Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

Supporting Information for:

Intermediates in the Rh-catalysed dehydrocoupling of Phosphine Boranes

Miguel A. Huertos and Andrew S. Weller*

Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, Oxford, OX1 6QR

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

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 130ºC 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.[1] CD_2Cl_2, C_6H_5F and 1,2-$F_2C_6H_4$ were distilled under vacuum from CaH_2 and stored over 3 Å molecular sieves. 1,2-$F_2C_6H_4$ was stirred over alumina for two hours prior to drying. $H_3B{\cdot}PPh_2H$, $H_3B{\cdot}P^tBu_2H$ and P^tBu_2H were purchased from Aldrich used as supplied. $[Rh(COD)_2][BAr^F_4]$,[2] $[Rh(P^iBu_3)_2(C_6H_5F)][BAr^F_4]$,[3] $[Rh(NBD)Cl]_2$,[4] (NBD = norbornadiene) and **2a**[5] were prepared as previously described and $[Rh(NBD)(P^tBu_2H)_2][BAr^F_4]$ was prepared by an adaptation of the published route using $NaBAr^F_4$[6] and PR_3.[7] NMR spectra were recorded on Varian Unity Plus 500 MHz spectrometers at room temperature unless otherwise stated. In 1,2-$F_2C_6H_4$, ^1H NMR spectra were referenced to the centre of the downfield solvent multiplet (δ = 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 µL/ 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 $[Rh(P^tBu_2H)_2(C_6H_5F)][BAr^F_4]$

A solution of $[Rh(NBD)(P^tBu_2H)_2][BAr^F_4]$ (50 mg, 0.074 mmol) in C_6H_5F (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 $[Rh(P^tBu_2H)_2(C_6H_5F)][BAr^F_4]$ as a pale orange powder (82 mg, 82%).

^1H NMR (500 MHz, C_6H_5F): δ 8.33 (s, 8H, BAr^F_4), 7.64 (s, 4H, BAr^F_4), 3.72 (AA'MM'XY, 2H, $^1J_{A\text{-}M}$= 355 Hz, $^3J_{A\text{-}M'}$= 12 Hz, $^2J_{M\text{-}M'}$= 25 Hz, $^2J_{A\text{-}X}\approx 0$, $^3J_{A\text{-}Y}\approx 0$, PH), 1.02 (d, 36H, $^3J_{H\text{-}P}$= 14 Hz, ^{t}Bu). Signals from C_6H_5F not observed.

$^{31}P\{^1H\}$ NMR (202 MHz, C_6H_5F): δ 87.1 (d, $J_{Rh\text{-}P}$= 200 Hz)

ESI-MS (C_6H_5F, 60ºC): positive ion: *m/z*, 491.19 $[M]^+$ (calc. 491.19).

Microanalysis: ($C_{54}BH_{55}P_2RhF_{25}$) Calc.: C, 47.88; H, 4.09. Found: C, 47.79; H, 3.94.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

Preparation of $[Rh(P^tBu_2H)_2(\eta^2\text{-}H_3B{\cdot}P^tBu_2BH_2{\cdot}P^tBu_2H)][BAr^F_4]$ (3a)

To a Youngs flask charged with $[Rh(P^tBu_2H)_2(C_6H_5F)][BAr^F_4]$ (50 mg, 0.037 mmol) and $H_3B{\cdot}P^tBu_2BH_2{\cdot}P^tBu_2H$ (**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 colour 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%).

^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$): δ 8.34 (s, 8H, BAr^F_4), 7.69 (s, 4H, BAr^F_4), 4.28 (dq, 1H, $^1J_{H\text{-}P}$= 366 Hz, $^2J_{H\text{-}B}$= 6 Hz, B-PH), 3.91 (AA'MM'XY, 2H, $^1J_{A\text{-}M}$= 330 Hz, $^3J_{A\text{-}M'}$= 20 Hz, $^2J_{M\text{-}M'}$= 23 Hz, $^2J_{A\text{-}X}\approx 0$, $^3J_{A\text{-}Y}\approx 0$, PH), 1.44 (d, 18H, $^3J_{H\text{-}P}$= 13 Hz, ^{t}Bu) 1.43 (d, 36H, $^3J_{H\text{-}P}$= 14 Hz, ^{t}Bu), 1.37 (d, 18H, $^3J_{H\text{-}P}$= 15 Hz, ^{t}Bu), 2-0.5 (vbr, 2H, BH_2), -1.91 (pcq, 3H, $^1J_{B\text{-}H}$= 86 Hz, BH_3).

^{31}P{^{1}H} NMR (202 MHz, 1,2-$F_2C_6H_4$): δ 91.6 (d, $J_{Rh\text{-}P}$= 174 Hz), 37.6 (br), 7.1 (br).

^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$): δ 8.1 (br), -38.5 (m).

ESI-MS (1,2-$F_2C_6H_4$, 60ºC): positive ion: *m/z*, 713.44 $[M]^+$ (calc. 713.44).

Microanalysis: ($C_{64}B_3H_{92}P_4RhF_{24}$) Calc.: C, 48.76; H, 5.88. Found: C, 48.69; H, 5.86.

Preparation of $[Rh(P^tBu_2H)_2(\eta^2\text{-}H_3B{\cdot}P^tBu_2H)][BAr^F_4]$ (4a)

To a Youngs flask charged with $[Rh(P^tBu_2H)_2(C_6H_5F)][BAr^F_4]$ (50 mg, 0.037 mmol) and $H_3B{\cdot}P^tBu_2H$ (**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 colour from pale orange to blue was observed. The resulting solution was layered with pentane and held at 5 ºC for 72 hours to afford the product as blue crystals (42 mg, 78%).

^{1}H NMR (500 MHz, $C_6H_4F_2$): δ 8.33 (s, 8H, BAr^F_4), 7.68 (s, 4H, BAr^F_4), 4.74 (d, 1H, $^1J_{H\text{-}P}$= 389 Hz, B-PH), 3.92 (AA'MM'XY, 2H, $^1J_{A\text{-}M}$= 345 Hz, $^3J_{A\text{-}M'}$= 22 Hz, $^2J_{M\text{-}M'}$= 25 Hz, $^2J_{A\text{-}X}\approx 0$, $^3J_{A\text{-}Y}\approx 0$, PH), 1.42 (d, 36H, $^3J_{H\text{-}P}$= 15 Hz, ^{t}Bu), 1.40 (d, 18H, $^3J_{H\text{-}P}$= 15 Hz, ^{t}Bu), -1.89 (pcq, 3H, $^1J_{B\text{-}H}$= 96 Hz, BH_3).

^{31}P{^{1}H} NMR (202 MHz, $C_6H_4F_2$): δ 90.5 (d, $J_{Rh\text{-}P}$= 175 Hz), 31.7 (br).

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ 0.3 (br).

ESI-MS ($C_6H_4F_2$, 60ºC): positive ion: *m/z*, 555.30 $[M]^+$ (calc. 555.30).

Microanalysis: ($C_{56}B_2H_{72}P_4RhF_{24}$) Calc.: C, 47.41; H, 5.12. Found: C, 47.63; H, 5.08.

Preparation of $[Rh(H_2)(P^tBu_2H)_2(\eta^2\text{-}H_3B{\cdot}P^tBu_2H)][BAr^F_4]$ (5a)

A solution of **4a** (10 mg, 0.007 mmol) in 1,2-$C_6H_4F_2$ (0.4 mL) was placed under hydrogen (4 atm) to form **5a** in quantitative yield. **5a** was characterised *in situ* by ^{1}H, ^{31}P{^{1}H}, ^{11}B NMR and ESI-MS.

^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$): δ 8.34 (s, 8H, BAr^F_4), 7.69 (s, 4H, BAr^F_4), 4.52 (dq, 1H, $^1J_{H\text{-}P}$= 369 Hz, $^2J_{H\text{-}B}$= 5 Hz, B-PH), 4.33 (d, 2H, $J_{H\text{-}P}$=318 Hz, PH), 1.39 (d, 36H, $^3J_{H\text{-}P}$= 14 Hz, ^{t}Bu), 1.35 (d, 18H, $^3J_{H\text{-}P}$= 15 Hz, ^{t}Bu), -0,94 (pcq, 3H, $^1J_{B\text{-}H}$= 104 Hz, BH_3), -17.67 (dt, 2H, $^1J_{H\text{-}Rh}$= 20 Hz, $^2J_{H\text{-}P}$= 15 Hz, Rh-H).

