**SUPPLEMENTARY INFORMATION**

**Novel B(Ar')$_2$(Ar'') hetero-tri(aryl)boranes: a systematic study of Lewis acidity**

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**Experimental**

**B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_2$(OH)**

$^1$H NMR (500.21 MHz, CD$_2$Cl$_2$, 25 °C, δ): +8.20 (s, 4H, Ar$_{F6}$ 2,6-H), +8.10 (s, 2H, Ar$_{F6}$ 4-H), +6.61 (s, 1H, OH); $^{11}$B NMR (160.49 MHz, CD$_2$Cl$_2$, 25 °C, δ): +44.3 (br.s); $^{13}$C{$^1$H} NMR (125.78 MHz, CD$_2$Cl$_2$, 25 °C, δ): +134.9 (br.q, $^3$J$_{CF}$ = 3.7 Hz, Ar$_{F6}$ 2,6-C), +131.9 (q, $^2$J$_{CF}$ = 33.0 Hz, Ar$_{F6}$ 3,5-C), +125.8 (sept., $^3$J$_{CF}$ = 3.7 Hz, Ar$_{F6}$ 4-C), +124.0 (q, $^1$J$_{CF}$ = 273 Hz, Ar$_{F6}$ 3,5-CF$_3$); $^{19}$F NMR (470.67 MHz, CD$_2$Cl$_2$, 25 °C, δ): −63.4 (s, 12F, Ar$_{F6}$ 3,5-CF$_3$).

**B{3,5-(CF$_3$)$_2$C$_6$H$_3$}(OMe)$_2$**

$^1$H NMR (500.21 MHz, C$_6$D$_6$, 25 °C, δ): +7.86 (s, 2H, Ar$_{F6}$ 2,6-H), +7.79 (s, 1H, Ar$_{F6}$ 4-H), +3.30 (s, 6H, OMe); $^{11}$B NMR (160.49 MHz, C$_6$D$_6$, 25 °C, δ): +27.2 (br.s); $^{19}$F NMR (470.67 MHz, C$_6$D$_6$, 25 °C, δ): −62.7 (s, 6F, Ar$_{F6}$ 3,5-CF$_3$).
SUPPLEMENTARY INFORMATION

X-ray Crystallography

To ensure the refinement of 6 converged it was necessary to treat the boron atom as isotropic. Additionally one of the CF$_3$ groups is modelled with crystallographic disorder of the fluoride atoms over two positions (58:42) due to rotation about the C(17)--C(20)F$_3$ bond.

**Figure S1a** X-ray crystallographic structure of B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_2$(C$_6$Cl$_5$)$_5$

**Figure S1b** X-ray crystallographic structure of B(C$_6$Cl$_5$)$_2$(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_6$
Supplementary Information

Computational Calculations – DFT

Figure S2a  DFT optimised structure of B(C₆F₅)₃ 1 (reproduced from reference 34)

Figure S2b  DFT optimised structure of B(C₆F₅)₂{3,5-(CF₃)₂C₆H₃} 2

Figure S2c  DFT optimised structure of B{3,5-(CF₃)₂C₆H₃}₄(C₆F₅) 3
Computational calculations were performed using density functional theory (DFT) using the Gaussian 09 (revision C.01) computational package. Calculations were carried out using the three-parameter exchange functional of Becke (B3) with the correlation functional of Lee, Yang, and Parr (LYP), B3LYP, together with applying the 6-311+G(d,p) basis set for all atoms. Structures were geometry optimised in the gas phase with the default convergence criteria, and confirmed as minima through frequency calculations.

**References**


**SUPPLEMENTARY INFORMATION**

Electrochemical Studies

![Cyclic voltammograms](image)

**Figure S3a**  Experimental (line) and simulated (open circles) cyclic voltammograms for the reduction of B(C₆F₅)₃ 1 (reproduced from reference 37)

![Cyclic voltammograms](image)

**Figure S3b**  Experimental (line) and simulated (open circles) cyclic voltammograms for the reduction of B{3,5-(CF₃)₂C₆H₃}₃ 4 (reproduced from reference 37)
Cyclic voltammograms were also obtained of a pure sample of $\text{B}\{3,5-(\text{CF}_3)_{2}\text{C}_6\text{H}_3\}_2(\text{OH})$, showing a one electron irreversible reduction at considerably more negative potentials (ca. $-2.3 \text{ V vs } [\text{FeCp}_2]^{0/+}$) than observed for any of the tri(aryl)boranes (Figure S4).

