Supporting Information

An Electrochemical Study of Frustrated Lewis Pairs: A Metal-free Route to Hydrogen Oxidation

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Contents

S1. Synthesis

S1.1. Na[HB(C$_6$F$_5$)$_3$]

To a solution of 1.0 M Na[HBEt$_3$] in toluene (3.7 mL, 3.7 mmol) was added a solution of B(C$_6$F$_5$)$_3$ (1.71 g, 3.3 mmol) in toluene (30 mL). The reaction mixture was left to stir under N$_2$ at room temperature for 2 h, during which time a white precipitate formed. The precipitate was left to settle before it was filtered and triturated with toluene (2 × 10 mL). The residue was dried *in vacuo* to yield Na[HB(C$_6$F$_5$)$_3$] (1.15 g, 2.1 mmol) as a fine white powder in 64 % yield. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ 3.56 (br. q, *J* = 87 Hz, 1H); ^{19}F NMR (282 MHz, [D$_6$]DMSO): δ −132.9 (m, 6F, *ortho*-F), −162.8 (m, 3F, *para*-F), −166.1 (m, 6F, *meta*-F); ^{11}B NMR (96.3 MHz, [D$_6$]DMSO): δ −25.2 ppm (d, *J* = 87 Hz); ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ 147.5 (dm, *J* = 236 Hz, *ortho*-C), 137.2 (dm, *J* = 243 Hz, *para*-C), 135.8 (dm, *J* = 246 Hz, *meta*-C), 124.9 (s, *ipso*-C).

S1.2. [^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$] ([^{n}Bu$_4$N]1)

A solution of ^{n}Bu$_4$NCl (0.45 g, 1.6 mmol) in CH$_2$Cl$_2$ (20 mL) was added to a white suspension of Na[HB(C$_6$F$_5$)$_3$] (0.86 g, 1.6 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature, with stirring under N$_2$. This resulted in the formation of a fine flocculent precipitate with the simultaneous breakup of the suspended material. The reaction mixture was left to stir overnight. The precipitate was then allowed to settle before it was filtered. The filtrate was concentrated in vacuo until a minimum quantity of solvent remained. A white precipitate was obtained at room temperature by layering the solution carefully with light petroleum ether (40/60, approximately twice the volume of solution was added). The precipitate was filtered and dried in vacuo to afford [^{n}Bu$_4$N]1 (0.89 g, 1.2 mmol) as a white powder in 74 % yield. Crystals suitable for X-ray crystallography (colourless plates) were grown by dissolving [^{n}Bu$_4$N]1 in a minimum quantity of CH$_2$Cl$_2$, warming to *ca.* 35 °C, adding an equal quantity of light petroleum ether and slow-cooling to room temperature. ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.60 (br. q, *J* = 82 Hz, 1H, BH), 3.07 (m, 8H, CH$_2$), 1.56 (m, 8H, CH$_2$), 1.32 (m, 8H, CH$_2$), 0.92 (t, *J* = 7.2 Hz, 12H, CH$_3$); ^{19}F NMR (282 MHz, CDCl$_3$): δ −133.6 (m, 6F, *ortho*-F), −163.4 (m, 3F, *para*-F), −166.7 (m, 6F, *meta*-F); ^{11}B NMR (96.3 MHz, CDCl$_3$): δ −25.4 (d, *J* = 82 Hz); ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 148.3 (dm, *J* = 240 Hz), 138.0 (dm, *J* = 245 Hz), 136.6 (dm, *J* = 248 Hz), 125.0, 58.9, 23.8, 19.6, 13.4. IR (ATR, cm^{-1}): 2424 (v_{B-H}, w). Anal. Calcd for C$_{34}$H$_{37}$BF$_{15}$N: C 54.06; H 4.94; N 1.85. Found: C 53.79; H 5.06; N 1.86.

S1.3. [TMPD][DB(C$_6$F$_5$)$_3$]

A clear yellow solution of 2,2,6,6-tetramethylpiperidine (TMP) (0.28 g, 1.95 mmol) in toluene (10 mL) was added to a clear colourless solution of B(C$_6$F$_5$)$_3$ (1.00 g , 1.95 mmol) in toluene (20 mL) to give a

clear, pale yellow solution. The sample was sparged with D_2 gas for 1 h. The pale yellow solution was then concentrated to *ca.* 5 mL and pentane (15 mL) was added to give a precipitate. The precipitate was allowed to settle and then filtered to give [TMPD][DB(C_6F_5)$_3$] (1.15 g, 1.75 mmol) as a white powder in 90 % yield. ^{1}H NMR (500 MHz, C_6D_6): δ 4.23 (t, *J* = 49 Hz, 1H, NH), 0.76 (m, 2H, CH_2), 0.67 (m, 4H, CH_2) 0.56 (s, 12H, CH_3); ^{19}F NMR (471 MHz, C_6D_6): δ −133.1 (m, 6F, *ortho*-F), −161.7 (m, 3F, *para*-F), −165.5 (m, 6F, *meta*-F); ^{11}B NMR (160 MHz, C_6D_6): δ −23.8 (s); [2]D NMR (556 MHz, CH_2Cl_2): δ 5.40 (d, *J* = 1.1 Hz, ND), 3.60 (br. m, BD).

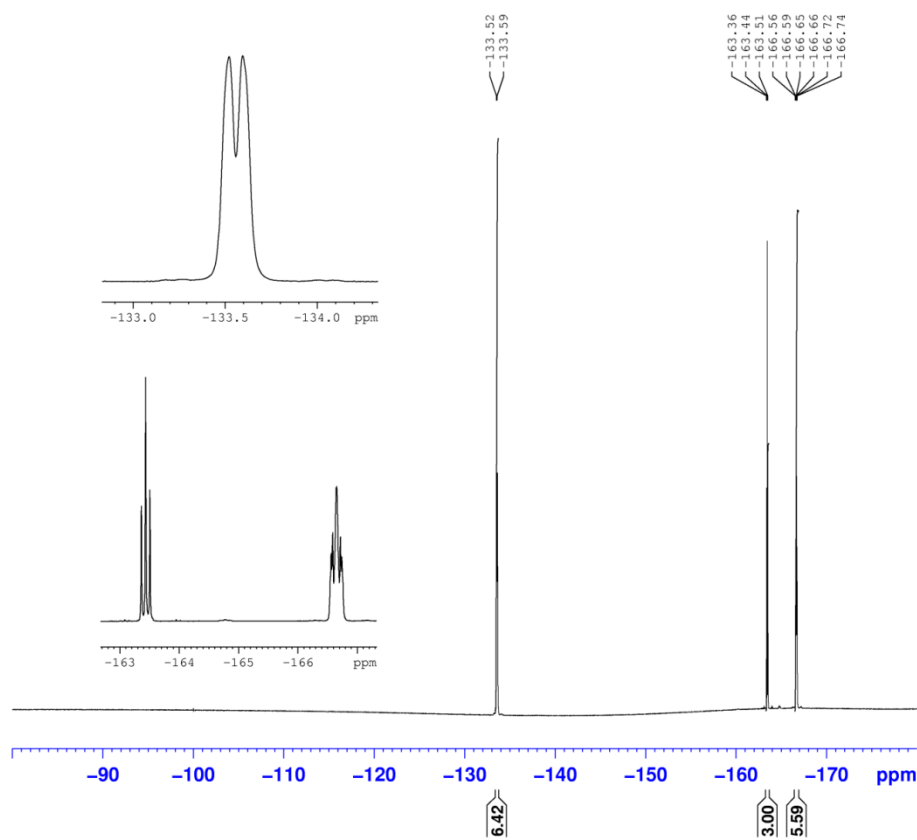### S1.4. [*n*Bu$_4$N][DB(C_6F_5)$_3$] ([*n*Bu$_4$N]1[D])

A clear colourless solution of [TMPD][DB(C_6F_5)$_3$] (0.31 g, 0.47 mmol) in toluene (20 mL) was added to NaH (11 mg, 0.47 mmol) to give some effervescence. The reaction mixture was left to stir at room temperature under N_2 overnight. The reaction mixture was then filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (10 mL) to give a clear colourless solution. To this was added a clear colourless solution of N*n*Bu$_4$Cl (0.13 g, 0.47 mmol) in CH_2Cl_2 (10 mL). A very fine precipitate rapidly formed. The reaction mixture was left to stir at room temperature for 1 h before it was filtered. The filtrate was concentrated to *ca.* 2 mL to give a white precipitate. This was filtered and the filtrated was concentrated *in vacuo* to yield a colorless viscous oil that solidified overnight to give [*n*Bu$_4$N]**1**[D] (0.10 g, 0.13 mmol) as an amorphous colorless solid in 28 % yield. ^{19}F NMR (471 MHz, CDCl$_3$): δ −133.5 (m, 6F, *ortho*-F), −163.4 (m, 3F, *para*-F), −166.6 (m, 6F, *meta*-F); ^{11}B NMR (160 MHz, CDCl$_3$): δ −25.3 (d, *J* = 82 Hz). [2]D NMR (556 MHz, CH_2Cl_2): δ 3.66 (br. s). IR (ATR, cm^{-1}): 1800 (v_{B-D}, w).

