Novel H_2 activation by a *Tris*[3,5-*bis*(trifluoromethyl)phenyl]borane Frustrated Lewis Pair

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Electronic Supplementary Information

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S1 Experimental details

All reactions and compounds were manipulated under N_2 using either a MBraun Labmaster DP glovebox or using standard Schlenk line techniques on a dual manifold vacuum/inert gas line. For the manipulation of moisture sensitive compounds, all glassware was heated to 170°C before use. Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel or Teflon cannulae, or via plastic syringes for volumes less than 20 ml. Filtrations were performed using either glassware containing sintered glass frits or modified stainless steel cannulae fitted with glass microfibre filters.

Reaction solvents (pentane, hexane, toluene, CH_2Cl_2) were dried using an Innovative Technology Pure Solv SPS-400; whereas Et_2O and THF were distilled from purple Na/benzophenone diketyl; all except CH_2Cl_2 and THF were stored over K-mirrored ampoules. H_2 was dried *via* passage through a column of pre-activated 3Å molecular sieves prior to use.

Deuterated NMR solvents were dried and freeze-thaw degassed over the appropriate drying agent: CD_2Cl_2, Pyridine-d_5 (activated 3Å molecular sieves); C_7D_8 (K) and purchased from Goss Scientific (99.8, 99.6 and 99.6% D respectively). $BF_3{\cdot}OEt_2$ (99.9%), ^{i}PrMgCl (2.0 M in THF), 1-bromo-3,5-*bis*(trifluoromethyl)benzene (99.9%), 2,2,6,6-tetramethylpiperidine (> 99%), *trans*-crotonaldehyde (> 99%) were purchased from Sigma Aldrich, all were used as received.

Assessment of Lewis acidity using the Gutmann-Beckett method followed a method described by D.W. Stephan *et al*. which used an excess of Lewis acid to Et_3PO (3:1) dissolved in CD_2Cl_2. To accurately record $\Delta\delta$, the solution was placed in an NMR tube along with a sealed reference capillary containing uncoordinated Et_3PO dissolved in CD_2Cl_2. The ^{31}P NMR shifts were recorded at 298K. The Childs method was performed as described by Childs *et al*; Lewis acid and *trans*-crotonaldehyde were mixed in a 1:1 ratio and placed in an NMR tube where the ^{1}H NMR chemical shift of the H_3 proton of crotonaldehyde was recorded.

NMR Spectra were recorded using Bruker AV-400 MHz and DRX-400 spectrometers. The ^{1}H and ^{13}C chemical shifts, δ, in parts per million (ppm) are referenced internally to the residual proton shift in the deuterated solvent employed. ^{11}B, ^{19}F and ^{31}P chemical shifts were referenced externally to $BF_3{\cdot}OEt_2$, $CFCl_3$ and 85 % H_3PO_4 ($\delta = 0$).

High resolution mass spectrometry samples (HRMS; EI & ESI) were recorded by Mr. J. Barton using either a Micromass Autospec Premier or a Micromass LCT Premier spectrometer.

IR spectra were recorded on a Perkin Elmer GX FT-IR spectrometer (range 4000-400 cm^{-1}, resolution 0.5 cm^{-1}) using KBr pellets.

Elemental analyses were conducted by Mr. S. Boyer of the London Metropolitan University.

S2 X-Ray Crystallography

Crystal data for **2**.Et_2O: $(C_{48}H_{19}B_2F_{36})(C_9H_{20}N)\cdot C_4H_{10}O$, M = 1517.63, triclinic, P-1 (no. 2), a = 12.0325(5), b = 15.7928(8), c = 17.3620(9) Å, α = 90.233(4), β = 92.367(4), γ = 100.933(4)°, V = 3236.4(3) $Å^3$, Z = 2, D_c = 1.557 g cm^{-3}, μ(Mo-Kα) = 0.164 mm^{-1}, T = 173 K, colourless tablets, Oxford Diffraction Xcalibur 3 diffractometer; 13209 independent measured reflections (R_{int} = 0.0305), F^2 refinement, R_1(obs) = 0.0822, wR_2(all) = 0.2509, 7684 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°], 1009 parameters.

The C(7), C(16), C(39), C(47) and C(48)-based CF_3 groups were found to be disordered. In each case two orientations were identified of *ca*. 69:31, 85:15, 80:20, 69:31 and 90:10% occupancy, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and only the major occupancy non-hydrogen atoms were refined anisotropically. The B–H–B and NH_2 hydrogen atoms were located from ΔF maps and refined freely, though the latter were subject to an N–H distance constraint of 0.90 Å. The hydrogen atoms of the C(57) and C(58)-based methyl groups of the 2,2,6,6-tetramethylpiperidinium cation were initially placed in idealised positions and refined using a simple riding model. However, this put them in a position where there was a *ca*. 1.69 Å H···H contact from one methyl group to the other, and so the handling was changed to one where the methyl group was allowed to rotate about the C–Me bond (using the SHELXL AFIX 137 command). Both groups slightly rotated such that the closest H···H contact between these two methyl groups in the final refinement is *ca*. 1.96 Å.

