Supporting Information

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

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Contents

S1. Synthesis S2
S2. NMR Spectra S4
S3. X-ray Crystallography S14
S4. Electrochemistry S17
S5. DFT Computational modeling S20
S1. Synthesis

S1.1. Na[HB(C₆F₅)]₃
To a solution of 1.0 M Na[HB₃] in toluene (3.7 mL, 3.7 mmol) was added a solution of B(C₆F₅)₃ (1.71 g, 3.3 mmol) in toluene (30 mL). The reaction mixture was left to stir under N₂ 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(C₆F₅)]₃ (1.15 g, 2.1 mmol) as a fine white powder in 64% yield.

S1.2. [nBu₄N][HB(C₆F₅)]₃ ([nBu₄N]1)
A solution of nBu₄NCl (0.45 g, 1.6 mmol) in CH₂Cl₂ (20 mL) was added to a white suspension of Na[HB(C₆F₅)]₃ (0.86 g, 1.6 mmol) in CH₂Cl₂ (20 mL) at room temperature, with stirring under N₂. 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 [nBu₄N]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 [nBu₄N]1 in a minimum quantity of CH₂Cl₂, warming to ca. 35 °C, adding an equal quantity of light petroleum ether and slow-cooling to room temperature. ¹H NMR (300 MHz, CDCl₃): δ 3.60 (br. q, J = 82 Hz, 1H, BH), 3.07 (m, 8H, CH₂), 1.56 (m, 8H, CH₂), 1.32 (m, 8H, CH₂), 0.92 (t, J = 7.2 Hz, 12H, CH₃); ¹⁹F NMR (282 MHz, CDCl₃): δ −133.6 (m, 6F, ortho-F), −163.4 (m, 3F, para-F), −166.7 (m, 6F, meta-F); ¹¹B NMR (96.3 MHz, CDCl₃): δ −147.5 (dm, J = 240 Hz), 137.2 (dm, J = 245 Hz), 135.8 (dm, J = 248 Hz), 124.9 (s, ipso-C), 125.0, 58.9, 23.8, 19.6, 13.4. IR (ATR, cm⁻¹): 2424 (νB–H, w).

Anal. Calcd for C₃₄H₃₇BF₁₅N: C 54.06; H 4.94; N 1.85. Found: C 53.79; H 5.06; N 1.86.

S1.3. [TMPD][DB(C₆F₅)]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(C₆F₅)₃ (1.00 g, 1.95 mmol) in toluene (20 mL) to give a
clear, pale yellow solution. The sample was sparged with D₂ 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(C₆F₅)₃] (1.15 g, 1.75 mmol) as a white powder in 90 % yield. ¹H NMR (500 MHz, C₆D₆): δ 4.23 (t, J = 49 Hz, 1H, NH), 0.76 (m, 2H, CH₂), 0.67 (m, 4H, CH₂) 0.56 (s, 12H, CH₃); ¹⁹F NMR (471 MHz, C₆D₆): δ −133.1 (m, 6F, ortho-F), −161.7 (m, 3F, para-F), −165.5 (m, 6F, meta-F); ¹¹B NMR (160 MHz, C₆D₆): δ −23.8 (s); ²D NMR (556 MHz, CH₂Cl₂): δ 5.40 (d, J = 1.1 Hz, ND), 3.60 (br. m, BD).

S1.4. [⁷⁷⁷Bu₄N][DB(C₆F₅)₃] ([⁷⁷⁷Bu₄N]¹³)

A clear colourless solution of [TMPD][DB(C₆F₅)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 N₂ overnight. The reaction mixture was then filtered and the filtrate was concentrated in vacuo. The residue was dissolved in CH₂Cl₂ (10 mL) to give a clear colourless solution. To this was added a clear colourless solution of N⁷⁷⁷Bu₄Cl (0.13 g, 0.47 mmol) in CH₂Cl₂ (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 [⁷⁷⁷Bu₄N]¹³ (0.10 g, 0.13 mmol) as an amorphous colorless solid in 28 % yield. ¹⁹F NMR (471 MHz, CDCl₃): δ −133.5 (m, 6F, ortho-F), −163.4 (m, 3F, para-F), −166.6 (m, 6F, meta-F); ¹¹B NMR (160 MHz, CDCl₃): δ −25.3 (d, J = 82 Hz). ²D NMR (556 MHz, CH₂Cl₂): δ 3.66 (br. s). IR (ATR, cm⁻¹): 1800 (νB–D, w).
S2. NMR Spectra

