# Electronic Supporting Information for 'Double Addition of H<sub>2</sub> to Transition Metal–Borane Complexes: a 'Hydride Shuttle' Process Between Boron and Transition Metal Centres'

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#### Experimental

General considerations: All manipulations were performed in a Braun glovebox with an O<sub>2</sub> and H<sub>2</sub>O atmosphere of below 5 ppm or by using standard Schlenk techniques. K[Tai],<sup>S1</sup>  $[Rh(NBD)Cl]_2^{S2}$  and  $2^{S3}$  were prepared according to literature procedures. PCyp<sub>3</sub> (Cyp = cyclopentyl) was purchased from Aldrich and was stored in the glovebox in a Young's ampoule as a 50 mg/mL solution in toluene. P<sup>t</sup>Bu<sub>3</sub> was purchased from Strem and was kept in the glovebox. PMe<sub>3</sub> was purchased from Aldrich as a 1.0 M solution in THF and stored in a Young's ampoule. Toluene was dried by refluxing over K and distilled under a N<sub>2</sub> atmosphere. THF was dried over Na/benzophenone and distilled under a N2 atmosphere. DCM was dried using a Grubbs' alumina system and kept in Young's ampoules under N<sub>2</sub> over molecular sieves (4 Å). Dry n-pentane (<0.05 ppm H<sub>2</sub>O) was purchased from Fluka and was kept in a flame-dried Young's ampoule under N<sub>2</sub> over molecular sieves (4 Å). Deuterated toluene and C<sub>6</sub>D<sub>6</sub> were degassed by three freeze-thaw cycles, dried by refluxing over K or Na/benzophenone respectively for 12 hours, vacuum distilled and kept in a flamedried Young's ampoule over 4 Å molecular sieves under N<sub>2</sub>. <sup>1</sup>H-NMR, <sup>11</sup>B{<sup>1</sup>H}-NMR, <sup>11</sup>B-NMR and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra were recorded on a JEOL ECP300 spectrometer operating at 300 MHz (<sup>1</sup>H). <sup>1</sup>H{<sup>11</sup>B}-NMR experiments were recorded on a JEOL Lamda 300 spectrometer operating at 300 MHz (<sup>1</sup>H). <sup>13</sup>C{<sup>1</sup>H}-NMR spectra and correlation experiments were recorded on a Varian VNMR S500 operating at 500 MHz (<sup>1</sup>H). The spectra were referenced internally, to the residual protic solvent  $(^{1}H)$  or the signals of the solvent  $(^{13}C)$ . <sup>11</sup>B{<sup>1</sup>H}-NMR and <sup>11</sup>B-NMR spectra were referenced externally relative to BF<sub>3</sub>•OEt<sub>2</sub>.  ${}^{31}P{}^{1}H$ -NMR were referenced externally relative to 85% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O. Mass spectra were recorded on a VG Analytic Quattro in ESI<sup>+</sup> mode. Elemental analyses were performed at the microanalytical laboratory of the School of Chemistry at the University of Bristol. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR spectrometer (solid state, neat) from 4000 cm<sup>-1</sup> to 650 cm<sup>-1</sup>.

### [Rh{ $\kappa^3$ -*NNB*-B(azaindolyl)<sub>3</sub>}(nortricycle)(PMe<sub>3</sub>)] (3):

A sample of  $[Rh \{\kappa^4-NNBN-B(azaindolyl)_3\}(nortricyclyl)]$  (2) (80 mg, 0.143 mmol) was charged into a Schlenk flask in the glovebox. The compound was dissolved in DCM (10 mL) and PMe<sub>3</sub> (190 µL of 1.0 M solution in THF, 1.3 mol eq.) was subsequently added. The colour of the solution changed from pink-orange to bright yellow and the reaction mixture stirred at room temperature overnight. After this time, all volatiles were removed and the residue extracted with pentane, (5-10 mL) and filtered. The pentane filtrate was left to stand at room temperature to yield yellow crystals of **3** which were isolated from the mother liquor by filtration and dried under vacuum. The spectroscopic data was consistent with the presence of two diasteromers in a ratio of 2:1 (A:B). Yield: 50 mg (55 %) Structural characterisation of a single crystal obtained from this sample also revealed a mixture of the two diastereomers in approximately 7: 3 ratio in the asymmetric unit.