S3 Synthesis of *tris*[(3,5-trifluromethyl)phenyl]borane ($BArF_{18}$); 1

i-PrMgCl (10.7 ml, 21.4 mmol, 2.0 M in Et_2O) was added slowly to a schlenk charged with a −20 °C stirred solution of 1-bromo-3,5-*bis*(trifluoromethyl)benzene (6.00 g, 3.5 ml, 20.5 mmol) in THF (100 ml). Over 30 minutes the solution was allowed to warm to 0 °C before being cooled to −50°C, whereupon $BF_3{\cdot}OEt_2$ (0.97 g, 0.84 ml, 6.8 mmol) was added dropwise using a syringe. The contents were warmed over the course of an hour, and followed by removal of all volatiles under vacuum. The amber oil was extracted using a toluene/pentane mixture (1:1, 3 x 50 ml) and removed under vacuum. The off-white solid was sublimed at 80°C under high vacuum (1 x 10^{-6} mbar) to produce analytically pure $BArF_{18}$ as a white powder (2.88 g, 67%, 4.4 mmol). Recrystallisation using a minimum quantity of toluene at 100°C, which is filtered and slow cooled to room temperature, produced an analytical sample.

S4 Synthesis of [TMPH][μ-H($BArF_{18}$)$_2$]; 2

Inside a glovebox, a 100 ml Rotaflo ampoule, equipped with stirrer bar, was charged with $BArF_{18}$ (0.5 g, 0.77 mmol) and TMP (0.07 ml, 0.41 mmol). The contents were transferred to a schlenk line and CH_2Cl_2 (50 ml) added. The mixture was degassed using a freeze-thaw method and sealed under H_2 (1 atm). After 4 hours, a flocculent white solid had precipitated by which point the solution was decanted off. The powder was washed with pentane (2 x 20 ml) and then dried. Yield 0.44g (0.30 mmol, 79 %).

Repeating this reaction in Et_2O (in the absence of stirring) provided a large crop of single crystals suitable for X-ray diffraction of **2**.Et_2O.

S5 Assessment of Lewis acidity

Gutmann Beckett in CD_2Cl_2. *$^{31}P\{^1H\}$ NMR:* $Et_3P{=}O$ reference capillary: δ = 50.7. $(Et_3P{=}O){\cdot}B(C_6F_5)_3$ reference adduct: δ = 77.3 ppm. Reference shift: $\Delta\delta$ = 26.6. $(Et_3P{=}O){\cdot}BArF_{18}$ adduct: δ = 78.9. Shift: $\Delta\delta$ = 28.2. Lewis-acidity relative to $B(C_6F_5)_3$: 106.0%. *$^{11}B\{^1H\}$ NMR (adduct)*: $(Et_3P{=}O){\cdot}B(C_6F_5)_3$ reference adduct: δ = – 2.5 ppm. $(Et_3P{=}O){\cdot}BArF_{18}$ adduct: δ = + 4.3 ppm.

Childs in CD_2Cl_2 at 298K. ^{1}H NMR: H_3C-CH=CH-CHO reference δ = 6.85 (m, 1H, *H-3*). (H_3C-CH=CH-CHO)-B(C_6F_5)$_3$ reference adduct: δ = 7.93 (m, 1H, *H-3*). Reference shift $\Delta\delta$ = 1.08. (H_3C-CH=CH-CHO)-BArF_{18} adduct: δ = 7.52 (m, 1H, *H-3*). Shift: $\Delta\delta$ = 0.67. Lewis-acidity relative to B(C_6F_5)$_3$: 62.0%. *$^{11}B\{^1H\}$ NMR (adduct)*: (H_3C-CH=CH-CHO)-B(C_6F_5)$_3$ reference adduct: δ = 3.4. (H_3C-CH=CH-CHO)-BArF_{18} adduct: δ = 10.7.

