SUPPLEMENTARY INFORMATION

Exploring Structural and Electronic Effects in Three Isomers of Tris{bis(trifluoromethyl)phenyl}borane: Towards the Combined Electrochemical-Frustrated Lewis Pair Activation of H_2

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Synthesis of authentic $[(^t\mathbf{Bu})_3\mathbf{PH}][\mathbf{HB}\{(\mathbf{CF_3})_2\mathbf{C_6H_3}]$ Equimolar amounts of Na[**2**−H] or Na[**3**−H] and $[(^t\mathrm{Bu})_3\mathrm{PH}]\mathrm{Cl}$ (synthesised from $P(t\mathrm{Bu})_3$ and HCl in Et_2O) are combined and dissolved in CD_2Cl_2. Colourless precipitate (NaCl) rapidly forms and NMR spectra obtained of the solution are consistent with $[(^t\mathrm{Bu})_3\mathrm{PH}][\mathbf{2}-\mathrm{H}]$ and $[(^t\mathrm{Bu})_3\mathrm{PH}][\mathbf{3}-\mathrm{H}]$ respectively; the spectra are unchanged over a 66 hour period.

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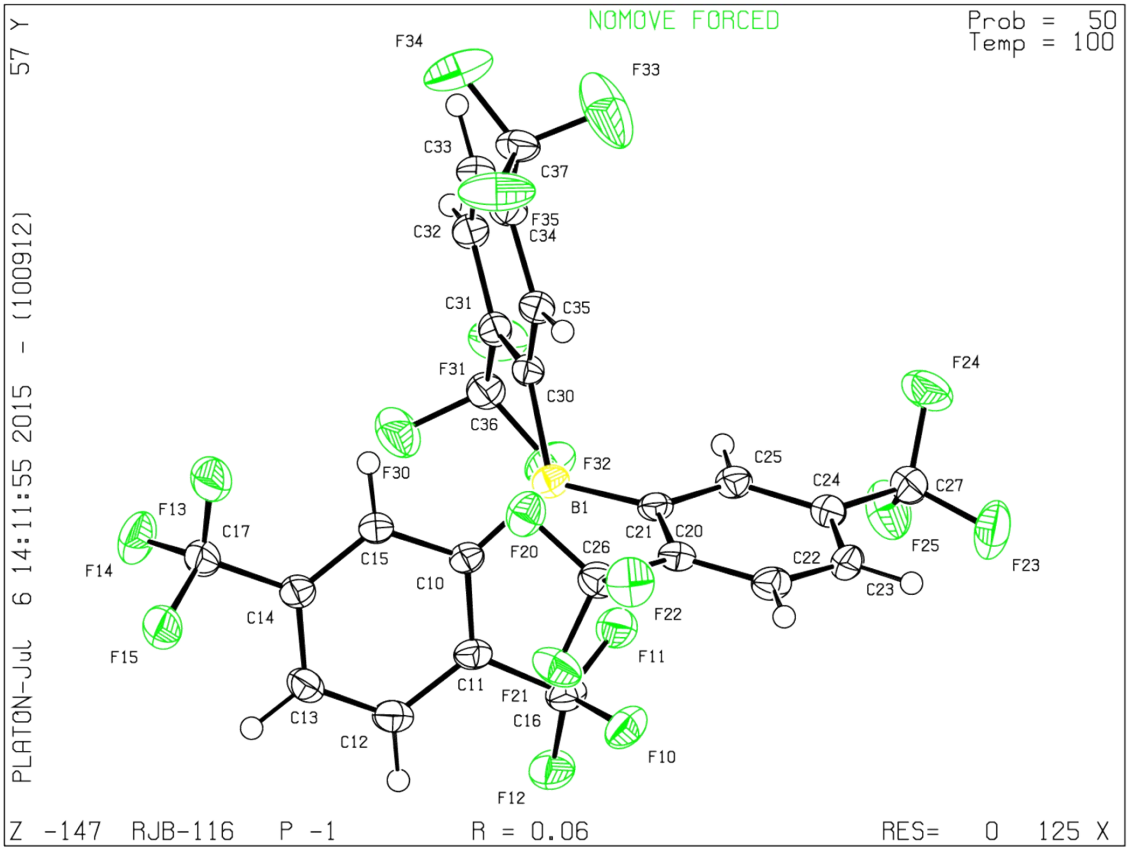

