3$^{3–}$. The value of $k_f$ is at least three orders of magnitude greater for the decomposition of 1$^{3–}$ than for 2$^{3–}$ or 3$^{3–}$, where, in the latter two cases, the presence of ortho-CF$_3$ groups provides significant steric shielding to the boron centre. It is worth noting here that these findings demonstrate the ease with which synthetic chemists working in this area can gain powerful insights into the chemistry of Lewis acidic species by the application of simple, rapid electrochemical characterization techniques in addition to the more ubiquitous crystallographic and spectroscopic characterization techniques. Simple examination of the shape and position of the voltammogram of each borane, obtained in a 20 minute experiment using inexpensive equipment can tell us qualitatively that in comparison to 1, boranes 2 and 3 are more sterically hindered, and less electrophilic, and therefore less Lewis acidic and less likely to be active FLP components for H$_2$ activation. The voltammetry even allows us to infer why this is so, given that the only thing boranes 2 and 3 have that 1 does not have and that could simultaneously sterically shield the borane and reduce the electronic demand at the boron centre are the o-CF$_3$ groups.
In comparison with the archetypal Lewis acid, B(C₆F₅)₃ (which is observed under the same conditions as a quasi-reversible reduction at \(E^0 = -1.518\) V vs. [FeCp₂]⁺⁺⁺ (see Fig. S2†), boranes 1–3 are all less electrophilic; while [B(C₆F₅)₃]⁻ is more stable (smaller \(k_f\) ) with respect to follow-on decomposition reactions than \(1^-\), but still considerably less stable than the ortho-(CF₃) stabilized \(2^-\) and \(3^-\).

**Borohydride oxidation.** Our combined electrochemical-FLP concept requires the electrochemical oxidation of borohydrides generated by the heterolytic cleavage of \(\text{H}_2\). Despite the only such species generated from the \(\text{B(C₆H₃(CF₃)₂)}₃\) isomers, being the previously reported bridging hydride \([\mu\text{-H}(1)]_2\)¹⁸, the ease of direct synthesis of the terminal hydrides \([\text{HB(C₆H₃(CF₃)₂)}₃]^-\) allows for their electrochemical study, to add to our understanding of the electrochemistry of the triaryl-borohydrides. Therefore, electrochemical studies of Na[1-H]–Na[3-H] and [tmpH][\(\mu\text{-H}(1)]_2\] were performed under the same conditions as their borane precursors (although Na1-H and [tmpH][\(\mu\text{-H}(1)]_2\] proved only sparingly soluble in CH₂Cl₂, and hence their concentrations cannot be accurately determined). In all cases a single irreversible oxidation wave is observed at scan rates up to 2.0 V s⁻¹.

For the terminal hydrides Na[1-H]–Na[3-H] (Fig. 5a–c) oxidations occurred with peak potentials of +1.08, +1.31, and 1.13 V vs. [FeCp₂]⁺⁺⁺ at a scan rate of 100 mV s⁻¹ respectively; with no evidence of electroactive product species (such as the parent boranes) being regenerated in sufficient quantities to be observed.

The bridging hydride [tmpH][\(\mu\text{-H}(1)]_2\] (Fig. 6) oxidation is observed as a shoulder on the edge of the solvent window, at ca. +1.55 V vs. [FeCp₂]⁺⁺⁺ at a scan rate of 100 mV s⁻¹ (observable distinct to the solvent/electrolyte breakdown at scan rates below 1.0 V s⁻¹), trace amounts of the terminal hydride species \([1^-\text{-H}]^-\) are also observed. Following oxidation of \([\mu\text{-H}(1)]_2^-\), sweeping to negative potentials results in observation (at 100 mV s⁻¹ scan rate and above) of an irreversible reduction wave at ca. −1.7 V vs. [FeCp₂]⁺⁺⁺ characteristic of the reduction wave observed for the parent borane 1.

In comparison to our previous studies on [HB(C₆F₅)₃]⁻,²⁵ all of the terminal-hydrides oxidize at more positive potentials,
whilst the bridging-hydride species, $[\mu-H]_2^-$, is oxidized at an even more positive potential approaching that of the direct oxidation of $\text{H}_2$ at a GCE (ca. +1.5 V vs. $[\text{FeCp}_2]^+$), and is effectively behaving as an electrolyte under these conditions.

