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H_2 Activation By A Highly Electron-Deficient Aralkylated Organoborane

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The electron-deficient and sterically bulky trialkylborane derivative tris[bis(pentafluorophenyl)methyl]borane [**1**, $B(CH(C_6F_5)_2)_3$], has been synthesised and comprehensively characterised; detailed ^1H and ^{19}F NMR studies reveal two dynamic bond rotational processes in the solution phase. Despite conventional probes (Gutmann-Beckett and Childs methods) implying that the compound has a very limited Lewis acidity, it was used to generate frustrated Lewis pairs capable of heterolytically activating H_2 in ethereal solutions, which suggests that the hydridophilicity of **1** is comparable to the potent Lewis acid $B(C_6F_5)_3$.

Introduction

Following the discovery by Stephan *et al*. in 2006 that combinations of sterically hindered Lewis acids and bases, termed "frustrated Lewis pairs" (FLPs), are capable of activating small molecules in solution, rapid progress has been made in this area of primarily main group chemistry.[1,2] Within such systems, the inability of the two components to form a dative covalent bond can lead to unquenched acidity and basicity allowing for the heterolytic activation of H_2. The most important application of such systems to date has been in the catalytic hydrogenation of polar,[3-5] and non-polar organic molecules,[6] as well as stoichiometric hydrogenations of CO_2 and CO – the latter both in syngas mixtures, and homogeneously on metal carbonyl complexes.[7-9]

A major factor in determining the thermodynamic ability of FLPs to cleave H_2 is thought to be the combined Lewis acidity and basicity of the system.[10, 11] Since its initiation, a focus for FLP chemistry has been around the use of strong Lewis acids such as $B(C_6F_5)_3$ (and related derivatives), which allow the cleavage of H_2 in the presence of relatively weak bases such as phosphines (e.g. $^tBu_3P$) and amines (e.g. 2,2,6,6-tetramethylpiperidine).[2] Trialkylboranes, by comparison, have not been widely investigated as Lewis acids in FLP systems due to their significantly lower Lewis acidity; for example, the $^tBu_3P/BEt_3$ FLP system does not react with H_2.[10,12] Supporting this observation are measurements using the Gutmann-Beckett method, which is a common spectroscopic probe to assess Lewis acidity based on the ^{31}P NMR shift difference upon coordination of $Et_3P{=}O$ relative to the free phosphine oxide; in C_6D_6 solution BEt_3 gives a value ($\Delta\delta$ = 11.6 ppm) less than half of that observed for $B(C_6F_5)_3$ ($\Delta\delta$ = 29.8 ppm) or BPh_3 (23.6 ppm).[13,14]

Although highly Lewis acidic boranes such as $B(C_6F_5)_3$ provide facile H_2 activation, the resultant borohydride anions are consequently fairly weakly hydride donors which can limit the scope of substrates that can be reduced in the hydride transfer step. Conversely, trialkylborohydrides are well known as powerful reducing agents, and $Li[Et_3BH]$ is commonly referred to as 'Super-Hydride'.[15] Generation of more powerful hydride donors from gaseous H_2 could allow a broader range of hydrogenation reactivity to be accessed. A key advance in this area was made by Bercaw *et al*. who demonstrated the first metal-free system capable of reversibly generating trialkylated borohydride anions directly from H_2 cleavage (Figure 1). However, this system requires use of a potent phosphazene Lewis base [^{t}BuNP(pyrrolidinyl)$_3$, P_1; pK_a(MeCN) $[HP_1]^+$ ~ 28];[9] the poor Brønsted acidity of this species subsequently hampers protonation of reduced substrates, which is necessary to close the catalytic cycle in an ionic hydrogenation process.[16] More recently, Krempner *et al.* have documented irreversible H_2 activation by BEt_3 in conjunction with a strongly basic zwitterionic organosodium base [pK_a(DMSO) = 22.5].[14]

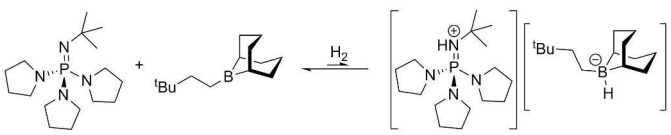


Figure 1. Activation of H_2 with an FLP consisting of $^tBuCH_2CH_2B(C_8H_{14})$ and ^{t}BuNP(pyrrolidinyl)$_3$

Despite the significant advances in FLP chemistry, no example has yet been reported of *electron deficient* trialkylboranes occupying the place of the Lewis acid in a H_2-activation system. This should attenuate the potency of the conjugate hydride donor, compared to traditional $[HB(alkyl)_3]^-$ species, concomitant with the ability to use weaker, more conventional FLP Lewis bases such as amines or phosphines.

Our aim in the current investigation was to augment the Lewis acidity of a trialkylborane *via* the incorporation of strongly electron withdrawing C_6F_5 substituents distal to the boron centre. In this manner we retain a boron centre which does not interact with the ligands through (p-p)π conjugation, as found in triarylborane compounds. Thus we report the first synthesis, characterisation and reactivity studies of the electron deficient homoleptic (aralkyl)borane compound, tris[bis(pentafluorophenyl)methyl]borane **1**, $B[CH(C_6F_5)_2]_3$.

Experimental

Unless stated otherwise all manipulations were performed under an atmosphere of dry N_2 using standard Schlenk line techniques, or in an MBraun Labmaster DP glovebox. All glassware was dried at 170 °C overnight before use. Pentane, toluene, hexane, CH_2Cl_2, and $CHCl_3$ were dried using an Innovative Technology Pure Solv SPS-400 system; THF and Et_2O were distilled from Na/fluorenone; tetrahydropyran (THP), dioxane, chlorobenzene and 1,2-difluorobenzene (DFB) were dried over 4 Å molecular sieves. Solvents were degassed, dried and stored in gas-tight ampoules over suitable drying agents; deuterated solvents were treated similarly: $CDCl_3$, CD_2Cl_2 and THF-d_8 (3 Å molecular sieves). CO_2 (5.0 Research Grade BOC) and H_2 (99.9999%, Air Liquide) were dried by passage through a Matheson gas purification column, D_2 (99.96 atom % D, Sigma-Aldrich) was dried in a gas ampoule over 3 Å molecular sieves, before being administered to the sample *via* a Toepler pump.