S6 Characterising Data for 1

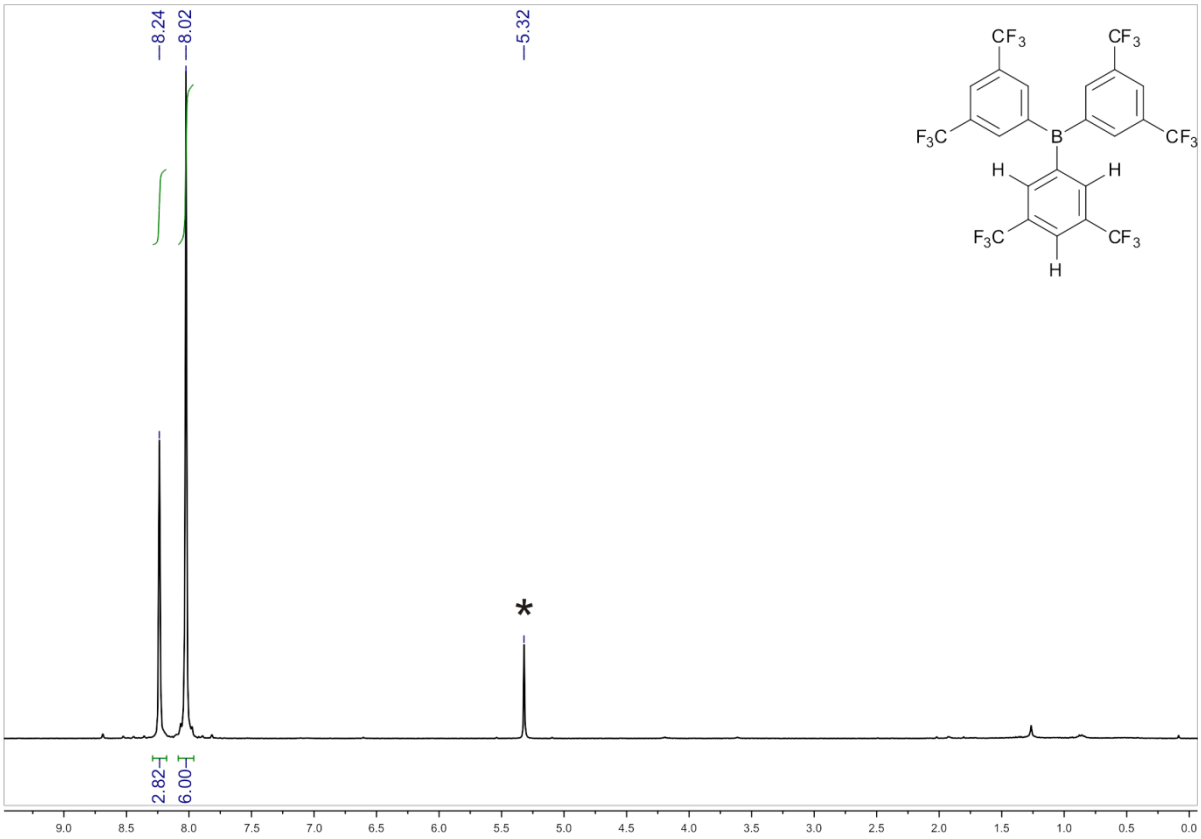

Figure 1. ^{1}H NMR for **1** in CD_2Cl_2. ***** denotes solvent.

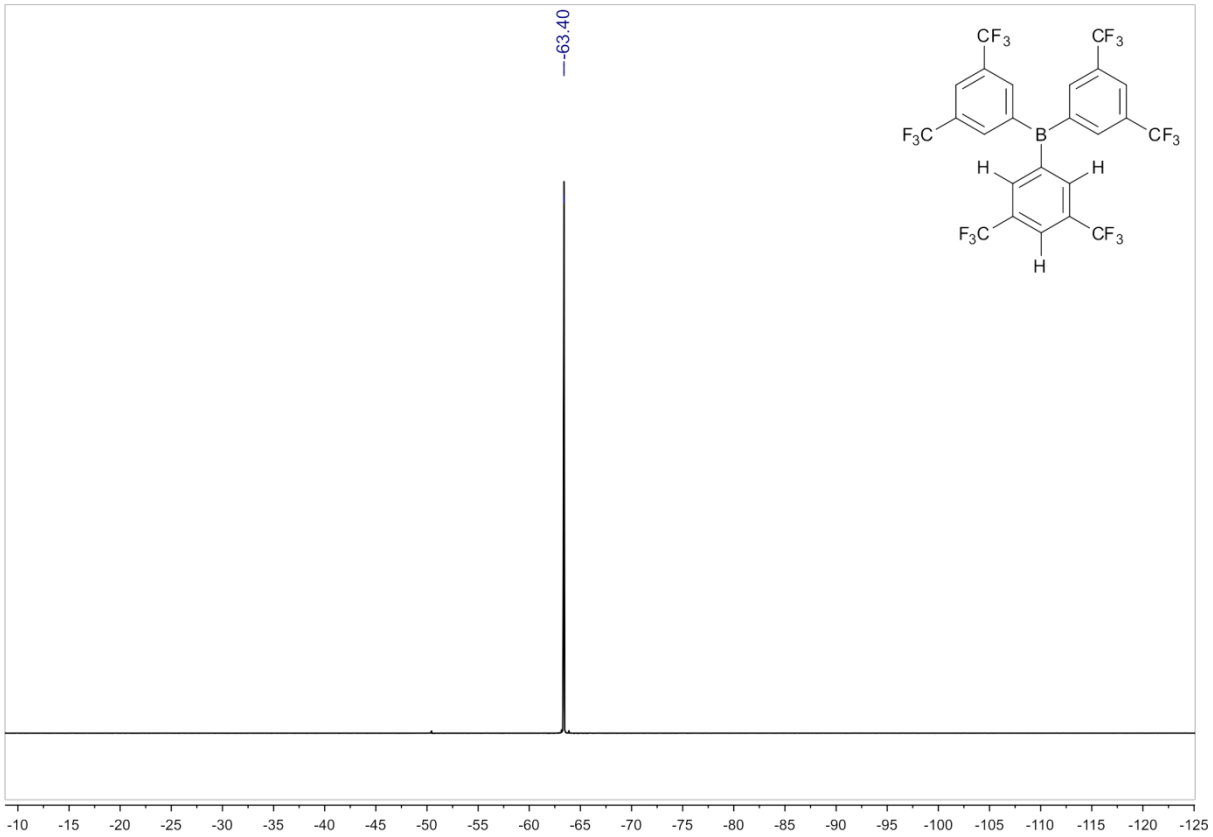

Figure 2. ^{19}F NMR for **1** in CD_2Cl_2.