Supplementary Figure S1. $^1$H NMR spectrum of [[$^0$Bu$_4$N][HB(C$_6$F$_5$)$_3$] [[$^0$Bu$_4$N]$_1$.}
Supplementary Figure S2. $^{19}$F NMR spectrum of [Bu$_4$N][HB(C$_6$F$_5$)$_3$] $^{19}$Bu$_4$N].
Supplementary Figure S3. $^{11}$B NMR spectrum of [Bu$_4$N][HB(C$_6$F$_5$)$_3$][Bu$_4$N]1.
Supplementary Figure S4. $^{13}$C NMR spectrum of $[\text{Bu}_4\text{N}][\text{HB(C}_6\text{F}_5)_3]$ $[\text{Bu}_4\text{N}]_1$. 

Current Data Parameters
NAME ELO000 SIMBAD13-HBu4 EXPNO 2 PROCNO 1

F1 - Acquisition Parameters
Data 20120801
Time 7.52
INSTRUM dp4300
PRODID 5 km Multinouei
POLEPROG suppy
TD 6556
SOLVENT CDCl3
NS 12115
DS 17865.61 Hz
FIDRES 6.274433 Hz
AQ 1.8219000 sec
M 7236.2
DS 27.800 usec
DE 60.000 usec
DS 8.400 usec
DI 2.0000000 sec
DIL 0.3000000 sec
DELTA 1.6999999 sec
TD 1
SF01 75.4782S3 MHz
HCB 130
DF 5.50 usec
PLM1 -1.0000000 W
PLM2 500.1515 MHz
PLM3 10 MHz
PLM4 10 MHz

F2 - Processing parameters
DS 23742
DF 75.667737 MHz
LOW 0
NB 0
LA 1.00 Hz
PC 1.40
Supplementary Figure S5. $^{19}$F NMR spectrum of [($^7$Bu$_4$N)[DB($C_6F_5$)$_3$]$^7$Bu$_4$N]$^1$D.
Supplementary Figure S6. $^{11}$B NMR spectrum of $[^7]$Bu$_4$N][DB(C$_6$F$_5$)$_3$] $[^7]$Bu$_4$N$^1$D.
Supplementary Figure S7. $^2$D NMR spectrum of [$^6$Bu₄N][DB(C₆F₅)₃] [$^6$Bu₄N]$_1^D$. 
Supplementary Figure S8. $^{19}$F NMR spectrum showing the progress of hydrogen cleavage by a B(C₆F₅)$_3$/ $^{1}$Bu₃P FLP under a H₂ atmosphere (1.1 bar) at 21 °C. The minor peaks that are highlighted by the dotted lines are attributable to the formation of (H₂O)B(C₆F₅)$_3$ [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 $\text{B(C}_6\text{F}_5)_3/\text{P}^3\text{Bu}_3$ FLP after 12 hours under a $\text{H}_2$ atmosphere (1.1 bar) at 21 °C.
### S3. X-ray Crystallography