![Experimental cyclic voltammograms for the reduction of B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_2$(OH)](image)

**Figure S4**  Experimental cyclic voltammograms for the reduction of $\text{B}\{3,5-(\text{CF}_3)_{2}\text{C}_6\text{H}_3\}_2(\text{OH})$
**SUPPLEMENTARY INFORMATION**

**Measurements of Lewis acidity**

“Gutmann-Beckett Method” B(Ar')_2(Ar'') (Lewis acid) is combined with a three-fold excess of OPEt_3 (Lewis base) in ca. 0.8 cm^3 CD_2Cl_2 in an NMR tube, rapidly generating the Lewis acid-base adduct Et_3POB(Ar')_2(Ar''), and ^1H, ^11B, ^19F and ^31P{^1H} NMR spectra obtained (Tables 3 & S1).

**Table S1** NMR spectral data for the Lewis acid/base adducts 1–OPEt_3 – 9–OPEt_3

<table>
<thead>
<tr>
<th>Adduct</th>
<th>NMR Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–OPEt_3</td>
<td>^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +1.92 (dq, J_HH = 13.44 Hz, J_HF = 7.7 Hz, 6H), +1.11 (dt, J_HH = 18.7 Hz, J_HF = 7.7 Hz, 9H); ^19F NMR (470.67 MHz, CD_2Cl_2, 25 °C, δ): −134.4 (m, 6F), −159.1 (t, J_FF = 19.9 Hz, 3F), −165.0 (m, 6F).</td>
</tr>
<tr>
<td>2–OPEt_3</td>
<td>^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +7.79 (s, 2H), +7.68 (s, 1H), +1.86 (dq, J_HH = 12.0 Hz, J_HF = 7.8 Hz, 6H); ^19F NMR (470.67 MHz, CD_2Cl_2, 25 °C, δ): −62.9 (s, 6F), −132.0 (m, 4F), −158.5 (t, J_FF = 19.9 Hz, 2F), −164.1 (m, 4F).</td>
</tr>
<tr>
<td>3–OPEt_3</td>
<td>^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +7.83 (s, 4H), +7.78 (s, 2H), +1.68 (dq, J_HH = 11.9 Hz, J_HF = 7.6 Hz, 6H), +1.11 (dt, J_HH = 18.4 Hz, J_HF = 7.6 Hz, 9H); ^19F NMR (470.67 MHz, CD_2Cl_2, 25 °C, δ): −63.1 (s, 12F), −131.8 (m, 2F), −158.9 (t, J_FF = 19.9 Hz, 1F), −163.9 (m, 2F).</td>
</tr>
<tr>
<td>4–OPEt_3</td>
<td>^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +7.79 (s, 6H), +7.74 (s, 3H), +1.68 (dq, J_HH = 11.9 Hz, J_HF = 7.7 Hz, 6H), +1.10 (dt, J_HH = 18.2 Hz, J_HF = 7.7 Hz, 9H); ^19F NMR (470.67 MHz, CD_2Cl_2, 25 °C, δ): −63.1 (s, 18F).</td>
</tr>
<tr>
<td>5–OPEt_3</td>
<td>^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +7.90 (s, 4H), +7.75 (s, 2H); ^19F NMR (470.67 MHz, CD_2Cl_2, 25 °C, δ): −63.1 (s, 12F).</td>
</tr>
<tr>
<td>6–OPEt_3</td>
<td>^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +7.94 (s, 2H), +7.65 (s, 1H); ^19F NMR (470.67 MHz, CD_2Cl_2, 25 °C, δ): −62.9 (s, 6F).</td>
</tr>
<tr>
<td>7–OPEt_3</td>
<td>no adduct formation</td>
</tr>
<tr>
<td>8–OPEt_3</td>
<td>^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +2.00 (br.m, 6H), +1.00 (br.m, 9H); ^19F NMR (470.67 MHz, CD_2Cl_2, 25 °C, δ): −130.0 (br.m, 1F), −133.1 (br.m, 1F), −158.5 (br.m, 1F), −164.0 (br.m, 1F), −165.9 (br.m, 1F).</td>
</tr>
<tr>
<td>9–OPEt_3</td>
<td>^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +1.96 (dq, J_HH = 12.4 Hz, J_HF = 7.7 Hz, 6H), +1.02 (dt, J_HH = 18.8 Hz, J_HF = 7.7 Hz, 9H); ^19F NMR (470.67 MHz, CD_2Cl_2, 25 °C, δ): −133.1 (m, 2F), −158.8 (t, J_FF = 20.3 Hz, 1F), −164.8 (m, 2F).</td>
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</table>