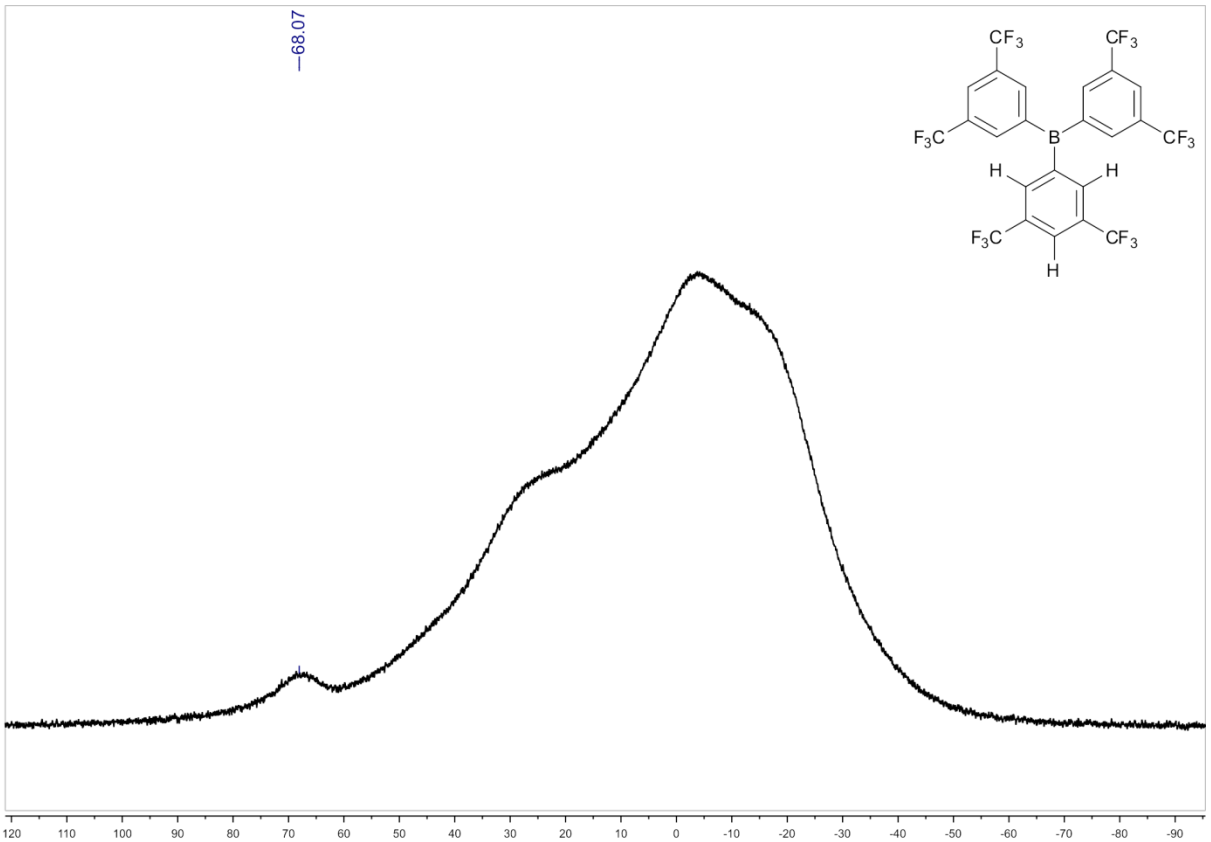

Figure 3. ^{11}B NMR spectrum of **1** in CD_2Cl_2

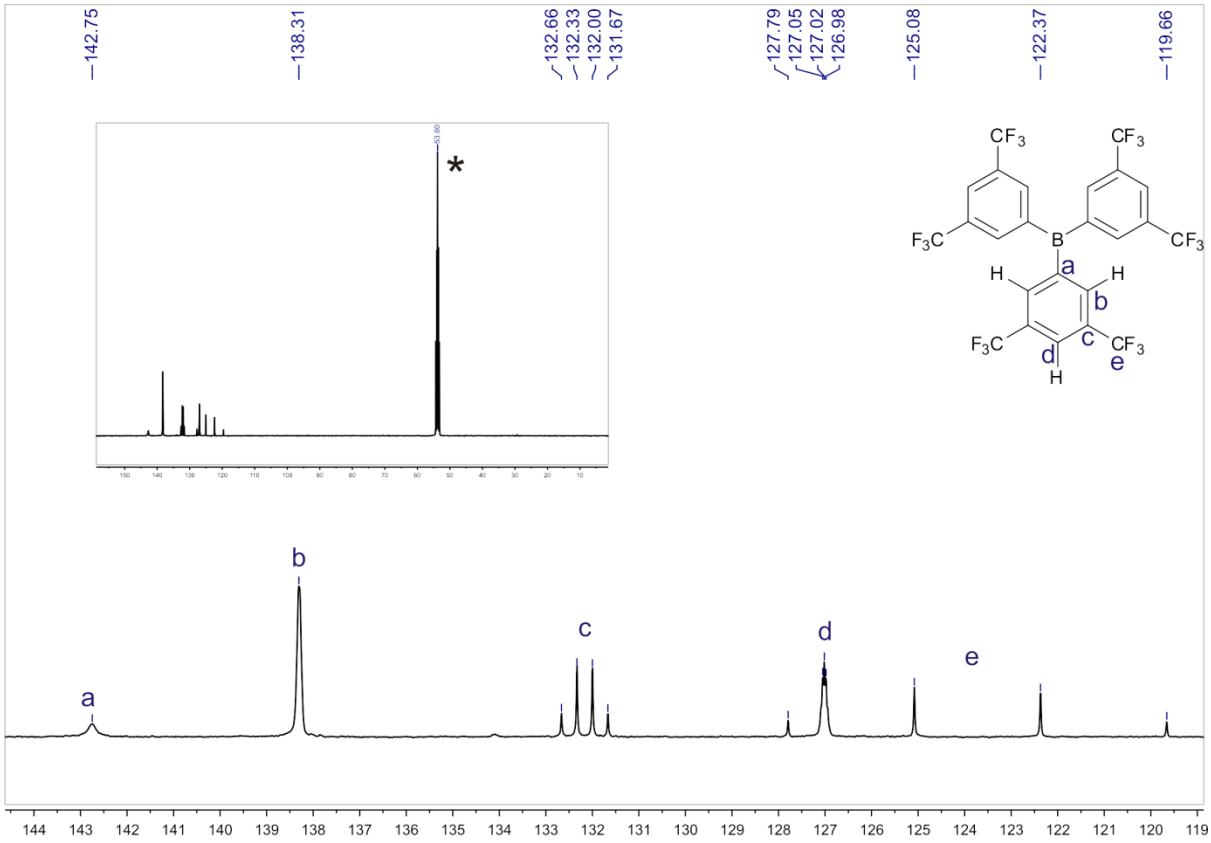

Figure 4. ^{13}C NMR for **1** in CD_2Cl_2. *Ortho* and *para* carbons (b and d) verified using HSQC. Inset displays full spectrum, solvent denoted by *.

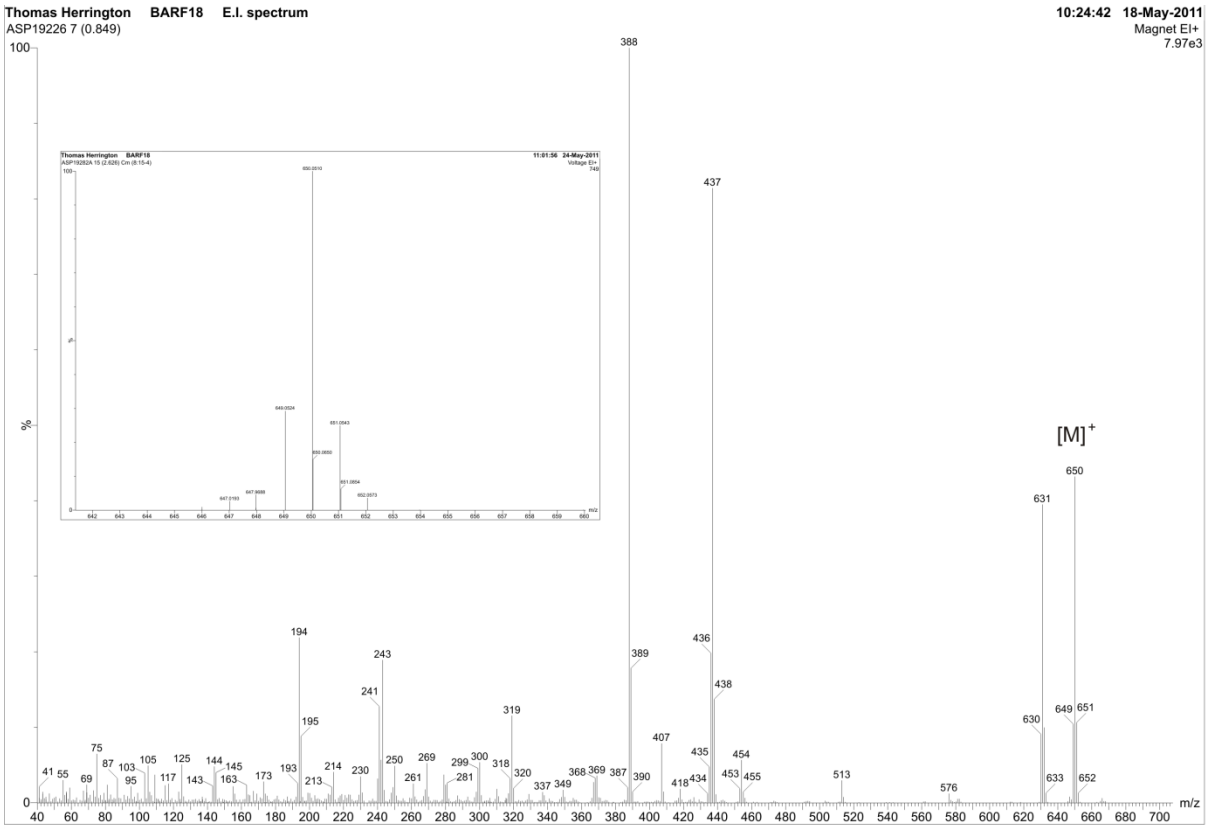

Figure 5 EI (m/z) Mass Spectrometry for **1**. Inset displays HRMS.

