SUPPLEMENTARY INFORMATION

H₂ activation using the first 1:1:1 hetero-tri(aryl)borane

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Figure S1  X-ray crystallographic structure of $\text{B(C₆F₅)}\{3,5-(\text{CF₃})₂\text{C₆H₃}\}(\text{C₆Cl₃})$ 3

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“Gutmann-Beckett method” for measurement of Lewis acidity

3 (Lewis acid) is combined with a three-fold excess of OPEt3 (Lewis base) in ca. 0.8 cm³ CD₂Cl₂ in a NMR tube, rapidly generating the Lewis acid-base adduct Et₃PO–3, and ¹H, ¹¹B, ¹⁹F and ³¹P{¹H} NMR spectra obtained.

Et₃POB(C₆F₅){3,5-(CF₃)₂C₆H₃}(C₆Cl₅)  Et₃PO–3

¹H NMR (500.2 MHz, CD₂Cl₂, 25 °C, δ): +7.81 (s, 2H, ArF₆ 2,6-H), +7.68 (s, 1H, ArF₆ 4-H), +1.89 (br.m, 6H, Et CH₂), +1.10 (br.m, 9H, Et CH₃); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): +2.51 (br.s);
¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): −62.9 (s, 6F, ArF₆ 3,5-CF₃), −131.3 (m, 2F, ArF₅ 2,6-F), −158.8 (t, ³JFF = 19.9 Hz, 1F, ArF₅ 4-F), −163.8 (m, 2F, ArF₅ 3,5-F), ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 25 °C, δ): +76.49 (s).
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**H₂ cleavage by FLPs**

Equimolar quantities (ca. 30 µmol) of Lewis acid (3) and Lewis base (either P(Bu)₃, 2,2,6,6-tetramethylpiperidine (tmp), or 2,6-lutidine) are combined in ca. 0.8 cm³ CD₂Cl₂ in a 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 1 bar H₂ (dried by passing through a P₂O₅ column). The NMR tube is allowed to warm to room temperature, shaken, and the resulting reaction monitored by ¹H and ¹¹B NMR spectroscopy. A final set of ¹H, ¹¹B, ¹⁹F and ³¹P {¹H} NMR spectra are then obtained.

\[ \text{[P(Bu)₃]HF[HB(C₆F₅)₂(C₆H₃)(C₆Cl₃)]} \] [P(Bu)₃HF][H–3]

Spectral data at 57% conversion (164 hours reaction time).

¹H NMR (500.2 MHz, CD₂Cl₂, 25 °C, δ): +7.68 (s, 2H, ArF₆ 2,6-H), +7.47 (s, 1H, ArF₆ 4-H), +5.10 (d, J⁹HF = 430 Hz, 1H), +4.08 (br.q, J₁HF = 88 Hz, 1H), +1.61 (d, J¹HF = 15.7 Hz, 27H); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): −14.3 (d, J₁HB = 88 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): −62.3 (s, 6F, ArF₆ 3,5-CF₃), −130.8 (br.m, 2F, ArF₅ 2,6-F), −160.4 (t, J₆FF = 20.3 Hz, 1F, ArF₅ 4-F), −167.2 (m, 2F, ArF₅ 3,5-F); ³¹P {¹H} NMR (202.5 MHz, CD₂Cl₂, 25 °C, δ): +59.9 (s).

\[ \text{[Me₃H₂C₆NH₂]HF[HB(C₆F₅)₂(C₆H₃)(C₆Cl₃)]} \] [tmp–H][H–3]

Spectral data at 38% conversion (164 hours reaction time); resonances for tmp correspond to a rapid equilibrium between [tmp–H]⁺ and free tmp.

¹H NMR (500.2 MHz, CD₂Cl₂, 25 °C, δ): +7.63 (s, 2H, ArF₆ 2,6-H), +7.52 (s, 1H, ArF₆ 4-H), +3.98 (br.q, J₁HF = 84 Hz, 1H), +2.90 (vbr.s, tmp NH₂), +1.67 (m, tmp 4-H), +1.42 (m, tmp 3,5-H), +1.17 (s, tmp 2,6-CH₃); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): −13.9 (d, J₁HB = 84 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): −62.5 (s, 6F, ArF₆ 3,5-CF₃), −130.9 (br.m, 2F, ArF₅ 2,6-F), −162.9 (t, J₆FF = 20.3 Hz, 1F, ArF₅ 4-F), −165.9 (m, 2F, ArF₅ 3,5-F).

\[ \text{[Me₃H₂C₆NH]HF[HB(C₆F₅)₂(C₆H₃)(C₆Cl₃)]} \] [lutidine–H][H–3]

Spectral data at 64% conversion (164 hours reaction time); resonances for lutidine correspond to a rapid equilibrium between [lutidine–H]⁺ and free lutidine.

¹H NMR (500.2 MHz, CD₂Cl₂, 25 °C, δ): +7.67 (s, 2H, ArF₆ 2,6-H), +7.62 (t, J₃HF = 7.7 Hz, lutidine 4-H), +7.45 (s, 1H, ArF₆ 4-H), +7.09 (d, J₃HF = 7.7 Hz, lutidine 3,5-H), +4.08 (br.q, J₁HF = 88 Hz, 1H), +2.50 (s, lutidine 2,6-CH₃); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): −14.3 (d, J₁HB = 88 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): −62.4 (s, 6F, ArF₆ 3,5-CF₃), −131.0 (br.m, 2F, ArF₅ 2,6-F), −160.5 (t, J₆FF = 21.2 Hz, 1F, ArF₅ 4-F), −167.3 (m, 2F, ArF₅ 3,5-F).
**Figure S2a** $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 3/P('Bu)$_3$ FLP

**Figure S2b** $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 3/P('Bu)$_3$ FLP
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*Figure S3a*  $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 3/tmp FLP

*Figure S3b*  $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 3/tmp FLP
**SUPPLEMENTARY INFORMATION**

*Figure S4a* $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 3/lutidine FLP

*Figure S4b* $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 3/lutidine FLP
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>90% consumed 3, is converted to the target H₂ cleavage product [H–3]⁻; non-negligible by-products are however observed in reactions where the Lewis base is P(Bu)₃ (Figure S2) or tmp (Figure S3). The signals in the range δB = -4 - +4 ppm are indicative of tetrahedral boron and it is speculated that these are the water adduct 3–OH₂, or the hydroxide [3–OH]⁻. Similarly, this explains the by-product resonances observable in aromatic region of the ¹H spectra.

**Figure S5**  Percentage conversion of 3 to [H–3]⁻ (monitored by ¹H NMR spectroscopy of ArF₆ 2,6-/4-H resonances), by reaction of a FLP with H₂ in CD₂Cl₂ at 20 °C, with varying Lewis base:

● P(Bu)₃, ▲ tmp, ■ lutidine.