Supporting Information for:

Hydroboration of an Alkene by Amine-Borane Catalysed by a \([\text{Rh(PR}_3)_2]^+\) fragment. Mechanistic Insight and Tandem Hydroboration/Dehydrogenation.

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**Experimental**

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk and glove-box techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. Pentane was dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles. 1-t-buty lethene (TBE) was dried over sodium, vacuum distilled and stored over 3 Å molecular sieves. 1,2-C₆H₄F₂ and CD₂Cl₂ were dried over CaH₂, vacuum distilled and stored over 3 Å molecular sieves. H₃B·NMe₃ was purchased from Aldrich and sublimed before use (5 × 10⁻² Torr, 298 K). H₃B·NMe₂H was purchased from Acros and sublimed twice before use (5 × 10⁻² Torr, 298 K). Na[BARF₄]₂, [Rh(P₂Bu₃tBu)₂][BARF₄] (B) were prepared by literature methods. All other chemicals are commercial products and were used as received. NMR spectra were recorded on a Varian Mercury VX 300 MHz or a Varian Unity Plus 500 MHz spectrometer at room temperature. In 1,2-C₆H₄F₂, ¹H NMR spectra were referenced to the centre of the downfield solvent multiplet (δ = 7.07). ³¹P NMR spectra and ¹¹B NMR spectra were referenced externally against 85% H₃PO₄ and BF₃.OEt₂ respectively. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicrOTOF-Q instrument interfaced with a glovebox. Microanalyses were performed by Elemental Microanalysis Ltd.

**Synthesis of new complexes**

[Rh(P₂Bu₃tBu)₂][BARCl₄]

Preparation same as the literature procedure for B substituting [BARF₄]¹⁻ for [BARCl₄]¹⁻ (ArCl₄⁻ = 3,5-C₆H₅Cl₂). Yield: 65 %.

¹H NMR (CD₂Cl₂, 500 MHz): δ 7.04 – 6.99 (m, 12H, BARCl₄), 1.90 – 1.74 (m, 8H, ’Bu{CH/CH₂}), 1.72 – 1.63 (m, 4H, ’Bu{CH₂}), 1.14 (dd, 18H, J = 7.5, J = 7.3, ’Bu{Me}), 1.00 – (–0.80) (br, 24H, ’Bu{Me}).

³¹P {¹H} NMR (CD₂Cl₂, 202 MHz): δ 64.2 (br).

[Rh(P₂Bu₂Bu)₂(η²-Me₂N₃H₂BCH₂CH₂CMe₃)][BARF₄] (2)

1,2-C₆H₄F₂ (1 mL) was added to a Young’s crystallisation tube containing B (0.050 g, 0.037 mmol) and H₃BNMe₃ (0.0027 g, 0.037 mmol). TBE (24 µL, 0.183 mmol) was then added and the tube sealed. After 5 days the purple solution was layered with pentane and held at 5 °C yielding the product as deep
purple crystals. Yield: 0.042 g (72 %). Crystals suitable for single crystal X-ray diffraction were grown by using \( \text{Rh} (\text{PBu}_2 \text{Bu})_2 [\text{BAR}^\text{Cl}_4] \).

\(^1\text{H} \text{NMR} \) (1,2-\( \text{C}_6\text{H}_4\text{F}_2 \), 500 MHz): \( \delta \) 8.34 (s, 8H, BAR\(^{\text{Cl}_4}\)), 7.69 (s, 4H, BAR\(^{\text{Cl}_4}\)), 2.94 (s, 9H, NMe\(^3\)), 2.18 (br, 4H, \( ^{1}\text{Bu}\{\text{CH}\} \)), 1.97 – 1.79 (m, 8H, \( ^{1}\text{Bu}\{\text{CH}_2\} \)), 1.73 – 1.70 (m, 2H, CH\(_2\)), 1.34 – 1.20 (m, 44H, \( ^{1}\text{Bu}\{\text{Me}\}, ^{1}\text{Bu}\{\text{Me}\}, \text{CH}_2 \)), 1.02 (s, 9H, C\{Me\}), -7.07 (br, 2H, BH\(_2\)).

\(^{11}\text{B} \text{NMR} \) (1,2-\( \text{C}_6\text{H}_4\text{F}_2 \), 160 MHz): \( \delta \) -0.83 (t, \( ^{1}\text{J}_{\text{BH}} = 96 \)).

**Catalytic Formation of 3**

1,2-\( \text{C}_6\text{H}_4\text{F}_2 \) (435 L) and TBE (15 L, 0.117 mmol) were added to a high pressure NMR tube containing B (0.0080 g, 0.006 mmol) and H\(_3\)B-NMe\(_3\) (0.0085 g, 0.117 mmol). The tube was sealed and in situ analysis by \(^1\text{H} \) and \(^{11}\text{B} \) NMR spectroscopy indicated the formation of 3. Only ~70% conversion is achieved with ~ 30% H\(_3\)B-NMe\(_3\) unreacted.

\(^1\text{H} \text{NMR} \) (1,2-\( \text{C}_6\text{H}_4\text{F}_2 \), 500 MHz): \( \delta \) 2.51 (s, 9H, NMe\(^3\)), 2.40 – 1.93 (m, 2H, BH\(_2\)), 1.43 – 1.40 (m, 2H, CH\(_2\)CH\(_2\)CMe\(_3\)), 1.02 (s, 9H, CMe\(_3\)), 0.55 (br, 2H, CH\(_2\)CH\(_2\)CMe\(_3\)).

