Supporting Information for:

Intermediates in the Rh-catalysed dehydrocoupling of Phosphine Boranes

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Experimental

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NMR and ESI-MS characterisation

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Catalytic study with [Rh(COD)2][BArF4]

Reactivity of [Rh(Ph3P)2(C6H5F)][BArF4]

Reactivity of [Rh(Ph3P)2(η2-H3B·Ph3P)][BArF4] (4a) with H3B·Ph3P (1a)

Reactivity of [Rh(COD)(Ph3P)2H)(η2-H3B·Ph3P)][BArF4] (6a) with H3B·Ph3P (1a)

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Crystallography

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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. Hexane and pentane were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles. CD$_2$Cl$_2$, C$_8$H$_5$F and 1,2-F$_2$C$_6$H$_4$ were distilled under vacuum from CaH$_2$ and stored over 3 Å molecular sieves. 1,2-F$_2$C$_6$H$_4$ was stirred over alumina for two hours prior to drying. H$_2$B-PPh$_2$H, H$_2$B-P'Bu$_2$H and P'Bu$_2$H were purchased from Aldrich used as supplied. [Rh(COD)$_2$][BAR$_4$]$_2$ [Rh(P'Bu$_3$)$_2$(C$_6$H$_5$F)][BAR$_4$]$_2$, [Rh(NBD)Cl]$_2$ [BAR$_4$]$_2$, [Rh(NBD)(P'Bu$_2$H)$_2$][BAR$_4$]$_2$ were prepared as previously described and [Rh(NBD)(P'Bu$_2$H)$_2$][BAR$_4$]$_2$ was prepared by an adaptation of the published route using NaBAR$_4$ and PR$_3$.$^7$ NMR spectra were recorded on Varian Unity Plus 500 MHz spectrometers at room temperature unless otherwise stated. In 1,2-F$_2$C$_6$H$_4$, $^1$H NMR spectra were referenced to the centre of the downfield solvent multiplet ($\delta = 7.07$). Chemical shifts are quoted in ppm and coupling constants in Hz. Pcq = partially collapsed quartet. ESI-MS were recorded on a Bruker MicrOTOF instrument. Typical acquisition parameters were: Sample flow rate (4 $\mu$L/ min), nebuliser gas pressure (0.4 bar), drying gas (argon at 60°C, flowing at 4L/ min), capillary voltage 4.5 kV, funnel voltage (200 V). MS samples were diluted to a concentration of 1 x 10$^{-6}$ M before running. Microanalyses were performed by Elemental Microanalysis Ltd and London Metropolitan University.

Synthesis of new complexes

Preparation of [Rh(P'Bu$_2$H)$_2$(C$_6$H$_5$F)][BAR$_4$]$_2$

A solution of [Rh(NBD)(P'Bu$_2$H)$_2$][BAR$_4$]$_2$ (50 mg, 0.074 mmol) in C$_8$H$_5$F (5 mL) was placed under 4 atm H$_2$. A colour change from bright orange to pale orange was observed upon warming the sample to room temperature. The solution was thoroughly degassed by freeze/pump/thaw methods, evaporated to dryness and the residue washed with pentane (3 x 5 mL) to yield [Rh(P'Bu$_2$H)$_2$(C$_6$H$_5$F)][BAR$_4$]$_2$ as a pale orange powder (82 mg, 82%).

$^1$H NMR (500 MHz, C$_8$H$_5$F): $\delta$ 8.33 (s, 8H, BAR$_4$), 7.64 (s, 8H, BAR$_4$), 3.72 (AA'MM'XY, 2H, $^1$J$_{A-M}$= 355 Hz, $^3$J$_{A-M}$= 12 Hz, $^2$J$_{M-M}$= 25 Hz, $^2$J$_{A-X}$= 0, $^3$J$_{A-Y}$= 0, PH), 1.02 (d, 36H, $^3$J$_{H-P}$= 14 Hz, 'Bu). Signals from C$_8$H$_5$F not observed.