The following chemicals were obtained from suppliers and used without further purification: CCl_4 (≥99.5% Sigma-Aldrich), ethyl formate (97%, Sigma-Aldrich), PCl_5 (95%, Sigma-Aldrich), Et_3PO (97%, Sigma-Aldrich), $BF_3{\cdot}OEt_2$ (≥46.5% BF_3 basis, Sigma-Aldrich), Iodine (99.9%, Sigma-Aldrich), bromopentafluorobenzene (99%, Fluorochem), Mg powder (98%, Fisher Scientific). The following were dried over 3 Å molecular sieves prior to use: *trans*-crotonaldehyde (≥99%, Sigma-Aldrich), 2,2,6,6-tetramethylpiperidine (TMP) (≥99%, Sigma-Aldrich), 1,2,2,6,6-pentamethylpiperidine (PMP) (97%, Sigma-Aldrich) and MeOTf (≥98%, Sigma-Aldrich). Decafluorobenzhydrol was prepared according to a previously reported method.[17]

IR spectra were recorded on a Perkin-Elmer GX FT-IR spectrometer using KBr pellets. The sample was finely ground with KBr and placed in a die in the glovebox, then pressed into a pellet and the spectrum recorded immediately. Elemental analyses were conducted by Mr S. Boyer of the London Metropolitan University. High resolution mass spectrometry (HRMS; ES) was performed by Dr L. Haigh using either a Micromass Autospec Premier or a Micromass LCT Premier spectrometer. NMR spectra were recorded using Bruker AV-400 (400 MHz) and Varian Unity-plus (500 MHz) spectrometers. Chemical shifts, δ, are reported in parts per million (ppm). ^1H and ^{13}C chemical shifts are given relative to Me_4Si and referenced internally to the appropriate residual solvent peak. ^{11}B, ^{19}F and ^{31}P chemical shifts were referenced externally to $BF_3{\cdot}OEt_2$, $CFCl_3$ and 85% aqueous H_3PO_4 ($\delta = 0$) respectively. Air or moisture sensitive samples were prepared inside the glovebox using NMR tubes fitted with J. Young valves.

Variable Temperature (VT) Line Shape Analysis of 1

A sample of **1** was run on a Varian Unity-plus with an 11.75 Tesla magnet; the ^1H NMR spectra were recorded at 499.9 MHz and ^{19}F at 490.3 MHz. The rates were extracted from the line shape simulations performed using gNMR (version 5.10) P. H. M. Budzelaar.

X-Ray Diffraction Experiments

Single crystal X-ray diffraction data were collected using an Oxford Diffraction Xcalibur unit. Crystals were prepared in the glovebox and mounted on a glass fibre using perfluoropolyether oil and mounted in a stream of dry N_2 at 173 K.

Lewis Acidity Measurements

Measurement of the Lewis acidity of **1** by the Gutmann-Beckett method followed the process established by Stephan *et al*. using an excess of Lewis acid to Et_3PO (3:1) dissolved in CD_2Cl_2.[18] The shift in the ^{31}P signal for the Et_3PO in the mixture was compared to an internal capillary containing uncoordinated Et_3PO dissolved in CD_2Cl_2. The Childs method was performed as described in the original paper;[19] Lewis acid and *trans*-crotonaldehyde were combined in a 1:1 ratio and placed in an NMR tube where the ^1H NMR chemical shift of the H_3 proton of the crotonaldehyde was recorded.

Synthesis of bis(pentafluorophenyl)methyl chloride, $CHCl(C_6F_5)_2$

In air a 250 mL RBF fitted with a condenser was charged with decafluorobenzhydrol (4.83 g, 13.3 mmol) and PCl_5 (2.76 g, 13.3 mmol). CCl_4 (50 mL) was added and the solution was refluxed for 4 hours, then allowed to cool to room temperature. All volatiles were removed on a rotary evaporator producing an oily brown residue. The oil was extracted with pentane (3 x 50 mL), dried over anhydrous Na_2SO_4 and filtered through a glass frit. The volatiles were once again removed with the aid of a rotary evaporator. Distillation (5 x 10^{-2} mbar, 90 °C) gave the product as a colourless oil. Yield 4.10 g (81%). ^1H NMR ($CDCl_3$): 6.62 (s, C*H*Cl(C_6F_5)$_2$). ^{19}F NMR ($CDCl_3$): –139.4 (m, *o*-CF), –151.5 (t, $^3J_{FF}$ = 21 Hz, *p*-CF), –160.7 (m, *m*-CF).[20]

Synthesis of tris[bis(pentafluorophenyl)methyl]borane, $B[CH(C_6F_5)_2]_3$ (1)