^{31}P{^{1}H} NMR (202 MHz, 1,2-$F_2C_6H_4$): δ 81.0 (d, $J_{Rh\text{-}P}$= 107.3 Hz), 27.4 (br).

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$): δ -20.4 (br).

ESI-MS (1,2-$F_2C_6H_4$, 60ºC): positive ion: *m/z*, 557.32 $[M]^+$ (calc. 557.32).

Preparation of [Rh(COD)(P^tBu_2H)(η^2-$H_3B{\cdot}P^tBu_2H$)][BAr^F_4] (6a)

To a Youngs flask charged with [Rh(COD)$_2$][BAr^F_4] (70 mg, 0.059 mmol) and $H_3B{\cdot}P^tBu_2H$ (**1a**) (19 mg, 0.120 mmol) was added 1,2-$F_2C_6H_4$ (10 mL). The solution was stirred at 40 ºC 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}H NMR (500 MHz, 1,2-$F_2C_6H_4$): δ 8.33 (s, 8H, BAr^F_4), 7.68 (s, 4H, BAr^F_4), 5.12 (s, 2H, COD), 4.10 (dq, 1H, $^1J_{H\text{-}P}$= 359 Hz, $^2J_{H\text{-}B}$= 5 Hz, B-PH), 5.12 (s, 2H, COD), 3.15 (d, 1H, $^1J_{H\text{-}P}$= 336 Hz, PH), 2.45 (m, 2H, COD), 2.28 (m, 2H, COD), 2.19 (m, 2H, COD), 2.05 (m, 2H, COD), 1.44 (d, 18H, $^3J_{H\text{-}P}$= 14 Hz, ^{t}Bu), 1.39 (d, 18H, $^3J_{H\text{-}P}$= 15 Hz, ^{t}Bu), -0.62 (pcq, 3H, $^1J_{B\text{-}H}$= 98 Hz, BH_3).

^{31}P{^{1}H} NMR (202 MHz, 1,2-$F_2C_6H_4$): δ 79.3 (d, $J_{Rh\text{-}P}$= 138 Hz), 28.5 (br).

^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$): δ -35.5 (br).

ESI-MS (1,2-$F_2C_6H_4$, 60ºC): positive ion: *m/z*, 517.29 $[M]^+$ (calc. 517.29).

Microanalysis: ($C_{56}B_2H_{65}P_2RhF_{24}$) Calc.: C, 48.72; H, 4.75. Found: C, 48.74; H, 4.80.

Preparation of [(P^tBu_2H)$_2BH_2$][BH_4] (7[BH_4])

Monobromoborane-metylsulfide complex (280 μL of 1.0 M CH_2Cl_2 solution, 0.280 mmol) was added to a stirred solution of di-*tert*-butylphosphine (100 μL, 0.540 mmol) in CH_2Cl_2 (10 mL). After 40 h, the volatiles were removed under vacuum, and the resulting white solid was washed with hexane and then dissolved in CH_2Cl_2 (5 mL). To this solution was added Li[BH_4] (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}H NMR (500 MHz, 1,2-$F_2C_6H_4$): δ 8.32 (s, 8H, BAr^F_4), 7.69 (s, 4H, BAr^F_4), 4.35 (dm, 2H, $^1J_{H\text{-}P}$= 372 Hz, PH), 2.32 (br, qu, 4H, $^1J_{H\text{-}B}$= 105 Hz, BH_4), 1.44 (d, 36H, $^3J_{H\text{-}P}$= 14 Hz, ^{t}Bu). Signals from BH_2 not observed.

^{31}P{^{1}H} NMR (202 MHz, 1,2-$F_2C_6H_4$): δ 34.9 (m, br).

^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$): δ -41.1 (m, br, 2B) BH_2 and BH_4 peaks are coincident.

ESI-MS (1,2-$F_2C_6H_4$, 60ºC): positive ion: *m/z*, 305.27 $[M]^+$ (calc. 305.27).

Preparation of [(P^tBu_2H)$_2BH_2$][BAr^F_4] (7[BAr^F_4])

Compound **7[BAr^F_4]** was made as described above for **7[BH_4]** but using Na[BAr^F_4] (248 mg, 0.280 mmol) (291 mg, 90%).

^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$): δ 8.32 (s, 8H, BAr^F_4), 7.69 (s, 4H, BAr^F_4), 4.54 (dm, 2H, $^1J_{H\text{-}P}$= 380 Hz, PH),

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

1.38 (d, 36H, $^{3}J_{H\text{-}P}$= 16 Hz, ^{t}Bu). Signals from BH_2 not observed.

$^{31}P\{^{1}H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$): δ 36.6 (m, br).

^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$): δ -41.1 (m, br).

NMR and ESI-MS characterisation

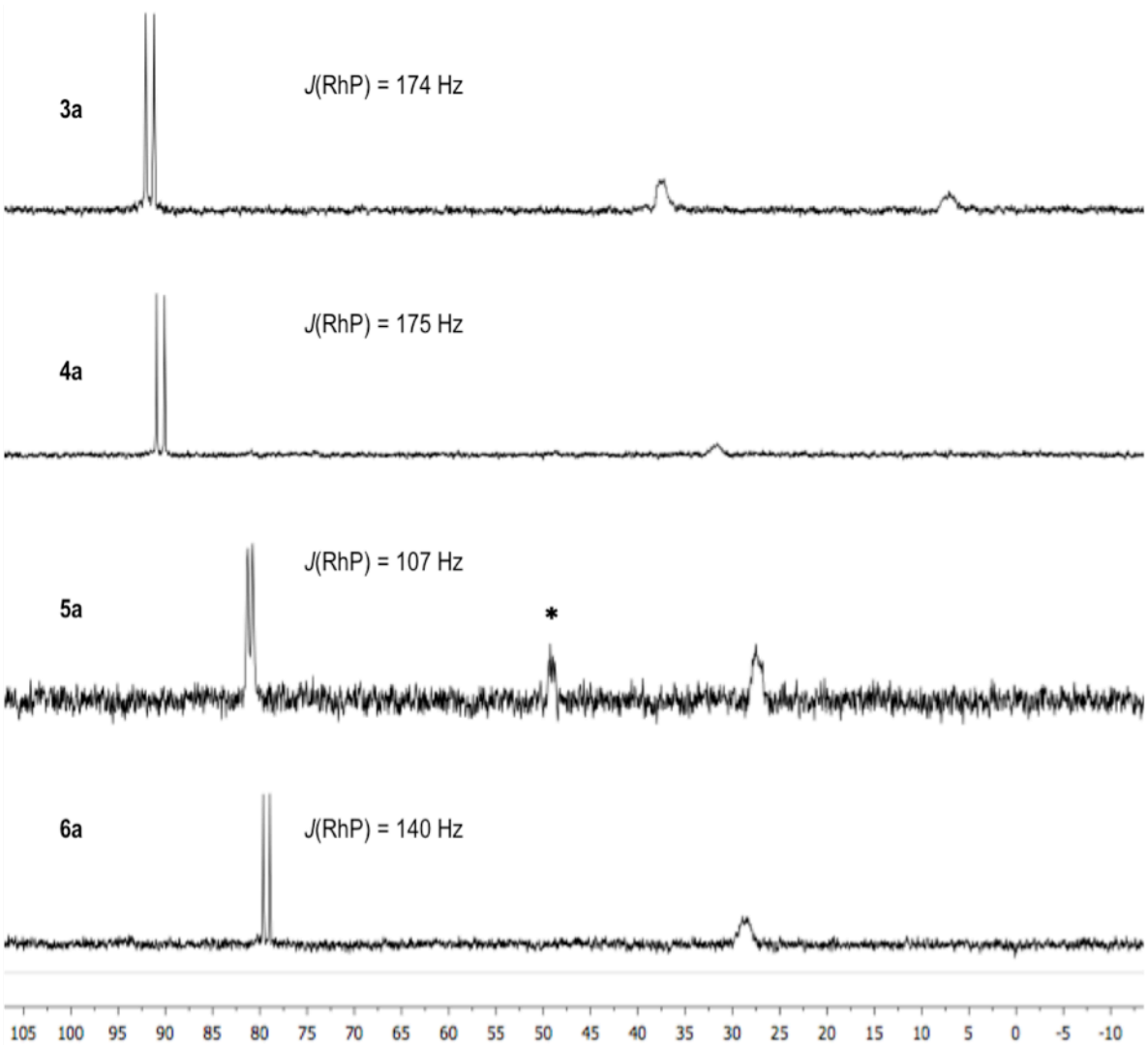


Figure S.1: $^{31}P\{^{1}H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$) spectra of **3a**, **4a, 5a** and **6a** all over the same chemicals shift range. ✱ = $H_3B{\cdot}P^{t}Bu_2H$ (**1a**).