<sup>1</sup>H-NMR ( $\delta$  CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): -0.20 (1H, m, nortricyclic, A), 0.34 (1H, t, <sup>3</sup>J<sub>HH</sub> = 5.5 Hz, nortricyclic, A), 0.61 (9H, dd,  ${}^{2}J_{PH} = 9.4$  Hz,  ${}^{3}J_{RhH} =$  unresolved, P(CH<sub>3</sub>)<sub>3</sub>, A), 0.63 (9H, dd,  ${}^{2}J_{\text{PH}} = 9.4 \text{ Hz}, {}^{3}J_{\text{RhH}} = \text{unresolved}, P(CH_{3})_{3}, \mathbf{B}), 0.66 (1H, m, nortricyclic, \mathbf{B}), 0.77 (2H, m, m)$ nortricyclic, B), 0.83 (1H, m, nortricyclic, A), 0.86 (1H, m, nortricyclic, B), 0.92 (2H, br s, nortricyclic, A), 1.01 (1H, m, nortricyclic, A), 1.27 (1H, br m, nortricyclic, A + 1H, br m, nortricyclic, **B**), 1.31 (1H, m, nortricyclic, **B**), 1.37 (1H, d,  ${}^{3}J_{\text{HH}} = 7.0$  Hz, nortricyclic, **B**), 1.62 (1H, d,  ${}^{3}J_{\text{HH}} = 9.5$  Hz, nortricyclic, A), 1.76 (1H, br s, nortricyclic, A), one signal corresponding to nortricyclic **B** was not located, 6.32 (1H, d,  ${}^{3}J_{HH} = 3.0$  Hz, 7-azaindole, **B**), 6.35 (1H, d,  ${}^{3}J_{HH} = 3.0$  Hz, 7-azaindole, A), 6.42 (1H, d,  ${}^{3}J_{HH} = 3.4$  Hz, 7-azaindole, A + 1H, d,  ${}^{3}J_{HH} = 3.4$  Hz, 7-azaindole, **B**), 6.54 (1H, d,  ${}^{3}J_{HH} = 3.4$  Hz, 7-azaindole, **A**), 6.57 (1H, d,  ${}^{3}J_{-1}$ <sub>HH</sub> = 3.4 Hz, 7-azaindole, **B**), 6.90 (2H, m, 7-azaindole, **A** + 2H, m, 7-azaindole, **B**), 6.97 (1H, m, 7-azaindole, A + 1H, m, 7-azaindole, B), 7.35 (1H, d,  ${}^{3}J_{HH} = 3.4$  Hz, 7-azaindole, A), 7.36 (1H, d,  ${}^{3}J_{\text{HH}}$  = 3.0 Hz, 7-azaindole, **B**), 7.39 (1H, d,  ${}^{3}J_{\text{HH}}$  = 3.0 Hz, 7-azaindole, **B**), 7.50  $(1H, d, {}^{3}J_{HH} = 3.4 \text{ Hz}, 7\text{-azaindole}, A), 7.59 (1H, d, {}^{3}J_{HH} = 3.4 \text{ Hz}, 7\text{-azaindole}, A), 7.63 (1H, d, {}^{3}J_{HH} = 3.4 \text{ Hz}, 7\text{-azaindole}, A)$ d,  ${}^{3}J_{HH} = 3.0$  Hz, 7-azaindole, **B**), 7.72 (1H, dd,  ${}^{4}J_{HH} = 1.2$  Hz,  ${}^{3}J_{HH} = 7.6$  Hz, 7-azaindole, **B**), 7.76 (2H, dd,  ${}^{4}J_{\text{HH}} = 1.2$  Hz,  ${}^{3}J_{\text{HH}} = 7.6$  Hz, 7-azaindole, A + 1H, overlapping with other signals, 7-azaindole, **B**), 7.87 (1H, dd, 7-azaindole, **A** + 1H, dd, 7-azaindole, **B**), 7.99 (1H, d, 7-azaindole, **A** + 1H, d, 7-azaindole, **B**), 8.09 (1H, dd,  ${}^{4}J_{HH} = 1.2$  Hz,  ${}^{3}J_{HH} = 4.9$  Hz, 7azaindole, A), 8.13 (1H, dd,  ${}^{4}J_{HH} = 1.2$  Hz,  ${}^{3}J_{HH} = 5.5$  Hz, 7-azaindole, B), 8.24 (1H, br s, 7azaindole, **A**), 8.27 (1H, br s, 7-azaindole, **B**). <sup>13</sup>C{<sup>1</sup>H}-NMR (δ CD<sub>2</sub>Cl<sub>2</sub>, 125.71 MHz): 11.5, 12.6, 12.8 (d,  ${}^{1}J_{RhC}$  = 29.3 Hz, P(CH<sub>3</sub>)<sub>3</sub>), 13.0, 13.2, 13.8 (d,  ${}^{1}J_{RhC}$  = 29.3 Hz, P(CH<sub>3</sub>)<sub>3</sub>), 18.6, 19.2 (d,  $J_{RhC} = 6.9$  Hz), 33.2 (d,  $J_{RhC} = 9.8$  Hz), 33.4 (d,  $J_{RhC} = 9.8$  Hz), 34.5 (CH<sub>2</sub>), 35.4 (CH<sub>2</sub>), 36.0 (CH<sub>2</sub>), 36.3, 37.4 (d, J<sub>RhC</sub> = 3.9 Hz), 100.9, 101.0, 102.8, 102.9, 115.0, 115.2, 115.5, 115.5, 120.5, 120.9, 124.0, 127.6, 127.7, 128.0, 128.4, 128.5, 129.4, 113.0, 132.7, 133.2, 134.9, 135.4, 140.0, 140.3, 140.4, 141.1, 141.3, 141.4, 141.8, 142.5, 152.4, 152.6, 153.0, 153.3, 153.8 (7-azaindolyl);  ${}^{11}B{}^{1}H{}-NMR$  ( $\delta$  CD<sub>2</sub>Cl<sub>2</sub>): -0.9 (unresolved multiplet signal,  $\mathbf{A} + \mathbf{B}$ ; <sup>11</sup>B-NMR ( $\delta$  CD<sub>2</sub>Cl<sub>2</sub>): -0.9 (unresolved multiplet signal,  $\mathbf{A} + \mathbf{B}$ ). <sup>31</sup>P{<sup>1</sup>H}-NMR ( $\delta$  CD<sub>2</sub>Cl<sub>2</sub>): 12.1 (d, <sup>1</sup>J<sub>RhP</sub> = 178.6 Hz, **A**), 11.9 (d, <sup>1</sup>J<sub>RhP</sub> = 180.5 Hz, **B**). MS (ESI<sup>+</sup>): 541.1  $[M-C_7H_9]^+$ ; Elem Anal.: Calc for C<sub>31</sub>H<sub>33</sub>BN<sub>6</sub>PRh•0.2 (n-pentane): C 59.24; H 5.50; N 12.95; Found: C 59.22; H 6.09; N 13.25.