A 250 mL RBF fitted with a condenser was charged with magnesium powder (1.93 g, 79.4 mmol) and Et_2O (50 mL). Following activation of the magnesium with a crystal of I_2 (0.1

g), $BF_3{\cdot}OEt_2$ (0.39 mL, 3.17 mmol) and bis(pentafluorophenyl)methyl chloride (7.60 mL, 9.93 mmol) were added *via* syringe. The solution was refluxed for 12 hours during which time the suspension darkened. The contents were allowed to cool to room temperature, the solvent decanted from excess Mg by cannula, and the light brown solution subsequently filtered through Celite®. The solvent was removed *in vacuo* to leave a light brown solid. Extraction with hot toluene (3 x 50 mL; 80 °C) was followed by removal of the solvent and washing of the gummy residue with hexanes. High vacuum sublimation (5 x 10^{-5} mbar, 160 °C) afforded **1** as a white powder (2.10 g, 63%). Crystals suitable for X-ray diffraction were grown from a saturated toluene solution cooled to –30 °C. ^{1}H NMR (CD_2Cl_2): 5.07 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 28.6 (s, B-*C*H(C_6F_5)$_2$), 112.4 (C_{ipso}, t, $^2J_{CF}$ = 18 Hz), 138.1 (dt, $^1J_{CF}$ = 254 Hz, *m*-CF), 141.4 (dt, $^1J_{CF}$ = 259 Hz, *p*-CF), 145.3 (dm, $^1J_{CF}$ = 247 Hz, *o*-CF). ^{19}F NMR (CD_2Cl_2): –138.2 (br, 12F, *o*-CF), –152.8 (t, 6F, $^3J_{FF}$ = 20 Hz, *p*-CF), –160.8 (s, 12F, *m*-CF). ^{11}B NMR (CD_2Cl_2): 80.3 (s, br). IR (KBr, cm^{-1}): 1655 (m), 1525 (s), 1500 (s), 1427 (w), 1301 (w), 1222 (m), 1161 (w), 1131 (m), 1115 (m), 1080 (m), 1055 (m), 1005 (s), 972 (s), 913 (m), 896 (w). Anal. Calcd. for $C_{39}H_3BF_{30}$: C 44.52; H 0.29; N 0.00. Found: C 44.42; H 0.29; N 0.00.

Synthesis of 2,2,6,6-tetramethylpiperidinium hydridotris[bis(pentafluorophenyl)methyl]borate, [TMP–H][H–B[CH(C_6F_5)$_2$]$_3$] (2)

In a glovebox a 100 mL Rotaflo ampoule, equipped with a magnetic stirrer bar, was charged with TMP (0.03 mL, 0.17 mmol) and **1** (0.15 g, 0.14 mmol). The contents were transferred to a Schlenk line and THF (20 mL) was added. The mixture was freeze-pump-thaw degassed and sealed under H_2 (1 atm). After heating for 5 days at 90 °C the solution was left to cool, the solvent removed and the product washed with pentane, then toluene to afford an amber oil. This oil was subsequently triturated with pentane to produce a cream coloured powder. Yield 0.1 g (0.08 mmol, 60 %). ^{1}H NMR (THF-d_8): 1.49 (s, 12H, NC(CH_3)$_2$CH$_2$), 1.51 (br, 1H, B*H*), 1.75 (m, 4H, NC(CH$_3$)$_2$C*H*$_2$), 1.88 (m, 2H, NC(CH$_3$)CH$_2$C*H*$_2$), 4.16 (d, $^3J_{HH}$ = 6.4 Hz, 3H, HB-C*H*(C_6F_5)$_2$), 7.35 (br, 2H, NH). $^{13}C\{^1H\}$ NMR (THF-d_8): 16.8 (s, 2C), 27.8 (s, 4C), 36.1 (s, 2C), 58.5 (s, 1C), 71.4 (s, 3C, B-*C*H(C_6F_5)$_2$), 136.6 (m), 139.1 (m), 145.4 (m), 147.9 (m). ^{19}F NMR (THF-d_8): –136.6 (br, 12F, *o*-CF), –163.4 (t, 6F, $^3J_{FF}$ = 20 Hz, *p*-CF), –166.8 (m, 12F, *m*-CF). ^{11}B NMR (THF-d_8): –14.6 (d, $^1J_{BH}$ = 87.6 Hz, BH). HRMS (ES+, *m*/z): for $[C_9H_{20}N]^+$ Calcd: 142.1596, found: 142.1592. HRMS (ES–, *m*/z): for $[C_{39}H_4BF_{30}]^-$ Calcd: 1052.9927, found: 1052.9921.

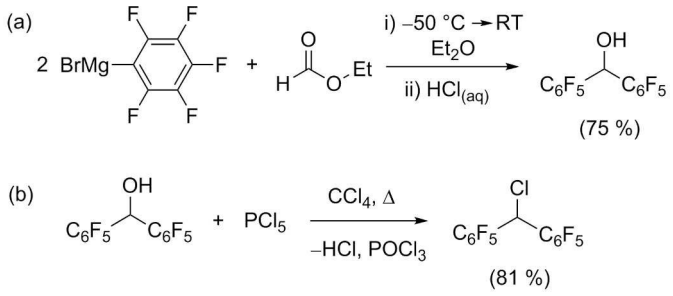
Representative procedure for admission of reactive gases for NMR experiments

Reagents were weighed out in a glovebox and transferred to an NMR tube fitted with a J. Young's tap, either as solutions or *via* microlitre syringe. The tube was transferred to a Schlenk or Toepler line and reactant gases added *via* a freeze-pump-thaw degassing method (1 bar at –196 °C, ~4 bar at RT).

Results and discussion

Synthesis of B[CH(C_6F_5)$_2$]$_3$, 1

A practical synthesis of the target borane was envisaged to occur through a Grignard reaction between $CHCl(C_6F_5)_2$ and $BF_3{\cdot}OEt_2$. Following a known procedure,[17] decafluorobenzhydrol was initially prepared and used in the synthesis of the desired alkyl chloride. Vorozhtsov *et al.* have previously detailed the synthesis of $CHCl(C_6F_5)_2$ *via* chlorination with PCl_5 in a solution of CCl_4.[20] Adaptation of this procedure allowed isolation of $CHCl(C_6F_5)_2$ in high yield (81%) and purity, following vacuum distillation (Scheme 1).