S2. NMR Spectra

Supplementary Figure S1. ^{1}H NMR spectrum of [^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$] [^{n}Bu$_4$N]**1**.
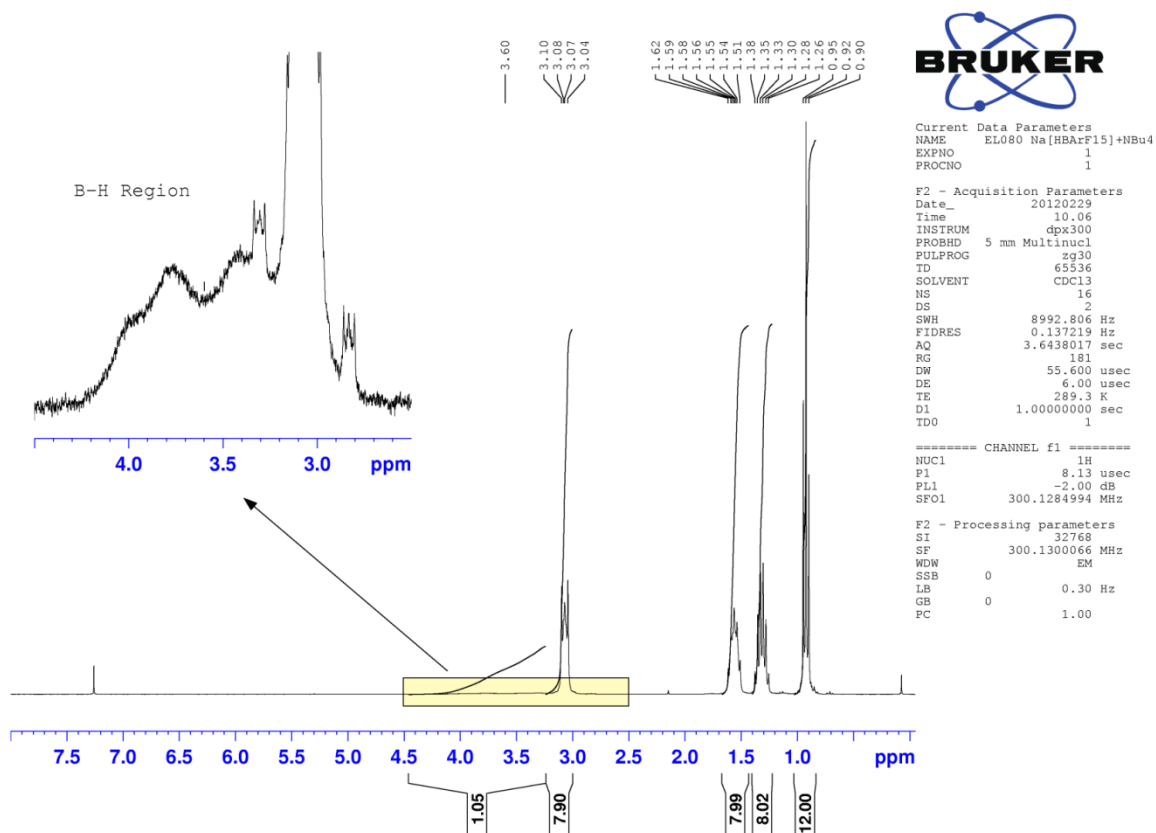
Supplementary Figure S2. ^{19}F NMR spectrum of [^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$] [^{n}Bu$_4$N]**1**.

Supplementary Figure S3. ^{11}B NMR spectrum of [^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$] [^{n}Bu$_4$N]**1**.