## [Rh{k<sup>3</sup>-NNH-HB(azaindolyl)<sub>3</sub>}(H)<sub>2</sub>(PCyp<sub>3</sub>)] (4)

In a glovebox,  $[Rh{\kappa^4-NNBN-B(azaindolyl)_3}(nortricyclyl)]$  (2) (150 mg, 0.27 mmol), 1.07 mL of a 50 mg/mL solution of tricyclopentylphosphine (PCyp<sub>3</sub>) in toluene and a further 15 mL of dry toluene were charged in a thick wall Young's ampoule. The contents of the ampoule were placed under vacuum after two freeze-thaw pump cycles. The orange-pink solution was left to warm to RT and then was pressurised with 2.5 bar H<sub>2</sub> and placed in an oil-bath thermostated at 85 °C and left at this temperature for 18 h to give a yellow solution. The flask was then allowed to equilibrate at RT and the mixture was filtered through glassmicrofibre canulla. All volatiles were subsequently removed under vacuum and the residue extracted with n-pentane (2 x 10 mL) and filtered as above. The volume of the filtrate was reduced until a dusky yellow solution appeared, upon which time pumping was stopped, the Schlenk was refilled with Ar and heated gently to produce a homogeneous yellow solution which was placed in the freezer (-30 °C) overnight to give a yellow microcrystalline precipitate (which contained 4 contaminated with small quantities of 6) that was isolated by filtration and dried under vacuum. The filtrate was further reduced until a cream white solid started forming and was again placed in the freezer (-30 °C) for 24 h. The precipitate was isolated by filtration and washed at -80 °C with n-pentane (3 x 2 mL) and dried under vacuum to give 4 as a cream white solid (60 mg; 32%).

<sup>1</sup>H-NMR ( $\delta$  C<sub>6</sub>D<sub>6</sub>, 300 MHz): -16.30 (2H, m, Rh*H*), -4.25 (1H, br q, <sup>1</sup>*J*<sub>BH</sub> = 72.9 Hz, B*H*), 1.00-1.30 (13H, m, PCyp<sub>3</sub>), 1.31-1.42 (4H, m, PCyp<sub>3</sub>), 1.44-1.65 (7H, m, PCyp<sub>3</sub>), 1.66-1.82 (3H, m, PCyp<sub>3</sub>), 6.37 (4H, m, 7-azaindole), 6.66 (1H, d,  ${}^{3}J_{HH} = 2.9$  Hz, 7-azaindole), 6.88 (1H, dd,  ${}^{3}J_{HH} = 4.4$  Hz,  ${}^{3}J_{HH} = 8.8$  Hz, 7-azaindole), 7.27 (1H, d,  ${}^{3}J_{HH} = 7.3$  Hz, 7-azaindole), 7.32 (1H, d,  ${}^{3}J_{\text{HH}}$  = 8.8 Hz, 7-azaindole), 7.55 (1H, d,  ${}^{3}J_{\text{HH}}$  = 2.9 Hz, 7-azaindole), 7.65 (1H, d,  ${}^{3}J_{HH} = 2.9$  Hz, 7-azaindole), 7.67 (1H, d,  ${}^{3}J_{HH} = 4.4$  Hz, 7-azaindole), 7.81 (1H, dd,  ${}^{3}J_{HH} =$ 2.9 Hz,  ${}^{3}J_{HH} = 7.3$  Hz, 7-azaindole), 8.25 (1H, d,  ${}^{3}J_{HH} = 4.4$  Hz, 7-azaindole), 8.50 (1H, dd,  ${}^{3}J_{\text{HH}} = 4.4 \text{ Hz}, {}^{4}J_{\text{HH}} = 1.5 \text{ Hz}, 7\text{-azaindole}), 8.63 (1H, br s, 7\text{-azaindole}); {}^{1}H{}^{11}B{}-\text{NMR} (\delta$  $C_6D_6$ , 300 MHz): -16.32 (two overlapping dddd and ddd), -4.25 (br s);  ${}^{13}C{}^{1}H$ -NMR ( $\delta$ C<sub>6</sub>D<sub>6</sub>, 125.71 MHz): 26.6 (two coinciding d,  ${}^{2}J_{PC} = 8.8$  Hz,  ${}^{2}J_{PC} = 7.8$  Hz, CH<sub>2</sub>, PCyp<sub>3</sub>), 30.1 (s,  $CH_2$ ,  $PCyp_3$ ), 30.4 (d,  ${}^{3}J_{PC} = 2.0 \text{ Hz } CH_2$ ,  $PCyp_3$ ), 38.3 (d,  ${}^{1}J_{PC} = 29.4 \text{ Hz}$ , CH,  $PCyp_3$ ), 102.2, 102.6, 103.0, 115.1, 115.3, 116.0, 124.1, 124.2, 127.8, 128.7, 128.8, 129.0, 131.3, 133.0, 133.5, 142.7, 146.4, 148.5, 153.6, 154.0 (7-azaindolyl); <sup>11</sup>B{<sup>1</sup>H}-NMR (δ C<sub>6</sub>D<sub>6</sub>): -0.6 (s,  $\Delta v_{1/2} = 19.6 \text{ Hz}$ ); <sup>11</sup>B-NMR: ( $\delta C_6 D_6$ ): -0.6 (dd, <sup>1</sup>J<sub>BH</sub> = 72.9 Hz, <sup>2</sup>J<sub>BH</sub> = 16.5 Hz); <sup>31</sup>P{<sup>1</sup>H}-NMR ( $\delta C_6 D_6$ ): 72.7 (d,  ${}^1J_{RhP} = 134$  Hz,  $PCyp_3$ ); IR (neat): 2157 cm<sup>-1</sup>, 2048.7 cm<sup>-1</sup>, 1937.0 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): 707.3 [M+H]<sup>+</sup>; Elem. Anal.: Calc for C<sub>36</sub>H<sub>45</sub>BN<sub>6</sub>PRh, C 61.20; H 6.42; N 11.90; Found: C 61.77; H 6.40; N 11.62.