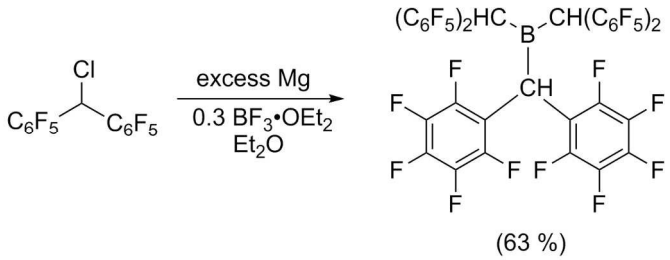


Scheme 1. Syntheses of (a) $CHOH(C_6F_5)_2$ from $BrMgC_6F_5$ and ethylformate in Et_2O and (b) $CHCl(C_6F_5)_2$ *via* chlorination with PCl_5 in CCl_4

Synthesis of **1** was initially achieved *via* the traditional approach: generating a Grignard using a suspension of Mg powder in Et_2O with the alkyl chloride, followed by the addition of $BF_3{\cdot}OEt_2$. However, this method gave only very low amounts of the product, as determined by ^{1}H NMR spectroscopic analysis of aliquots of the reaction solution.

Brown *et al.* have reported a direct route to a variety of triorganylboranes, *via* the *in situ* preparation of the Grignard in the presence of $BF_3{\cdot}OEt_2$.[21] We found this procedure both saved considerable time and prevented side reactions such as Wurtz coupling. Employing this protocol a one-pot synthesis of **1** could be achieved from $CHCl(C_6F_5)_2$ (Scheme 2). Purification using high vacuum sublimation gave the product as a white, microcrystalline solid in moderate yield (63%). The high molecular weight of **1** required temperatures in excess of 150 °C and very low pressures (5 x 10^{-5} mbar) for sublimation.

Solutions of **1** in CD_2Cl_2 display a broad peak in the ^{11}B NMR spectrum at 80.3 ppm; this may be compared to the related tribenzylborane $B(CH_2Ph)_3$, which shows a resonance at 82.8 ppm (Et_2O solvent).[21] **1** is slightly soluble in aromatics and significantly more so in polar organics such as CH_2Cl_2, DFB and THF. Presumably, due to the steric bulk of the $CH(C_6F_5)_2$ groups, **1** does not significantly bind typical donor solvents such as Et_2O, THF or pyridine, as evidenced by the almost identical shift observed for the compound at *ca.* 80 ppm in the ^{11}B NMR spectrum in all of these media.



Scheme 2. Preparation of $B[CH(C_6F_5)_2]_3$ from *in situ* formation of $[(C_6F_5)_2CH]MgCl$ in the presence of $BF_3{\cdot}OEt_2$

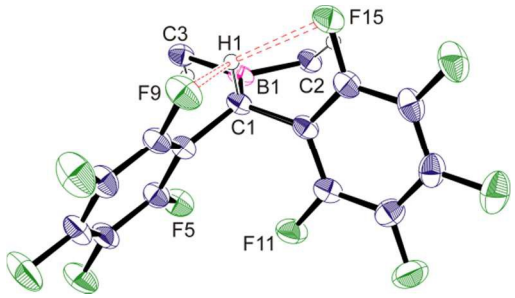


Figure 3. Fragment ORTEP diagram showing the hydrogen bonding between an *ortho*-F on each aryl ring and the neighbouring proton, thermal ellipsoids shown at 50% probability. Selected C_6F_5 rings removed for clarity.

X-ray diffraction studies of $B[CH(C_6F_5)_2]_3$

Clear prisms of **1**·1.5(C_7H_8) were grown by slow cooling a saturated toluene solution of **1** to –30°C. Despite the prevalence of the B–C_6F_5 motif in Lewis acidic boranes, no structural data exist for a borane incorporating this electron withdrawing group in which all ligands are separated by B–CH_n (n = 1, 2) bonds; **1** thus represents the first structurally characterised electron deficient trialkylborane derivative where C_6F_5 groups are not directly attached to the boron centre. The B–$CH_2(C_6F_5)$ moiety has been reported in the crystallographically characterised borane-oxy-borate, $[(C_6F_5)CH_2B(C_6F_5)OB(C_6F_5)_3]^-$ (formed in the reaction of $^tBu_3P/B(C_6F_5)_3$ with CO and H_2), however this borane is both electronically and sterically very different to **1** due to the B–O and pendant $B(C_6F_5)_3$ fragments.[8]

As expected for a three-coordinate boron compound the arrangement around the boron centre is trigonal planar (Figure 2), as evidenced by the near-zero deviation of the B atom from the plane of the three directly bound C atoms, in addition to the sum of the CBC angles = 359.4°.

The B-C bond lengths for **1** (see Table 1) are comparable to those reported for other sterically bulky trialkylboranes such as BCy_3 (Cy = cyclohexyl; range 1.5833(3)-1.5893(4) Å)[22] and B^tBu_3 (1.618(3) Å).[23]

In the case of **1**, since the C_6F_5 groups are incapable of displaying any π-donation effects to the empty boron *p*-orbital (as observed in B–C_6F_5 compounds)[24] the average torsion angle – the angle between the plane of the C_3B unit and the aryl ring – is expected to depend solely on the steric influence of crowding the six C_6F_5 rings around the boron centre; values close to the ideal torsion angle of 60° are accordingly observed in the structure. In this "propeller"-like configuration, **1** displays two protons above the C_3B plane and one proton below. The two protons projected above the plane are inequivalent; the angle from the plane of their respective BCH unit and that of the C_3B plane yields values of 80.4° and 43.1° for H1 and H2 respectively. Interestingly, these protons show evidence of H-bonding interactions with one *ortho*-F of each aryl ring, with average F···H separations of 2.34 Å; this is significantly less than the sum of the van der Waals radii [r_w(F) + r_w(H) = 2.67 Å, Figure 3].