**Supplementary Table S1.** Crystallographic data for compound $[^6]$Bu$_4$N$\cdot$1.

|                     | \[n\]Bu$_4$N$\cdot$HB(C$_6$F$_5$)$_3$ | \[n\]Bu$_4$N$\cdot$1 |
|---------------------|--------------------------------------|----------------------|
| Elemental formula   | C$_{16}$H$_{36}$N, C$_{18}$H$_{15}$BF$_{15}$ |                      |
| Formula weight      | 755.46                               |                      |
| Temperature / K     | 100                                  |                      |
| Crystal system      | Monoclinic                           |                      |
| Space group         | $P2_1/\text{n}$                       |                      |
| $a$ / Å             | 10.141(4)                            |                      |
| $b$ / Å             | 18.471(7)                            |                      |
| $c$ / Å             | 18.792(7)                            |                      |
| $\alpha$ / °        | 90                                   |                      |
| $\beta$ / °         | 100.504(7)                           |                      |
| $\gamma$ / °        | 90                                   |                      |
| Volume / Å$^3$       | 3461 (2)                             |                      |
| $Z$                 | 4                                    |                      |
| $\rho_{\text{calc}}$ / mg mm$^{-3}$ | 1.450                               |
| $\mu$ / mm$^{-1}$   | 0.140                                |                      |
| F(000)              | 1552                                 |                      |
| Crystal size / mm$^3$ | 0.21 × 0.11 × 0.04                   |
| Reflections collected | 25957                              |
| Independent reflections | 6049                          |
| ‘Observed’ data [I≥2σ(I)] | [R(int) = 0.030]                    |
| Data / restraints / parameters | 6049 / 0 / 548                    |
| Goodness-of-fit on $R^2$ | 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 $[^n\text{Bu}_4\text{N}]1$, 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-C1 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 $[^n\text{Bu}_4\text{N}]1$ 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 $\vartheta_{max} = 25 ^\circ$, was 25957 of which 6049 were unique ($R_{int} = 0.030$); 5559 were 'observed' with $I > 2\sigma_I$.

Data were processed using the CrystalClear-SM Expert program,\textsuperscript{1} incorporating absorption corrections. The structure was determined by the direct methods routines in the SHELXS-97 program\textsuperscript{2} and refined by full-matrix least-squares methods, on $F^2$'s, in SHELXL-97.\textsuperscript{2} In the preliminary refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in idealized positions and their $U_{iso}$ values were set to ride on the $U_{eq}$ 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$_6$F$_5$ 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 $w = [a^2(F_o^2) + (0.0486P)^2 + 1.975P]^{-1}$ 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. Computer programs used in this analysis have been noted above, and were run through WinGX on a Dell Precision 370 PC at the University of East Anglia.

The data for ["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 CH₃CN solvent containing 0.1 M [nBu₄N][PF₆] 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 CH₂Cl₂ 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 N₂ atmosphere in CH₂Cl₂ containing 0.05-0.10 M [nBu₄N][B(C₆F₅)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 [\textit{n}Bu_4\textit{N}]1 in CH_2Cl_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 $\text{H}_2$ containing 2.3 mM $\text{Cp}_2\text{Fe}^{0/+}$ as internal reference in $\text{CH}_2\text{Cl}_2$ 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.
DFT Computational modeling

DFT calculations were performed using the Gaussian 09 computational package. Geometry optimization calculations have been carried out using the three-parameter exchange functional of Becke and the correlation functional of Lee, Yang, and Parr (LYP), B3LYP. The 6-311+G(d,p) basis set has been implemented for all atoms. 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 1- species and the SOMO of the 1* intermediate lends further support to our proposed mechanism (See main text). Interestingly, partial charge calculations for 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 1- is a weak hydride donor, and is consistent with the results of previous studies involving the FLP reduction of small molecules. The B–C and B–H bond dissociation energies for the 1- were calculated as ΔH_{B-C} = 408.1 kJmol⁻¹ and ΔH_{B-H} = 312.2 kJmol⁻¹ respectively, whilst for 1* the values were found to be ΔH_{B-C} = 71.7 kJmol⁻¹ and ΔH_{B-H} = 34.0 kJmol⁻¹ respectively. This indicates that the electrochemical oxidation of 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(C₆F₅)₃⁺ and H⁺. Note that these are gas phase DFT calculations; it is likely that heterolytic cleavage of the B–H bond in 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
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 | -1.1043930000 |
| C | 4.248665001 | -1.047254000 | -0.247912000 |
| B | 3.946437000 | -0.347799000 | 0.914030000 |
| B | -0.010553000 | 2.179049000 | -0.780960000 |
| B | -0.373937000 | 3.484843000 | -1.106802000 |
| B | -1.224437000 | 4.1893701 | -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 |
| F | -3.499473000 | -1.988683000 | -2.289244000 |
| F | -1.671320000 | -0.128092000 | -1.711421000 |
| F | -0.685744000 | -2.397958000 | 2.356870000 |
| F | -2.509123000 | -4.253914000 | 1.746291000 |
| F | 0.798584000 | 1.561745000 | -1.669034000 |
| F | 0.079424000 | 4.070289000 | -2.234115000 |
| F | -1.592134000 | 5.450539000 | -0.560173000 |
| F | -2.525247000 | 4.243210000 | 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 | 2.240252000 |
| F | 4.940943000 | 0.015550000 | 1.750240000 |
| F | 2.415010000 | 0.656057000 | 2.342724000 |
| H | 0.001589000 | -0.001320000 | 2.034661000 |