Computational studies

To further our understanding of the tris[bis(trifluoromethyl)phenyl]borane isomers 1-3 we have investigated them and their associated radical-anions $1^{--}-3^{--}$ using density functional theory (DFT).

For all the neutral boranes 1-3 the LUMOs (Fig. 7) showed a high degree of boron p$_z$ character (19, 22, 19% respectively, the majority of the remaining contributions being from the phenyl π-systems) as do the SOMOs (Fig. S4†) for the radical-anions $1^{--}-3^{--}$.

Total molecular energy calculations indicate that the ground state of 1 is lower in energy than those of 2 and 3 by ca. 43 kJ mol$^{-1}$. Analysis of calculated Mulliken atomic charges for 1-3 show that any stabilisation of 1 compared to 2 and 3 cannot be attributed to electron withdrawing effects of the aryl rings; and therefore may be attributed to the reduced steric hindrance caused by the lack of ortho-CF$_3$ groups in 1.

As noted previously, the ortho-CF$_3$ groups in 2 and 3 are orientated such that there is potential for B⋯F bonding interactions. Such interactions are clearly identified by the calculated bonding parameters: the B⋯F bonding parameter for 2 is 0.065, whilst for 3 it is 0.076 (in both cases averaged over all contributing B⋯F pairs). As expected, in 1, where no interaction occurs, the B⋯F bonding parameter to the meta-CF$_3$ groups is <0.001.

Conclusions

We have investigated three structural isomers of tris[bis(trifluoromethyl)phenyl]borane in terms of both their electrochemical redox chemistries and also as the Lewis acidic components of an FLP for the heterolytic cleavage of $\text{H}_2$.

The two isomers of tris[bis(trifluoromethyl)phenyl]borane that incorporate ortho-CF$_3$ groups were not found to be active as the Lewis acidic component of FLPs for $\text{H}_2$ cleavage reactions. This lack of reactivity is due to a combination of, kinetic effects resulting from in part steric shielding of the boron centre; but also quenching of the boranes’ electrophilicity through B⋯F bonding interactions, which are quantified by DFT calculations and electrochemical measurements. Whilst electrochemical studies show that all three isomers are less electrophilic than the archetypal Lewis acid B(C$_6$F$_5$)$_3$ the link between Lewis acidity, activity towards $\text{H}_2$ in an FLP, and electrophilicity, as shown in our previous studies$^{20,25,26}$ and those of other groups$^{33-35}$ is complex and requires further study.

The direct synthesis of all three tris[bis(trifluoromethyl)phenyl]borohydride species under mild conditions allows for their reduction potentials to be measured, and their propensity for combined electrochemical-frustrated Lewis pair catalysis to be screened in a straightforward manner. The oxidation potentials of all three terminal borohydrides studied were found to be more positive than that of [HB(C$_6$F$_5$)$_3$]$^-$ yet are still less than the potential required for the direct oxidation of $\text{H}_2$ at a GCE under identical conditions.

Electrochemical studies of the bridging hydride formed when $\text{H}_2$ is cleaved by the B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_3$/mp FLP, show that this species is oxidized at comparable potentials to that of the direct oxidation of $\text{H}_2$. However, following oxidation, the regeneration of the parent borane species is clearly observed, which is not the case for any of the terminal borohydride Na[1-H]-Na[3-H] species studied.

What this report demonstrates is the utility of electrochemical characterization methods to enable synthetic chemists to rapidly screen prospective new Lewis acids using simple electrochemical techniques to gain insights into the chemical behaviour of new species. It also provides insights to guide the design of new Lewis acids for researchers wishing to employ the combined electrochemical-frustrated Lewis pair activation of $\text{H}_2$, which is the focus of our ongoing studies.

Experimental

All reactions and manipulations were performed under an atmosphere of dry, oxygen-free $\text{N}_2$, using either standard Schlenk techniques or in either a MBraun UNItlab or LABmaster
glovebox. All solvents were dried prior to use by refluxing over an appropriate drying agent (Na/benzophenone for petroleum ether (b.p 40–60 °C) and diethyl ether; Na for toluene; CaH₂ for dichloromethane), collected by distillation under an inert N₂ atmosphere and stored over 4 Å molecular sieves prior to use. All other reagents were obtained from commercial suppliers and used as received.