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

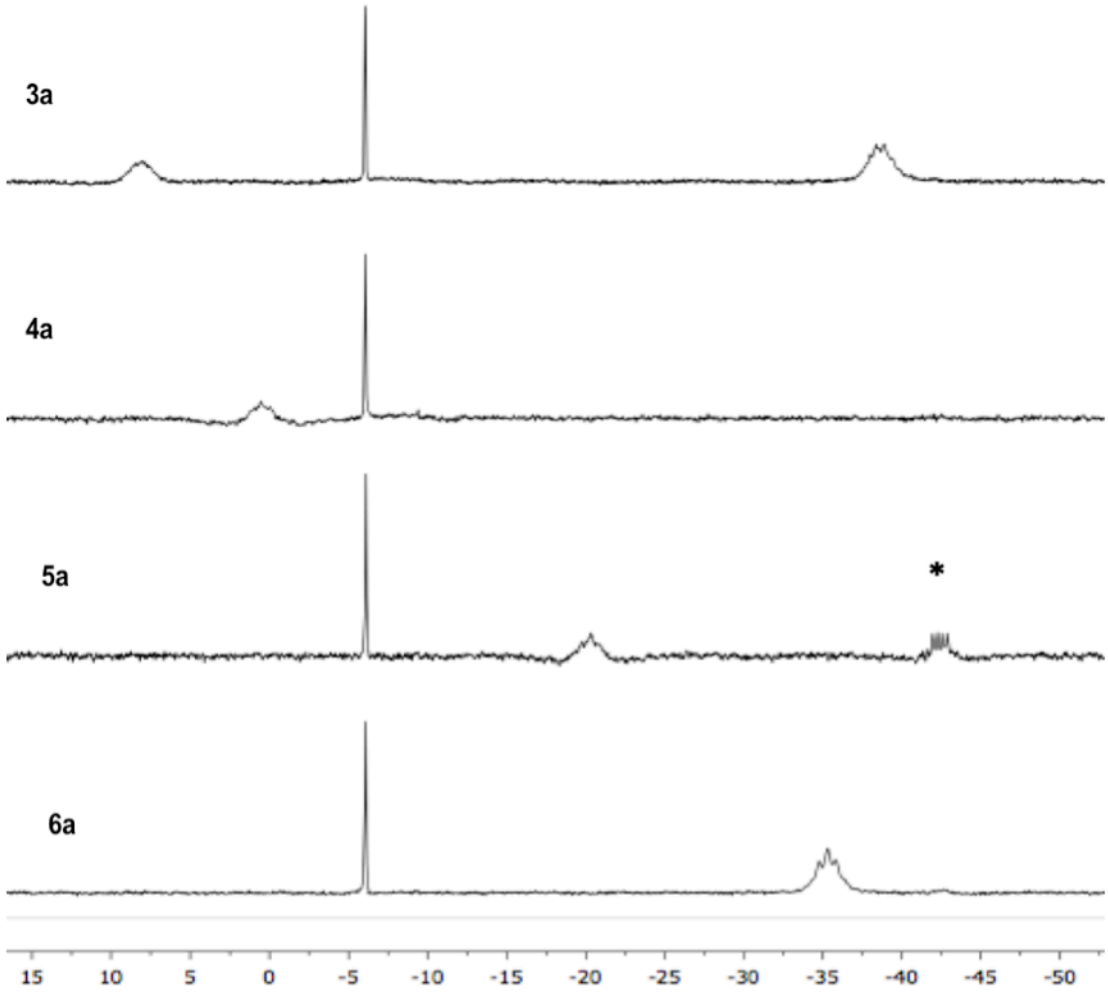


Figure S.2: ^{11}B NMR (160 MHz, 1,2-$F_2C_6H_4$) spectra of **3a**, **4a, 5a** and **6a** all over the same chemicals shift range. ✱ = $H_3B{\cdot}P^tBu_2H$ (**1a**).

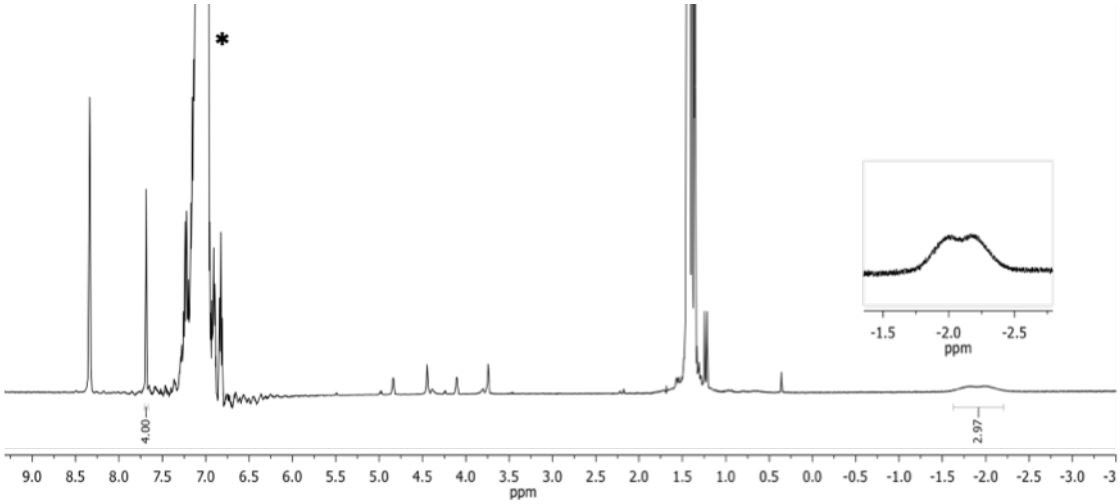


Figure S.3: ^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$) spectrum of **3a**. ✱ = 1,2-$F_2C_6H_4$.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

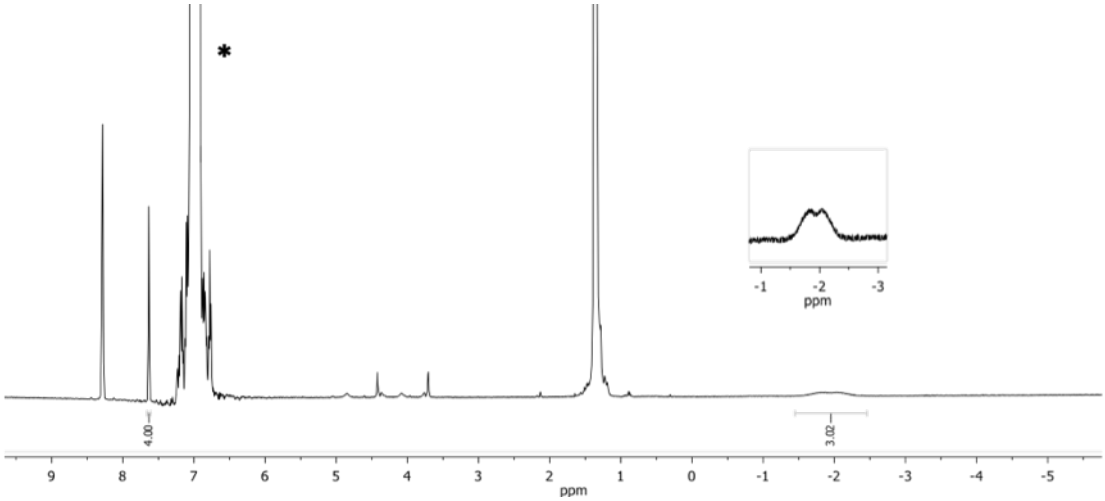


Figure S.4: ^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$) spectrum of **4a**. ✱ = 1,2-$F_2C_6H_4$.