Total Energy $E = -2209.456570$ au
Total Enthalpy $H = -2209.455626$ au
| B | C | C | C | C | C | F | F | F | F | F | F | H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.00441100 | -1.09226400 | 0.43776400 | 1.54090600 | 2.61849100 | 1.90451700 | 3.21630000 | 4.24866500 | 3.94643700 | 2.94866700 | 3.94573200 | 2.50912200 | 0.00158900 |
| -0.00190800 | -1.13990200 | 1.51556100 | -0.38041800 | -0.03132200 | -1.06789100 | -0.00155300 | -1.41101100 | -1.13990200 | -0.38041800 | -0.00155300 | -1.41101100 | -0.00155300 |
| 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 |
| 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 |
| 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 |
| 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 | 0.37844700 | 0.37144700 | 0.82914500 |

**B(C_F_3)_2**

Total Energy $E = -2208.744497$ au

Total Enthalpy $H = -2208.743553$ au
Total Energy $E = -1481.366365$ au
Total Enthalpy $H = -1481.365421$ au
\[
\begin{array}{ccc}
C & -3.98753600 & -0.48558800 \\
C & -3.79982300 & 0.76696000 \\
C & -2.51828700 & 1.30457200 \\
F & -0.62645800 & -1.32860800 \\
F & -3.09195700 & -2.38016800 \\
F & -5.20828700 & -1.01359900 \\
F & -4.84633600 & 1.43417900 \\
F & -2.38556100 & 2.51091700 \\
F & 0.62693700 & -1.32858400 \\
F & 3.09258700 & -2.38001300 \\
F & 5.20836800 & -1.01334700 \\
F & 4.84581000 & 1.43442400 \\
F & 2.38496900 & 2.51063000 \\
H & -0.00013100 & 2.52044600 \\
\end{array}
\]

\[
(C_6F_5)^* \\
C & 0.00000000 & -1.64768400 \\
C & -1.21774100 & -1.01086700 \\
C & 1.21773600 & -1.01086600 \\
C & 1.21451700 & 0.38829200 \\
C & 0.00000300 & 1.07628000 \\
C & -1.21451300 & 0.38828700 \\
F & 2.38094400 & -1.67006500 \\
F & 2.36458100 & 1.06957500 \\
F & -0.00000500 & 2.41200900 \\
F & -2.36457000 & 1.06958300 \\
F & -2.38095000 & -1.67006400 \\
\]

Total Energy E = -727.864035 au \\
Total Enthalpy H = -727.863091 au
**Supplementary Figure S14.** View of the geometry optimized structure of $\mathbf{1}^-$ with partial charges shown for each atom, based on Mulliken electron population analysis.

**Supplementary Figure 15.** View of the SOMO of $\mathbf{1}^+$. 
**Supplementary Figure 16.** View of the SOMO of B(C₆F₅)₃⁻.

**Supplementary Figure 17.** View of the LUMO of B(C₆F₅)₃.
Supplementary Figure 18. View of the HOMO of B(C_F)_3.

References
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