Supplementary Figure S4. ^{13}C NMR spectrum of [^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$] [^{n}Bu$_4$N]**1**.
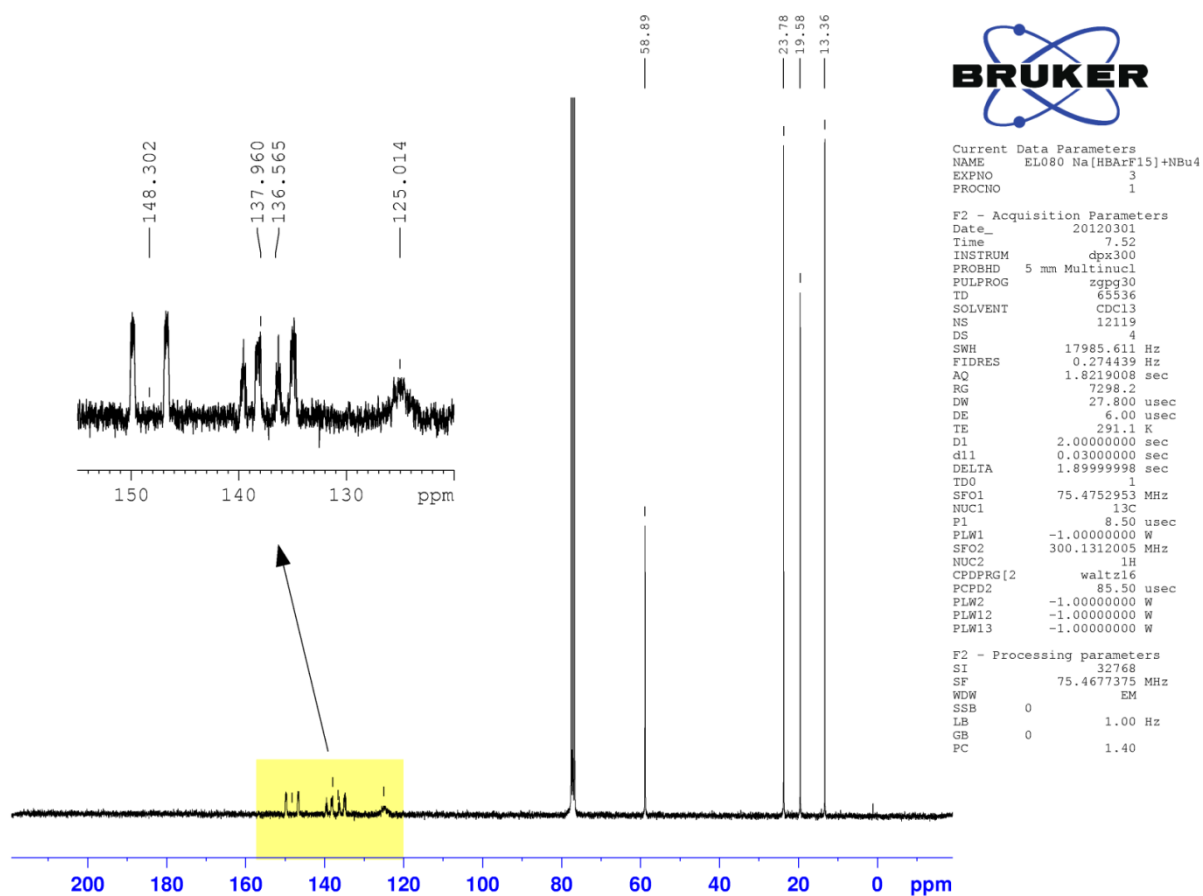
Supplementary Figure S5. ^{19}F NMR spectrum of [$^{n}Bu_4N$][$DB(C_6F_5)_3$] [$^{n}Bu_4N$]**1**^{D}.
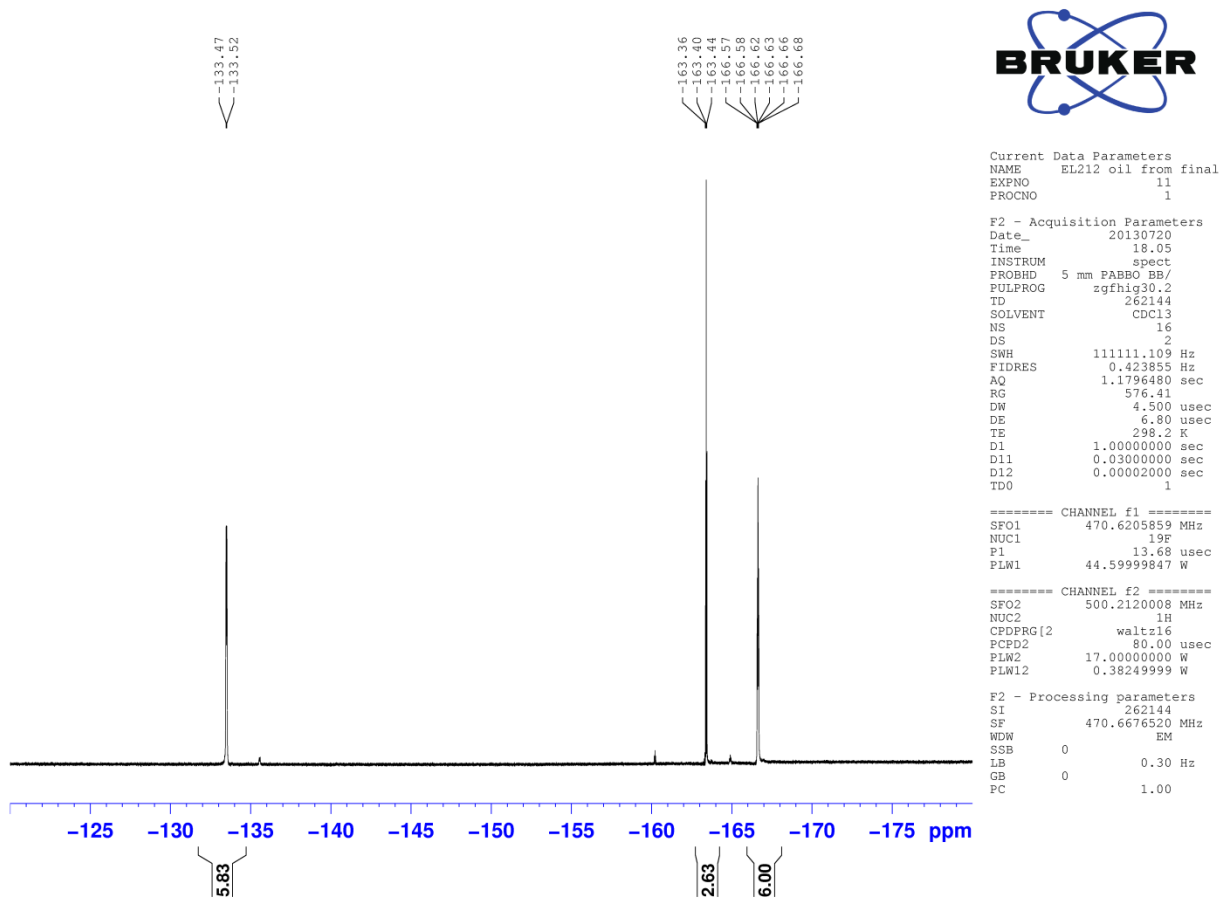
Supplementary Figure S6. ^{11}B NMR spectrum of [^{n}Bu$_4$N][DB(C$_6$F$_5$)$_3$] [^{n}Bu$_4$N]**1^{D}**.
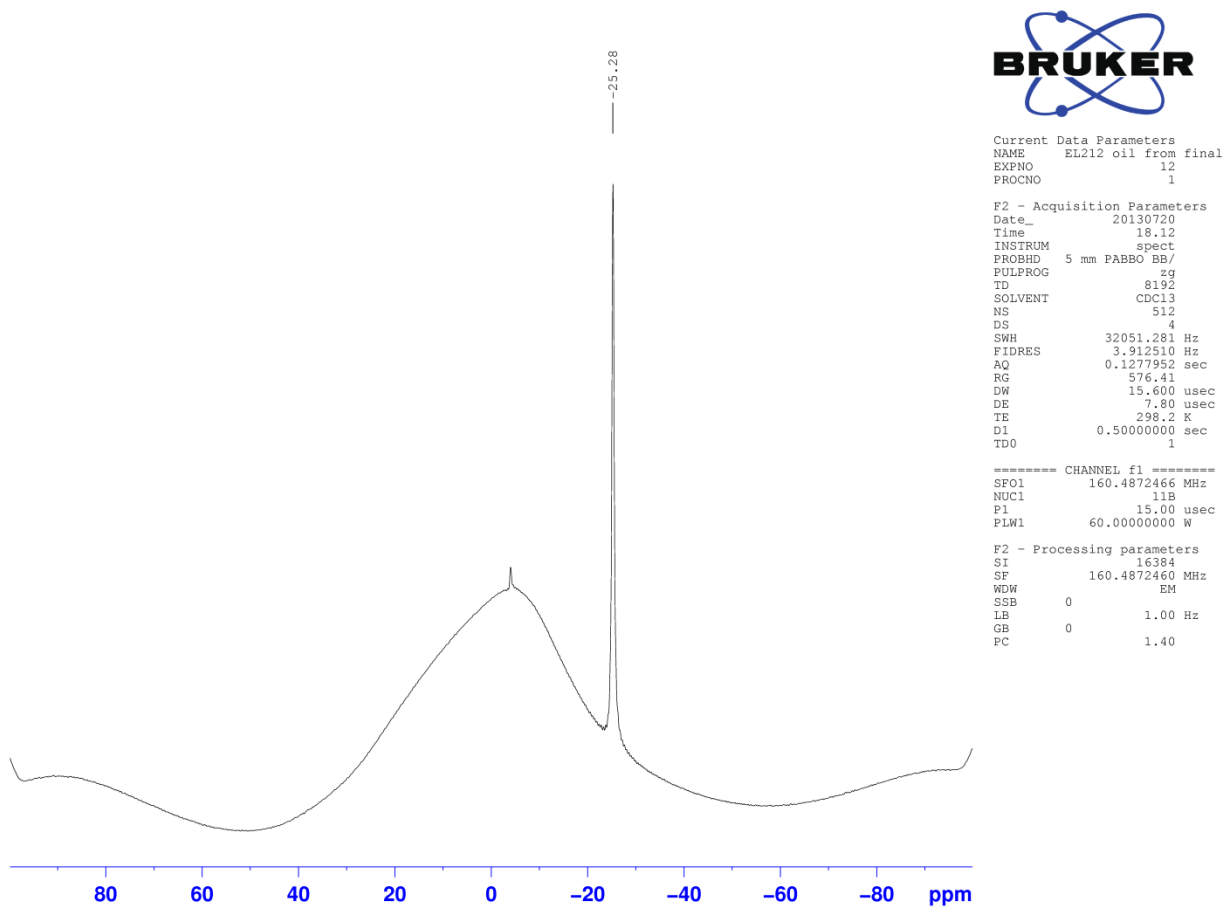
Supplementary Figure S7. ^{2}D NMR spectrum of [^{n}Bu$_4$N][DB(C$_6$F$_5$)$_3$] [^{n}Bu$_4$N]**1^D**.
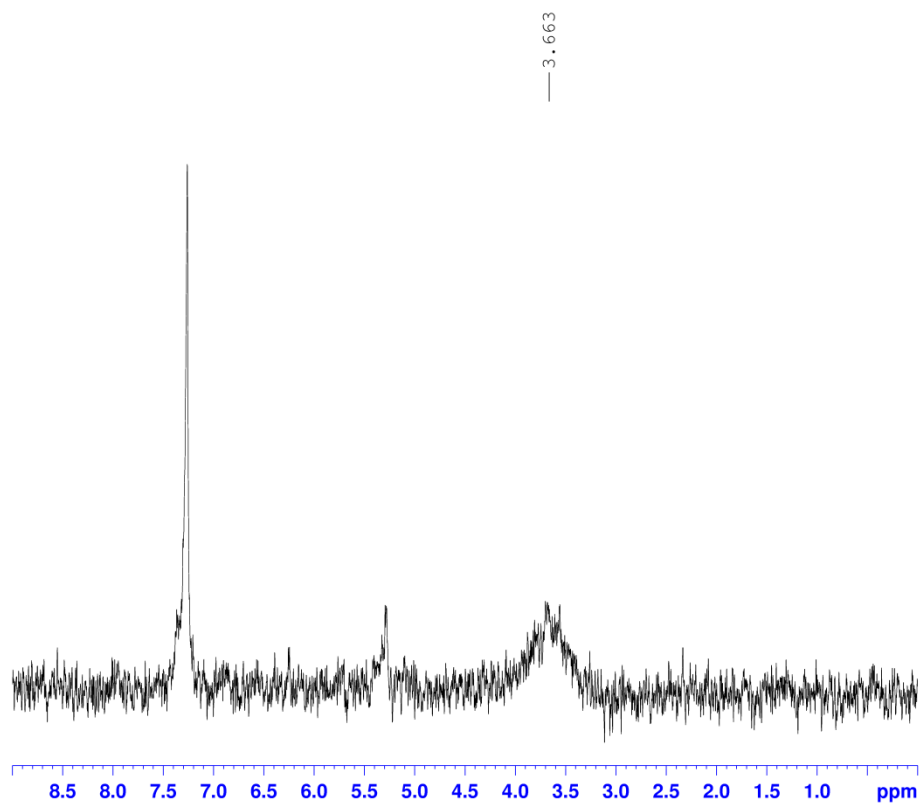
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EXPNO   10
PROCNO   1