S7 ^{11}B NMR data for 1·OEt$_2$

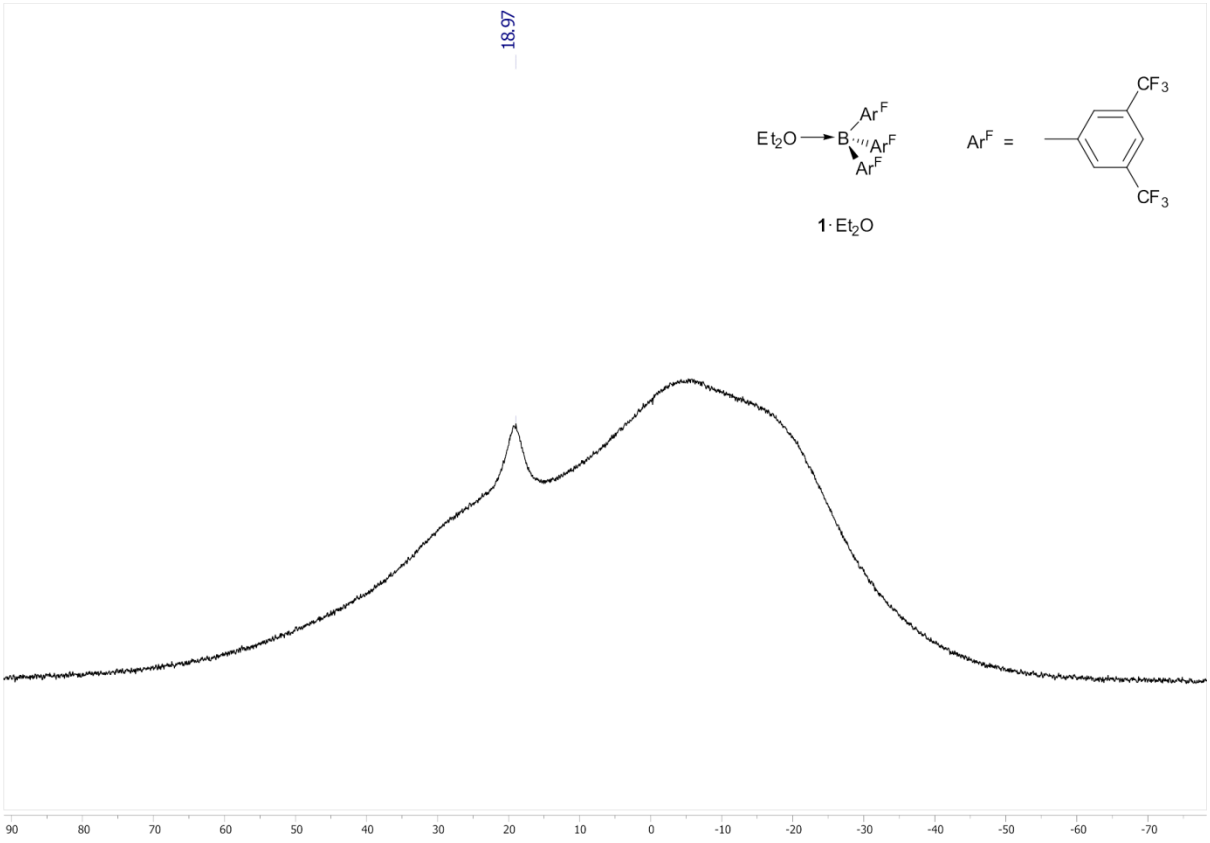

Figure 6. ^{11}B NMR spectrum of **1** in Et$_2$O solution.