$^{31}$P($^1$H) NMR (202 MHz, C$_8$H$_5$F): $\delta$ 87.1 (d, $J_{Rh-P}$= 200 Hz)

ESI-MS (C$_8$H$_5$F, 60°C): positive ion: m/z, 491.19 [M]$^+$ (calc. 491.19).

Microanalysis: (C$_{54}$H$_{75}$P$_2$RhF$_{25}$) Calc.: C, 47.88; H, 4.09. Found: C, 47.79; H, 3.94.
Preparation of [Rh(P^Bu_2H)\_2(\eta^2-H\_2B-P^Bu_2BH)]\[BAR^f_4\] (3a)

To a Youngs flask charged with [Rh(P^Bu_2H)\_2(C_6H_5F)]\[BAR^f_4\] (50 mg, 0.037 mmol) and H\_2B-P^Bu_2BH (2a) (12 mg, 0.038 mmol) was added 1,2-F\_2C\_6H\_4 (5 mL). The solution was stirred at room temperature for 1 hour and a change in the color from pale orange to blue was observed. The diffusion of pentane (15 mL) into the solution gave 3a as a blue microcrystalline solid (39 mg, 67%).

\( ^1H \) NMR (500 MHz, 1,2-F\_2C\_6H\_4): \( \delta 8.34 \) (s, 8H, BAR\^f\_4), 7.69 (s, 4H, BAR\^f\_4), 4.28 (dq, 1H, \( J_{H-F} = 366 \) Hz, \( J_{H-B} = 6 \) Hz, B-PH), 3.91 (AA' MM' XY, 2H, \( J_{A-M} = 330 \) Hz, \( J_{A-X} = 20 \) Hz, \( J_{M-M} = 23 \) Hz, \( J_{A-Y} = 0 \), \( J_{A-V} = 0 \), PH), 1.44 (d, 18H, \( J_{H-P} = 13 \) Hz, \( \beta \)Bu), 1.37 (d, 18H, \( J_{H-P} = 15 \) Hz, \( \beta \)Bu), 2.0-5 (vbr, 2H, BH\_2), -1.91 (pcq, 3H, \( J_{B-H} = 86 \) Hz, BH\_3).

\( ^31P(\text{'H}) \) NMR (202 MHz, 1,2-F\_2C\_6H\_4): \( \delta 91.6 \) (d, \( J_{R-P} = 174 \) Hz), 37.6 (br), 7.1 (br).

\( ^11B \) NMR (160 MHz, 1,2-F\_2C\_6H\_4): \( \delta 8.1 \) (br), -38.5 (m).

ESI-MS (1,2-F\_2C\_6H\_4, 60°C): positive ion: m/z, 713.44 [M]^+ (calc. 713.44).

Microanalysis: (C\_66B\_3H\_92P\_4Rh\_24) Calc.: C, 48.76; H, 5.88. Found: C, 48.69; H, 5.86.

Preparation of [Rh(P^Bu_2H)\_2(\eta^2-H\_2B-P^Bu_2H)]\[BAR^f_4\] (4a)

To a Youngs flask charged with [Rh(P^Bu_2H)\_2(C_6H_5F)]\[BAR^f_4\] (50 mg, 0.037 mmol) and H\_2B-P^Bu_2H (1a) (6 mg, 0.038 mmol) was added 1,2-F\_2C\_6H\_4 (5 mL). The solution was stirred at room temperature for 1 hour and a change in the color from pale orange to blue was observed. The resulting solution was layered with pentane and held at 5°C for 72 hours to afford the product as blue crystals (42 mg, 78%).