# $[Rh{\kappa^3-NNH-HB(azaindolyl)_3}(H)_2(P^tBu_3)] (5)$

In a glovebox,  $[Rh{\kappa^{4}-NNBN-B(azaindolyl)_{3}}(nortricycle)]$  (2) (150 mg, 0.27 mmol), P<sup>t</sup>Bu<sub>3</sub> (45.4 mg, 0.27 mmol) and toluene (15 mL) were charged into a thick wall Young's ampoule. The contents of the ampoule were placed under vacuum after two freeze-thaw pump cycles. The orange-pink solution was left to warm to RT and then was pressurised with 2.5 bar H<sub>2</sub> and placed in an oil-bath thermostated at 85 °C and heated overnight to give a brown yellow solution. The mixture was allowed to equilibrate at RT and filtered through glass-microfibre canulla. The NMR spectra of the reaction mixture revealed the presence of **5** and **6** in an approximately ratio of 4:1 as determined by <sup>11</sup>B{<sup>1</sup>H}-NMR and <sup>1</sup>H-NMR spectroscopy. All volatiles were subsequently removed under vacuum and the residue extracted with n-pentane (20 mL) and filtered as above. The yellow extract was then placed in the freezer (-30 °C) overnight to give a mixture of **5** and **6**. The mother liquor was isolated by filtration and placed in a -80 °C freezer to yield a cream white powder (10 mg) which was a pure sample of **5** and was isolated by filtration. The supernatant was reduced to half and stored at -80 °C to give a second crop of **5** (40 mg) which was contaminated by approx 25% P<sup>t</sup>Bu<sub>3</sub>. Further crops of **5** were only isolated after several recrystallisation steps.

<sup>1</sup>H-NMR ( $\delta C_6 D_6$ , 300 MHz): -17.21 (1H, br s, Rh*H*), -16.92 (1H, ddd, <sup>2</sup>*J*<sub>HH</sub> = 9.2 Hz, <sup>2</sup>*J*<sub>PH</sub> = 13.7 Hz,  ${}^{1}J_{RhH} = 28.4$  Hz, RhH), -0.70 (1H, q,  ${}^{1}J_{BH} = 77.6$  Hz, BH), 1.11 (27H, d,  ${}^{3}J_{PH} = 11.9$ Hz, P{C(CH<sub>3</sub>)<sub>3</sub>}), 6.27 (2H, m, 7-azaindole), 6.31 (1H, dd,  ${}^{3}J_{HH} = 3.7$  Hz,  ${}^{3}J_{HH} = 2.8$  Hz, 7azaindole), 6.50 (1H, dd,  ${}^{3}J_{HH} = 5.5$  Hz,  ${}^{3}J_{HH} = 7.3$  Hz, 7-azaindole), 6.67 (1H, d,  ${}^{3}J_{HH} = 3.7$ Hz, 7-azaindole), 6.90 (1H, dd,  ${}^{3}J_{HH} = 4.6$  Hz,  ${}^{3}J_{HH} = 8.3$  Hz, 7-azaindole), 7.21 (1H, dd,  ${}^{4}J_{HH}$ = 1.8 Hz,  ${}^{3}J_{HH}$  = 8.3 Hz, 7-azaindole), 7.29 (1H, dd,  ${}^{4}J_{HH}$  = 1.8 Hz,  ${}^{3}J_{HH}$  = 7.3 Hz, 7azaindole), 7.45 (1H, d,  ${}^{3}J_{HH} = 3.7$  Hz, 7-azaindole), 7.77 (1H, d,  ${}^{3}J_{HH} = 2.8$  Hz, 7-azaindole), 7.80 (1H, d,  ${}^{3}J_{HH} = 3.7$  Hz, 7-azaindole), 7.84 (1H, dd,  ${}^{4}J_{HH} = 1.8$  Hz,  ${}^{3}J_{HH} = 8.3$  Hz, 7azaindole), 8.33 (1H, dd,  ${}^{4}J_{HH} = 1.8$  Hz,  ${}^{3}J_{HH} = 4.6$  Hz, 7-azaindole), 8.44 (1H, dd,  ${}^{3}J_{HH} = 2.8$ Hz,  ${}^{3}J_{\text{HH}} = 8.3$  Hz, 7-azaindole), 8.63 (1H, d,  ${}^{3}J_{\text{HH}} = 5.5$  Hz, 7-azaindole);  ${}^{1}\text{H}\{{}^{11}\text{B}\}$ -NMR ( $\delta$ C<sub>6</sub>D<sub>6</sub>, 300 MHz): -17.2 (dddd [appears as ddt],  ${}^{2}J_{HH} = 9.2$  Hz,  ${}^{2}J_{HH} = 10.1$  Hz,  ${}^{2}J_{PH} = 13.7$ Hz,  ${}^{1}J_{RhH} = 28.4$  Hz, Rh*H*), -16.92 (ddd,  ${}^{2}J_{HH} = 9.2$  Hz,  ${}^{2}J_{PH} = 13.7$  Hz,  ${}^{1}J_{RhH} = 28.4$  Hz, Rh*H*), -0.70 (br s, B*H*); <sup>13</sup>C{<sup>1</sup>H}-NMR (δ C<sub>6</sub>D<sub>6</sub>, 125.71 MHz): 32.7 (br s, P{C(CH<sub>3</sub>)<sub>3</sub>}<sub>3</sub>), 39.7 (d,  ${}^{1}J_{PC} = 13.7$  Hz, P{C(CH<sub>3</sub>)<sub>3</sub>}), 102.0, 102.4, 103.2, 115.1, 115.4, 116.0, 124.5, 124.3, 124.0, 129.0, 129.2, 129.4, 131.7, 133.0, 133.2, 143.0, 146.5, 148.4, 153.4, 153.8, 154.1 (7-azaindolyl); <sup>11</sup>B{<sup>1</sup>H}-NMR ( $\delta C_6D_6$ ): -0.7 (s,  $\Delta v_{1/2} = 7.7$  Hz); <sup>11</sup>B-NMR ( $\delta C_6D_6$ ): -0.7 (dd,  ${}^{1}J_{BH} = 77.6$  Hz,  ${}^{2}J_{BH} = 14.1$  Hz);  ${}^{31}P{}^{1}H$ -NMR ( $\delta C_{6}D_{6}$ ): 108.8 (d,  ${}^{1}J_{RhP} = 137.7$  Hz,  $P^{t}Bu_{3}$ ; MS (ESI<sup>+</sup>): 693.3 [M+Na]<sup>+</sup> (40%), 671.3 [M+H]<sup>+</sup> (100%). Elem. Anal.: Calc for C<sub>33</sub>H<sub>45</sub>BN<sub>6</sub>PRh.<sup>1</sup>/<sub>4</sub>P<sup>t</sup>Bu<sub>3</sub>: C 59.97; H 7.23; N 11.66; Found: C 59.40; H 7.44; N 11.31.