Figure S1 Crystallographic molecular structure of **3** (ellipsoids at 50% probability level)

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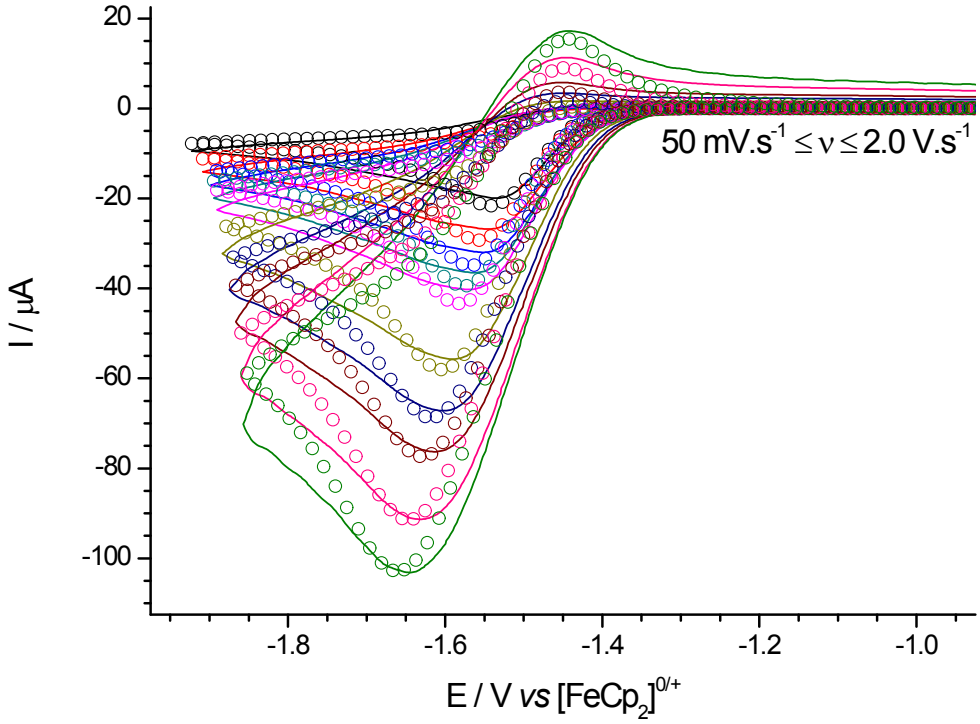

Figure S2 Experimental (line) and simulated (open circles) cyclic voltammograms for the reduction of $B(C_6F_5)_3$

WE = glassy carbon disc; CE = platinum wire; *pseudo*-RE = silver wire; $CH_2Cl_2/[^nBu_4N][B(C_6F_5)_4]$

Simulated using an *EC*-mechanism with:

$E^0 = -1.518$ V *vs* $[FeCp_2]^{0/+}$; $\alpha = 0.379$; $k^0 = 1.45\times10^{-2}$ cm.s^{-1}; $k_f = 9.2$ s^{-1};

$D\{B(C_6F_5)_3\} = D\{B(C_6F_5)_3^{\bullet-}\} = 0.85\times10^{-5}$ cm^2.s^{-1} diffusion constant obtained *via* ^{19}F DOSY NMR spectroscopy

Table S1 Relative ground state molecular energies and orbital energies

	E / kJ.mol^{-1} [a]	E (HOMO) / Ha	E (SOMO) / Ha	E (LUMO) / Ha
$B\{3,5\text{-}(CF_3)_2C_6H_3\}_3$ **1**	−46.0	−0.31412	-	−0.13356
$B\{2,4\text{-}(CF_3)_2C_6H_3\}_3$ **2**	0.0	−0.30144	-	−0.12319
$B\{2,5\text{-}(CF_3)_2C_6H_3\}_3$ **3**	−3.1	−0.29809	-	−0.11971
$[B\{3,5\text{-}(CF_3)_2C_6H_3\}_3]^{\bullet-}$ **1**$^{\bullet-}$	−280.3	-	−0.04756	+0.02745
$[B\{2,4\text{-}(CF_3)_2C_6H_3\}_3]^{\bullet-}$ **2**$^{\bullet-}$	−221.8	-	−0.04618	−0.02729
$[B\{2,5\text{-}(CF_3)_2C_6H_3\}_3]^{\bullet-}$ **3**$^{\bullet-}$	−213.4	-	−0.03962	+0.02719

[a] Total molecular energies are all reported relative to **2**.