\( ^1H \) NMR (500 MHz, C\_6H\_12F\_2): \( \delta 8.33 \) (s, 8H, BAR\^f\_4), 7.68 (s, 4H, BAR\^f\_4), 4.74 (d, 1H, \( J_{H-P} = 389 \) Hz, B-PH), 3.92 (AA' MM' XY, 2H, \( J_{A-M} = 345 \) Hz, \( J_{A-X} = 22 \) Hz, \( J_{M-M} = 25 \) Hz, \( J_{A-Y} = 0 \), \( J_{A-V} = 0 \), PH), 1.42 (d, 36H, \( J_{H-P} = 15 \) Hz, \( \beta \)Bu), 1.40 (d, 18H, \( J_{H-P} = 15 \) Hz, \( \beta \)Bu), -1.89 (pcq, 3H, \( J_{B-H} = 96 \) Hz, BH\_3).

\( ^31P(\text{'H}) \) NMR (202 MHz, C\_6H\_12F\_2): \( \delta 90.5 \) (d, \( J_{R-P} = 175 \) Hz), 31.7 (br).

\( ^11B \) NMR (160 MHz, C\_6H\_12F\_2): \( \delta 0.3 \) (br).

ESI-MS (C\_6H\_12F\_2, 60°C): positive ion: m/z, 555.30 [M]^+ (calc. 555.30).

Microanalysis: (C\_56B\_2H\_24P\_4Rh\_24) Calc.: C, 47.41; H, 5.12. Found: C, 47.63; H, 5.08.

Preparation of [Rh(H\_2)(P^Bu_2H)\_2(\eta^2-H\_2B-P^Bu_2H)]\[BAR^f_4\] (5a)

A solution of 4a (10 mg, 0.007 mmol) in 1,2-C\_6H\_12F\_2 (0.4 mL) was placed under hydrogen (4 atm) to form 5a in quantitative yield. 5a was characterised in situ by \( ^1H \), \( ^31P(\text{'H}) \), \( ^11B \) NMR and ESI-MS.

\( ^1H \) NMR (500 MHz, 1,2-F\_2C\_6H\_4): \( \delta 8.34 \) (s, 8H, BAR\^f\_4), 7.69 (s, 4H, BAR\^f\_4), 4.52 (dq, 1H, \( J_{H-P} = 369 \) Hz, \( J_{H-B} = 5 \) Hz, B-PH), 4.33 (d, 2H, \( J_{H-P} = 318 \) Hz, PH), 1.39 (d, 36H, \( J_{H-P} = 14 \) Hz, \( \beta \)Bu), 1.35 (d, 18H, \( J_{H-P} = 15 \) Hz, \( \beta \)Bu), -0.94 (pcq, 3H, \( J_{B-H} = 104 \) Hz, BH\_3), -17.67 (dt, 2H, \( J_{H-Rh} = 20 \) Hz, \( J_{H-H} = 15 \) Hz, Rh-H).

\( ^31P(\text{'H}) \) NMR (202 MHz, 1,2-F\_2C\_6H\_4): \( \delta 81.0 \) (d, \( J_{R-P} = 107.3 \) Hz), 27.4 (br).
Preparation of \([\text{Rh} \text{(COD)}[\text{P}^1\text{Bu}_2\text{H}]\{(\eta^2-\text{H}_2\text{B-P}^1\text{Bu}_2\text{H})][\text{BAr}^6\text{d}]}\) (6a)

To a Youngs flask charged with \([\text{Rh} \text{(COD)}]\)\([\text{BAr}^6\text{d}]}\) (70 mg, 0.059 mmol) and \(\text{H}_3\text{B-P}^1\text{Bu}_2\text{H}\) (1a) (19 mg, 0.120 mmol) was added 1,2-\(\text{F}_2\text{C}_6\text{H}_4\) (10 mL). The solution was stirred at 40 °C for 24 hours and a change in the colour from pale orange to yellow was observed. The diffusion of pentane (20 mL) into the solution gave 3a as a pale yellow microcrystalline solid (67 mg, 82%).