S8 ^{1}H NMR data for 2

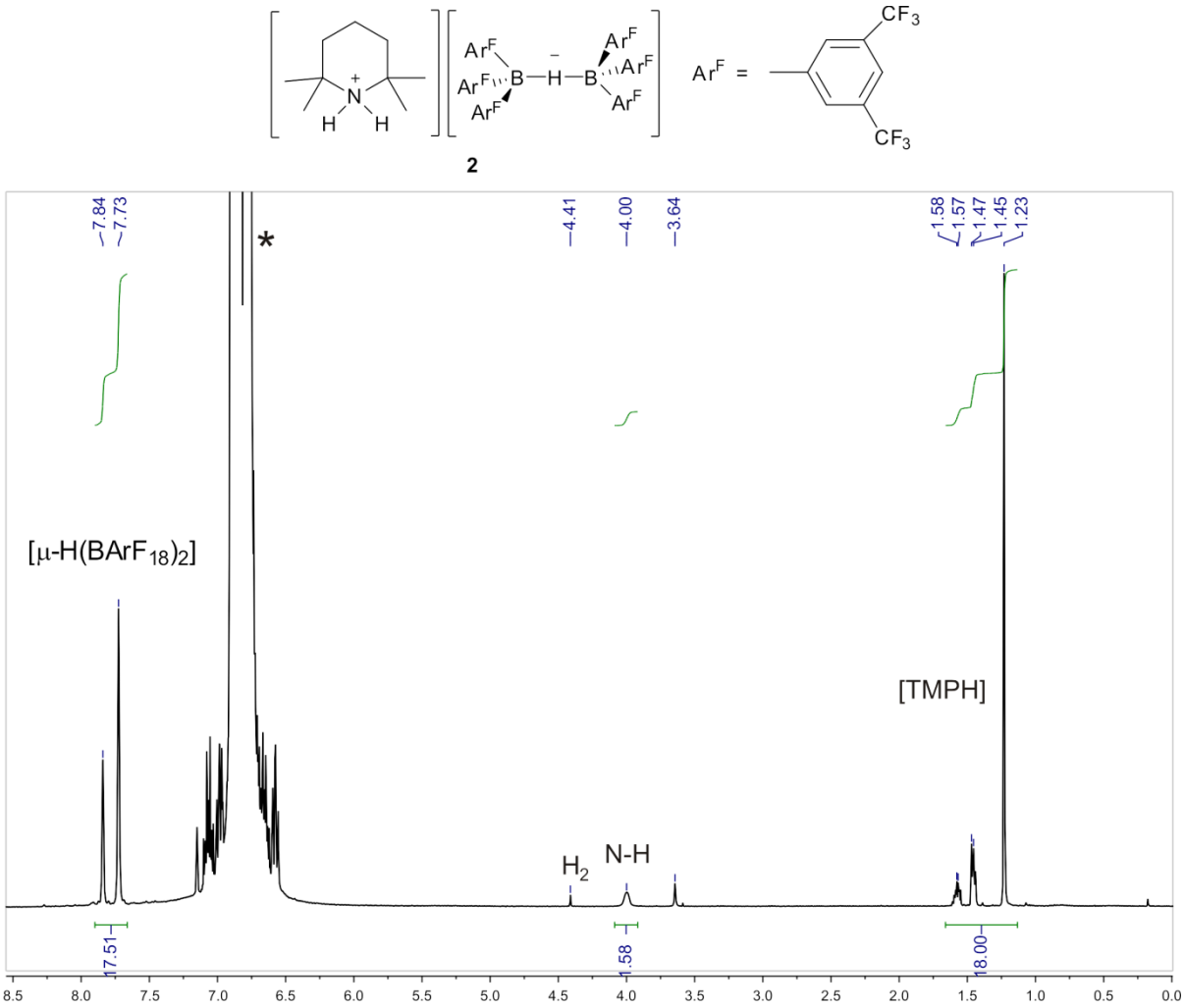

Figure 7. ^{1}H NMR for **2** in 1,2-difluorobenzene ($C_6H_4F_2$) at 80ºC. Small quantities of H_2 evolved at this temperature, solvent signals (4,5-H positions referenced to δ = 6.75 ppm) denoted by *.