If resonances corresponding to the ethyl groups of the adduct are not specified, the resonances are co-incident with / obscured by free Et_3PO: ^1H NMR (500.21 MHz, CD_2Cl_2, 25 °C, δ): +1.64 (dq, J_HH = 11.7 Hz, J_HF = 7.7 Hz), +1.11 (dt, J_HH = 16.1 Hz, J_HF = 7.7 Hz) ^11B NMR (160.49 MHz, CD_2Cl_2, 25 °C, δ) and ^31P{^1H} NMR (202.49 MHz, CD_2Cl_2, 25 °C, δ) spectral data reported in Table 3.
**Figure S5**  Correlation between: (a) $E^\circ$(borane) and $\delta_B$(borane); (b) $E^\circ$(borane) and $\delta_P$(adduct); (c) $E^\circ$(borane) and $\delta_B$(adduct); (d) $\delta_B$(borane) and $\delta_P$(adduct); (e) $\delta_B$(borane) and $\delta_B$(adduct); (f) $\delta_P$(adduct) and $\delta_B$(adduct).
SUPPLEMENTARY INFORMATION

H₂ cleavage by FLPs

Equimolar quantities of B(Ar')₂(Ar'') (Lewis acid) and P('Bu)₃ (Lewis base) are combined in ca. 0.8 cm³ CD₂Cl₂ (ca. 40 mM acid/base concentrations) in an NMR tube fitted with a J.Young valve. ¹H, ¹¹B, ¹⁹F and ³¹P{¹H} NMR spectra are obtained. The solution is degassed in the NMR tube by three freeze-pump-thaw cycles, before being frozen and the head-space of the NMR tube filled with dry H₂. The NMR tube is allowed to warm to room temperature (giving a H₂ pressure of ca. 4 bar), shaken, and the resulting reaction monitored by ¹H and ¹¹B NMR spectroscopy. (Spectra obtained at intervals between 90 min and 12 hours until reaction reaches completion / spectra cease changes). Upon completion of the reaction a final set of ¹H, ¹¹B, ¹⁹F and ³¹P{¹H} NMR spectra are obtained (data reported in Tables 4 and S2). Reaction mixture was maintained at room temperature (ca. +20 °C) throughout.

Table S2 NMR spectral data for the terminal hydride, H₂ cleavage products for the 1-9/P('Bu)₃ FLPs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ)</th>
<th>¹¹B NMR (160.49 MHz, CD₂Cl₂, 25 ºC, δ) spectral data reported in Table 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HP('Bu)₃]⁺</td>
<td>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ): +5.12 (d, ¹J_HP = 430 Hz, 1H), +1.58 (d, ³¹J_HP = 15.7 Hz, 27H); ³¹P{¹H} NMR (202.49 MHz, CD₂Cl₂, 25 ºC, δ): +59.8 (s).</td>
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<tr>
<td>[H1]⁻</td>
<td>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ): +3.60 (br.q, ¹J_HB = 93.9 Hz, 1H); ¹⁹F NMR (470.67 MHz, CD₂Cl₂, 25 ºC, δ): −133.6 (m, 6F), −163.4 (m, 3F), −166.7 (m, 6F).</td>
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<tr>
<td>[H2]⁻</td>
<td>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ): +7.74 (s, 4H), +7.51 (s, 2H), +3.71 (br.q, ¹J_HB = 86.1 Hz, 1H); ¹⁹F NMR (470.67 MHz, CD₂Cl₂, 25 ºC, δ): −62.5 (s, 6F), −131.6 (m, 4F), −163.9 (t, ³¹J_FF = 19.9 Hz, 2F), −166.8 (m, 4F).</td>
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</tr>
<tr>
<td>[H3]⁻</td>
<td>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ): +7.75 (s, 4H), +7.51 (s, 2H), +3.71 (br.q, ¹J_HB = 86.1 Hz, 1H); ¹⁹F NMR (470.67 MHz, CD₂Cl₂, 25 ºC, δ): −62.5 (s, 6F), −131.8 (br.m, 1F), −163.6 (t, ³¹J_FF = 19.9 Hz, 1F), −166.0 (m, 2F).</td>
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</tr>
<tr>
<td>[H4]⁻</td>
<td>no terminal hydride formation</td>
<td></td>
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<tr>
<td>[H5]⁻</td>
<td>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ): +7.75 (s, 4H), +7.48 (s, 2H), +4.22 (br.q, ¹J_HB = 86.1 Hz, 1H); ¹⁹F NMR (470.67 MHz, CD₂Cl₂, 25 ºC, δ): −62.5 (s, 2F).</td>
<td></td>
</tr>
<tr>
<td>[H6]⁻</td>
<td>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ): +7.63 (br.s, 2H), +7.47 (s, 1H), +4.24 (br.q, ¹J_HB = 88.0 Hz, 1H); ¹⁹F NMR (470.67 MHz, CD₂Cl₂, 25 ºC, δ): −62.5 (s, 6F).</td>
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</tr>
<tr>
<td>[H7]⁻</td>
<td>no reaction</td>
<td></td>
</tr>
<tr>
<td>[H8]⁻</td>
<td>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ): +4.11 (br.q, ¹J_HB = 86.1 Hz, 1H); ¹⁹F NMR (470.67 MHz, CD₂Cl₂, 25 ºC, δ): −133.9 (m, 4F), −164.8 (m, 2F), −167.7 (m, 4F).</td>
<td></td>
</tr>
<tr>
<td>[H9]⁻</td>
<td>¹H NMR (500.21 MHz, CD₂Cl₂, 25 ºC, δ): +3.94 (br.q, ¹J_HB = 90.0 Hz, 1H); ¹⁹F NMR (470.67 MHz, CD₂Cl₂, 25 ºC, δ): −133.5 (m, 4F), −164.9 (m, 2F), −167.6 (m, 4F).</td>
<td></td>
</tr>
</tbody>
</table>
Figure S6a  $^1$H NMR spectra showing the progress of H$_2$ cleavage by the I/P(Bu)$_3$ FLP post H$_2$ addition spectra at ca. 90 min intervals