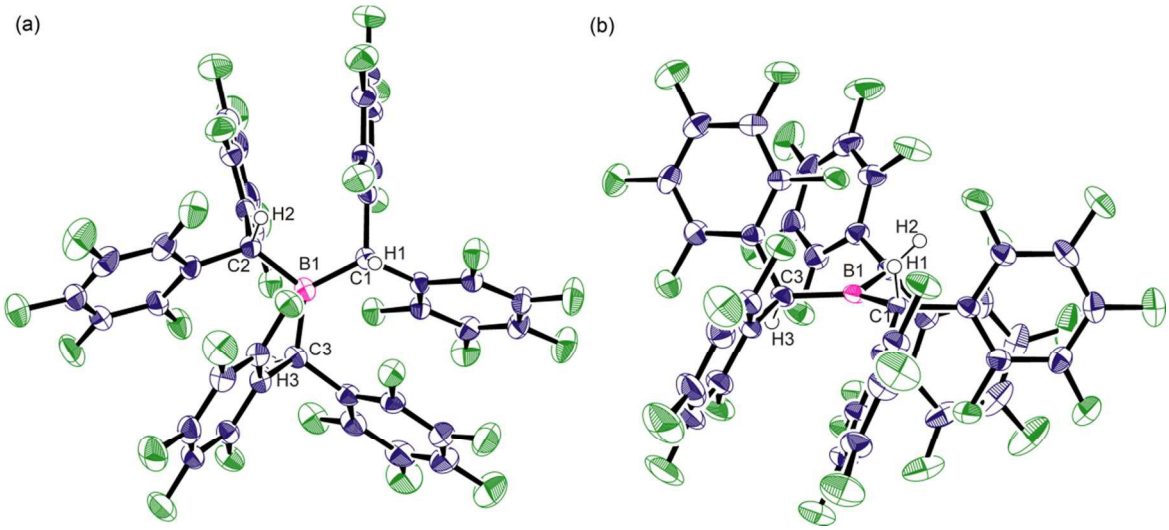


Figure 2. ORTEP diagram of **1**, thermal ellipsoids shown at 50% probability; (a) plan of the BC_3 plane and (b) side-on views; H: white, B: pink, C: blue, F: green

Table 1. Selected bond lengths and angles for **1**, numbers in parentheses are estimated standard deviation (esd) values.

	1
B1-C1 (Å)	1.600(4)
B1-C2 (Å)	1.615(4)
B1-C3 (Å)	1.595(4)
Range H···F (Å)	2.264-2.499(4)
Range (C_6F_5)^(CH)B[CH$(C_6F_5)_2]_2$ (º)	62.3–89.6º

NMR spectroscopy of $B[CH(C_6F_5)_2]_3$

Complete characterisation of **1** by ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopy was undertaken. The NMR spectra reveal that two key exchange processes occur in the solution phase, each of which have different coalescence temperatures, T_c, and hence distinct rates: rotation about the C-(C_6F_5) bonds (hereafter referred to as Process **A**; T_c = 313 K) and rotation about the B-C bonds (Process **B**; T_c = 228 K) (Figure 4).

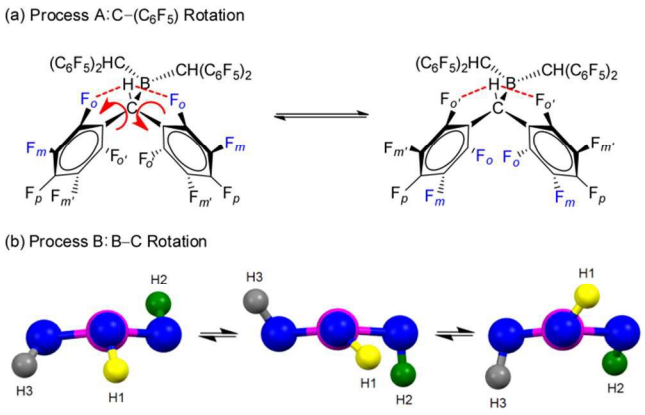


Figure 4. Exchange processes in **1**. Schematic diagrams demonstrating (a) the two inequivalent *ortho*-F atoms of each C_6F_5 ring, and (b) the three inequivalent $CH(C_6F_5)_2$ ligands. Illustration based on crystal structure conformation.

At elevated temperatures the ^{19}F NMR spectrum displays a single resonance for each of the *ortho*-, *meta*- and *para*-fluorine environments, and the fluxional processes are in the fast exchange regime (Figure 5). As the temperature is lowered the *ortho*-F resonance is observed to split in two, as a result of a decreased rate in Process **A**, which renders the two *ortho*-F environments inequivalent in each C_6F_5 ring (see Figure 5(a)). Further reduction in the temperature induces separation of the *ortho* and *meta*-F resonances, as Process **B** approaches the slow exchange limit. Finally, at 203 K, six *ortho*-F environments are observed (two degenerate) and six *meta*-F resonances (three partially superimposed), indicative of rotational 'freeze-out' of both Processes **A** and **B**; these observations are supported by the short F···H contacts seen in the solid state. Accordingly at low temperature each $CH(C_6F_5)_2$ ligand is rendered inequivalent, within which the *ortho*- and *meta*-F resonances are split depending on their spatial disposition to the C–H bond vector, for the C_6F_5 substituents.

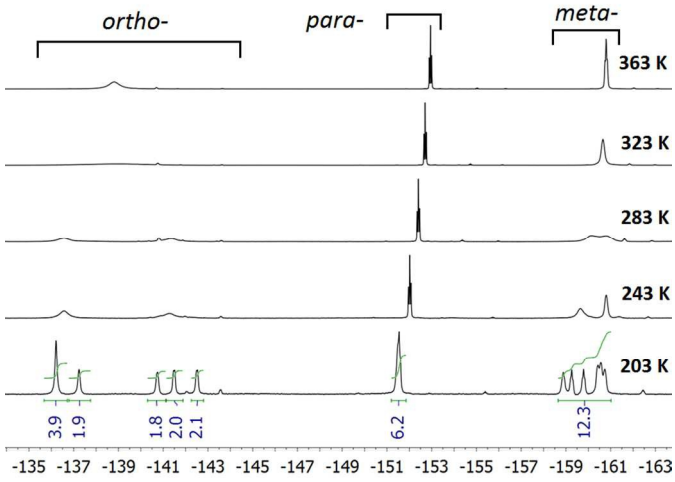


Figure 5. Variable temperature ^{19}F NMR spectroscopy of **1** (C_7D_8 solvent).