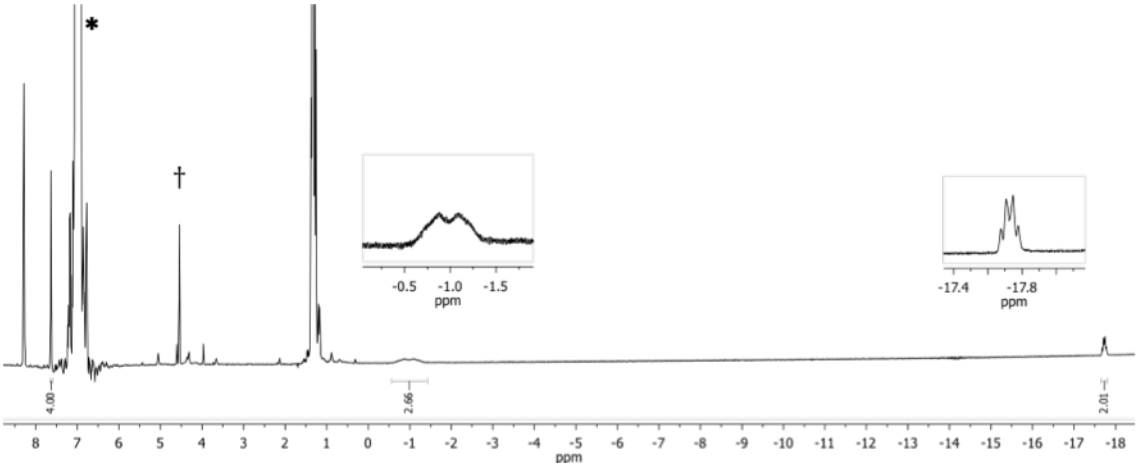


Figure S.5: ^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$) spectrum of **5a**. ✱ =1,2-$F_2C_6H_4$, † = H_2.

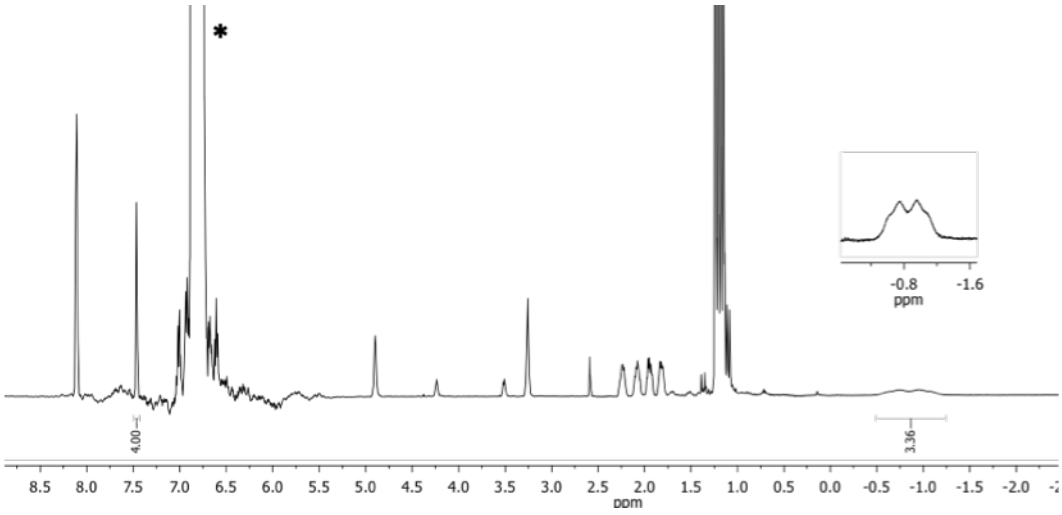


Figure S.6: ^{1}H NMR (500 MHz, 1,2-$F_2C_6H_4$) spectrum of **6a**. ✱ = 1,2-$F_2C_6H_4$.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

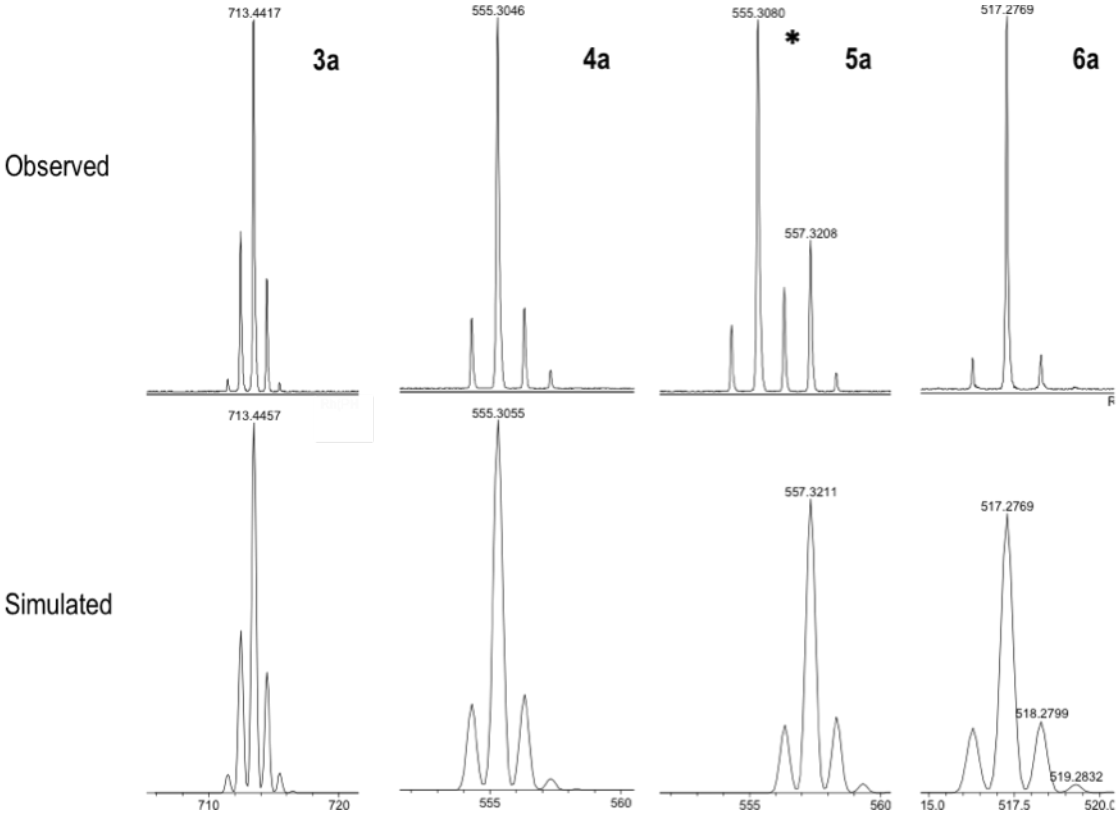
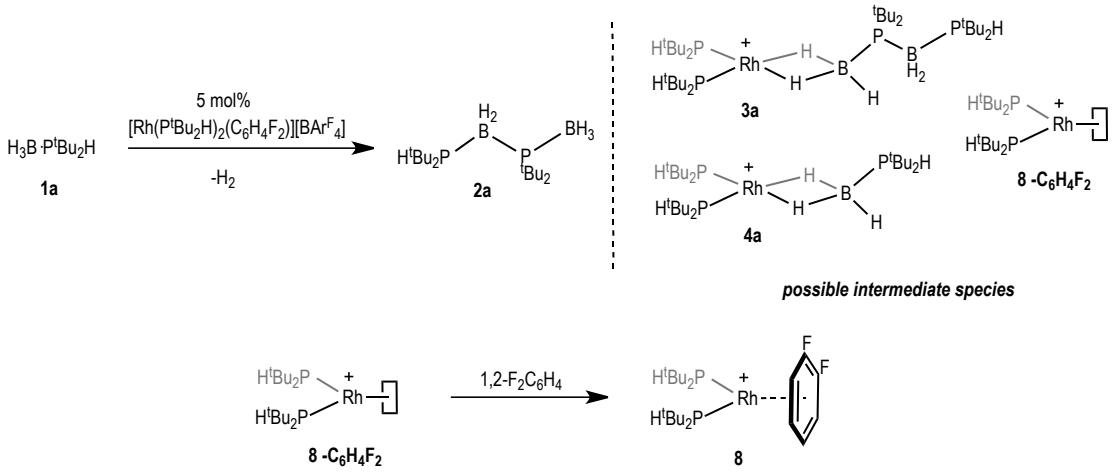


Figure S.7: Observed (top) and simulated (bottom) ESI-MS of **3a**, **4a, 5a** and **6a** in 1,2-$F_2C_6H_4$. ✱ = **4a** (**5a** loses H_2 under Ar atmosphere to give $[M\text{-}H_2]^+$).