S9 ^{11}B NMR data for 2 in pyridine-d_5

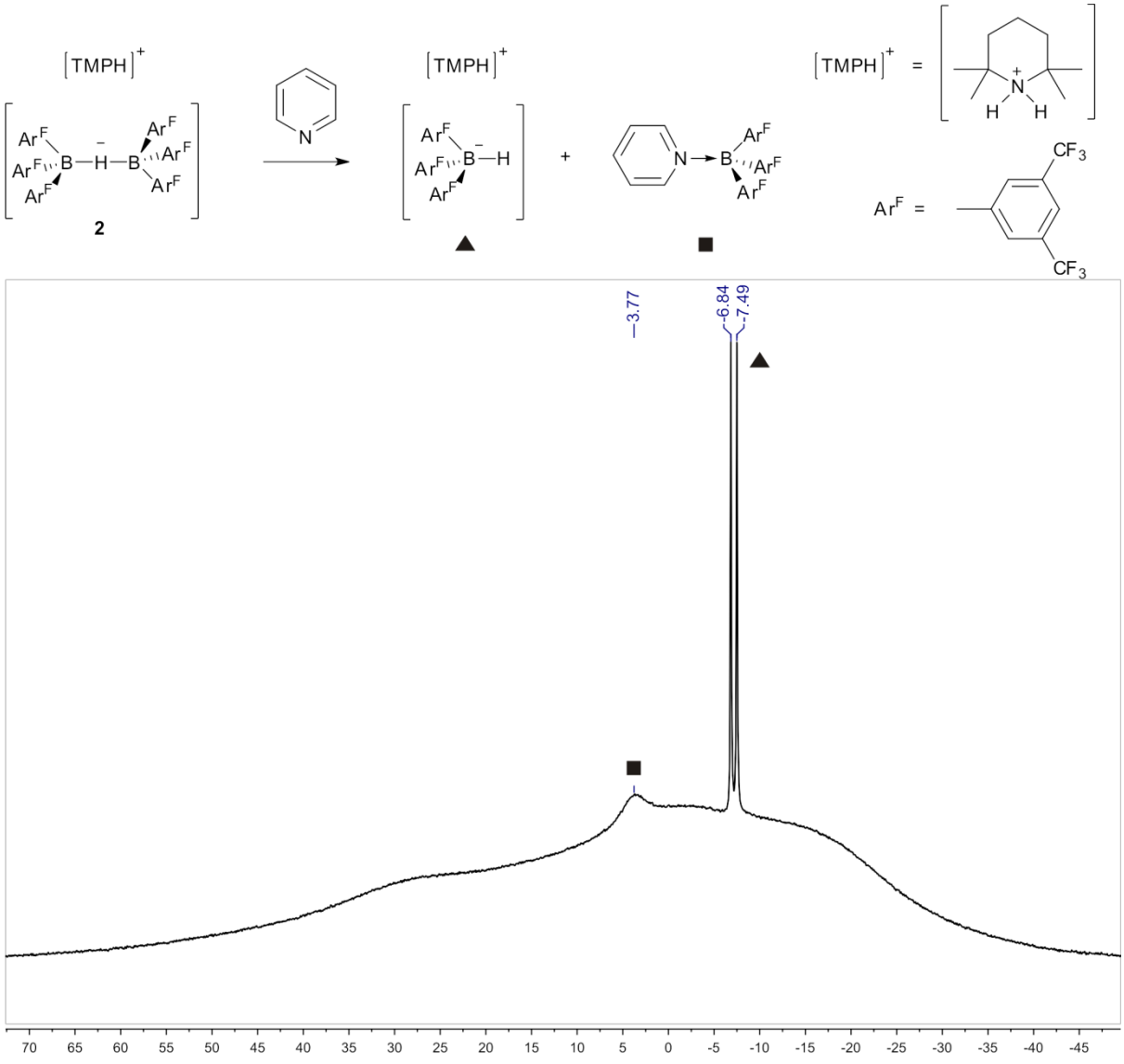

Figure 8. ^{11}B NMR spectra of **2** following dissolution in pydridine-d_5. ▲ and ■ denote the pyrdine·$BArF_{18}$ and terminal hydride respectively.

S10 Free volume calculations in $C_5H_5N{\cdot}A$ (A = $B(C_6F_5)_3$, 1) adducts

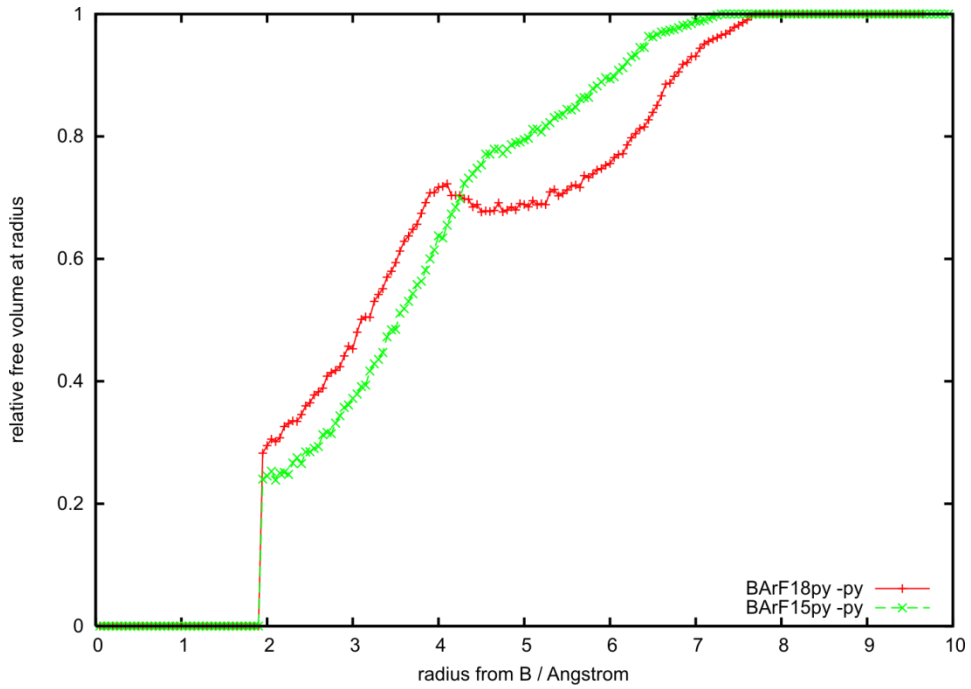

Figure 9. The relative free volume at a given radius from the boron centre for **1** and $B(C_6F_5)_3$ (defined as the percentage of a surface area of sphere of that radius centred on the boron not enclosed by the van der Waals surface). Calculated by a Monte Carlo integration with 10000 samples per radius. The estimates of standard error for each point was < 0.005.

Free volume calculations were performed to investigate the differences in steric factors around $B(C_6F_5)_3$ and **1**. Beginning with crystal structures for the tetrahedral pyridine adducts $C_5H_5N{\cdot}A$ (A = $B(C_6F_5)_3$, **1**; see main text for references) the pyridine was excised, leaving a pyramidal A structural residue. Using the van der Waals radii of Bondi,[1] and, for Boron, Martina *et al.*,[2] the van der Waals surface of each pyramidal A was constructed. The relative free volume at a given radius from the boron was defined as the percentage of a surface area of sphere of that radius centred on the boron which was not enclosed by the van der Waals surface, and was calculated by a Monte Carlo integration.

S11 References

1. A. Bondi, *J. Phys. Chem.*, **1964**, *68*, 441-451.

2. M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A*, **2009**, *113*, 5806–5812.