The impact of Process **B** may also be seen in the ^{1}H NMR spectrum, which at 298 K displays a broad singlet at 5.07 ppm. As the temperature is lowered this resonance splits into two separate broad peaks with a relative integration of 2:1 (Figure 6). Since three environments cannot be resolved at 203 K, it is assumed that the resonances for two of these overlap, as observed in the ^{19}F NMR spectrum for the *ortho*-F at this temperature, which explains the integral ratio.

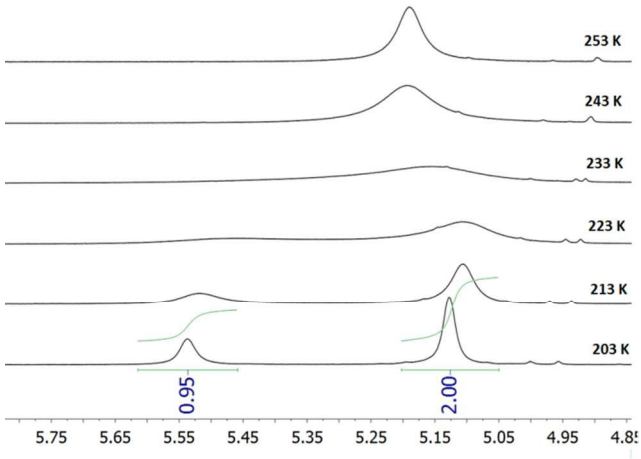


Figure 6. Variable temperature ^{1}H NMR spectroscopy of **1** (C_7D_8 solvent).

Eyring analysis of the ^{19}F NMR spectra for Process **A** and the ^{1}H and ^{19}F NMR spectra for Process **B** as a function of temperature permitted extraction of the activation parameters for the restricted rotations (Table 2). In the case of Process **B**, line shape analysis using ^{1}H and ^{19}F NMR spectra gave consistent results.

Table 2. Activation parameters determined by variable temperature ^{19}F and ^{1}H NMR for Process **A** (range examined 303-332 K) and Process **B** (range examined 209-244 K).

NMR nucleus	Process (T_c)	$\Delta H^{\ddagger}$ (kJ.mol^{-1})	$\Delta S^{\ddagger}$ (J.mol^{-1}.K^{-1})	$\Delta G^{\ddagger}$ (T_c, kJ.mol^{-1})
^{19}**F**	**A** (313 K)	32.1(5)	–75(2)	55.5(4)
^{19}**F**	**B** (228 K)	28(2)	–84(10)	48(3)
^{1}**H**	**B** (228 K)	32(1)	–71(4)	48(1)

Lewis acidity measurements of B[CH(C$_6$F$_5$)$_2$]$_3$

In order to probe the Lewis acidity of **1**, measurements were taken in CD_2Cl_2 solution using the Gutmann-Beckett and Childs spectroscopic methods (Figure 7), with the results reported in Table 3 in comparison with $B(C_6F_5)_3$; the former suggests that **1** has 1.9 % Lewis acidity relative to $B(C_6F_5)_3$, whereas the latter method gave a value of 0 %. It is thought that the considerable steric shielding around the boron centre imparted by the large $CH(C_6F_5)_2$ impedes access of the Lewis base probes to an extent that neither method can truly assess the Lewis acidity.

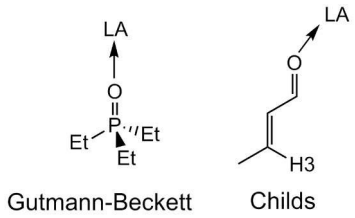


Figure 7. Gutmann-Beckett and Childs Lewis acidity probes

These findings correlate with the observation by Ashley and O'Hare that substitution of the C_6F_5 ligands on $B(C_6F_5)_3$ with C_6Cl_5 resulted in a lower recorded Lewis acidity by both Gutmann Beckett and Childs methods, despite the higher electron withdrawing capacity of the chlorinated ligands as predicted by Hammett parameters and measured by cyclic voltammetry; this was attributed to the increased steric effects of the bulkier C_6Cl_5 substituents.[24]

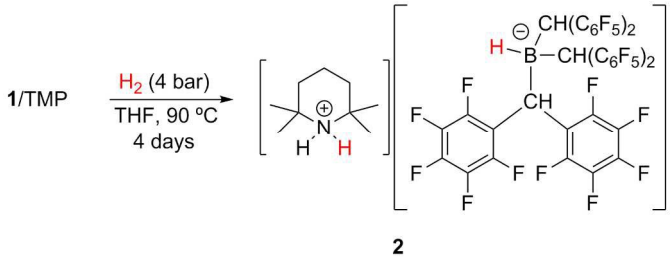
Table 3. ^{31}P and ^{1}H NMR spectral data for Lewis acidity measurements of $B(C_6F_5)_3$ and **1**

Lewis acid	Et_3PO		*trans*-Crotonaldehyde	
	^{31}P NMR /ppm	$\Delta\delta$ /ppm[i]	^{1}H NMR /ppm	$\Delta\delta$ /ppm[ii]
None	50.0	–	6.87	–
$B(C_6F_5)_3$	77.3	27.3	7.93	1.06
1	50.5	0.5	6.87	0

[i] $\Delta\delta = \delta[Et_3PO(\text{coordinated})] - \delta[Et_3PO(CD_2Cl_2)]$; [ii] $\Delta\delta = \delta[H_3(\text{coordinated})] - \delta[H_3(CD_2Cl_2)]$

Heterolytic cleavage of H$_2$ by 1 in the presence of Lewis bases

In contrast to $B(C_6F_5)_3$, which strongly coordinates THF,[25] **1** does not bind ethereal solvents and is stable in THF solution indefinitely at elevated temperatures (90 °C). Addition of either 2,2,6,6-tetramethylpiperidine (TMP) or 1,2,2,6,6-pentamethylpiperidine (PMP) to **1** in THF led to the formation of an FLP mixture as evidenced by the absence of any change in the ^{1}H, ^{11}B or ^{19}F NMR spectra of the borane; heating these solutions resulted in neither decomposition of **1** nor the solvent. Surprisingly, considering the supposedly negligible Lewis acidity of the borane as judged by standard methods, heating a solution of **1** and TMP in THF under an atmosphere of H_2 (~4 bar, 90 °C) resulted in the appearance of new resonances in the ^{1}H, ^{19}F and ^{11}B NMR spectra which correspond to the borohydride salt [TMP–H][H–B[CH(C$_6$F$_5$)$_2$]$_3$] (**2**) (see Scheme 3 and Figure 8).