\(^1\text{H} \text{NMR (500 MHz, 1,2-\(\text{F}_2\text{C}_6\text{H}_4\)): } \delta 8.33 \text{ (s, 8H, BAr}^6\text{d}]), 7.68 \text{ (s, 4H, BAr}^6\text{d}]), 5.12 \text{ (s, 2H, COD)}, 4.10 \text{ (dq, 1H, } 1^\text{J}_{\text{H}-\text{P}}= 359 \text{ Hz, } 2^\text{J}_{\text{H}-\text{PH}}= 5 \text{ Hz, B-PH}), 5.12 \text{ (s, 2H, COD)}, 3.15 \text{ (d, 1H, } 1^\text{J}_{\text{H}-\text{P}}= 336 \text{ Hz, PH}), 2.45 \text{ (m, 2H, COD), 2.28 \text{ (m, 2H, COD), 2.19 \text{ (m, 2H, COD), 2.05 \text{ (m, 2H, COD})}}, 1.44 \text{ (d, 18H, } 3^\text{J}_{\text{H}-\text{P}}= 14 \text{ Hz, } 1^\text{Bu}), 1.39 \text{ (d, 18H, } 3^\text{J}_{\text{H}-\text{P}}= 15 \text{ Hz, } 1^\text{Bu}), -0.62 \text{ (pcq, 3H, } 1^\text{V}_{\text{B-H}}= 98 \text{ Hz, BH}_3\).

\(^{31}\text{P}^{1}(\text{H}) \text{NMR (202 MHz, 1,2-\(\text{F}_2\text{C}_6\text{H}_4\)): } \delta 79.3 \text{ (d, } 1^\text{J}_{\text{H}-\text{P}}= 138 \text{ Hz, } 28.5 \text{ (br).}

\(^{11}\text{B} \text{NMR (160 MHz, 1,2-\(\text{F}_2\text{C}_6\text{H}_4\)): } \delta -35.5 \text{ (br).}

ESI-MS (1,2-\(\text{F}_2\text{C}_6\text{H}_4\), 60°C): positive ion: \(m/z\), 517.29 \text{ [M]+ (calc. 517.29).}

Microanalysis: \((\text{C}_{56}\text{B}_2\text{H}_{65}\text{P}_2\text{RhF}_{24})\) Calc.: C, 48.72; H, 4.75. Found: C, 48.74; H, 4.80.

Preparation of \([\text{P}^1\text{Bu}_2\text{H}_2]\text{BH}_3\)[\text{BAr}^6\text{d}]}\) (7[BH]d)

Monobromoborane-methylsulfide complex (280 μL of 1.0 M CH₂Cl₂ solution, 0.280 mmol) was added to a stirred solution of di-tert-butylphosphine (100 μL, 0.540 mmol) in CH₂Cl₂ (10 mL). After 40 h, the volatiles were removed under vacuum, and the resulting white solid was washed with hexane and then dissolved in CH₂Cl₂ (5 mL). To this solution was added Li[BH]d (10 mg, 0.280 mmol), and then stirred for 12 h before filtering to removed LiCl. The solution was evaporated to dryness, the residue washed with hexane (3 x 5 mL) and dried under vacuum (83 mg, 74%).

\(^1\text{H} \text{NMR (500 MHz, 1,2-\(\text{F}_2\text{C}_6\text{H}_4\)): } \delta 8.32 \text{ (s, 8H, BAr}^6\text{d}]), 7.69 \text{ (s, 4H, BAr}^6\text{d}]), 4.35 \text{ (dm, 2H, } 1^\text{J}_{\text{H}-\text{P}}= 372 \text{ Hz, PH}), 2.32 \text{ (br, qu, 4H, } 1^\text{J}_{\text{H}-\text{P}}= 105 \text{ Hz, BH}_3\)), 1.44 \text{ (d, 36H, } 3^\text{J}_{\text{H}-\text{P}}= 14 \text{ Hz, } 1^\text{Bu}). \text{Signals from BH}_2 \text{ not observed.}

\(^{31}\text{P}^{1}(\text{H}) \text{NMR (202 MHz, 1,2-\(\text{F}_2\text{C}_6\text{H}_4\)): } \delta 34.9 \text{ (m, br).}