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TE   298.0 K
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TD0   1

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WDW   EM
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GB   0
PC   1.00

S10

Supplementary Figure S8. ^{19}F NMR spectrum showing the progress of hydrogen cleavage by a $B(C_6F_5)_3/$ $^tBu_3P$ FLP under a H_2 atmosphere (1.1 bar) at 21 °C. The minor peaks that are highlighted by the dotted lines are attributable to the formation of $(H_2O)B(C_6F_5)_3$ [see: Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* 2007, *129*, 1880–1881].
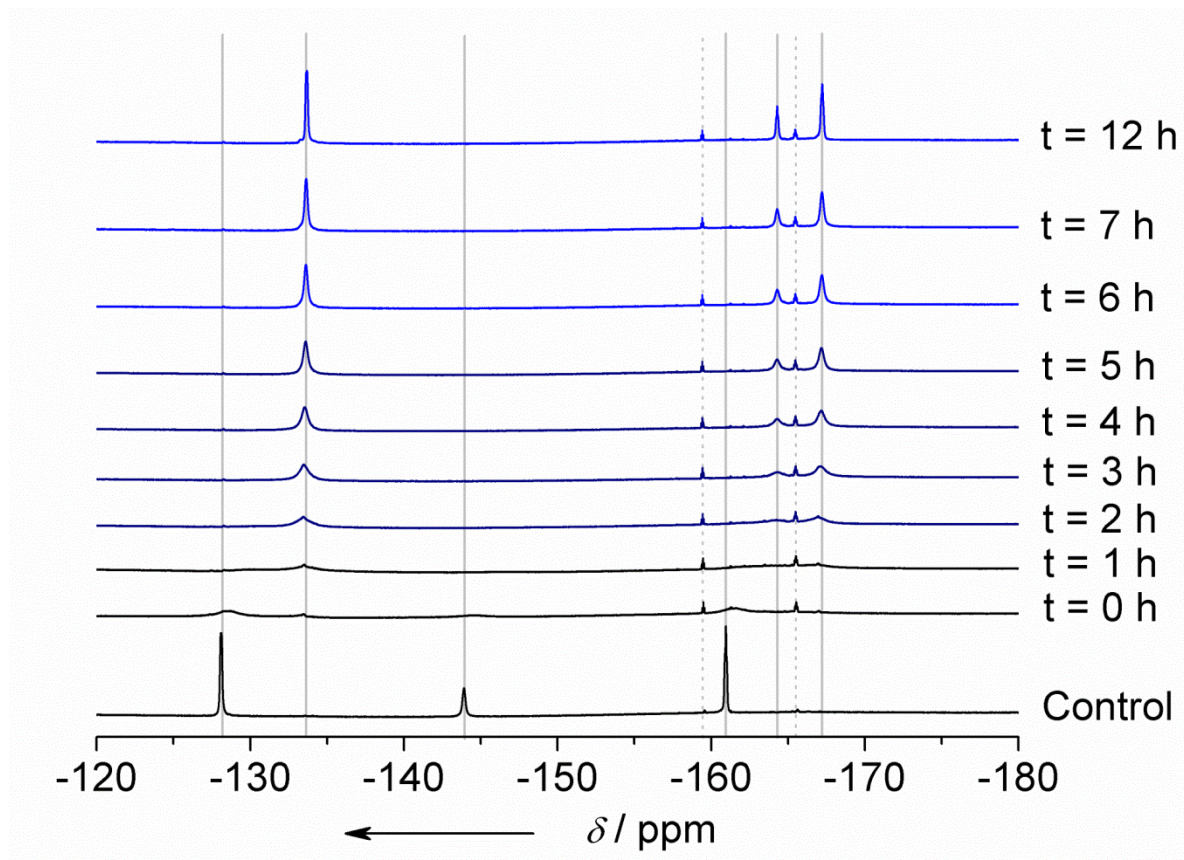
Supplementary Figure S9. ^{11}B NMR spectrum showing the progress of hydrogen cleavage by a B(C$_6$F$_5$)$_3$/P^{t}Bu$_3$ FLP under a H$_2$ atmosphere (1.1 bar) at 21 °C.
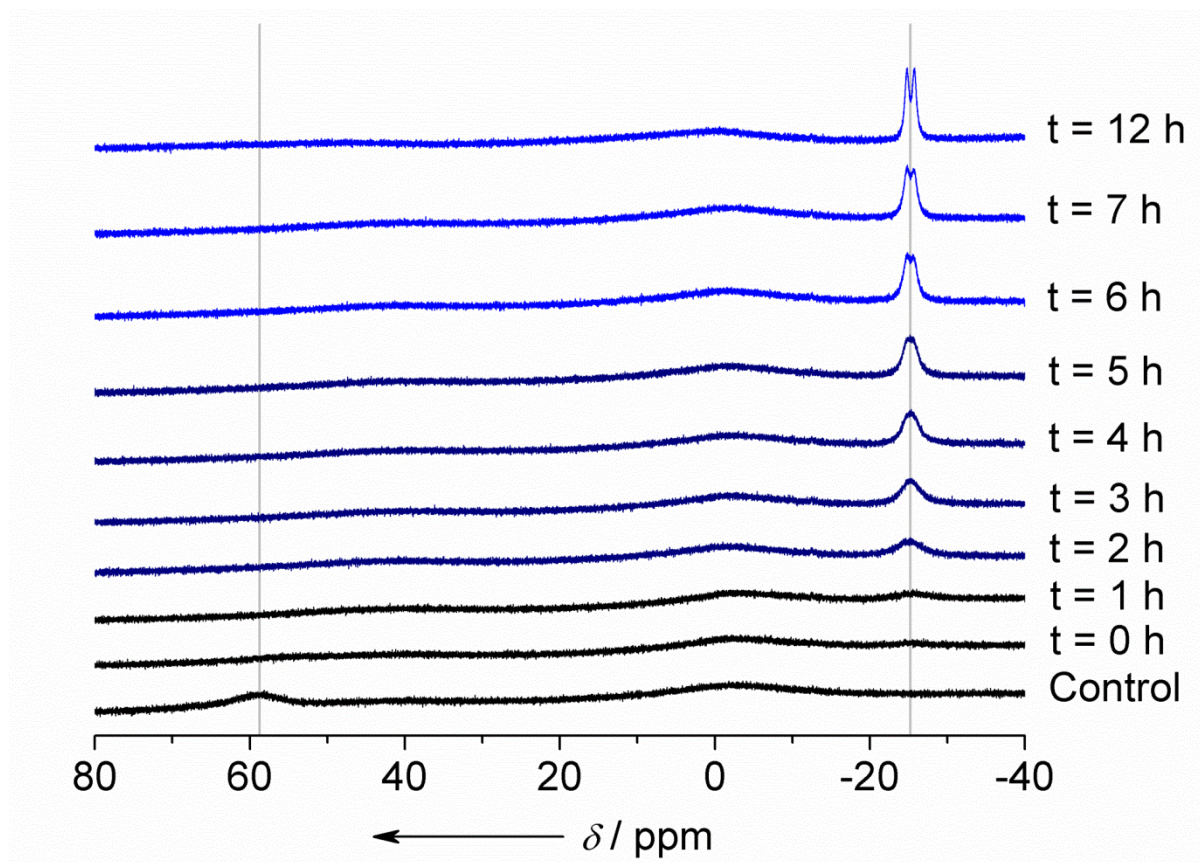
Supplementary Figure S10. ^{31}P {^{1}H} NMR spectrum showing the product of hydrogen cleavage by a B(C$_6$F$_5$)$_3$/P^{t}Bu$_3$ FLP after 12 hours under a H$_2$ atmosphere (1.1 bar) at 21 °C.
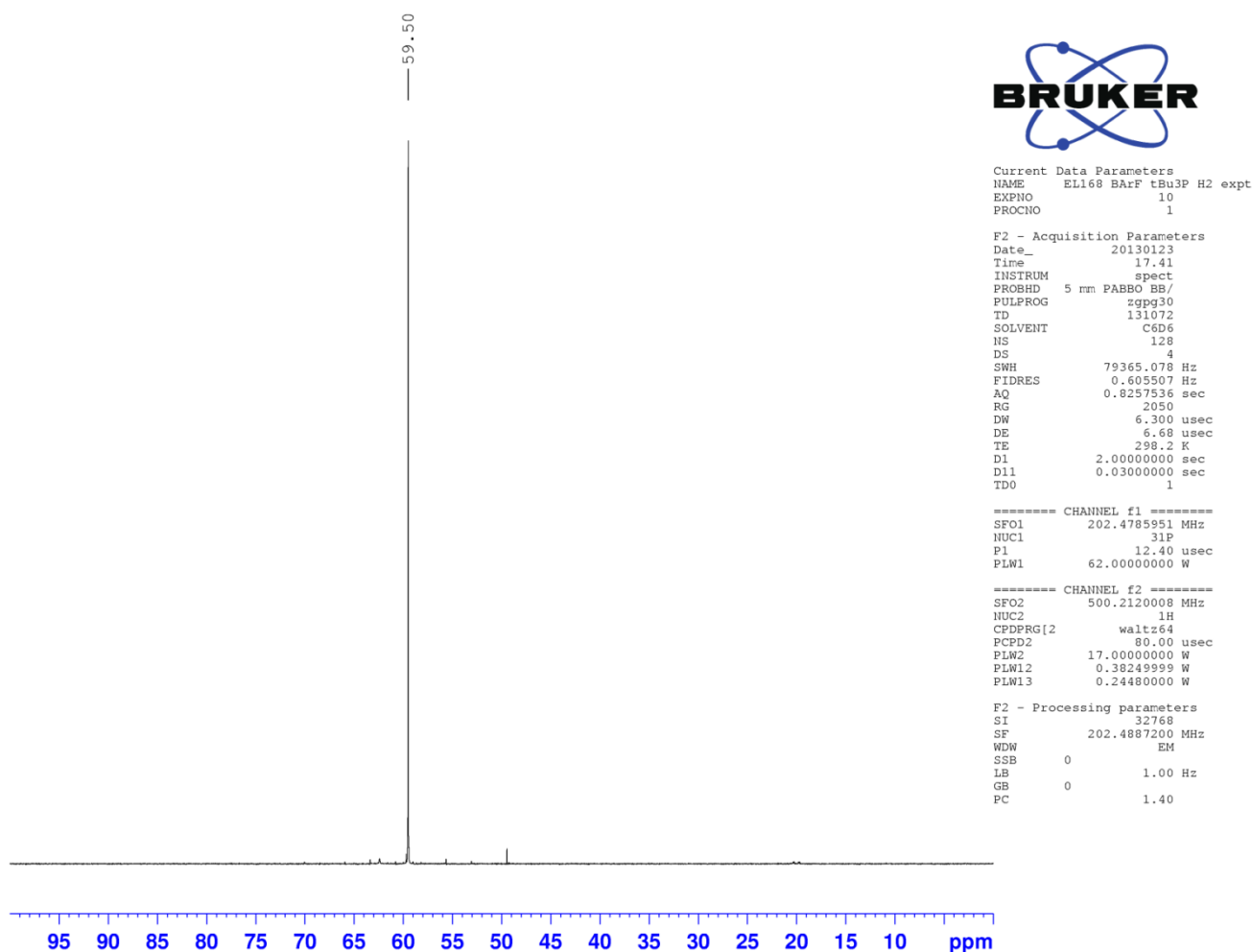
S3. X-ray Crystallography