## [(Rh{ $\kappa^3$ -NNB-B(azaindolyl)\_3)<sub>2</sub>( $\mu$ -H)( $\mu$ -7-azaindolyl)] (6)

In a glovebox,  $[Rh{\kappa^4-NNBN-B(azaindolyl)_3}(nortricyclyl)]$  (2) (80 mg, 0.14 mmol), 7azaindole (8.5 mg, 0.071 mmol) and toluene (10 mL) were charged in a thick wall Young's ampoule. The contents of the ampoule were placed under vacuum after two freeze-thaw pump cycles. The orange-pink solution was left to warm to RT and then was pressurised with 2.5 bar H<sub>2</sub> and placed in an oil-bath thermostated at 85 °C and heated overnight to give a yellow solution. This was then allowed to equilibrate at RT and filtered through glassmicrofibre canulla. A pale yellow solid was obtained when the volume of the solution was reduced to ca. 3 mL. This solid was washed with two portions of hexane (5 mL) and dried under reduced pressure to provide 6 as a pale yellow microcrystalline solid. Yield 27 mg (37 %). Complex 6 was also observed as the major product when a toluene solution of complex 2 was placed under 2.5 bar of H<sub>2</sub> and placed in a thermostated at 85 °C overnight. In this case however significant decomposition was observed.

<sup>1</sup>H-NMR ( $\delta$  C<sub>7</sub>D<sub>8</sub>, 300 MHz): -22.16 (1H, br t, <sup>1</sup>J<sub>RhH</sub> = 24.9 Hz), <sup>84</sup> 5.25 (1H, d, <sup>3</sup>J<sub>HH</sub> = 2.9 Hz, 7-azaindole), 5.64 (1H, br, 7-azaindole), 5.74 (4H, m, 7-azaindole), 6.04 (2H, m, 7azaindole), 6.12 (2H, dd,  ${}^{3}J_{HH} = 4.7$  Hz,  ${}^{3}J_{HH} = 3.3$  Hz, 7-azaindole), 6.27 (1H, d,  ${}^{3}J_{HH} = 2.9$ Hz, 7-azaindole), 6.30 (1H, d,  ${}^{3}J_{HH} = 3.3$  Hz, 7-azaindole), 6.53 (2H, m, 7-azaindole), 7.17 (8H, m, 7-azaindole), 7.39 (1H, d,  ${}^{3}J_{HH} = 2.9$  Hz, 7-azaindole), 7.44 (1H, d,  ${}^{3}J_{HH} = 3.3$  Hz, 7azaindole), 7.60 (3H, m, 7-azaindole), 8.00 (1H, vbr m, 7-azaindole), 8.73 (1H, vbr m, 7azaindole) several signals where very broad and could not be resolved from the baseline or overlapped with residual toluene solvent; <sup>1</sup>H-NMR (δ C<sub>7</sub>D<sub>8</sub>, 300 MHz, -60°C): -21.87 (1H, br, t,  ${}^{1}J_{RhH} = 23.5$  Hz), 5.34 (1H, d,  ${}^{3}J_{HH} = 2.9$  Hz, 7-azaindole), 5.75 (2H, m, 7-azaindole), 5.80 (2H, br m, 7-azaindole), 5.91 (2H, m, 7-azaindole), 6.14 (6H, m, 7-azaindole), 6.36 (2H, t,  ${}^{3}J_{\rm HH} = 3.7$  Hz, 7-azaindole), 6.42 (1H, d,  ${}^{3}J_{\rm HH} = 3.7$  Hz, 7-azaindole), 6.47 (4H, m, 7azaindole), 7.22 (2H, br d,  ${}^{3}J_{HH} = 5.1$  Hz, 7-azaindole), 7.29 (2H, dd,  ${}^{3}J_{HH} = 7.3$  Hz,  ${}^{4}J_{HH} =$ 1.5 Hz7-azaindole), 7.37 (2H, m, 7-azaindole), 7.46 (1H, d,  ${}^{3}J_{HH} = 2.9$  Hz, 7-azaindole), 7.60 (1H, dd,  ${}^{3}J_{HH} = 7.3$  Hz,  ${}^{4}J_{HH} = 1.5$  Hz, 7-azaindole), 7.66 (1H, dd,  ${}^{3}J_{HH} = 7.3$  Hz,  ${}^{4}J_{HH} = 1.5$ Hz, 7-azaindole), 8.14 (1H, d,  ${}^{3}J_{HH} = 5.1$  Hz, 7-azaindole), 8.24 (1H, d,  ${}^{3}J_{HH} = 5.1$  Hz, 7azaindole), 8.78 (2H, br m, 7-azaindole), 2 protons overlapping with residual toluene solvent; <sup>1</sup>H-NMR ( $\delta$  C<sub>7</sub>D<sub>8</sub>, 300 MHz, 80°C): -22.74 (1H, br t, <sup>1</sup>J<sub>RhH</sub> = 24.7 Hz), 5.22 (1H, br, 7azaindole), 5.68 (4H, m, 7-azaindole), 5.86 (1H, br, 7-azaindole), 6.00 (2H, m, 7-azaindole), 6.11 (2H, m, 7-azaindole), 6.19 (1H, br, 7-azaindole), 6.26 (2H, m, 7-azaindole), 6.58 (3H, m, 7-azaindole), 7.24 (6H, m, 7-azaindole), 7.41 (2H, m, 7-azaindole), 7.59 (3H, m, 7azaindole), 7.69 (1H, br, 7-azaindole), 7.83 (1H, br, 7-azaindole), 7.98 (1H, br d,  ${}^{3}J_{HH} = 4.6$ Hz, 7-azaindole), 8.56 (1H, br, 7-azaindole), 8.68 (1H, br, 7-azaindole), 3 protons overlapping with residual toluene solvent.  ${}^{11}B{}^{1}H$ -NMR ( $\delta C_7D_8$ , 96.4 MHz): 3.3 (s), 3.7 (s); <sup>11</sup>B-NMR ( $\delta$  C<sub>7</sub>D<sub>8</sub>): 3.3 (s), 3.7 (s). <sup>11</sup>B{<sup>1</sup>H}-NMR ( $\delta$  C<sub>7</sub>D<sub>8</sub>, 128.3 MHz): 3.3 (s,  $\Delta v_{1/2} =$ 30 Hz), 3.7 (s,  $\Delta v_{1/2} = 30$  Hz); <sup>11</sup>B-NMR ( $\delta C_7 D_8$ , 128.3 MHz): 3.3 (s), 3.7 (s). MS (ESI<sup>+</sup>): 1071.1 [M+Na]<sup>+</sup> (10%), 1049.1 [M+H]<sup>+</sup> (100%), 931.1 [M-azaindolyl]<sup>+</sup> (40%). Calc for C49H36B2N14Rh2: C 56.14; H 3.46; N 18.71; Found: C 56.48; H 3.85; N 16.66. We were unable to obtain good data for the nitrogen content on samples of this compound despite several attempts.