2

Scheme 3. Formation of **2** from heterolytic H_2 activation

The ^{11}B NMR spectrum of **2** displays a broad doublet at –14.5 ppm ($^{1}J_{BH}$ = 87.6 Hz), indicating the [B-H] unit (c.f [H–BEt_3]$^-$ δ = –12.1 ppm in THF)[26] with a corresponding broad resonance in the ^{1}H NMR spectrum at 1.51 ppm (overlapping signal with Me resonance from the tetramethylpiperidinium ion) which is attributed to the hydride resonance. In the ^{19}F NMR spectrum the *ortho*-F resonances are extremely broad, whereas those for both *meta*- and *para*-F positions are sharp. The difference in shift between the *meta*- and *para*-environments also narrows appreciably in **2** when compared with **1** ($\Delta\delta_{m,p}$ = 3.38 and 7.93 ppm for **2** and **1** respectively).

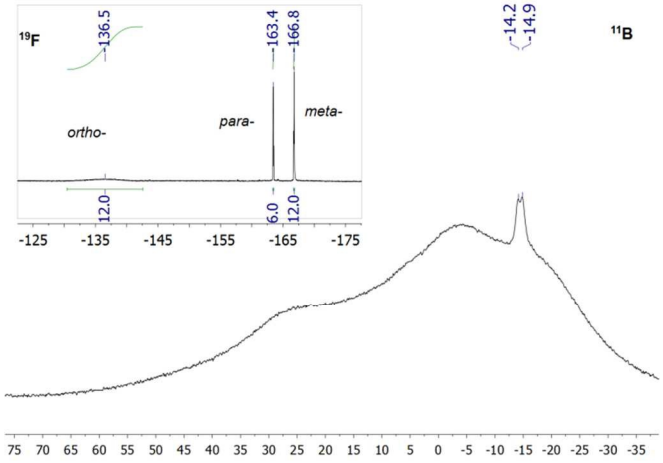


Figure 8. ^{11}B and ^{19}F (inset) NMR spectra of **2** (THF-d_8)

In addition to characterisation by NMR spectroscopy, HRMS (ES+/ES–) clearly showed the formation of **2** (see ESI), with the major mass ion peak in the positive mode corresponding to the $[TMPH]^+$ fragment, and the major peak in the negative mode at exact mass for the molecular ion $[HB(CH(C_6F_5)_2)_3]^-$. Unfortunately, attempts to grow crystals suitable for X-ray diffraction were unsuccessful; the only isolable product was an amber oil.

In order to confirm the source of the hydrogen incorporated into the borohydride anion, isotopic labelling studies were undertaken using D_2 gas. A solution of PMP/**1** in THF-d_8 was heated under an atmosphere of H_2 (~2 bar, 90 °C) produced a clear doublet in the ^{11}B NMR spectrum, as described above using TMP as Lewis base. However, a solution of PMP/**1** in proteo-THF under a D_2 atmosphere and treated otherwise identically, showed a broad singlet in the ^{11}B NMR spectrum at –14.5 ppm (Figure 9) corresponding to the borodeuteride anion $[D–B(CH(C_6F_5)_2)_3]^-$; as previously reported, the B-D coupling is not resolved in the ^{11}B NMR spectrum.[1] These experiments confirm that the source of the deuterium in the compound cannot be from the solvent.

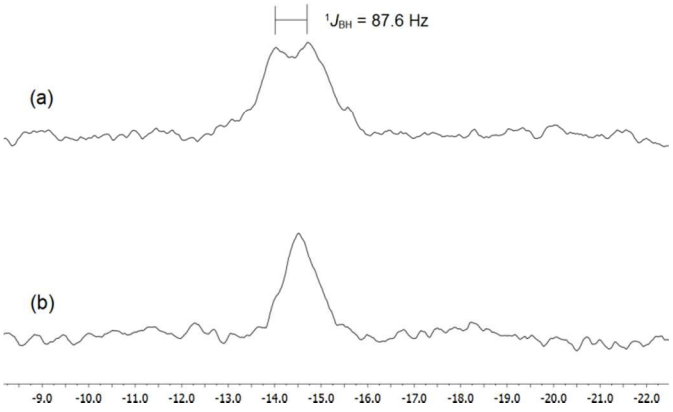


Figure 9. ^{11}B NMR spectra of (a) $[PMPH][HB(CH(C_6F_5)_2)_3]$ and (b) $[PMPD][DB(CH(C_6F_5)_2)_3]$ (expanded).

Due to the considerable steric bulk around the boron atom in **1**, the generation of **2** was initially unexpected, as TMP and PMP are unlikely to be able to approach close enough to the boron centre in order to form the encounter complex usually invoked for a concerted H_2 cleavage mechanism by an FLP.[27-29] Interestingly, when the reactions were performed in either non-polar solvents such as toluene, or non-donor polar organics (i.e. PhCl, DFB) no H_2 activation products were observed. Furthermore, while searching for other possible bases to incorporate into an FLP system with **1** it became apparent that an appreciably weaker triarylphosphine base could be used for H_2 cleavage in THF; using $P(Mes)_3$ [pK_a = 7.3][30] resulted in the appearance of a singlet in the $^{31}P\{^1H\}$ NMR spectrum at –27.2 ppm, and a doublet in the ^1H NMR spectrum at 8.6 ppm ($^1J_{PH}$ = 490 Hz), which are consistent with formation of the trimesitylphosphonium ion, $[Mes_3P–H]^+$.