\(^{11}\text{B} \text{NMR (160 MHz, 1,2-\(\text{F}_2\text{C}_6\text{H}_4\)): } \delta -41.1 \text{ (m, br, 2B) BH}_2 \text{ and BH}_3 \text{ peaks are coincident.}

ESI-MS (1,2-\(\text{F}_2\text{C}_6\text{H}_4\), 60°C): positive ion: \(m/z\), 305.27 \text{ [M]+ (calc. 305.27).}

Preparation of \([\text{P}^1\text{Bu}_2\text{H}_2]\text{BH}_3\)[\text{BAr}^6\text{d}]}\) (7[BH]d)

Compound 7[BH]d was made as described above for 7[BH]d but using Na[BAr]d (248 mg, 0.280 mmol) (291 mg, 90%).

\(^1\text{H} \text{NMR (500 MHz, 1,2-\(\text{F}_2\text{C}_6\text{H}_4\)): } \delta 8.32 \text{ (s, 8H, BAr}^6\text{d}]), 7.69 \text{ (s, 4H, BAr}^6\text{d}]), 4.54 \text{ (dm, 2H, } 1^\text{J}_{\text{H}-\text{P}}= 380 \text{ Hz, PH),}
1.38 (d, 36H, \( J_{\text{H-P}} = 16 \text{ Hz, } \text{tBu} \)). Signals from BH\(_2\) not observed.

\(^{31}\text{P}\{^1\text{H}\} \text{ NMR} (202 \text{ MHz, 1,2-F}_2\text{C}_6\text{H}_4)\): \( \delta 36.6 \) (m, br).

\(^{11}\text{B} \text{ NMR} (160 \text{ MHz, 1,2-F}_2\text{C}_6\text{H}_4)\): \( \delta -41.1 \) (m, br).

NMR and ESI-MS characterisation

Figure S.1: \(^{31}\text{P}\{^1\text{H}\} \text{ NMR} (202 \text{ MHz, 1,2-F}_2\text{C}_6\text{H}_4)\) spectra of 3a, 4a, 5a and 6a all over the same chemicals shift range. \( \star = \text{H}_2\text{B}è^3\text{Bu}_2\text{H} (1a) \).
Figure S.2: $^{11}$B NMR (160 MHz, 1,2-F$_2$C$_6$H$_4$) spectra of 3a, 4a, 5a and 6a all over the same chemical shift range. $\star$ = H$_3$B·PBU$_3$H (1a).

Figure S.3: $^1$H NMR (500 MHz, 1,2-F$_2$C$_6$H$_4$) spectrum of 3a. $\star$ = 1,2-F$_2$C$_6$H$_4$. 
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Figure S.4: $^1$H NMR (500 MHz, 1,2-F$_2$C$_6$H$_4$) spectrum of 4a. $\star$ = 1,2-F$_2$C$_6$H$_4$.

Figure S.5: $^1$H NMR (500 MHz, 1,2-F$_2$C$_6$H$_4$) spectrum of 5a. $\star$ = 1,2-F$_2$C$_6$H$_4$, $\dagger$ = H$_2$.

Figure S.6: $^1$H NMR (500 MHz, 1,2-F$_2$C$_6$H$_4$) spectrum of 6a. $\star$ = 1,2-F$_2$C$_6$H$_4$. 
Figure S.7: Observed (top) and simulated (bottom) ESI-MS of 3a, 4a, 5a and 6a in 1,2-F$_2$C$_6$H$_4$. * = 4a (5a loses H$_2$ under Ar atmosphere to give [M-H$_2$]$^+$).
Catalytic study with [Rh(P\textsubscript{t}Bu\textsubscript{2}H\textsubscript{2})(C\textsubscript{6}H\textsubscript{5}F)][BAr\textsubscript{F\textsubscript{4}}]