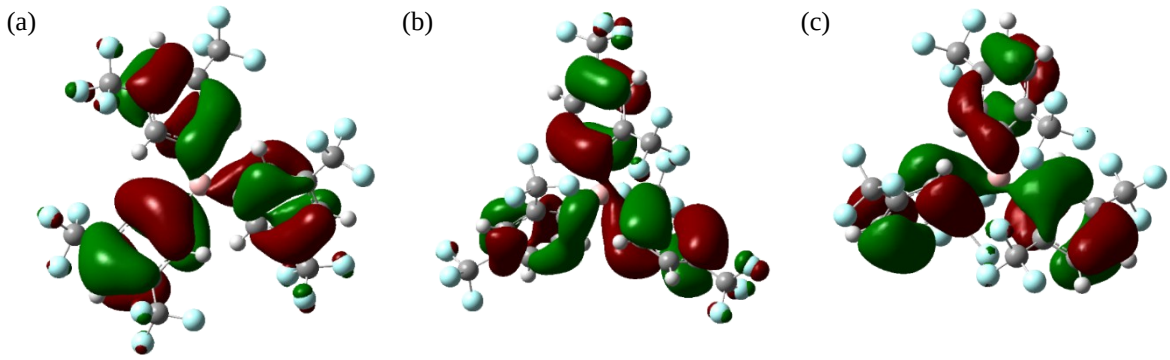

Figure S3 Highest occupied molecular orbitals (HOMOs) for (a) **1**, (b) **2**, and (c) **3**

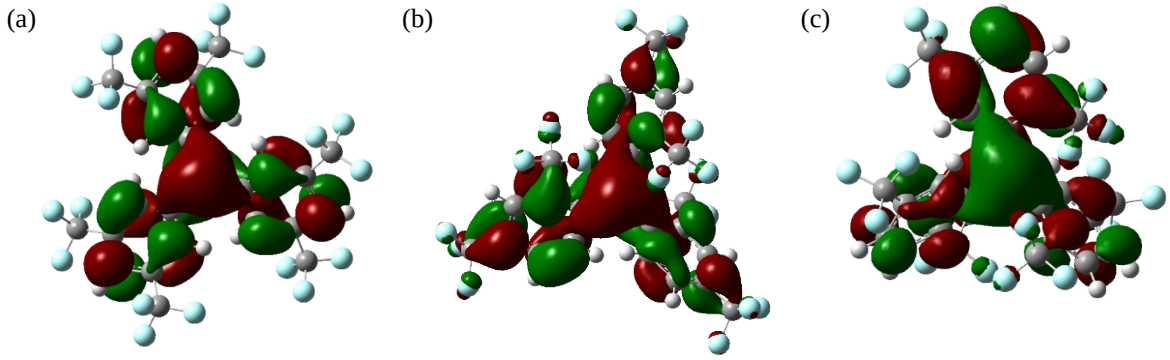

Figure S4 Singularly occupied molecular orbitals (SOMOs) for (a) $\mathbf{1}^{\bullet-}$, (b) $\mathbf{2}^{\bullet-}$, and (c) $\mathbf{3}^{\bullet-}$

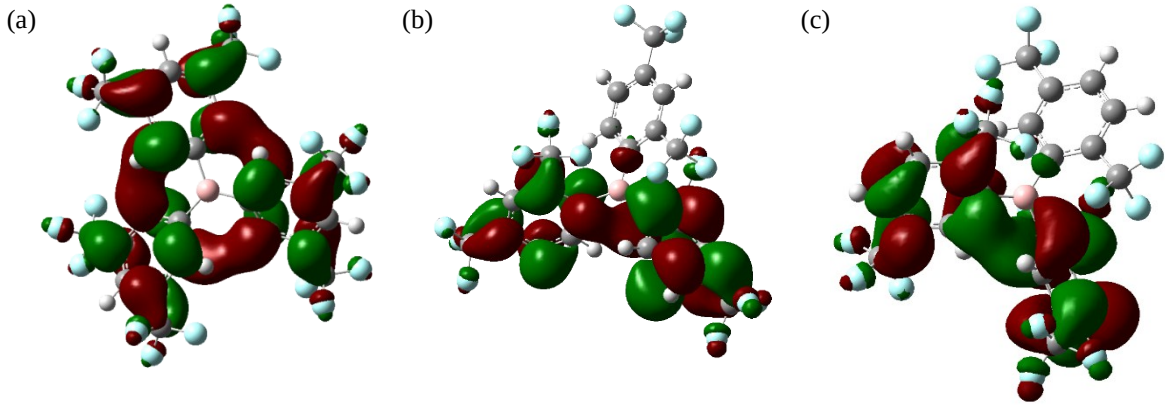

Figure S5 Lowest unoccupied molecular orbitals (LUMOs) for (a) $\mathbf{1}^{\bullet-}$, (b) $\mathbf{2}^{\bullet-}$, and (c) $\mathbf{3}^{\bullet-}$