Figure S6b  $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the I/P(Bu)$_3$ FLP post H$_2$ addition spectra at ca. 90 min intervals
**Figure S7a**  $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 2/P(Bu)$_3$ FLP post H$_2$ addition spectra at ca. 90 min intervals

**Figure S7b**  $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 2/P(Bu)$_3$ FLP post H$_2$ addition spectra at ca. 90 min intervals
**Figure S8a**  1H NMR spectra showing the progress of H₂ cleavage by the 3/P(‘Bu)₃ FLP post H₂ addition, 12 spectra at ca. 90 min intervals, subsequently at ca. 12 hour intervals.

**Figure S8b**  11B NMR spectra showing the progress of H₂ cleavage by the 3/P(‘Bu)₃ FLP post H₂ addition, 12 spectra at ca. 90 min intervals, subsequently at ca. 12 hour intervals.
Figure S9a  \(^1\)H NMR spectra showing the progress of \(\text{H}_2\) cleavage by the \(\text{4/P('Bu)}_3\) FLP post \(\text{H}_2\) addition spectra at ca. 90 min intervals

Figure S9b  \(^{11}\)B NMR spectra showing the progress of \(\text{H}_2\) cleavage by the \(\text{4/P('Bu)}_3\) FLP post \(\text{H}_2\) addition spectra at ca. 90 min intervals
**Supplementary Information**

*Figure S10a* $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 5/P(tBu)$_3$ FLP post H$_2$ addition spectra at ca. 8 hour intervals

*Figure S10b* $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 5/P(tBu)$_3$ FLP post H$_2$ addition spectra at ca. 8 hour intervals
**Figure S11a** $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 6/P(tBu)$_3$ FLP post H$_2$ addition spectra at ca. 8 hour intervals

**Figure S11b** $^1$B NMR spectra showing the progress of H$_2$ cleavage by the 6/P(tBu)$_3$ FLP post H$_2$ addition spectra at ca. 8 hour intervals
**Figure S12a** $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 7/Pt(Bu)$_3$ FLP post H$_2$ addition spectra at ca. 12 hour intervals

**Figure S12b** $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 7/Pt(Bu)$_3$ FLP post H$_2$ addition spectra at ca. 12 hour intervals
**Figure S13a** $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 8/P(Bu)$_3$ FLP post H$_2$ addition spectra at ca. 12 hour intervals

**Figure S13b** $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 8/P(Bu)$_3$ FLP post H$_2$ addition spectra at ca. 12 hour intervals
**Figure S14a** $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 9/P('Bu)$_3$ FLP post H$_2$ addition spectra at ca. 90 min intervals

**Figure S14b** $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 9/P('Bu)$_3$ FLP post H$_2$ addition spectra at ca. 90 min intervals