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

Catalytic study with $[Rh(P^tBu_2H)_2(C_6H_5F)][BAr^F_4]$

Dehydrocoupling of $H_3B{\cdot}P^tBu_2H$ (**1a**) using 5 mol% of $[Rh(P^tBu_2H)_2(C_6H_5F)][BAr^F_4]$ at 140 ºC in melt conditions led to compound **2a** in approximately 65% conversion in 20 hours. Monitoring the melt reaction using $^{31}P\{^1H\}$ NMR spectroscopy and ESI-MS (in 1,2-$F_2C_6H_4$ solutions for both) showed as well as **2a**, PH^tBu_2 (free phosphine) and $[^tBu_2HP{\cdot}BH_2{\cdot}PH^tBu_2]^+$ (**7**$^+$) assumed to be the $[BH_4]^-$ salt (Figure S.8). By monitoring the same reaction but using 20 mol% of $[Rh(P^tBu_2H)_2(C_6H_5F)][BAr^F_4]$ we have identified possible intermediate species (Figures S.9 and S.10).



Scheme S.1: Catalytic dehydrocoupling of **1a** to give **2a** (left) and possible intermediate species (right). **Bottom:** Reaction of **8 –$C_6H_4F_2$** when you solve it in difluorobenzene, formation of **8**.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

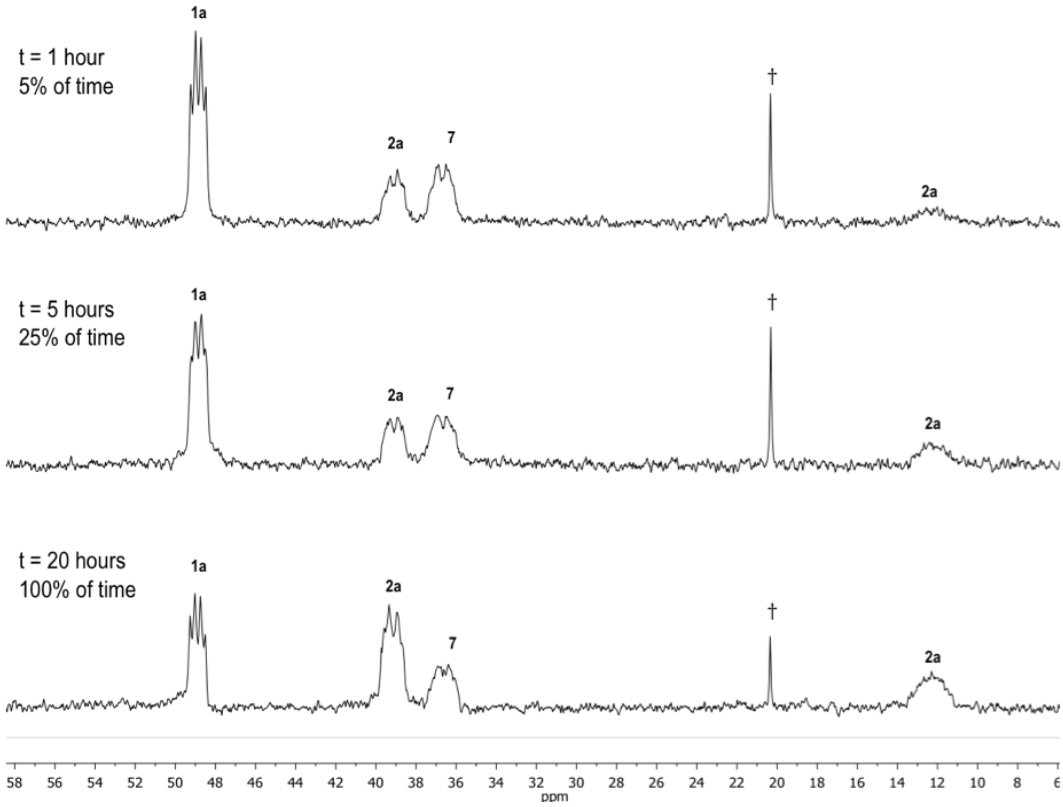


Figure S.8: $^{31}P\{^{1}H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$) spectra for the catalytic dehydrocouplin of **1a** to give **2a** (melt, 140 ºC) at 1 hour (top), 5 hours (middle) and 20 hours (bottom). † = PH^tBu_2. After 30 hours no changes observed.

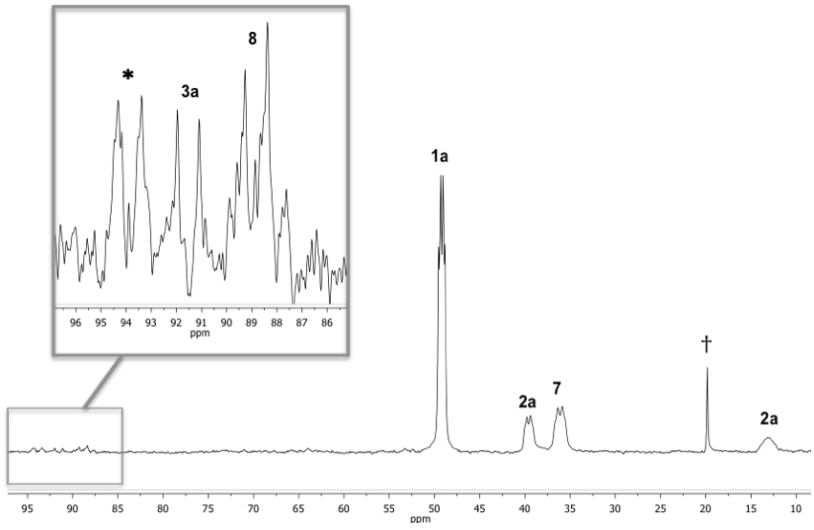


Figure S.9: $^{31}P\{^{1}H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$) spectrum for the catalytic dehydrocoupling of **1a** to give **2a** (melt, 140 ºC) at 5 hours using 20 mol% of $[Rh(P^tBu_2H)_2(C_6H_5F)][BAr^F_4]$. In the box, signals for intermediate species **8** and **3a**. † = free PH^tBu_2. ✱ = unknown species.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