SUPPLEMENTARY INFORMATION

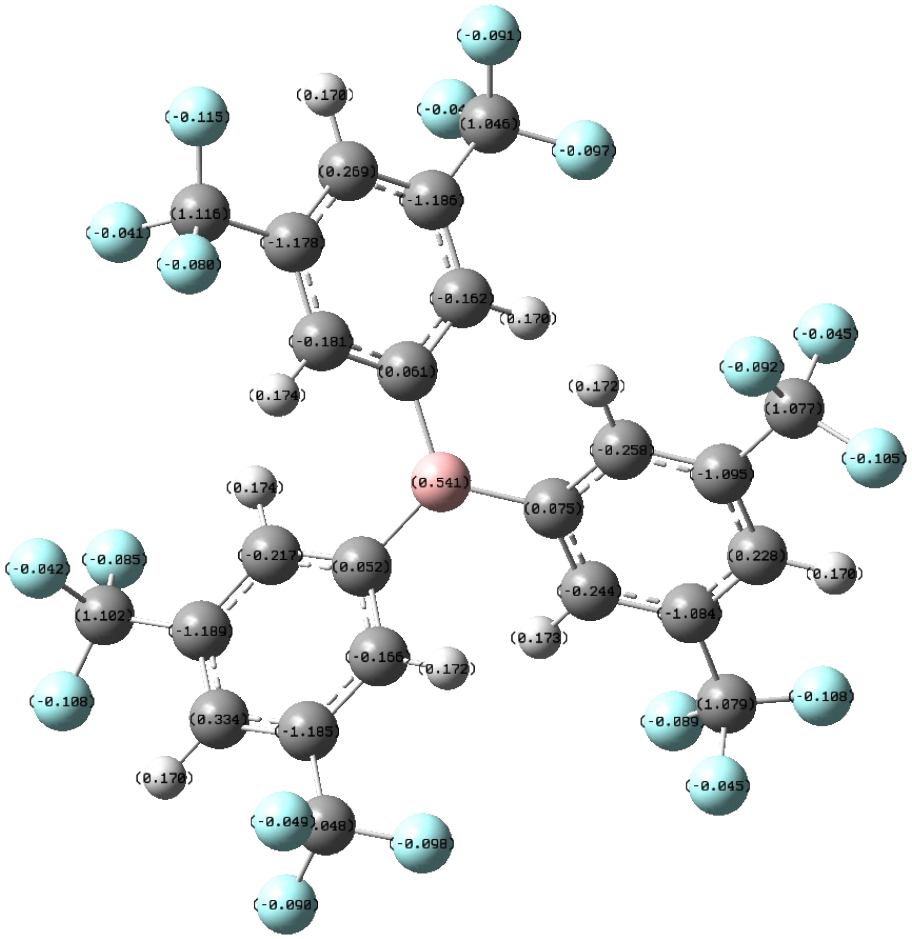

Figure S6a Calculated Mulliken atomic charges for B{3,5-$(CF_3)_2C_6H_3$}$_3$ **1**