Dehydrocoupling of H\textsubscript{3}B·P\textsubscript{t}Bu\textsubscript{2}H (1\textsubscript{a}) using 5 mol\% of [Rh(P\textsubscript{t}Bu\textsubscript{2}H\textsubscript{2})(C\textsubscript{6}H\textsubscript{5}F)][BAr\textsubscript{F\textsubscript{4}}] at 140 °C in melt conditions led to compound 2\textsubscript{a} in approximately 65\% conversion in 20 hours. Monitoring the melt reaction using \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectroscopy and ESI-MS (in 1,2-F\textsubscript{2}C\textsubscript{6}H\textsubscript{4} solutions for both) showed as well as 2\textsubscript{a}, PH\textsubscript{t}Bu\textsubscript{2} (free phosphine) and [Bu\textsubscript{2}HP·BH\textsubscript{2}·PH\textsubscript{t}Bu\textsubscript{2}]\textsuperscript{+} (7\textsuperscript{+}) assumed to be the [BH\textsubscript{4}]\textsuperscript{-} salt (Figure S.8). By monitoring the same reaction but using 20 mol\% of [Rh(P\textsubscript{t}Bu\textsubscript{2}H\textsubscript{2})(C\textsubscript{6}H\textsubscript{5}F)][BAr\textsubscript{F\textsubscript{4}}] we have identified possible intermediate species (Figures S.9 and S.10).

Scheme S.1: Catalytic dehydrocoupling of 1\textsubscript{a} to give 2\textsubscript{a} (left) and possible intermediate species (right). Bottom: Reaction of 8 -C\textsubscript{6}H\textsubscript{4}F\textsubscript{2} when you solve it in difluorobenzene, formation of 8.
Figure S.8: $^{31}$P($^1$H) NMR (202 MHz, 1,2-F$_2$C$_6$H$_4$) spectra for the catalytic dehydrocoupling of 1a to give 2a (melt, 140 °C) at 1 hour (top), 5 hours (middle) and 20 hours (bottom). † = PH$^t$Bu$_2$. After 30 hours no changes observed.

Figure S.9: $^{31}$P($^1$H) NMR (202 MHz, 1,2-F$_2$C$_6$H$_4$) spectrum for the catalytic dehydrocoupling of 1a to give 2a (melt, 140 °C) at 5 hours using 20 mol% of [Rh($^t$Bu$_2$H)$_2$C$_6$H$_5$F][BAr$_4$^4]. In the box, signals for intermediate species 8 and 3a. † = free PH$^t$Bu$_2$. * = unknown species.
Figure S.10: Observed ESI-MS for the catalytic dehydrocoupling of 1a to give 2a (melt, 140 °C) at 5 hours. 

✱ = unknown species. We see no evidences from the specie [(Bu₂HP·BH₂·PhBu₂·BH₂·PhBu₂H]+ by NMR spectroscopy and assume arises from fragmentation in the ESI-MS.
Catalytic study with [Rh(COD)$_2$][BAR$_6$]

Dehydrocoupling of H$_3$B·P$^*$Bu$_2$H (1a) using 5 mol% of [Rh(COD)$_2$][BAR$_6$] at 140 °C in melt conditions led to compound 2a in approximately 65% of conversion in 20 hours. Monitoring the melt reaction, after 5 hours, using $^{31}$P($^1$H) NMR spectroscopy and ESI-MS (in 1,2-F$_2$C$_6$H$_4$ solutions for both) showed as well as 2a, PH$^*$Bu$_2$ (free phosphine) and [Bu$_2$HP·BH$_3$·PH$^*$Bu$_2$]$^+$ (7$^+$). We have also identified possible organometallic intermediate species (Figure S.11).

Figure S.11: Left: $^{31}$P($^1$H) NMR (202 MHz, 1,2-F$_2$C$_6$H$_4$) spectrum for the catalytic dehydrocoupling of 1a to give 2a (melt, 140 °C) at 5 hours. In the box, signals for intermediate species 8 and 3a. † = free PH$^*$Bu$_2$. ∗ = unknown species. Right: Observed ESI-MS for the catalytic dehydrocoupling of 1a (melt, 140 °C) at 5 hours.
Reactivity of \([\text{Rh}(\text{PBu}_3)_2(\text{C}_6\text{H}_5\text{F})][\text{BARF}_4]\)