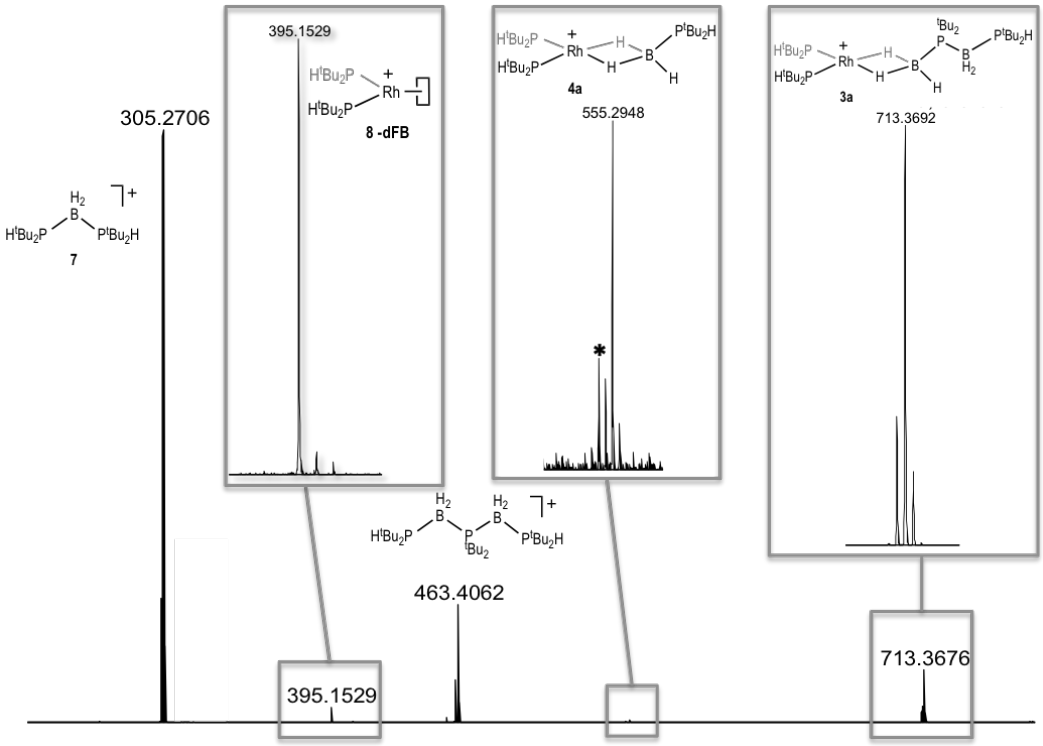


Figure S.10: Observed ESI-MS for the catalytic dehydrocoupling of **1a** to give **2a** (melt, 140 ºC) at 5 hours.

✱ = unknown species. We see no evidences from the specie $[^{t}Bu_2HP{\cdot}BH_2{\cdot}P^{t}Bu_2{\cdot}BH_2{\cdot}P^{t}Bu_2H]^{+}$ by NMR spectroscopy and assume arises from fragmentation in the ESI-MS.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

Catalytic study with $[Rh(COD)_2][BAr^F{}_4]$

Dehydrocoupling of $H_3B{\cdot}P^tBu_2H$ (**1a**) using 5 mol% of $[Rh(COD)_2][BAr^F{}_4]$ at 140 ºC in melt conditions led to compound **2a** in approximately 65% of conversion in 20 hours. Monitoring the melt reaction, after 5 hours, using $^{31}P\{^1H\}$ NMR spectroscopy and ESI-MS (in 1,2-$F_2C_6H_4$ solutions for both) showed as well as **2a**, PH^tBu_2 (free phosphine) and $[^tBu_2HP{\cdot}BH_3{\cdot}PH^tBu_2]^+$ (**7**$^+$). We have also identified possible organometallic intermediate species (Figure S.11).

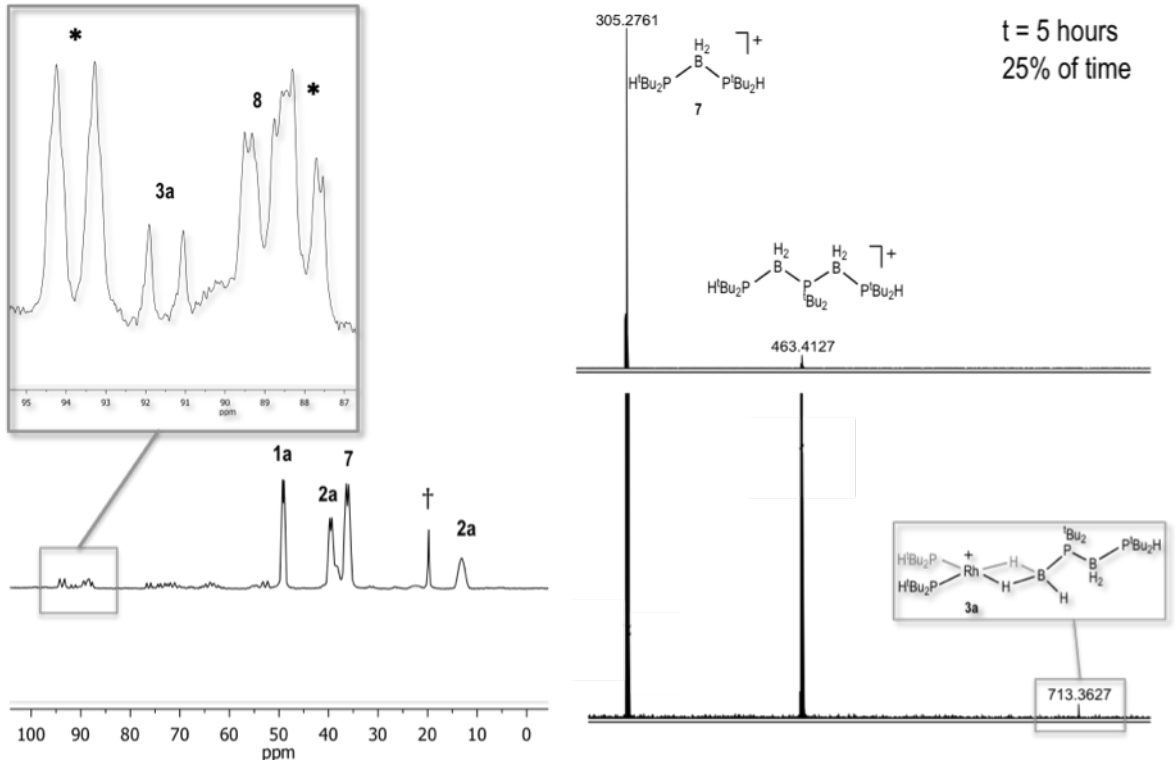
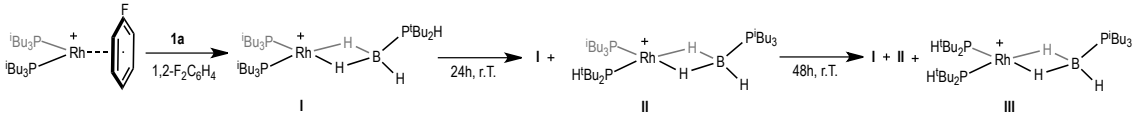


Figure S.11: Left: $^{31}P\{^1H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$) spectrum for the catalytic dehydrocoupling of **1a** to give **2a** (melt, 140 ºC) at 5 hours. In the box, signals for intermediate species **8** and **3a**. † = free PH^tBu_2. ✱ = unknown species. **Right:** Observed ESI-MS for the catalytic dehydrocoupling of **1a** (melt, 140 ºC) at 5 hours.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

Reactivity of $[Rh(P^iBu_3)_2(C_6H_5F)][BAr^F_4]$

To a Youngs NMR tube charged with $[Rh(P^iBu_3)_2(C_6H_5F)][BAr^F_4]$ (10 mg, 0.007 mmol) an equimolar amount of $H_3B{\cdot}P^tBu_2H$ (**1a**) (1.2 mg, 0.007 mmol) was added 1,2-$F_2C_6H_4$ (0.4 mL). Instantaneously, a change in the colour from pale orange to blue was observed and the products of this reaction were characterised *in situ* by ^1H, $^{31}P\{^1H\}$ and ^{11}B NMR spectroscopy and interrogated by NMR spectroscopy after 24 and 72 hours at room temperature (Figure S.12).



Scheme S.2: Reaction of $[Rh(P^iBu_3)_2(C_6H_5F)][BAr^F_4]$ with **1a**. Formation of the sustances $[Rh(P^iBu_3)_n(P^tBu_2H)_{2-n}(H_3B{\cdot}PR_3)][BAr^F_4]$ (PR_3 = P^iBu_3, P^tBu_2H; n = 2–0) (**I**, **II** and **III**).