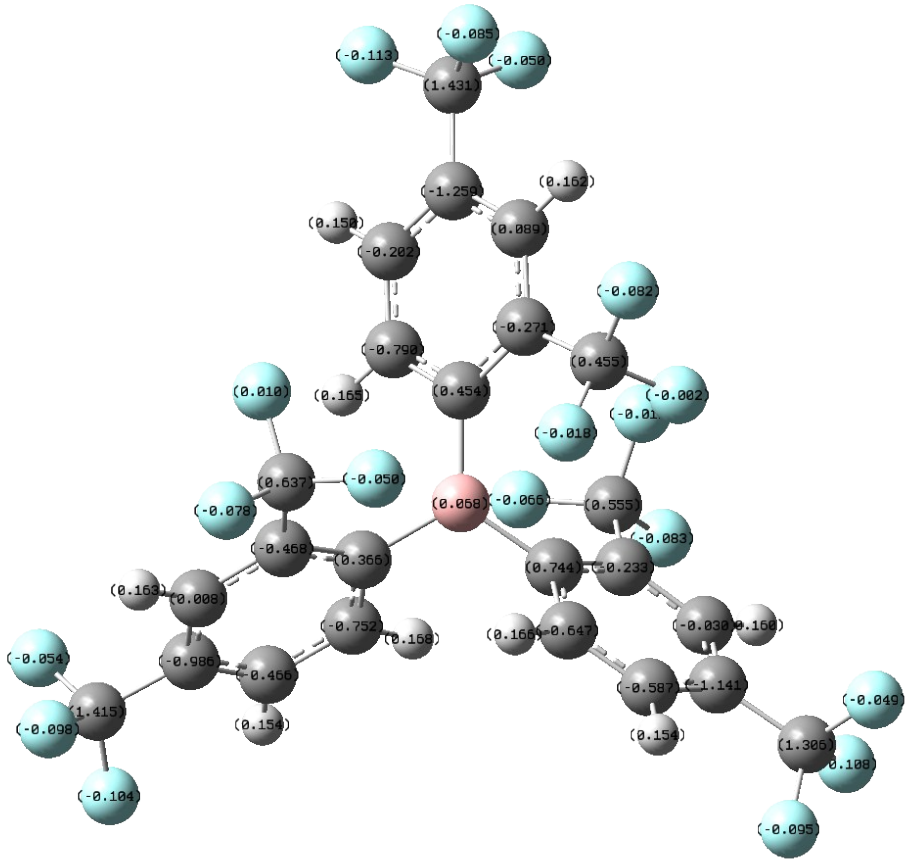

Figure S6b Calculated Mulliken atomic charges for B{2,4-$(CF_3)_2C_6H_3$}$_3$ **2**

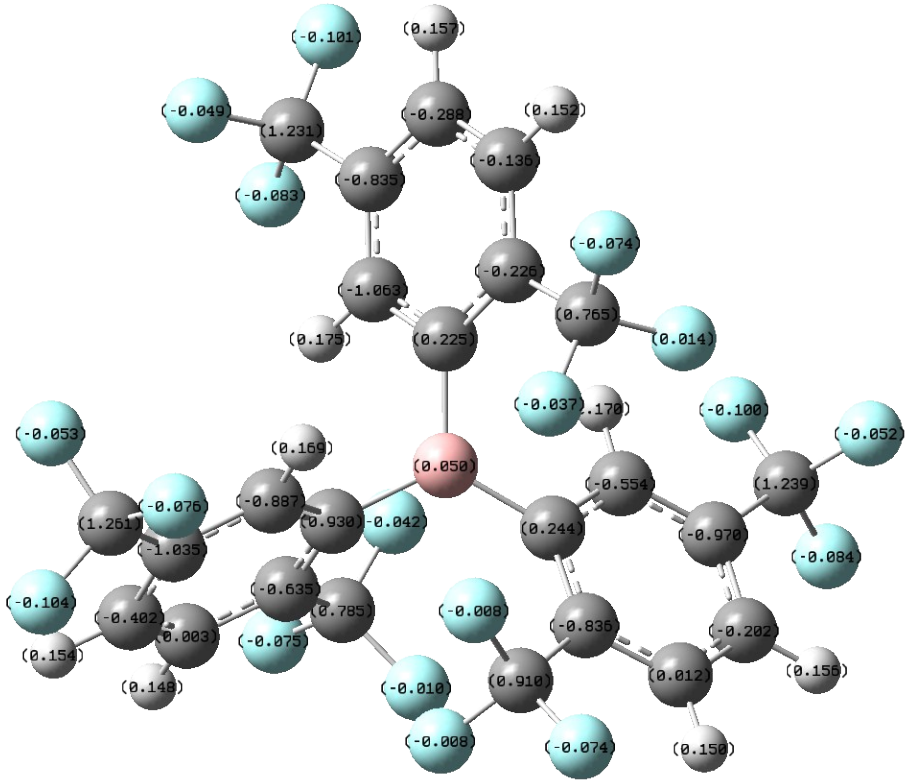

Figure S6c Calculated Mulliken atomic charges for B{2,5-$(CF_3)_2C_6H_3$}$_3$ **3**