To a Youngs NMR tube charged with \([\text{Rh}(\text{PBu}_3)_2(\text{C}_6\text{H}_5\text{F})][\text{BARF}_4]\) (10 mg, 0.007 mmol) an equimolar amount of \(\text{H}_3\text{B}·\text{PtBu}_2\text{H}\) (1a) (1.2 mg, 0.007 mmol) was added 1,2-\(\text{F}_2\text{C}_6\text{H}_4\) (0.4 mL). Instantaneously, a change in the colour from pale orange to blue was observed and the products of this reaction were characterised \textit{in situ} by \(^1\text{H}, \quad ^{31}\text{P}^\{^1\text{H}\}\) and \(^{11}\text{B}\) NMR spectroscopy and interrogated by NMR spectroscopy after 24 and 72 hours at room temperature (Figure S.12).

\[\text{Scheme S.2: Reaction of [Rh(PBu)_3_2(C_6H_5F)][BARF_4] with 1a. Formation of the substances [Rh(PBu)_n(PtBu_2H)_2-n(H_3B PR_3)][BARF_4] (PR_3 = PBu_3, PBu_2H; n = 2–0) (I, II and III).}\]

\[\text{Figure S.12: } ^{31}\text{P}^\{^1\text{H}\}\text{ NMR (202 MHz, 1,2-\(\text{F}_2\text{C}_6\text{H}_4\)) spectra of the reaction between [Rh(PBu)_3_2(C_6H_5F)][BARF_4] and 1a after 0 hours (top), 24 hours (middle) and 72 hours (bottom).}\]
Reactivity of \([\text{Rh}(\text{P}^\text{tBu}_2\text{H})_2(\eta^2-\text{H}_3\text{B}-\text{P}^\text{tBu}_2\text{H})][\text{BAr}_4^\text{F}_4]\) (4a) with \(\text{H}_3\text{B}-\text{P}^\text{tBu}_2\text{H}\) (1a)

A Youngs NMR tube charged with \([\text{Rh}(\text{P}^\text{tBu}_2\text{H})_2(\eta^2-\text{H}_3\text{B}-\text{P}^\text{tBu}_2\text{H})][\text{BAr}_4^\text{F}_4]\) (4a) (10 mg, 0.007 mmol), an equimolar amount of \(\text{H}_3\text{B}-\text{P}^\text{tBu}_2\text{H}\) (1.2 mg, 0.007 mmol) (1a) and 1,2-F\(_2\)C\(_6\)H\(_4\) (0.4 mL) was heated for 5 hours at 60 °C and for 15 hours at 75 °C. The mixture of reaction changed in colour from blue to yellow with the formation of 5a.

**Scheme S.3:** Reaction of 4a with 1a. Formation of 5a and 3a.

**Figure S.13**: \(^{31}\text{P}\{\text{H}\}\) NMR (202 MHz, 1,2-F\(_2\)C\(_6\)H\(_4\)) spectra of the reaction of 4a and 1 eq. of 1a after 0 hours (top), 5 hours at 60 °C (middle) and 15 hours at 75 °C (bottom). Only the Rh-PHBu\(_2\) area is shown for clarity.
Reactivity of $[\text{Rh(COD)}(\text{P}^2\text{Bu}_2\text{H})(\eta^2-\text{H}_3\text{B} \cdot \text{P}^2\text{Bu}_2\text{H})][\text{BAr}_4^+]$ (6a) with $\text{H}_3\text{B} \cdot \text{P}^2\text{Bu}_2\text{H}$ (1a)

A Youngs NMR tube charged with $[\text{Rh(COD)}(\text{P}^2\text{Bu}_2\text{H})(\eta^2-\text{H}_3\text{B} \cdot \text{P}^2\text{Bu}_2\text{H})][\text{BAr}_4^+]$ (6a) (10 mg, 0.007 mmol), 2 equivalents of $\text{H}_3\text{B} \cdot \text{P}^2\text{Bu}_2\text{H}$ (1a) (2.4 mg, 0.014 mmol) and 1,2-\text{F}_2\text{C}_6\text{H}_4 (0.4 mL) was heated for 48 hours at 75 °C until 5a was formed in almost quantitative yield.