NMR Spectra were obtained on either a Bruker Avance III 500 MHz or Bruker AV 400 MHz spectrometer, all deuterated solvents were dried over 4 Å molecular sieves prior to use. For 1H spectra residual protio-solvent was used as an internal standard; for 13C the solvent resonance(s) were used as an internal standard;46 for 19F spectra CFCl₃ was used as an external standard; for 11B spectra BF₄Et₂O was used as an external standard. 1H and 19F DOSY experiments were performed on a Bruker Avance III 500 MHz spectrometer equipped with a broadband multinuclear probe, using a longitudinal eddy current delay incorporating bipolar gradients for diffusion and spoil gradients (ledbpgp2s) pulse sequence.37

Mass spectrometry was performed by the EPSRC Mass Spectrometry Service at the University of Swansea for 3, or by Dr L. Haigh at Imperial College using a Micromass Autospec Premier spectrometer for 2. Elemental analyses were performed by Mr S. Boyer of the Elemental Analysis Service at London Metropolitan University.

Single crystals of 3 were grown by slow diffusion of a saturated CH₂Cl₂ solution of the compound into n-hexane; data collection and processing was performed at the UK National Crystallographic Service at the University of Southampton.30 Using Olex2, the structure was solved and space group assigned with SuperFlip/EDMA using charge flipping, and then refined with the ShelXL version 2014/7 refinement program using least squares minimization.

CCDC 1061234 contains the supplementary crystallographic data for this paper.

Electrochemical studies were carried out using a Metrohm Autolab PGSTAT302N potentiostat linked to a computer running Metrohm Autolab NOVA version 1.11 software, in conjunction with a three electrode cell comprising: a glassy carbon disc working electrode (Bioanalytical Systems Inc, ca. 7.0 mm² area calibrated using the [FeCp₂]⁺/² redox couple), a platinum wire (99.99% purity) counter electrode, and a silver wire (99.99% purity) pseudo-reference electrode; all electrodes were polished with 0.3 μm α-alumina and dried prior to use. All electrochemical measurements were performed at ambient temperature under a dry N₂ atmosphere, in CH₂Cl₂ containing 0.05 M [Bu₄N][B(C₆F₅)₄] as the supporting electrolyte and between 1.0 and 2.0 mM of the analyte species of interest. Cyclic voltammetric measurements were Ir-compensated using positive-feedback to within 0.5% of the uncompensated solution resistance. [Bu₄N][B(C₆F₅)₄] was synthesized according to published methods.31 All potentials were referenced to the [FeCp₂]⁺/² redox couple, which was added as an internal standard. Simulations of electrochemical processes were performed using ElchSoft DigiElch version 7.096 software.42

DFT calculations were performed using the Gaussian 09 computational package.43 Geometry optimization calculations have been carried out using the three-parameter exchange functional of Becke44 (B3) and the correlation functional of Lee, Yang, and Parr (LYP), B3LYP.45 The 6-311+G(d,p) basis set has been implemented for all atoms.46 Structures were geometry optimized in the gas phase with the default convergence criteria and confirmed as minima through frequency calculations. All optimized structures were confirmed as minima by frequency analysis with thermodynamic properties extracted for the gas phase at 298.15 K and 1 atm. Bonding parameters between B and F atoms were calculated as the absolute values of the associated non-diagonal elements of the condensed to atoms electron density matrix. Density matrices were computed in a separate calculation taking into consideration basis set superposition error (BSSE) correction using an unrestricted Hartree–Fock (H–F) calculation with counterpoise (CP) correction approach as implemented in Gaussian suite.

B[3,5-(CF₃)₂C₆H₃]₃ 1,18,27 and [tmpH][μ-H][B[3,5-(CF₃)₂C₆H₃]₃]₂ [tmpH][μ-H(1)₂]₁₈ were synthesized as previously reported.