### Reaction of 2 with P<sup>t</sup>Bu<sub>3</sub>

In the glovebox a Young's NMR tube was charged with 20 mg (0.036 mmol) of **2** and 7.3 mg  $P^tBu_3$  and  $d^8$ -toluene (0.5 mL) was added to give an orange-pink solution. The tube was sealed and degassed with three freeze-pump-thaw cycles. It was left to reach RT and placed in a thermostated at 85 °C overnight. <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H}, <sup>11</sup>B and <sup>31</sup>P{<sup>1</sup>H}-NMR spectroscopy showed no reaction.

### Reaction of 3 with H<sub>2</sub>

In a glovebox a Young's NMR tube was charged with 15 mg (0.023 mmol) of **3** and dissolved in d<sup>8</sup>-toluene. The tube was sealed and degassed with three freeze-pump-thaw cycles. It was left to reach RT, pressurised with 2.5 bar H<sub>2</sub> and placed in a thermostated at 85 °C overnight. <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H}, <sup>11</sup>B and <sup>31</sup>P{<sup>1</sup>H}-NMR spectroscopy showed no reaction under these conditions.

### **Catalytic Tests**

General procedure for styrene and cyclooctene hydrogenation using 2 or 4.

For 1 mol% loadings using **2**: A Young's ampule was charged with 2 mmol of styrene (230  $\mu$ L) or cyclooctene (260  $\mu$ L), and the contents degassed with 3 freeze-thaw pump cycles. Complex **2** (11.2 mg, 0.02 mmol), dry C<sub>6</sub>D<sub>6</sub> (2 mL) and 1,3,5-trimethoxybenzene (37.3 mg, 0.22 mmol) were subsequently added under an atmosphere of Ar. The ampoule was degassed with 3 further freeze-thaw pump cycles, allowed to warm to room temperature and pressurised to 2.5 bar of H<sub>2</sub>. The resulting mixture was heated at 85 °C for 18 h. The conversion of the substrate to the hydrogenated product was measured by the relative integration against the internal standard (1,3,5-trimethoxybenzene).

For 0.1 mol% loadings using **2** and **4**: A Young's ampule was charged with 7 mmol of styrene (805  $\mu$ L) or cyclooctene (910  $\mu$ L), and its contents degassed with 3 freeze-thaw pump cycles. Complex **2** (3.9 mg, 0.007 mmol) or complex **4** (4.9 mg, 0.007 mmol), dry C<sub>6</sub>D<sub>6</sub> (1 mL) and 1,3,5-trimethoxybenzene (131 mg, 0.78 mmol) were subsequently added under Ar. The ampoule was degassed with 3 further freeze-thaw pump cycles, allowed to warm to room temperature and pressurised to 2.5 bar of H<sub>2</sub>. The resulting mixture was heated at 85 °C for 18 h. The conversion of the substrate to the hydrogenated product was measured by the relative integration against the internal standard (1,3,5-trimethoxybenzene).