Supplementary Table S1. Crystallographic data for compound [^{n}Bu$_4$N]**1**.

	[^{n}Bu$_4$N][HB(C$_6$F$_5$)$_3$] [^{n}Bu$_4$N]**1**
Elemental formula	C$_{16}$ H$_{36}$ N, C$_{18}$ H B F$_{15}$
Formula weight	755.46
Temperature / K	100
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	10.141(4)
b / Å	18.471(7)
c / Å	18.792(7)
α / °	90
β / °	100.504 (7)
γ / °	90
Volume / Å^3	3461 (2)
Z	4
ρ_{calc} / mg mm^{-3}	1.450
μ / mm^{-1}	0.140
F(000)	1552
Crystal size / mm^3	0.21 × 0.11 × 0.04
Reflections collected	25957
Independent reflections	6049 [R(int) = 0.030]
'Observed' data [I≥2σ(I)]	5559
Data / restraints / parameters	6049 / 0 / 548
Goodness-of-fit on F^2	1.128
Final R indexes [I≥2σ(I)]	R_1 = 0.054 wR_2 = 0.117
Final R indexes [all data]	R_1 = 0.061 wR_2 = 0.121
Largest difference peak / hole /e.Å^{-3}	0.41 / −0.30
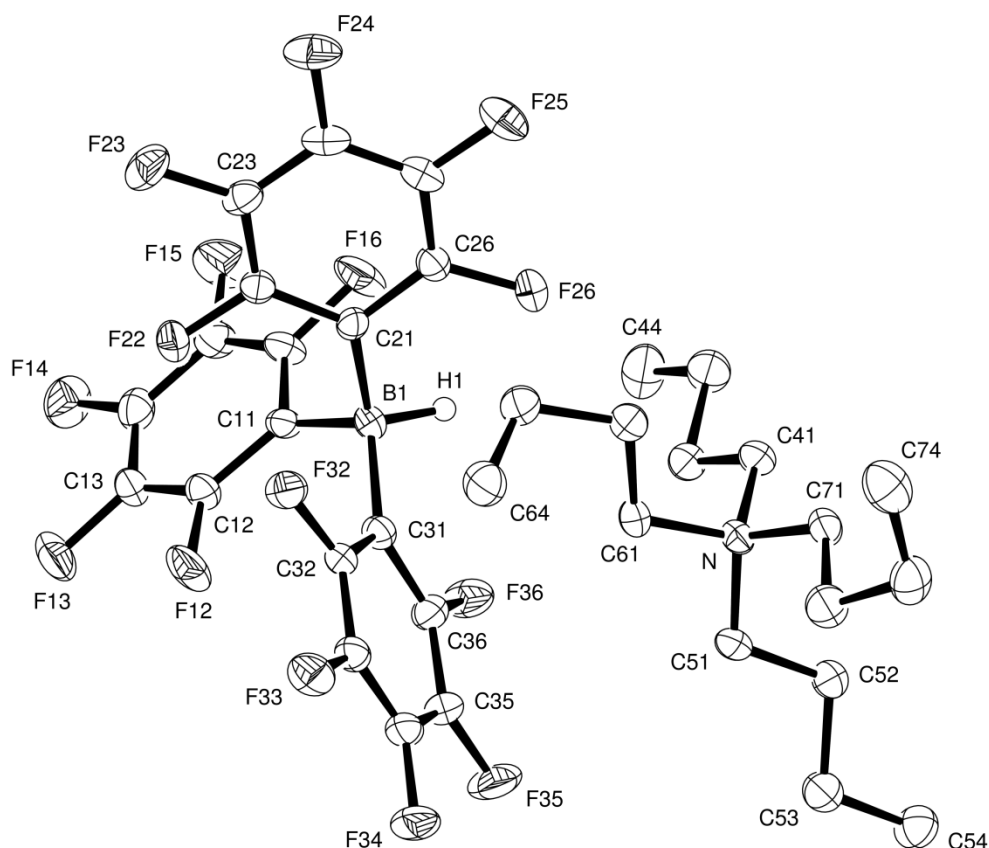
Supplementary Figure S11. View of the ions of [^{n}Bu$_4$N]**1**, indicating the atom numbering scheme. Only the major conformations of disordered groups are shown. Hydrogen atoms of the cation have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: B1-H1 1.10, B1-C11 1.637(3), B1-C21 1.637(3), B1-C31 1.631(3); C31-B1-C21 115.47(19), C31-B1-C11 112.18(18), C21-B1-C11 109.9(2), C31-B1-H1 106.4, C21-B1-H1 105.2, C11-B1-H1 107.1.

Crystals of [^{n}Bu$_4$N]**1** are colorless plates. From a sample under oil, one, *ca.* 0.21 x 0.11 x 0.04 mm, was mounted on a glass fibre and fixed in the cold nitrogen stream on an AFC12 (Right): Kappa 3 circle/CCD diffractometer (at the EPSRC UK National Crystallography Service) equipped with *Mo-Kα* radiation and confocal mirrors monochromator. Intensity data were measured by thin-slice ω-scans. Total no. of reflections recorded, to ϑ_{max} = 25 °, was 25957 of which 6049 were unique (*Rint* = 0.030); 5559 were 'observed' with $I > 2\sigma_I$.