B[2,4-(CF₃)₂C₆H₃]₂ 2

2,4-Bis(trifluoromethyl)bromobenzene (2.00 g, 1.16 cm³, 6.83 mmol) and Et₂O (100 cm³) were combined and the solution cooled to −77 °C. With the aid of rapid stirring, BuLi (2.87 cm³, 7.17 mmol, 2.5 M in hexanes) was added slowly by means of a syringe. Following one hour of stirring, BCl₃ (2.28 cm³, 2.28 mmol, 1.0 M in heptane) was syringed into the amber solution and the mixture permitted to slowly warm to room temperature. The volatiles were removed in vacuo and the off white residue extracted with CH₂Cl₂ (3 × 25 cm³) and filtered through Celite. Volatiles were removed under vacuum, following a high vacuum sublimation step (10⁻⁶ mbar) at 85 °C, a pure white solid was obtained. Yield 1.33 g (2.04 mmol, 90%).

1H NMR (400.4 MHz, CD₂Cl₂, 25 °C, δ): +8.06 (s, 3H, 3-H), +7.87 (d, 3H, 3'H = 8 Hz, 5-H), +7.46 (d, 3H, 3'H = 8 Hz, 6-H); 11B NMR (128.4 MHz, CD₂Cl₂, 25 °C, δ): +74.0 (br.s); 13C(1H) NMR (100.6 MHz, CD₂Cl₂, 25 °C, δ): +144.2 (br, 1-C), +135.9 (s, 6-CH), +134.2 (q, JCF = 34 Hz, 2/4-C), +133.7 (q, JCF = 34 Hz, 2/4-C), +127.9 (q, JCF = 3 Hz, 5-CH), +123.9 (q, JCF = 273 Hz, 2/4-CF₃), +123.6 (sept., JCF = 3 Hz, 3-CH), +123.6 (q, JCF = 273 Hz, 2/4-CF₃). 19F NMR (376.8 MHz, CD₂Cl₂, 25 °C, δ): −56.6 (s, 9F, 2-CF₃), −63.8 s, 9F 4-CF₃; HRMS-EI (m/z): [M⁺] calc. for C₂₄H₁₉BF₁₈ 650.0510; found, 650.0491. Elemental analysis (calc. for C₂₄H₁₉BF₁₈): C 44.34 (44.48), H 1.29 (1.47).

B[2,5-(CF₃)₂C₆H₃]₃ 3

2,5-Bis(trifluoromethyl)bromobenzene (3.1 cm³, 17.9 mmol) and Et₂O (100 cm³) were combined and cooled to -77 °C. "BuLi (11 cm³, 17.6 mmol, 1.6 M in hexanes) was added to the stirred solution. After one hour BCl₃ (5.8 cm³, 5.8 mmol, 1.0 M in heptane) was added to the orange solution and the mixture permitted to slowly warm to room temperature. The volatiles were removed in vacuo and the pale yellow residue extracted.
with CH₂Cl₂ (3 × 25 cm³) and filtered (via cannula). The product is then recrystallized from CH₂Cl₂/hexane and isolated as a white micro-crystalline solid. Yield 2.89 g (4.44 mmol, 77%).

\[ ^{1} \text{H NMR} \quad (500.21 \text{ MHz, CD₂Cl₂, 25 °C, } \delta) \quad +7.95 \ (s, 3 \text{H, 3/4-H}), +7.98 \ (s, 3 \text{H, 3/4-H}), +8.47 \ (s, 3 \text{H, 3-H}) \]

\[ ^{11} \text{B NMR} \quad (160.49 \text{ MHz, CD₂Cl₂, 25 °C, } \delta) \quad +70.7 \ (br.s) \]

\[ ^{13} \text{C} \{^{1} \text{H}\} \text{ NMR} \quad (125.78 \text{ MHz, CD₂Cl₂, 25 °C, } \delta) \quad +141.5 \ (br.s, 1-CH), +137.1 \ (q, J_{CF} = 33 \text{ Hz, 2/5-C}), +133.3 \ (q, J_{CF} = 33 \text{ Hz, 2/5-C}), +132.4 \ (q, J_{CF} = 3.7 \text{ Hz, 3/4/6-C}), +129.3 \ (q, J_{CF} = 3.7 \text{ Hz, 3/4/6-C}), +127.8 \ (br.m, 3/4/6-C), +124.1 \ (q, J_{CF} = 275 \text{ Hz, 2/5-CF₃}), +123.9 \ (q, J_{CF} = 273 \text{ Hz, 2/5-CF₃}) \]

\[ ^{19} \text{F NMR} \quad (70.67 \text{ MHz, CD₂Cl₂, 25 °C, } \delta) \quad -56.5 \ (s, 9 \text{F, 2-CF₃}), -63.7 \ (s, 9 \text{F, 5-CF₃}) \]


