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

Robin J. Blagg and Gregory G. Wildgoose

School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, NR4 7TJ, U.K.

Figure S1  X-ray crystallographic structure of $\text{B}(\text{C}_6\text{F}_5)\{3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3\}(\text{C}_6\text{Cl}_5)_3$
“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(C₄F₅){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, ³J₉F = 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).
**SUPPLEMENTARY INFORMATION**

H₂ cleavage by FLPs

Equimolar quantities (ca. 30 µmol) of Lewis acid (3) and Lewis base {either P(Ph)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.

[(⁺⁻Bu)₃PF][HB(C₆F₃)₃(3,5-(CF₃)₂C₆H₃)(C₆Cl₃)]  [(⁺⁻Bu)₃PF][H⁺–H⁻]  [(⁺⁻Bu)₃PF][H⁺]

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

¹H NMR (500.2 MHz, CD₂Cl₂, 25 °C, δ): +7.68 (s, 2H, Ar¹F, 2,6-H), +7.47 (s, 1H, Ar¹F 4-H), +5.10 (d, JHP = 430 Hz, 1H), +4.08 (br.q, JHH = 88 Hz, 1H), +1.61 (d, JHP = 15.7 Hz, 27H); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): −14.3 (d, JHH = 88 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): −62.3 (s, 6F, Ar¹F 3,5-CF₃), −130.8 (br.m, 2F, Ar¹F 2,6-F), −160.4 (t, JFF = 20.3 Hz, 1F, Ar¹F 4-F), −167.2 (m, 2F, Ar¹F 3,5-F); ³¹P {¹H} NMR (202.5 MHz, CD₂Cl₂, 25 °C, δ): +59.9 (s).

[Me₂H₂C₂NH₂][HB(C₆F₃)₃(3,5-(CF₃)₂C₆H₃)(C₆Cl₃)]  [tmp–H⁺][H⁻–H⁻]  [tmp–H⁺]  [tmp–H⁻]  [tmp–H⁺][H⁻]  [tmp–H⁻][H⁺]

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, Ar¹F, 2,6-H), +7.52 (s, 1H, Ar¹F 4-H), +3.98 (br.q, JHP = 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, JHH = 88 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): −62.5 (s, 6F, Ar¹F 3,5-CF₃), −130.9 (br.m, 2F, Ar¹F 2,6-F), −162.9 (t, JFF = 20.3 Hz, 1F, Ar¹F 4-F), −165.9 (m, 2F, Ar¹F 3,5-F).

[Me₂H₂C₂NH][HB(C₆F₃)₃(3,5-(CF₃)₂C₆H₃)(C₆Cl₃)]  [lutidine–H⁺][H⁻–H⁻]  [lutidine–H⁺]  [lutidine–H⁻]  [lutidine–H⁺][H⁻]  [lutidine–H⁻][H⁺]

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, Ar¹F, 2,6-H), +7.62 (t, JHH = 7.7 Hz, lutidine 4-H), +7.45 (s, 1H, Ar¹F 4-H), +7.09 (d, JHH = 7.7 Hz, lutidine 3,5-H), +4.08 (br.q, JHP = 88 Hz, 1H), +2.50 (s, lutidine 2,6-CH₃); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): −14.3 (d, JHH = 88 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): −62.4 (s, 6F, Ar¹F 3,5-CF₃), −131.0 (br.m, 2F, Ar¹F 2,6-F), −160.5 (t, JFF = 21.2 Hz, 1F, Ar¹F 4-F), −167.3 (m, 2F, Ar¹F 3,5-F).
Figure S2a  $^1$H NMR spectra showing the progress of H$_2$ cleavage by the 3/P(tBu)$_3$ FLP.

Figure S2b  $^{11}$B NMR spectra showing the progress of H$_2$ cleavage by the 3/P(tBu)$_3$ FLP.
**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
**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
SUPPLEMENTARY INFORMATION

>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(tBu)₃ (Figure S2) or tmp (Figure S3). The signals in the range δ_B ≈ -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 Ar²F₅ 2,6-/4-H resonances), by reaction of a FLP with H₂ in CD₂Cl₂ at 20 °C, with varying Lewis base:

- ● P(tBu)₃
- ▲ tmp
- ■ lutidine.