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Supporting Information for:

Revealing the P–B coupling event in the rhodium catalysed dehydrocoupling of phosphine boranes, $H_3B{\cdot}PR_2H$ (R = ^{t}Bu, Ph)

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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 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-$C_6H_4F_2$ were distilled under vacuum from CaH_2 and stored over 3 Å molecular sieves, 1,2-$C_6H_4F_2$ was stirred over alumina for two hours prior to drying. $H_3B{\cdot}PPh_2H$, $H_3B{\cdot}P^tBu_2H$, bis-(diphenylphosphinepropane) (dpp3), $BD_3{\cdot}THF$, Ph_2HP and $^tBu_2HP$ were purchased from Aldrich. $[Rh(NBD)Cl]_2$,[2] $[Rh(NBD)(dpp3)][BArF_4]$,[3] $^tBu_2HP{\cdot}BH_2{\cdot}P^tBu_2{\cdot}BH_3$[4] and $Ph_2HP{\cdot}BH_2{\cdot}PPh_2{\cdot}BH_3$[5] were prepared as previously described. NMR spectra were recorded on Varian Unity Plus 500 MHz spectrometer at room temperature unless otherwise stated. In $C_6H_4F_2$, ^1H NMR spectra were referenced to the centre of the downfield solvent multiplet (δ = 7.07), ^{31}P and ^{11}B NMR spectra were referenced against 85% H_3PO_4 (external) and $BF_3.OEt_2$ (external) respectively. The spectrometer was pre-locked and pre-shimmed using a C_6D_6 (0.1 mL) and 1,2-$C_6H_4F_2$ (0.3 mL) sample. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicrOTOF instrument. In all ESI-MS spectra there was a good fit to both the principal molecular ion and the overall isotopic distribution.

Synthesis of new complexes

Synthesis of [Rh(dpp3)(η^2-$H_3B{\cdot}P^tBu_2H$)][BAr^F_4] (4)

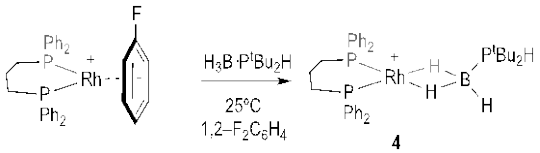
To a Youngs flask charged with [Rh(dpp3)(C_6H_5F)][BAr^F_4] (50 mg, 0.034 mmol) and $H_3B{\cdot}P^tBu_2H$ (6 mg, 0.038 mmol) was added 1,2-$C_6H_4F_2$ (15 mL). The solution was stirred at room temperature for 10 minutes and a change in the colour from pale orange to blue was observed. Complex **4** was Isolated as a blue oil, and was characterized in situ by NMR and ESI-MS as attempts to purify it lead to rapid decomposition. The reaction was quantitative (i.e. > 95%) by NMR spectroscopy.

^1H NMR (500 MHz, $C_6H_4F_2$): δ 8.32 (s, 8H, BAr^F_4), 7.68 (s, 4H, BAr^F_4), 3.90 (d, 1H, $^1J_{H\text{-}P}$= 380, B-PH), 2.39 (m, 4H, 2 CH_2), 1.96 (m, 2H, CH_2), 1.17 (d, 18H, $^3J_{H\text{-}P}$= 14, ^{t}Bu), -0.50 (br, 3H, BH_3). Ph-region is overlapped by $C_6H_4F_2$.

$^{31}P\{^1H\}$ NMR (202 MHz, $C_6H_4F_2$): δ 34.3 (d, $J_{Rh\text{-}P}$= 170), 38.7 (br).

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ -1.5 (br), -6.2 (BAr^F_4).

ESI-MS ($C_6H_4F_2$, 60ºC): positive ion: *m/z*, 675.32 $[M]^+$ (calc. 675.40).