Additional investigation showed that the phenomenon was not unique to THF as solvent; tetrahydropyran (THP) also gave H_2 activation products, albeit at a slower rate. This led us to suspect that the amine or phosphine may not be directly involved in H_2 activation, and instead the THF or THP solvent mediates H_2 heterolysis as the Lewis base, in conjunction with **1**. In support of this hypothesis, ethers have previously been reported to behave in such a fashion with strong triarylboron Lewis acids. The Stephan group provided evidence for the formation of a $[Et_2O–H–OEt_2]^+$ species from the reaction of H_2 with the $Et_2O/B(C_6F_5)_3$ FLP system in CH_2Cl_2 solvent.[6] More recently our group, in separate studies, showed that THF (Figure 10) and other ether solvents can act as effective Lewis bases in FLP systems for the catalytic reduction of polar organic compounds, including carbonyls.[4, 5] In the current system, the transiently formed THF/THP-solvated proton would subsequently be levelled to the much stronger auxiliary base present (pK_a $[THF–H]^+$ = –2.08 in aqueous H_2SO_4; pK_a $[TMP–H]^+$ = 11.07 in H_2O).[31-33]

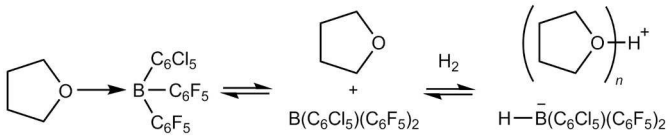


Figure 10. Reversible activation of H_2 by $B(C_6Cl_5)(C_6F_5)_2$ in THF solvent.[34]

In spite of the propensity for THF to polymerise in the presence of powerful Lewis acids,[25] this was never observed for solutions of **1**, even after prolonged heating (90 °C; sealed NMR tube) for several days. However, when identical solutions were heated under an atmosphere of H_2, evidence for the formation of polymerised THF was seen in the ^1H NMR spectra (see ESI), in addition to a marked increase in viscosity; collectively these results suggest generation of a strong Brønsted acid under these conditions. The combination of these two observations – that H_2 activation products, such as **2**, are observed only in THF or THP solutions, and that H_2 activation is apparent in the absence of other bases – lead us to propose that **1**/(THF/THP) FLP is the primary source of H_2 activation in this study. The fact that the reaction is faster in THF than in THP is presumably due to the larger size of the six-membered ring of THP, which likely makes formation of an encounter complex with **1** less favourable, although still accessible. This indicates that the cleavage of H_2 by **1** and ethers is somewhat finely balanced, with subtle changes in the solvent resulting in measurable changes in reactivity.

Since the Brønsted basicity of the ethereal solvents is substantially lower relative to the typical amine or phosphine bases commonly utilised in FLP chemistry, our results indicate that, in order for the system to activate H_2, the Lewis acidity (or more correctly the hydridophilicity) of **1** must be comparable to the strong Lewis acids $B(C_6F_5)_3$ or $B(C_6Cl_5)(C_6F_5)_2$; this is in clear contradiction to the outcome of the Gutmann-Beckett and Childs Lewis acidity tests. Britovsek has noted that a simple

linear correlation does not exist for these two methods for boron-based Lewis acids, and the hardness or softness of the acceptor site can needs to be taken into account.[35] In line with studies on the $B(C_6Cl_5)_x(C_6F_5)_{3-x}$ (x = 0-3) series,[24] our findings further demonstrate that steric factors can also have a powerful impact on these spectroscopic techniques.

Unfortunately, attempts to effect hydride reduction of unsaturated organic substrates in THF (PhCOPh, MeCOMe and $PhCH{=}NCH_2Ph$) by the H_2-generated trialkylborohydride anion $[HB(CH(C_6F_5)_2)_3]^-$ led to no observable reaction; even the small, potent electrophiles MeOTf or MeI could not be reduced. This lack of reactivity may be attributed to both the high hydridophilicity of **1** and the very large steric hindrance around the boron centre; together thermodynamic *and* kinetic factors are unfavourable for accomplishing hydride transfer.

Conclusion

The novel tri(aralkyl)borane $B[CH(C_6F_5)_2]_3$ **1** has been prepared and characterised by single crystal X-ray diffraction and multinuclear NMR spectroscopy; this is the first example of an electron-deficient homoleptic borane bearing saturated α-$C(sp^3)$ ligands. The compound displayed dynamic behaviour in the ^1H and ^{19}F NMR spectra which is due to restricted rotation about both the B–C and C–C_6F_5 bonds; kinetic parameters were extracted for both of these processes. Both Gutmann-Beckett and Childs measurements suggested negligible Lewis acidity for **1**. In light of this result it was surprising that H_2 heterolysis is mediated by **1** in the presence of amine or phosphine Lewis bases, yet this is only observed when the solvent was THF or THP; deuterium labelling was used to unequivocally establish the source of proton and hydride in the ammonium/phosphonium borohydride products. It is proposed that the ether itself is the primary partner of this FLP system, which subsequently shuttles the resultant protons to the stronger 'spectator' auxiliary base. Collectively, experimental results suggest that **1** is actually a rather potent hydridophile, in addition to being a highly sterically hindered Lewis acid.

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray crystallographic details for **1**·1.5(C_7H_8), CCDC 1048650. Full characterising data for **1** and **2.** See DOI: 10.1039/b000000x/

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Table of contents entry

- A novel, highly-electron deficient aralkylated homoleptic borane is able to activate dihydrogen wherein the ethereal solvent acts as Lewis base.