### Crystallography

A summary of the crystallographic data collection parameters and refinement details is presented in the supplementary information (Table S1). Anisotropic parameters, bond lengths and (torsion) angles for 3, 3', 5, 6 and 6' are available from the cif file. The data for complexes 3, 5 and 6' were collected on a Bruker Apex II diffractometer with a fine-focus sealed tube Mo-K<sub> $\alpha$ </sub> (wavelength 0.71073 Å) radiation source. The data for **3**' were collected on a Bruker Proteum diffractometer with rotating anode (Mo- $K_{\alpha}$  radiation). The data for 6 were collected on an Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo- $K_{\alpha}$  radiation). Collections of all data were performed using a CCD area detector from single crystals mounted on a glass fibre using silicon grease. Intensities were integrated<sup>S5</sup> from several series of exposures measuring  $0.5^{\circ}$  in  $\omega$ . Absorption corrections were based on equivalent reflections using SADABS,<sup>S6</sup> and structures were refined against all  $F_0^2$  data with hydrogen atoms riding in calculated positions using SHELXL.<sup>87</sup> The hydrogen atoms H1, H2 and H3 in complex 5 were found in the difference map. The position of H1 was tied to B1 whereas the positions of H2 and H3 were allowed to freely refine. In complex 6 (and 6'), a peak was observed in the difference map where a hydride is expected to be according to the spectroscopic evidence. Thus this was assigned as H1 and its position in the structure was allowed to refine freely (see ESI). The difficulty in locating hydrogen atoms adjacent to heavy atoms is recognised by the authors and the danger of mistaking Fourier ripples caused by a sharp cut-off in the high angle data for hydrogen atoms. Nevertheless, the hydrogen atoms have been included in this model based on the evidence from the spectroscopic data.

Single crystals of complex **3** were obtained by slow diffusion of pentane into a toluene solution of **3**. A second polymorph, **3'**, was obtained by leaving a pentane solution of **3** stand at RT. In both structures disorder is observed at the nortricyclic rings. This disorder models for the two possible diastereomers (R- and S-isomers). This ratio is similar to that observed in the spectroscopic data for **3** (see above). Single crystals of complex **5** were obtained by layering a toluene solution of **5** with pentane. This structure contains one half molecule of disordered pentane for each complex. Single crystals of complex **6** were obtained by allowing a diethyl ether solution stand at -30 °C overnight. This structure contains two molecules of diethyl ether for each complex. A second polymorph, **6'**, was obtained by slow evaporation of a benzene solution of the complex. This structure contains two molecules of benzene per molecule of **6**.

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Figure S1 – Ortep representations of  $[Rh{\kappa^3-NNB-B(azaindolyl)_3}(nortricycle) (PMe_3)]$  (3) (hydrogen atoms have been removed for clarity, ellipsoids drawn at 50% probability level). The two polymorphs are shown 3 on the left and 3' on the right.



Figure S2 – Ortep representation of  $[(Rh{\kappa^3-NNB-B(azaindolyl)_3})_2(\mu-H)(\mu-azaindolyl)]$  (6') (hydrogen atoms with the exception of H1 have been removed for clarity, ellipsoids drawn at 50% probability level). Two polymorphs were obtained the first one, **6**, is presented in the manuscript; the second polymorph **6'** is shown here.

| Compound reference                            | Complex 3   | Complex 3'  | Complex 5  | Complex 6                       | Complex 6'  |
|---|---|---|--|---------------------------------|---|
| Chemical formula                              | C <sub>31</sub> H <sub>33</sub> BN <sub>6</sub> PRh | C <sub>31</sub> H <sub>33</sub> BN <sub>6</sub> PRh | $C_{33}H_{45}BN_6PRh$<br>•0.5(C <sub>5</sub> H <sub>12</sub> ) | $C_{57}H_{56}B_2N_{14}O_2 Rh_2$ | $C_{49}H_{36}B_2N_{14}Rh_2$<br>•2(C <sub>6</sub> H <sub>6</sub> ) |
| Formula Mass                                  | 634.32  | 634.32  | 706.51   | 1196.60                         | 1204.57   |
| Crystal system                                | Triclinic   | Orthorhombic  | Monoclinic   | Triclinic                       | Triclinic   |
| a/Å   | 9.9941(3)   | 19.3135(17)   | 11.6549(8)   | 11.3780(3)                      | 11.5334(5)  |
| b/Å   | 11.5950(3)  | 20.0036(17)   | 12.9893(9)   | 11.9021(3)                      | 15.3688(6)  |
| $c/{ m \AA}$                                  | 13.1114(3)  | 14.4432(13)   | 22.6123(15)  | 20.7067(6)                      | 15.8442(6)  |
| a/°   | 84.798(1)   | 90  | 90   | 74.070(2)                       | 93.813(2)   |
| β/°   | 71.666(1)   | 90  | 90.483(3)  | 78.342(2)                       | 100.089(2)  |
| $\gamma/^{\circ}$                             | 77.102(2)   | 90  | 90   | 80.084(2)                       | 111.872(2)  |
| Unit cell volume/Å <sup>3</sup>               | 1405.51(6)  | 5580.0(8)   | 3423.1(4)  | 2620.47(12)                     | 2539.17(18)   |
| Temperature/K                                 | 100(2)  | 100(2)  | 100(2)   | 100(2)                          | 100(2)  |
| Space group                                   | $P\overline{1}$                                     | Pbcn  | P21/c  | $P\overline{1}$                 | $P\overline{1}$   |
| No. of formula units per unit cell, $Z$       | 2   | 8   | 4  | 2                               | 2   |
| Absorption coefficient, $\mu/\text{mm}^{-1}$  | 0.697   | 5.745   | 0.580  | 0.689                           | 0.709   |
| No. of reflections measured                   | 28766   | 30600   | 109624   | 53963                           | 81749   |
| No. of independent reflections                | 6492  | 4607  | 21767  | 12055                           | 24532   |
| R <sub>int</sub>                              | 0.0310  | 0.0485  | 0.0298   | 0.0941                          | 0.0541  |
| Final $R_I$ values $(I > 2\sigma(I))$         | 0.0260  | 0.0290  | 0.0298   | 0.0504                          | 0.0401  |
| Final $wR(F^2)$ values<br>$(I > 2\sigma(I))$  | 0.0586  | 0.0696  | 0.0743   | 0.1015                          | 0.0814  |
| Final <i>R</i> <sub>1</sub> values (all data) | 0.0321  | 0.0394  | 0.0402   | 0.0972                          | 0.0710  |
| Final $wR(F^2)$ values (all data)             | 0.0610  | 0.0734  | 0.0807   | 0.1164                          | 0.0932  |
| CCDC number                                   | 783205  | 783206  | 783207   | 783208                          | 783209  |