\(^{11}\text{B} \text{NMR} \) (1,2-\( \text{C}_6\text{H}_4\text{F}_2 \), 160 MHz): \( \delta \) -0.83 (t, \( ^{1}\text{J}_{\text{BH}} = 96 \)).

**Oxidation of 3**

1,2-\( \text{C}_6\text{H}_4\text{F}_2 \) (0.4 mL) and TBE (350 \( \mu \text{L} \), 1.4 mmol) were added to a Young’s NMR tube containing B (0.038 g, 0.028 mmol) and H\(_3\)B-NMe\(_3\) (0.100 g, 1.371 mmol). After 6 days the solution was transferred to a round bottomed flask and THF (2 mL) followed by EtOH (2 mL), NaOH (2M, 2 mL) and H\(_2\)O\(_2\) (35%
aq. solution, 3 mL) were added. The solution was stirred at 40 °C for 16 hours to ensure complete oxidation. The reaction mixture was extracted with Et₂O (3 x 20 mL), and the organic phase washed with a 2M aq. NaOH solution (20 mL), H₂O (20 mL) and finally brine (20 mL). The organic layer was dried over MgSO₄, filtered and concentrated to yield the expected HOCH₂CH₂Bu as the only product (¹H NMR spectroscopy).

**Kinetics**

5 mol% of B

1,2-C₆H₄F₂ (435 µL) and TBE (15 µL, 0.117 mmol) were added to a high pressure NMR tube containing B (0.0080 g, 0.006 mmol) and H₃B·NMe₃ (0.0085 g, 0.117 mmol). The sample was shaken twice and then immediately followed by ¹¹B NMR spectroscopy. Catalysis had slowed dramatically at ~70% completion at which point the solution was transferred to another NMR tube containing a further 20 equivalents of TBE (15 µL, 0.117 mmol) and H₃B·NMe₃ (0.0085 g, 0.117 mmol). Catalysis was seen to restart at a slightly lower initial rate (1 x 10⁻⁶ Ms⁻¹ versus 4 x 10⁻⁶ Ms⁻¹).

![Figure S-1: Plot of concentration versus time for the hydroboration of TBE by H₃B·NMe₃ catalysed by B (5 mol%)](image)
10 mol% of B

1,2-C₆H₄F₂ (435 µL) and TBE (15 µL, 0.117 mmol) were added to a high pressure NMR tube containing B (0.0160 g, 0.0117 mmol) and H₃B·NMe₃ (0.0085 g, 0.117 mmol). The sample was shaken twice and then immediately followed by ¹¹B NMR spectroscopy. An initial rate of $7 \times 10^{-6}$ M s⁻¹ was seen over the first 2100 seconds.
2 fold excess of TBE at 5 mol% of B

1,2-C₆H₄F₂ (420 µL) and TBE (30 µL, 0.234 mmol) were added to a high pressure NMR tube containing B (0.0080 g, 0.006 mmol) and H₃B·NMe₃ (0.0085 g, 0.117 mmol). The sample was shaken twice and then immediately followed by ¹¹B NMR spectroscopy. An initial rate of 8 x 10⁻⁶ Ms⁻¹ was seen over the first 2100 seconds.

![Graph](image1.png)

Figure S-4: Initial rate over 2100 seconds with a 2 fold excess of TBE (5 mol% B)

10 fold excess of TMAB at 5 mol% of B

1,2-C₆H₄F₂ (435 µL) and TBE (15 µL, 0.117 mmol) were added to a high pressure NMR tube containing B (0.0080 g, 0.006 mmol) and H₃B·NMe₃ (0.085 g, 1.17 mmol). The sample was shaken twice and then immediately followed by ¹¹B NMR spectroscopy. An initial rate of 4 x 10⁻⁶ Ms⁻¹ was seen over the first 2100 seconds.

![Graph](image2.png)

Figure S-5: Initial rate over 2100 seconds with a 10 fold excess of TMAB (5 mol% B)
**Equilibrium constant**

350 $\mu$L of a 0.0187 M solution of $\text{H}_3\text{B-NMe}_3$ in 1,2-$\text{C}_6\text{H}_4\text{F}_2$ was added to a high pressure NMR tube containing 2 (0.010 g, 0.0065 mmol). After 3 hours, analysis by $^1\text{H}$ NMR spectroscopy gave an equilibrium constant, $K$ of 1.62.

$$K = \frac{[2][\text{TMAB}]}{[1][3]}$$

**DMAB + TBE**

10 fold excess of TBE at 5 mol%

A solution of DMAB (0.0086 g, 0.146 mmol) in 1,2-$\text{C}_6\text{H}_4\text{F}_2$ (2 mL) was added dropwise with stirring over a period of 30 minutes to a Young's flask containing $\text{B}$ (0.010 g, 7.3x10$^{-3}$ mmol), TBE (0.188 mL, 1.46 mmol) and 1,2-$\text{C}_6\text{H}_4\text{F}_2$ (3 mL). After 2 hours, analysis by $^{11}\text{B}$ NMR spectroscopy showed 3 major products; 4, 5 and [H$_2$BNMe$_2$]$_2$.

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**Figure S-6:** $^{11}\text{B}$ NMR spectrum from the reaction of H$_3$B-NMe$_3$H and TBE catalysed by B (5 mol%) showing tandem hydroboration/dehydrogenation. (R = CH$_2$CH$_2$Bu)
References