Elemental analysis (calc. for C₂₄H₁₀BF₁₈Na, 631.0519): C 42.83 (42.76), H 1.57 (1.50).

To a solution of 1 (0.40 g, 0.62 mmol) in toluene (10 cm³) was added Na[HB{3,5-(CF₃)₂C₆H₃}₃Na][Na-H] (0.6 mmol, 1.0 M in toluene), the reaction mixture was stirred for 6 hours to give a colourless solution. All volatiles were removed in vacuo to give a white solid. Yield 0.207 g (0.31 mmol, 74%).

\[ ^{1} \text{H NMR} \quad (500.21 \text{ MHz, CD₂Cl₂, 25 °C, } \delta) \quad +7.70 \ (d, J_{HH} = 8.2 \text{ Hz, 3H, 3/4-H}), +7.45 \ (d, J_{HH} = 8.5 \text{ Hz, 3H, 3/4-H}), +7.23 \ (br.s, 3H, 6-H), +3.06 \ (br.q, J_{HH} = 82 \text{ Hz, 9F, 2/5-CF₃}), +123.9 \ (q, J_{CF} = 3.7 \text{ Hz, 3/4/6-C}), +127.1 \ (q, J_{CF} = 3.7 \text{ Hz, 3/4/6-C}), +134.8 \ (q, J_{CF} = 28.0 \text{ Hz, 2/5-CF₃}), +133.7 \ (q, J_{CF} = 3.7 \text{ Hz, 3/4/6-C}), +132.3 \ (q, J_{CF} = 31.0 \text{ Hz, 2/5-CF₃}), +127.1 \ (q, J_{CF} = 275 \text{ Hz, 2/5-CF₃}), +126.3 \ (br.m, 3/4/6-C), +118.5 \ (s, 4-C), +165.0 \ (q, J_{CF} = 9 \text{ Hz, 1-C}) \]

Elemental analysis (calc. for C₂₄H₁₃BF₁₈Na: C 42.95 (42.76), H 1.61 (1.50)).

**Na[HB{2,5-(CF₃)₃C₆H₃}₃Na][3-H]**

To a solution of 3 (0.275 g, 0.42 mmol) in toluene (8 cm³) was added Na[HB{3,5-(CF₃)₂C₆H₃}₃Na][Na-H] (0.43 cm³, 0.43 mmol, 1.0 M in toluene), the reaction mixture was stirred for 4 hours to give a colourless solution. The reaction mixture was concentrated in vacuo reducing its volume to ca. 2 cm³, and the product crystallized by addition of petroleum ether and cooling to −25 °C. The white crystalline solid was isolated by filtration and dried in vacuo. Yield 0.207 g (0.31 mmol, 74%).

**Acknowledgements**

G. G. W. and A. E. A. thank the Royal Society for financial support by University Research Fellowships. E. J. L. thanks the EPSRC for financial support by a DTA studentship under grant number EP/J500409. The research leading to these results has received funding from the European Research Council under the ERC Grant Agreement no. 307061 (PIHOMER).

We thank Dr C. MacDonald (University of East Anglia) for assistance with the ¹H and ¹⁹F DOSY NMR experiments.

We acknowledge the use of the EPSRC funded National Chemical Database Service hosted by the Royal Society of Chemistry, and the EPSRC UK National Mass Spectrometry Facility (NMSF) at the University of Swansea. We thank the EPSRC UK National Crystallography Service at the University of Southampton for the collection of the crystallographic data. We thank the Research Computing Service at the University of East Anglia for access to the high performance computing cluster.

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