Table S1 - Crystallographic data collection parameters and refinement details for complexes **3**, **5** and **6** 

#### Selected bond lengths (Å) and angles (°) for 3, 3', 5, 6 and 6'

**3**: Rh1-N4 2.1289(16), Rh1-N2 2.1680(15), Rh1-B1 2.1735(19), Rh1-P1 2.2307(5), Rh1-C25 2.0911(18), B1-N1 1.538(2), B1-N3 1.557(2), B1-N5 1.521(2), C25-Rh1-N4 91.80(7), N2-Rh1-N4 88.63(6), C25-Rh1-B1 94.93(7), N4-Rh1-B1 84.20(7), N2-Rh1-B1 83.53(6), C25-Rh1-P1 89.92(6), N2-Rh1-P1 89.66(4), B1-Rh1-P1 96.10(6), N5-B1-N1 113.37(14), N5-B1-N3 107.66(14), N1-B1-N3 110.46(15), N5-B1-Rh1 121.99(13), N1-B1-Rh1 102.44(11), N3-B1-Rh1 99.94(11).

**3**': Rh1-N4 2.117(2), Rh1-N2 2.181(2), Rh1-B1 2.158(3), Rh1-P1 2.2238(7), Rh1-C25 2.099(3), B1-N1 1.533(3), B1-N3 1.551(3), B1-N5 1.524(3), C25-Rh1-N4 92.92(10), N2-Rh1-N4 89.06(8), C25-Rh1-B1 93.38(11), N4-Rh1-B1 84.40(10), N2-Rh1-B1 83.03(9), C25-Rh1-P1 90.24(8), N2-Rh1-P1 88.17(6), B1-Rh1-P1 100.93(8), N5-B1-N1 111.5(2), N5-B1-N3 109.5(2), N1-B1-N3 109.0(2), N5-B1-Rh1 122.14(18), N1-B1-Rh1 102.77(16), N3-B1-Rh1 100.87(17).

**5**: Rh1-N4 2.1159(7), Rh1-N2 2.1896(8), Rh1-P1 2.2928(3), Rh1-H2 1.586(15), Rh1-H3 1.442(15), Rh1-H1 1.800(16), N1-B1 1.5336(13), N3-B1 1.5386(12), N5-B1 1.5323(14), B1-H1 1.244(15), N4-Rh1-N2 89.09(3), N2-Rh1-P1 105.07(2), N4-Rh1-H2 90.0(5), P1-Rh1-H2 76.2(5), N4-Rh1-H3 88.1(6), N2-Rh1-H3 98.8(6), P1-Rh1-H3 81.1(6), H2-Rh1-H3 77.9(8), N2-Rh1-H1 86.1(5), P1-Rh1-H1 93.1(5), H2-Rh1-H1 97.1(8), H3-Rh1-H1 174.5(8), N5-B1-N1 111.38(8), N5-B1-N3 111.57(8), N1-B1-N3 109.79(8), N5-B1-H1 105.4(7), N1-B1-H1 108.7(7), N3-B1-H1 109.9(7).

**6**: Rh1-N14 2.027(3), Rh1-N2 2.100(3), Rh1-N4 2.024(3), Rh1-B1 2.171(4), Rh1-Rh2 2.8803(4), Rh2-N13 2.046(3), Rh2-N8 2.095(3), Rh2-N10 2.095(3), Rh2-B2 2.139(5), N5-B1-N3 115.4(3), N5-B1-N1 108.2(3), N3-B1-N1 110.6(3), N5-B1-Rh1 118.1(3), N3-B1-Rh1 102.1(3), N1-B1-Rh1 101.5(2), N11-B2-N9 115.1(3), N11-B2-N7 110.3(3), N9-B2-N7 110.9(3), N11-B2-Rh2 114.8(3), N9-B2-Rh2 102.7(3), N7-B2-Rh2 102.1(3).

**6**': Rh1-N14 2.0410(15), Rh1-N10 2.0467(14), Rh1-N8 2.0897(15), Rh1-B2 2.148(2), Rh1-Rh2 2.8873(2), Rh2-N13 2.0418(14), Rh2-N4 2.0525(14), Rh2-N2 2.0945(15), Rh2-B1 2.1559(19), N5-B1-N3 111.89(14), N5-B1-N1 109.67(14), N3-B1-N1 109.70(14), N5-B1-Rh2 121.71(13), N3-B1-Rh2 101.66(11), N1-B1-Rh2 101.29(11), N11-B2-N9 112.45(14), N11-B2-N7 112.50(14), N9-B2-N7 111.70(15), N11-B2-Rh1 115.95(13), N9-B2-Rh1 101.93(11), N7-B2-Rh1 101.42(11).

#### References

- S1 D. Song, W. L. Jia, G. Wu and S. Wang, *Dalton Trans.*, 2005, 433.
- S2 E. W. Abel. M. A. Bennett and G. Wilkinson, J. Chem. Soc., 1959, 3178.
- N. Tsoureas, T. Bevis, C. P. Butts, A. Hamilton and G. R. Owen, *Organometallics* 2009, 28, 5222.
- S4 A similar coupling constant was found in a hydride ligand bridging two rhodium centres: see M. D. Fryzuk and W. E. Piers, *Polyhedron*, 1988, **7**, 1001.
- S5 Bruker-AXS SAINT V7.60A
- S6 G. M. Sheldrick, SADABS V2008/1-2, University of Göttingen, Germany.
- **S7** G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.