Data were processed using the CrystalClear-SM Expert program,[1] incorporating absorption corrections. The structure was determined by the direct methods routines in the SHELXS-97 program[2] and refined by full-matrix least-squares methods, on F^2's, in SHELXL-97.[2] In the preliminary refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in idealized positions and their *Uiso* values were set to ride on the *Ueq* values of the parent

carbon and boron atoms. The array of difference peaks (highest peak 0.8 eÅ^{-3}) suggested disorder in the anion, where an alternative orientation for each of the three C_6F_5 rings (by rotation in the ring plane) was clear; the minor fluorine component atoms were readily identified and refined (isotropically) well, all with site occupancies of 0.081(1); the minor carbon sites were less well resolved and the three C_6 rings were refined with geometrical constraints. The carbon and nitrogen atoms of the cation were refined anisotropically and hydrogen atoms were included as described above; only at the end of one butyl chain was any disorder found – an alternative site for C74 was refined. At the conclusion of the refinement, wR_2 = 0.121 and R_1 = 0.061[2] for all 6049 reflections weighted $w = [\sigma^2(F_o^2) + (0.0486P)^2 + 1.975P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data only, R_1 = 0.054.

In the final difference map, the highest peak (*ca* 0.4 eÅ^{-3}) was close to H(73B).

Scattering factors for neutral atoms were taken from the literature.[3] Computer programs used in this analysis have been noted above, and were run through WinGX[4] on a Dell Precision 370 PC at the University of East Anglia.

The data for [^{n}Bu$_4$N]**1** has been deposited at the Cambridge Crystallographic Data Centre with CCDC number 958238.

References

1   CrystalClear-SM Expert 2.0 r13, An integrated program for the collection and processing of area detector data, (Rigaku Corporation, 2011).

2   Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* **A64,** 112–122 (2008).

3   International Tables for X-ray Crystallography 3rd Ed, Vol. C (Ed.: Th. Hahn), pp. 500, 219 and 193 (Kluwer Academic Publishers, Dordrecht, 1992).

4   Farrugia; L. J. *J. Appl. Cryst.* **45**, 849-854 (2012).

S4. Electrochemistry

All electrochemical experiments were performed using either an Autolab PGSTAT 30 or PGSTAT 302N computer-controlled potentiostat. Cyclic voltammetry (CV) was performed using a three-electrode configuration consisting of a glassy carbon macrodisk working electrode (GCE) (nominal diameter of 3 mm; BASi, Indiana, USA) combined with a Pt wire counter electrode (99.99 %; GoodFellow, Cambridge, UK) and a Ag wire pseudoreference electrode (99.99 %; GoodFellow, Cambridge, UK). The GCE was polished between experiments using successive grades of diamond paste slurries from 3.0 to 0.1 μm (Kemet, Maidstone, UK). The electrodes were briefly sonicated in distilled water and rinsed with ethanol between each polishing step, to remove any adhered microparticles. The electrodes were then dried in an oven at 100 °C to remove any residual traces of water. The GCE electroactive area was calibrated for each experiment using a 5 mM ferrocene solution in CH_3CN solvent containing 0.1 M $[^nBu_4N][PF_6]$ as the supporting electrolyte. The electroactive area was accurately determined by construction of a Randles-Sevcik plot from cyclic voltammograms recorded at varying scan rates (50-750 mVs^{-1}).[1] The Ag wire pseudoreference electrodes were calibrated to the ferrocene/ferrocenium couple in CH_2Cl_2 at the end of each run to allow for any drift in potential, following IUPAC recommendations.[2] Controlled potential bulk electrolysis was performed using a three-electrode configuration consisting of a carbon felt (99.0 %; Alfa Aesar, Massachusetts, USA) working electrode combined with a Ag wire pseudo-reference electrode (99.99 %, GoodFellow, Cambridge, UK) and a Pt gauze counter electrode (52 mesh woven from 0.1 mm diameter wire, 99.9 %; Alfa Aesar, Massachusetts, USA). The working and pseudo-reference electrodes were separated from the counter electrode compartment by a porous glass frit. All electrochemical measurements were performed at ambient temperatures under an inert N_2 atmosphere in CH_2Cl_2 containing 0.05-0.10 M $[^nBu_4N][B(C_6F_5)_4]$ as the supporting electrolyte. All electrochemical measurements were iR-compensated to within 80 ± 5 % of the solution uncompensated resistance.
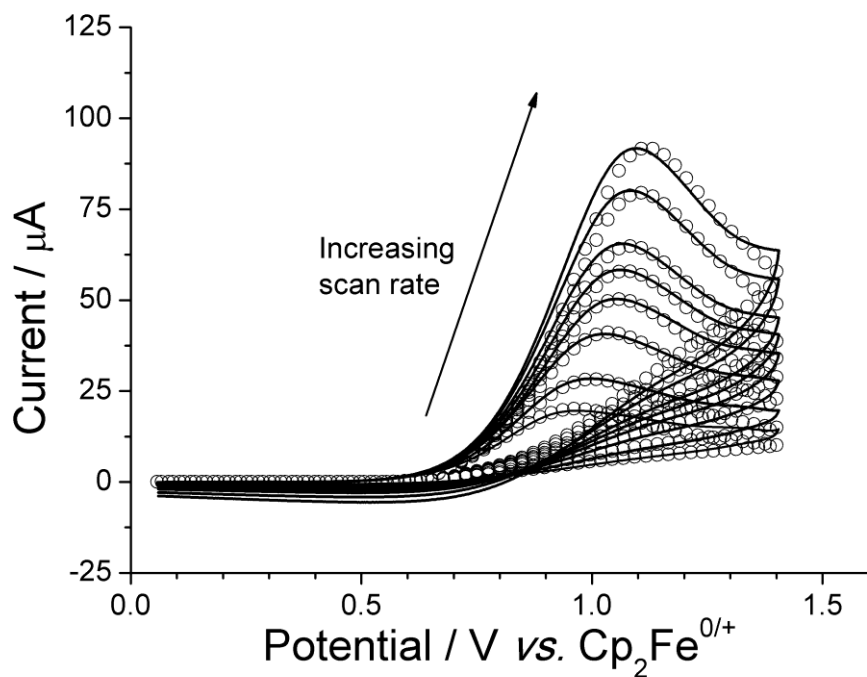
Supplementary Figure S12. Cyclic voltammetry of a 2.9 mM solution of [^{n}Bu$_4$N]**1** in CH$_2$Cl$_2$ recorded at voltage scan rates of 50, 100, 200, 300, 400, 500, 750, and 1000 mVs^{-1}: Solid lines are experimental data; open circles are best fit simulated data (see main text, Table 1).
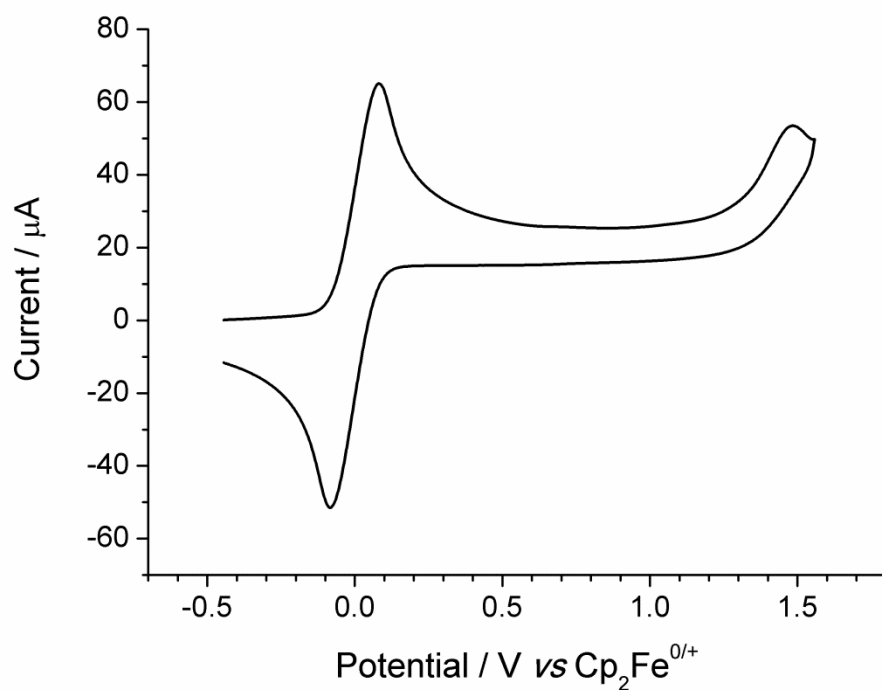
Supplementary Figure S13. Cyclic voltammetry of a saturated solution of H_2 containing 2.3 mM $Cp_2Fe^{0/+}$ as internal reference in CH_2Cl_2 recorded at a voltage scan rate of 100 mVs^{-1}.