Scheme S.4: Reaction of 6a with 1a. Formation of 4a and 5a.

Figure S.14: $^{31}\text{P}^{1\text{H}}$ NMR (202 MHz, 1,2-\text{F}_2\text{C}_6\text{H}_4) spectra of the reaction of 6a and 2 eq. of 1a after 0 hours (top), 24 hours (middle) and 48 hours (bottom). * = unidentified product (< 5%).
4a + D₂

A solution of 4a (10 mg, 0.007 mmol) in 1,2-F₂C₆H₄ (0.4 mL) was placed under D₂ (4 atm) and the resulting mixture was characterised in situ by ¹H and ²H NMR experiments after 1 hour. A ¹H NMR experiment shows a small hydride peak growing in at -17.9 ppm and the ²H NMR experiment shows a small peak for Rh-D-B (Figure S.15). We propose that at first the D₂ oxidatively adds to the Rh (I) compound to give a Rh(III) compound, and then slowly exchanges with the BH₃ hydrogen atoms via reversible B-H activation process (Scheme S.5).

Scheme S.5: Reaction of 4a with D₂.

Figure S.15: ²H NMR (500 MHz, 1,2-F₂C₆H₄) spectrum of the reaction between 3a and D₂ at 4 atm.
Crystallography

Relevant details about structure refinement are given in Table S.1. Data were collected on a Enraf Nonious Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low temperature device; data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK. The structures were solved by direct methods using SIR92 and refined full-matrix least squares on F² using SHELX-97. All non-hydrogen atoms were refined anisotropically. H1, H2, H3, H001 and H002 were located on the Fourier difference map. All other hydrogen atoms were placed in calculated positions using the riding model. Disorder of the solvent molecule (1,2-F₂C₆H₄) was treated by modelling the fluorine substituent in the 6 sites in the molecule and restraining all of C-F distances. Disorder of the phosphine-borane ligand was treated by modelling it over two sites and restraining its geometry. Rotational disorder of the CF₃ groups of the anion was treated by modelling the fluorine atoms over three sites and restraining their geometry in respect to both the ipso and methyl carbons on which they were present. Rigid geometric restraints applied to 6 of the 8 CF₃ groups on the counter anion, disordered phosphine-borane ligand and solvent molecule (1,2-F₂C₆H₄) are responsible for the high number of restraints in the final structure.

| 4a | CCDC number | 865050 |
| 4a | Formula | C₅₉H₇₄B₂F₁₅P₃Rh |
| 4a | M | 1475.62 |
| 4a | Crystal System | Triclinic |
| 4a | Space group | P-1 |
| 4a | T [K] | 150(2) |
| 4a | a [Å] | 12.8587(1) |
| 4a | b [Å] | 13.3769(1) |
| 4a | c [Å] | 20.2366(2) |
| 4a | α [deg] | 87.9016(4) |
| 4a | β [deg] | 80.6774(4) |
| 4a | γ [deg] | 82.2782(5) |
| 4a | V [Å³] | 3403.73(5) |
| 4a | Z | 2 |
| 4a | Density [gcm⁻³] | 1.440 |
| 4a | µ [mm⁻¹] | 0.426 |
| 4a | θ range [deg] | 5.11 ≤ θ ≤ 27.52 |
| 4a | Reflgs collected | 23970 |
| 4a | Rint | 0.0174 |
| 4a | Completeness | 98.5% |
| 4a | Data/restr/param | 15457 / 1028 / 1082 |
| 4a | R₁ [I > 2σ(I)] | 0.0427 |
| 4a | wR₂ [all data] | 0.1087 |
| 4a | GoF | 1.041 |
| 4a | Largest diff. pk and hole [eÅ⁻³] | 0762, -0.555 |

Table S.1: Crystallographic data for 4a.
References