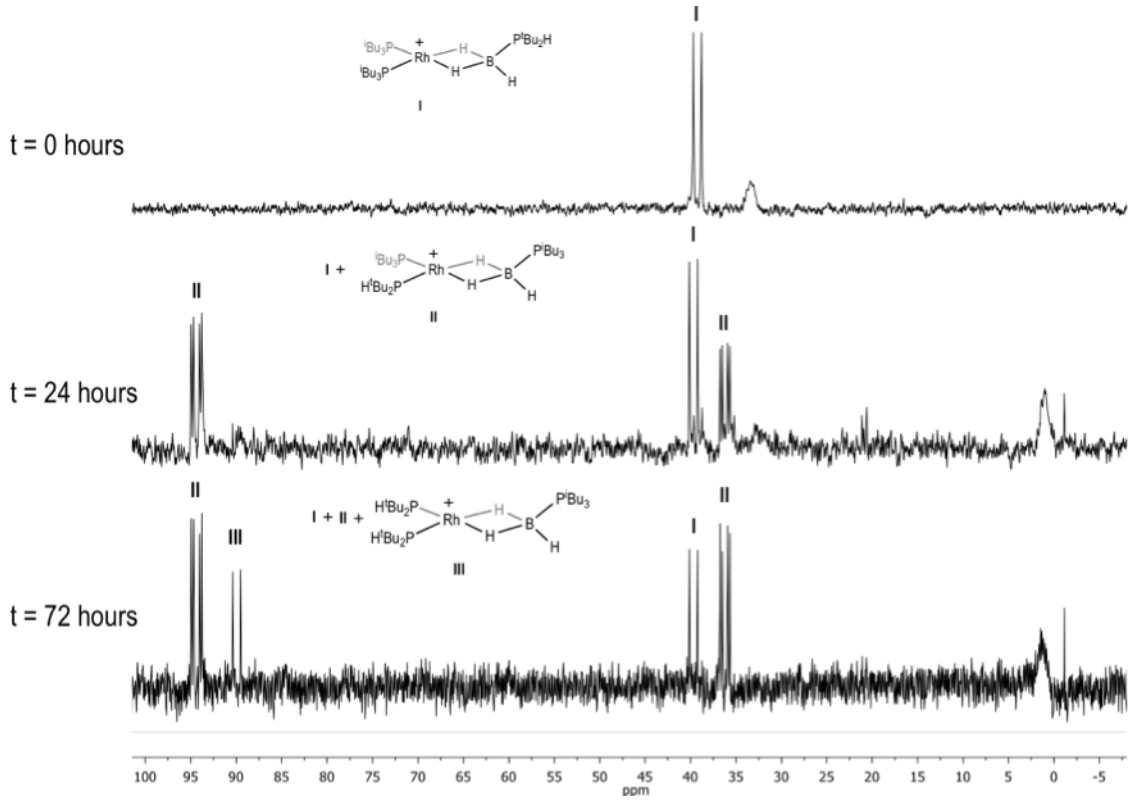
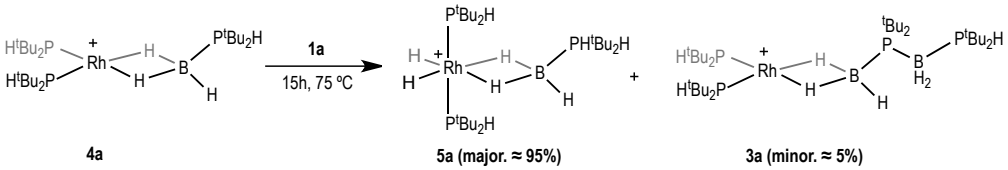


Figure S.12: $^{31}P\{^1H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$) spectra of the reaction between $[Rh(P^iBu_3)_2(C_6H_5F)][BAr^F_4]$ and **1a** after 0 hours (top), 24 hours (middle) and 72 hours (bottom).

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

Reactivity of [Rh(P^tBu_2H)$_2$(η^2-$H_3B{\cdot}P^tBu_2H$)][BAr^F_4] (4a) with $H_3B{\cdot}P^tBu_2H$ (1a)

A Youngs NMR tube charged with [Rh(P^tBu_2H)$_2$(η^2-$H_3B{\cdot}P^tBu_2H$)][BAr^F_4] (**4a**) (10 mg, 0.007 mmol), an equimolar amount of $H_3B{\cdot}P^tBu_2H$ (1.2 mg, 0.007 mmol) (**1a**) and 1,2-$F_2C_6H_4$ (0.4 mL) was heated for 5 hours at 60 ºC and for 15 hours at 75 ºC. 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**.

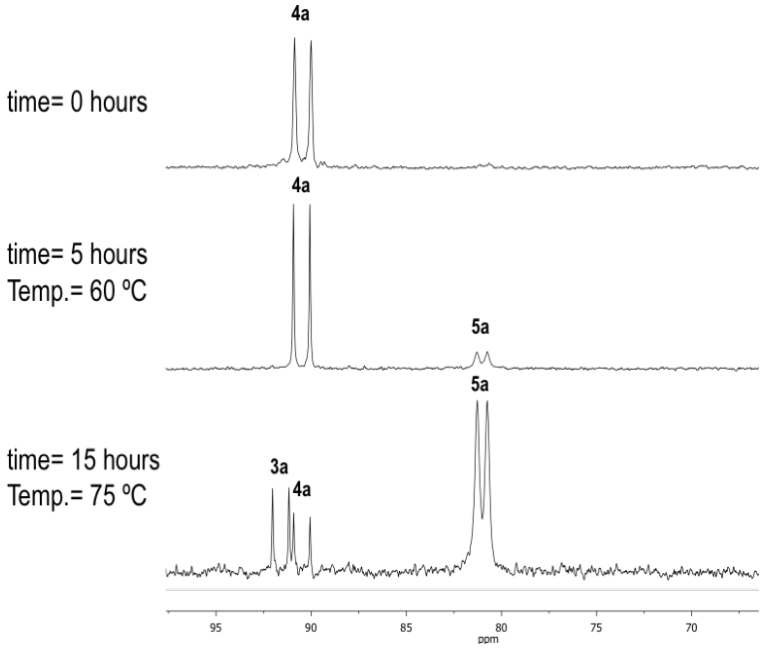
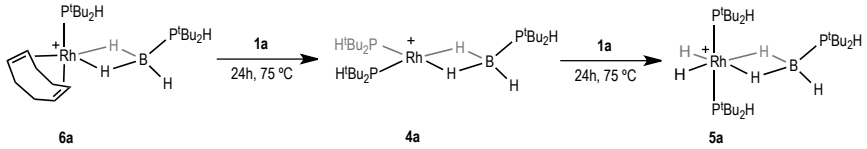


Figure S.13 : $^{31}P\{^1H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$) spectra of the reaction of **4a** and 1 eq. of **1a** after 0 hours (top), 5 hours at 60 ºC (middle) and 15 hours at 75 ºC (bottom). Only the Rh-PH^tBu_2 area is shown for clarity.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

Reactivity of [Rh(COD)(P^tBu_2H)(η^2-$H_3B{\cdot}P^tBu_2H$)][BAr^F_4] (6a) with $H_3B{\cdot}P^tBu_2H$ (1a)

A Youngs NMR tube charged with [Rh(COD)(P^tBu_2H)(η^2-$H_3B{\cdot}P^tBu_2H$)][BAr^F_4] (**6a**) (10 mg, 0.007 mmol), 2 equivalents of $H_3B{\cdot}P^tBu_2H$ (**1a**) (2.4 mg, 0.014 mmol) and 1,2-$F_2C_6H_4$ (0.4 mL) was heated for 48 hours at 75 ºC until **5a** was formed in almost quantitative yield.