References

1   Compton, R. G.; Banks, C. E. *Understanding Voltammetry*; 2nd Revised edition.; Imperial College Press, 2011.

2   Gritzner, G.; Kůta, J. *Electrochimica Acta* **1984**, *29*, 869–873.

S5. DFT Computational modeling

DFT calculations were performed using the Gaussian 09 computational package[1]. Geometry optimization calculations have been carried out using the three-parameter exchange functional of Becke[2] (B3) and the correlation functional of Lee, Yang, and Parr (LYP), B3LYP.[3] The 6-311+G(d,p) basis set has been implemented for all atoms.[4] All calculations have been performed at spin-unrestricted level of theory. Structures were geometry optimized in the gas phase with the default convergence criteria and confirmed as minima through frequency calculations. Thermodynamic properties were calculated at 298.15 K/1atm. Bond dissociation energies were calculated by taking the difference in the total enthalpies between the original structure and optimized fragments, assuming homolytic cleavage. The enthalpies included both electronic contributions and thermal corrections. The charge distribution shown in **Supplementary Figure S14** is based on Mulliken electron population analysis.

Cartesian coordinates and total energies for the optimised calculated structures are given in the table below.

Computational modelling of the HOMO and LUMO of the geometry optimized $\mathbf{1}^-$ species and the SOMO of the $\mathbf{1}^{\bullet}$ intermediate lends further support to our proposed mechanism (See main text). Interestingly, partial charge calculations for $\mathbf{1}^-$ reveal that the B–H bond is not particularly polar, as verified by the computed partial charges on the atoms (−0.099 and +0.078 on H and B respectively – see Supplementary Fig. S13); this indicates that $\mathbf{1}^-$ is a weak hydride donor, and is consistent with the results of previous studies involving the FLP reduction of small molecules.[5, 6] The B–C and B–H bond dissociation energies for the $\mathbf{1}^-$ were calculated as $\Delta H_{B-C} = 408.1$ kJmol^{-1} and $\Delta H_{B-H} = 312.2$ kJmol^{-1} respectively, whilst for $\mathbf{1}^{\bullet}$ the values were found to be $\Delta H_{B-C} = 71.7$ kJmol^{-1} and $\Delta H_{B-H} = 34.0$ kJmol^{-1} respectively. This indicates that the electrochemical oxidation of $\mathbf{1}^-$ strongly facilitates B–H bond cleavage. The spin density of the SOMO is predominantly located in the B–H bond, whose strength in the radical intermediate is *almost* comparable to a hydrogen bonding interaction between $B(C_6F_5)_3^{\bullet-}$ and H$^+$.[7] Note that these are gas phase DFT calculations; it is likely that heterolytic cleavage of the B–H bond in $\mathbf{1}^-$ to produce charged ions (Fig. 4) is energetically favourable in the solution phase and rapid, as determined from our digital simulations of the redox process.

Supplementary Table S2. Cartesian coordinates and total energies for the optimised calculated structures

1•

Total Energy E= -2209.257260 au
Total Enthalpy H = -2209.256315 au

B	0.004411000	-0.001908000	0.829145000
C	-1.092264000	-1.139902000	0.369817000
C	-0.437764000	1.515561000	0.371447000
C	1.540906000	-0.380419000	0.378447000
C	2.618491000	-0.031323000	1.198114000
C	1.904517000	-1.067892000	-0.781752000
C	3.216299000	-1.411012000	-1.104393000
C	4.248665001	-1.047254000	-0.247912000
C	3.946437000	-0.347779000	0.914030000
C	-0.010553000	2.179049000	-0.780960000
C	-0.373937000	3.484843000	-1.106802000
C	-1.224437000	4.188937001	-0.262809000
C	-1.694019000	3.571538000	0.890025000
C	-1.298403000	2.266126000	1.178225000
C	-3.030383000	-3.138791000	-0.275068000
C	-2.298668000	-3.221799000	0.903133000
C	-1.356888000	-2.235990000	1.196275000
C	-1.845869000	-1.115145000	-0.805973000
C	-2.801374000	-2.073907000	-1.138436000
F	-3.945733000	-4.079465000	-0.579013000
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F	-1.671320000	-0.128092000	-1.711421000
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F	0.798584000	1.561745000	-1.669034000
F	0.079424000	4.070289000	-2.234115000
F	-1.592134000	5.450539001	-0.560173000
F	-2.525247000	4.243210001	1.713692000
F	-1.806172000	1.740293000	2.313884000
F	0.967947000	-1.439680000	-1.681322000
F	3.498639000	-2.081180000	-2.240252000
F	5.524600001	-1.364067000	-0.542793000
F	4.940943001	0.015550000	1.750240000
F	2.415010000	0.656057000	2.342742000
H	0.001589000	-0.001320000	2.034661000

1⁻

Total Energy E = -2209.456570 au
Total Enthalpy H = -2209.455626 au

```
B      0.00441100  -0.00190800   0.82914500
C     -1.09226400  -1.13990200   0.36981700
C     -0.43776400   1.51556100   0.37144700
C      1.54090600  -0.38041800   0.37844700
C      2.61849100  -0.03132200   1.19811400
C      1.90451700  -1.06789100  -0.78175200
C      3.21630000  -1.41101100  -1.10439300
C      4.24866500  -1.04725300  -0.24791200
C      3.94643700  -0.34777800   0.91403000
C     -0.01055400   2.17904900  -0.78096000
C     -0.37393800   3.48484300  -1.10680200
C     -1.22443800   4.18893700  -0.26280900
C     -1.69402000   3.57153800   0.89002500
C     -1.29840400   2.26612600   1.17822500
C     -3.03038200  -3.13879200  -0.27506800
C     -2.29866700  -3.22180000   0.90313300
C     -1.35688700  -2.23599000   1.19627500
C     -1.84586900  -1.11514600  -0.80597300
C     -2.80137300  -2.07390800  -1.13843600
F     -3.94573200  -4.07946600  -0.57901300
F     -3.49947200  -1.98868400  -2.28924400
F     -1.67132000  -0.12809200  -1.71142100
F     -0.68574300  -2.39795800   2.35687000
F     -2.50912200  -4.25391500   1.74629100
F      0.79858400   1.56174500  -1.66903400
F      0.07942300   4.07028900  -2.23411500
F     -1.59213600   5.45053900  -0.56017300
F     -2.52524800   4.24320900   1.71369200
F     -1.80617300   1.74029200   2.31388400
F      0.96794800  -1.43968000  -1.68132200
F      3.49864000  -2.08117900  -2.24025200
F      5.52460000  -1.36406500  -0.54279300
F      4.94094300   0.01555200   1.75024000
F      2.41501000   0.65605800   2.34274200
H      0.00158900  -0.00132000   2.03466100
```

<u>B(C$_6$F$_5$)$_3$</u>

Total Energy E = -2208.744497 au
Total Enthalpy H = -2208.743553 au

```
B     -0.00095600  -0.00155300   0.00191400
C      1.18252900  -1.03148400   0.00267700
C     -1.48525000  -0.50956600   0.00065800
C      0.30107200   1.53827700   0.00120100
```

C	-0.48366300	2.45791700	0.71461300
C	1.37499000	2.09201000	-0.71343100
C	1.65189400	3.45400500	-0.73458500
C	0.84761900	4.32368500	-0.00107500
C	-0.22534200	3.82351200	0.73374500
C	-2.50239100	0.14488300	-0.71221900
C	-3.82061600	-0.29579800	-0.73316600
C	-4.17140400	-1.42820800	-0.00104400
C	-3.20113700	-2.10880900	0.73160700
C	-1.88909500	-1.65002900	0.71236200
C	3.32498300	-2.89347000	-0.00030300
C	3.42681700	-1.71362600	0.73395900
C	2.37142700	-0.80923100	0.71536300
C	1.12670700	-2.23879600	-0.71119700
C	2.16965300	-3.15757600	-0.73300700
F	4.32988600	-3.76723700	-0.00215500
F	2.07526500	-4.28514300	-1.44462200
F	0.04251000	-2.54078900	-1.44438200
F	2.52057900	0.30549500	1.44985700
F	4.53139800	-1.46372100	1.44388300
F	-2.22066600	1.23463500	-1.44529300
F	-4.74869300	0.35280200	-1.44351400
F	-5.43123600	-1.85949400	-0.00130900
F	-3.53845300	-3.19033400	1.44094300
F	-0.99935400	-2.33937900	1.44533000
F	2.17673500	1.30313300	-1.44770400
F	2.67607200	3.93420900	-1.44671400
F	1.10377300	5.63043500	-0.00257900
F	-0.99211000	4.65652100	1.44427900
F	-1.52436900	2.03126500	1.44881200