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

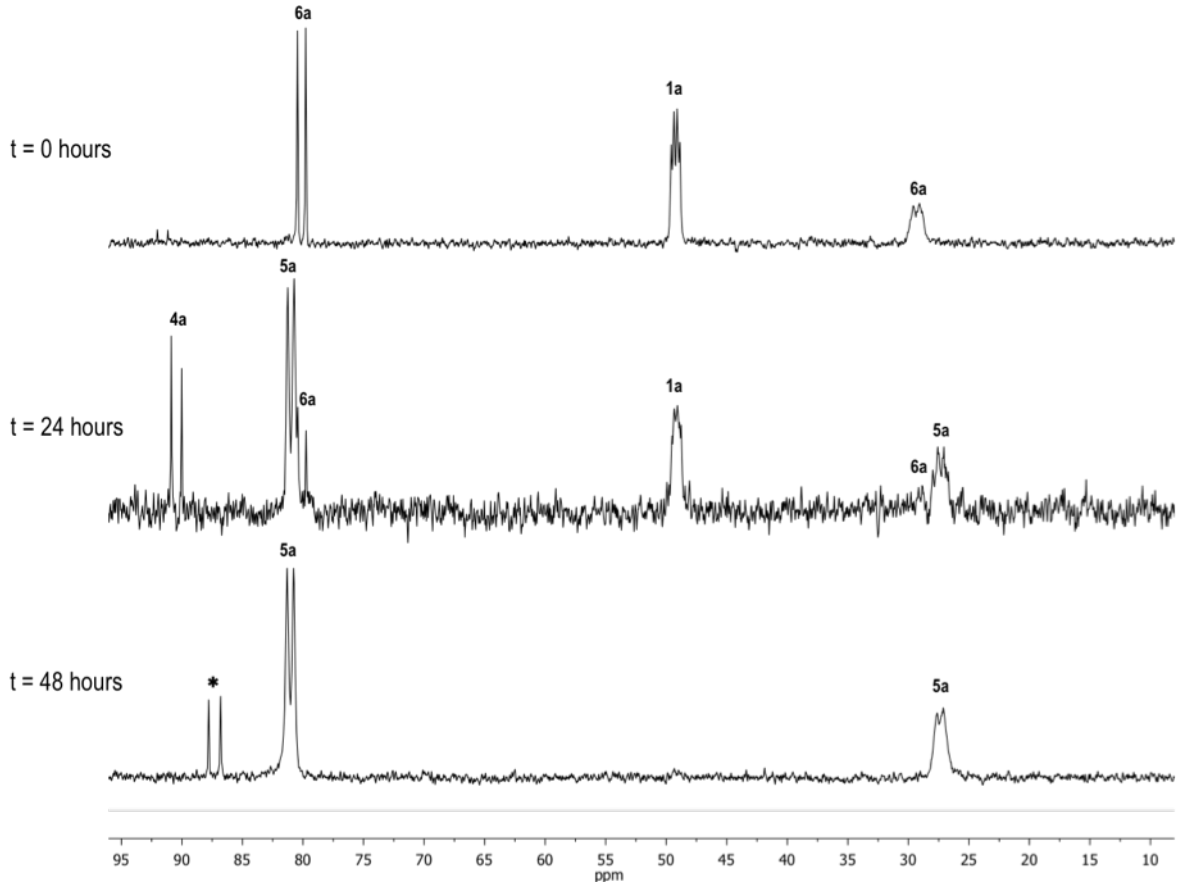
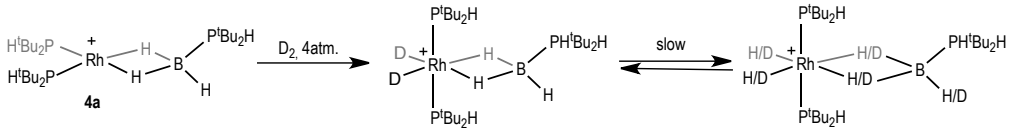


Figure S.14 : $^{31}P\{^1H\}$ NMR (202 MHz, 1,2-$F_2C_6H_4$) spectra of the reaction of **6a** and 2 eq. of **1a** after 0 hours (top), 24 hours (middle) and 48 hours (bottom). ✱ = unidentified product (< 5%).

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

4a + D_2

A solution of **4a** (10 mg, 0.007 mmol) in 1,2-$F_2C_6H_4$ (0.4 mL) was placed under D_2 (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 D_2 oxidatively adds to the Rh (I) compound to give a Rh(III) compound, and then slowly exchanges with the BH_3 hydrogen atoms via reversible B-H activation process (Scheme S.5).



Scheme S.5: Reaction of **4a** with D_2.

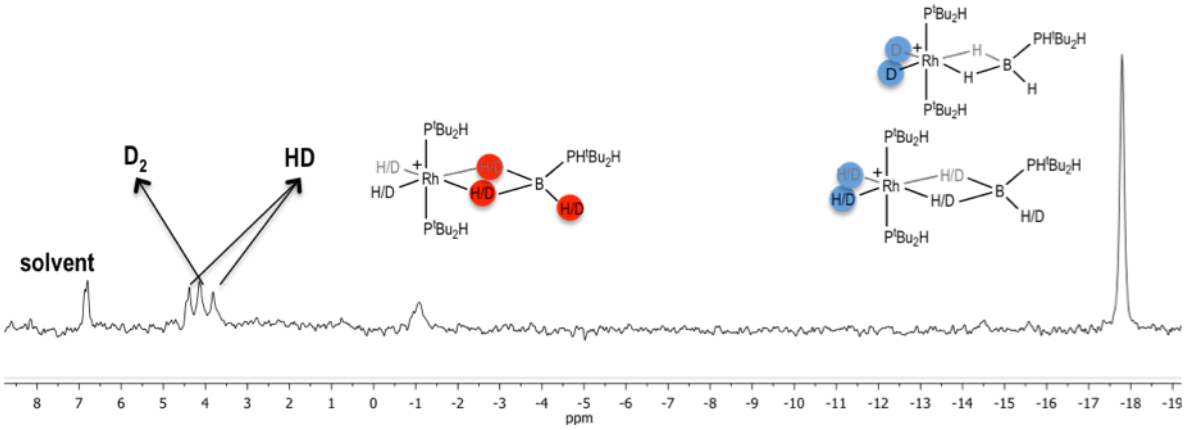


Figure S.15: ^2H NMR (500 MHz, 1,2-$F_2C_6H_4$) spectrum of the reaction between **3a** and D_2 at 4 atm.

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

Crystallography

Relevant details about structure refinement are given in Table S.1. Data were collected on a Enraf Nonious Kappa CCD difractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low temperature device;[8] data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK.[9] The structures were solved by direct methods using SIR92[10] and refined full-matrix least squares on F^2 using SHELX-97.[11] All non-hydrogen atoms were refined anysotropically. 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-$F_2C_6H_4$) 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 CF_3 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 CF_3 groups on the counter anion, disordered phosphine-borane ligand and solvent molecule (1,2-$F_2C_6H_4$) are responsible for the high number of restraints in the final structure.

	4a
CCDC number	865050
Formula	$C_{59}H_{74}B_2F_{25}P_3Rh$
M	1475.62
Crystal System	Triclinic
Space group	*P*-1
T [K]	150(2)
a [Å]	12.8587(1)
b [Å]	13.3769(1)
c [Å]	20.2366(2)
α [deg]	87.9016(4)
β [deg]	80.6774(4)
γ [deg]	82.2782(5)
V [Å^3]	3403.73(5)
Z	2
Density [gcm^{-3}]	1.440
μ [mm^{-1}]	0.426
θ range [deg]	$5.11 \le \theta \le 27.52$
Reflns collected	23970
R_{int}	0.0174
Completeness	98.5%
Data/restr/param	15457 / 1028 / 1082
R_1 [I > 2σ(I)]	0.0427
wR_2 [all data]	0.1087
GoF	1.041
Largest diff. pk and hole [eÅ^{-3}]	0762, -0.555

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

Supplementary Material (ESI) for Chemical Communications
This Journal is (c) The Royal Society of Chemistry 2012

References

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518.
2. E. Neumann, A. Pfaltz, *Organometallics* **2005**, *24*, 2008.
3. A. B. Chaplin, A. I. Poblador-Bahamonde, H. A. Sparkles, J. A. K. Howard, S. A. Macgregor and A. S. Weller, *Chem. Commun.*, **2009**, 244.
4. W. E. Abel, M. A. Bennet, G. J. Wilkinson, *J. Chem. Soc.*, **1959**, 3178.
5. H. Dorn, E. Vejzovic, A. J. Lough and I. Manners, *Inorg. Chem.* **2001,** *40,* 4327.
6. W. E. Buschman, J. S. Miller, K. Bowmn-James and C. N. Miller, *Inorg. Synth.*, **2002**, *33*, 83.
7. A. Rifat, V. E. Laing, G. Kociok-Köhn, M. F. Mahon, G. D. Ruggiero and A. S Weller, J. Organometallic Chem. 2003, 680, 127.
8. J. Cosier and M. A. Glazer, *J. Appl. Cryst.*, **1986**, *19*, 105.
9. Z. Otwinowski, Z. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol. **1997**, 276, Eds C. W. Carter, R. M. Sweet, Academic Press.
10. A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camali. *J. Appl. Cryst.*, **1994**, *27*, 435.
11. G. M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112.