1 $^{•-}$

Total Energy E = -1481.366365 au
Total Enthalpy H = -1481.365421 au

B	-0.00006700	1.33064200	0.00060100
C	-1.38542500	0.62932000	-0.04378200
C	1.38539200	0.62942100	0.04452200
C	2.51797800	1.30472800	-0.44496100
C	1.63021200	-0.62765300	0.62334900
C	2.90003600	-1.18698700	0.70216800
C	3.98757600	-0.48534900	0.18272300
C	3.79955200	0.76716800	-0.39868900
C	-1.62996900	-0.62777100	-0.62272200
C	-2.89973500	-1.18715800	-0.70214500

C	-3.98753600	-0.48558800	-0.18315900
C	-3.79982300	0.76696000	0.39830200
C	-2.51828700	1.30457200	0.44515600
F	-0.62645800	-1.32860800	-1.16915400
F	-3.09195700	-2.38016800	-1.27419100
F	-5.20828700	-1.01359900	-0.24546700
F	-4.84633600	1.43417900	0.89523900
F	-2.38556100	2.51091700	1.01181100
F	0.62693700	-1.32858400	1.17007400
F	3.09258700	-2.38001300	1.27408800
F	5.20836800	-1.01334700	0.24445000
F	4.84581000	1.43442400	-0.89615500
F	2.38496900	2.51106300	-1.01163800
H	-0.00013100	2.52044600	0.00091700

$(C_6F_5)^\bullet$

Total Energy E = -727.864035 au
Total Enthalpy H = -727.863091 au

| C	0.00000000	-1.64768400	0.00038900
C	-1.21774100	-1.01086700	0.00053900
C	1.21773600	-1.01086600	0.00052300
C	1.21451700	0.38829200	0.00045500
C	0.00000300	1.07628000	0.00020700
C	-1.21451300	0.38828700	0.00043300
F	2.38094400	-1.67006500	-0.00057200
F	2.36458100	1.06957500	-0.00011400
F	-0.00000500	2.41200900	-0.00032700
F	-2.36457000	1.06958300	-0.00015500
F	-2.38095000	-1.67006400	-0.00052900
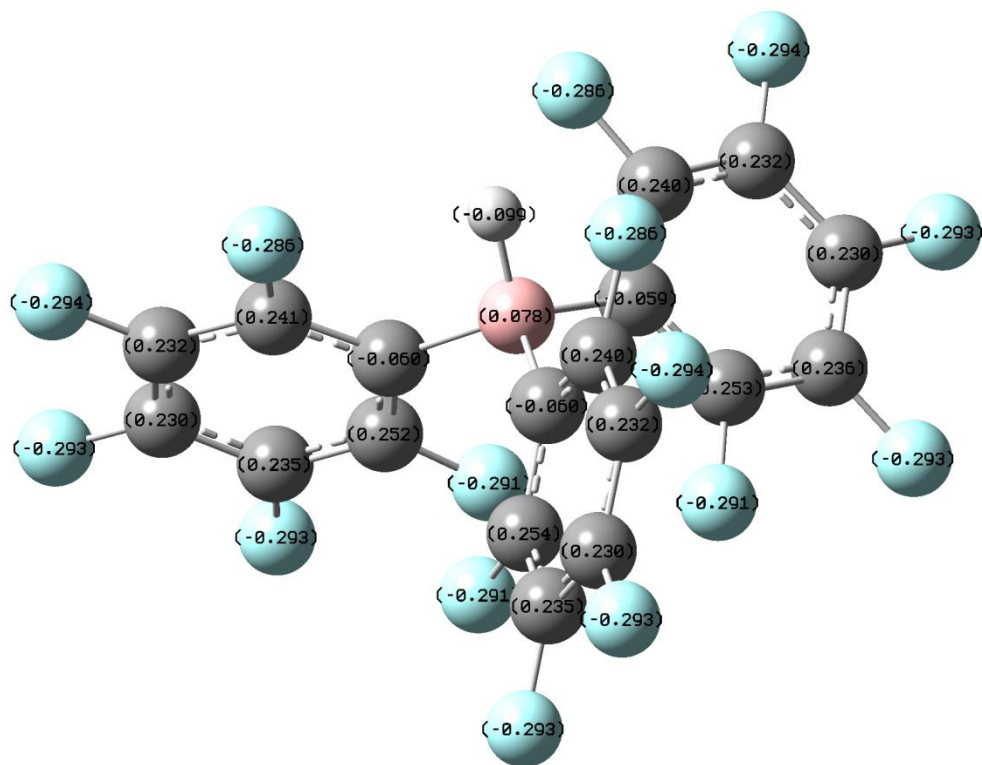
Supplementary Figure S14. View of the geometry optimized structure of **1**⁻ with partial charges shown for each atom, based on Mulliken electron population analysis.
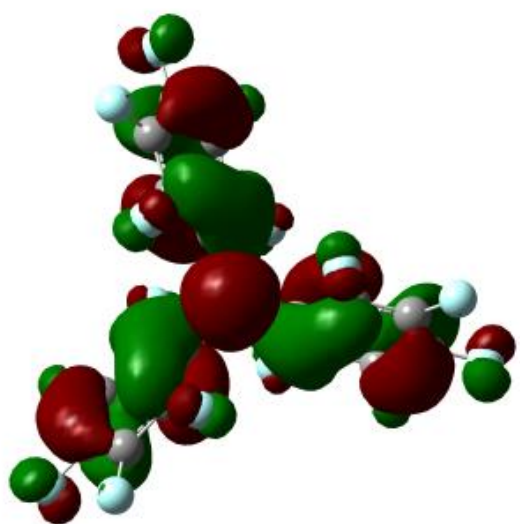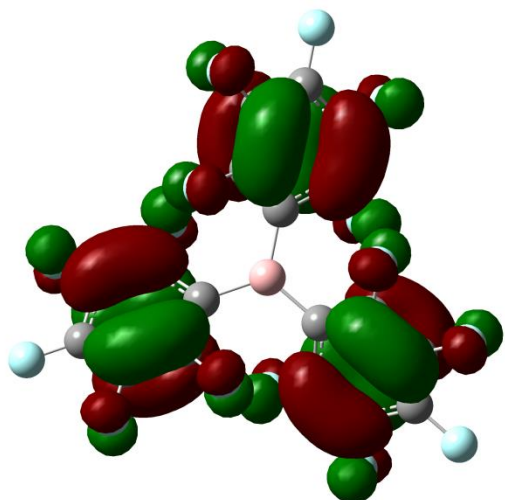

Supplementary Figure 15. View of the SOMO of **1**•.
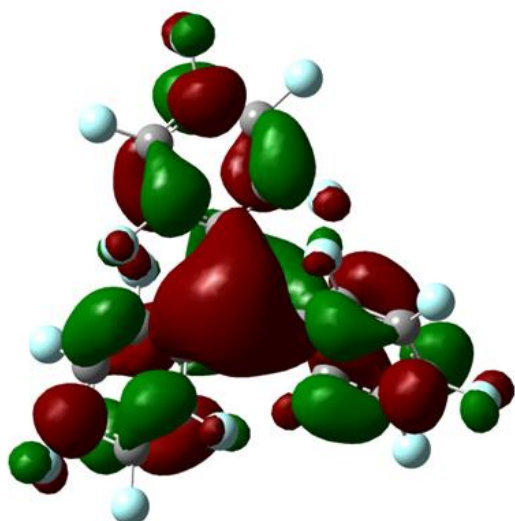
Supplementary Figure 16. View of the SOMO of B(C$_6$F$_5$)$_3$$^{\bullet-}$.
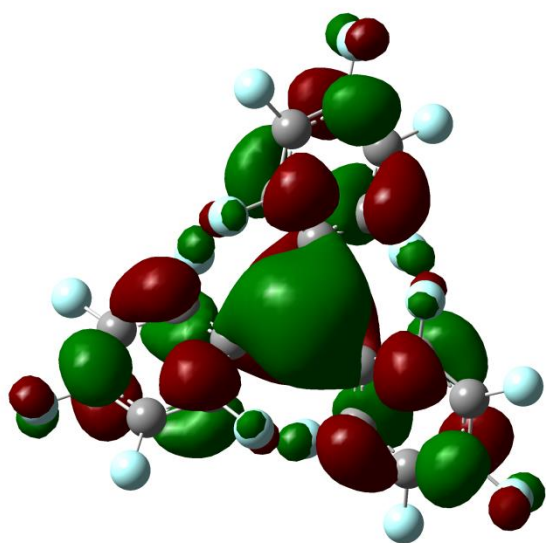
Supplementary Figure 17. View of the LUMO of B(C$_6$F$_5$)$_3$.

Supplementary Figure 18. View of the HOMO of $B(C_6F_5)_3$.

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