Scheme S.1. Synthesis of complex **4**

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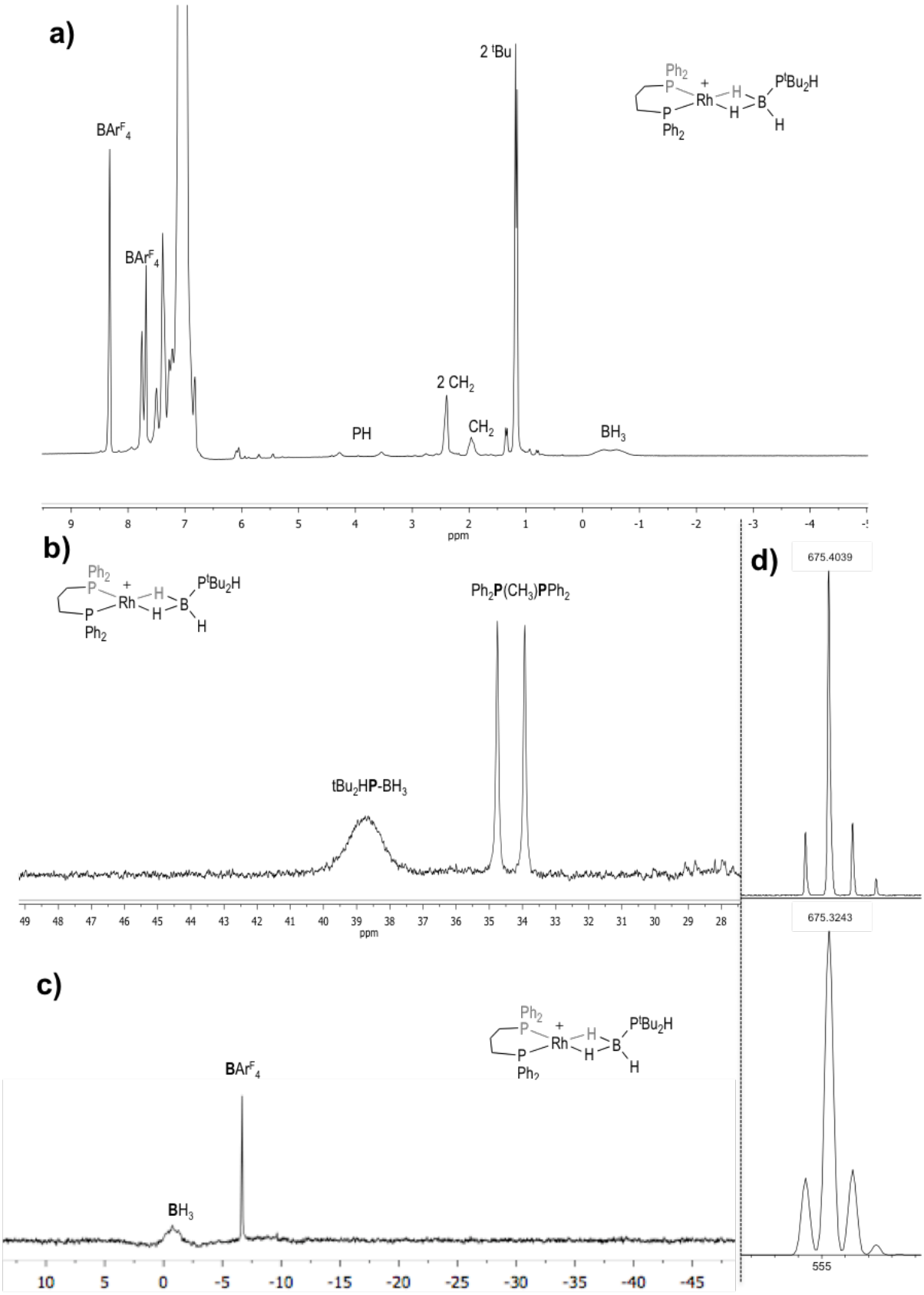

Figure S.1. a) ^{1}H NMR spectrum for complex **4**. **b)** ^{31}P{^{1}H} NMR spectrum for complex **4**. **c)** ^{11}B NMR spectrum for complex **4**. **d)** ESI.MS for compound **4$^+$.**

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Synthesis of [Rh(dpp3)(η^2-$H_3B{\cdot}P^tBu_2BH_2{\cdot}P^tBu_2H$)][$BAr^F{}_4$] (5)

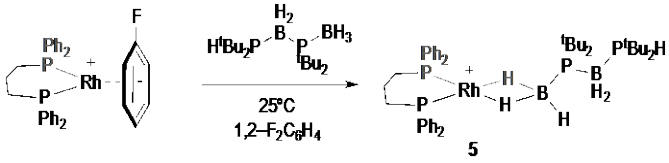
To a Youngs flask charged with [Rh(dpp3)(C_6H_5F)][$BAr^F{}_4$] (20 mg, 0.014 mmol) and $H_3B{\cdot}P^tBu_2BH_2{\cdot}P^tBu_2H$ (4.5mg, 0.014 mmol) was added 1,2-$C_6H_4F_2$ (5 mL). The solution was stirred at room temperature for 1 hour and a change in the colour from pale orange to blue was observed. Compound **5** was isolated as a blue oil, and was characterized in situ by NMR and ESI-MS as attempts to purify it lead to rapid decomposition. The reaction was quantitative (i.e. > 95%) by NMR spectroscopy.

^{1}H NMR (500 MHz, $C_6H_4F_2$): δ 8.33 (s, 8H, $BAr^F{}_4$), 7.68 (s, 4H, $BAr^F{}_4$), 3.99 (d, 1H, $^1J_{H\text{-}P}$= 368, B-PH), 2.35 (m, 4H, 2 CH_2), 1.95 (m, 2H, CH_2), 1.19 (d, 18H, $^3J_{H\text{-}P}$= 13, ^{t}Bu), 1.16 (d, 18H, $^3J_{H\text{-}P}$= 15, ^{t}Bu), 1.50-0.30 (br, 2H, P-BH_2-P overlapped by the ^{t}Bu signal), -1.38 (br, 3H, BH_3). Ph-region is overlapped by $C_6H_4F_2$.

^{31}P{^{1}H} NMR (202 MHz, $C_6H_4F_2$): δ 35.8 (d, $J_{Rh\text{-}P}$= 183), 36.8 (br, B-*P*), 7.9 (br, B-*P*-B).

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ 0.1 (br), -6.2 ($BAr^F{}_4$) -38.5 (br).

ESI-MS ($C_6H_4F_2$, 60ºC): positive ion: *m/z*, 833.35 $[M]^+$ (calc. 833.35).



Scheme S.2. Synthesis of complex **5**

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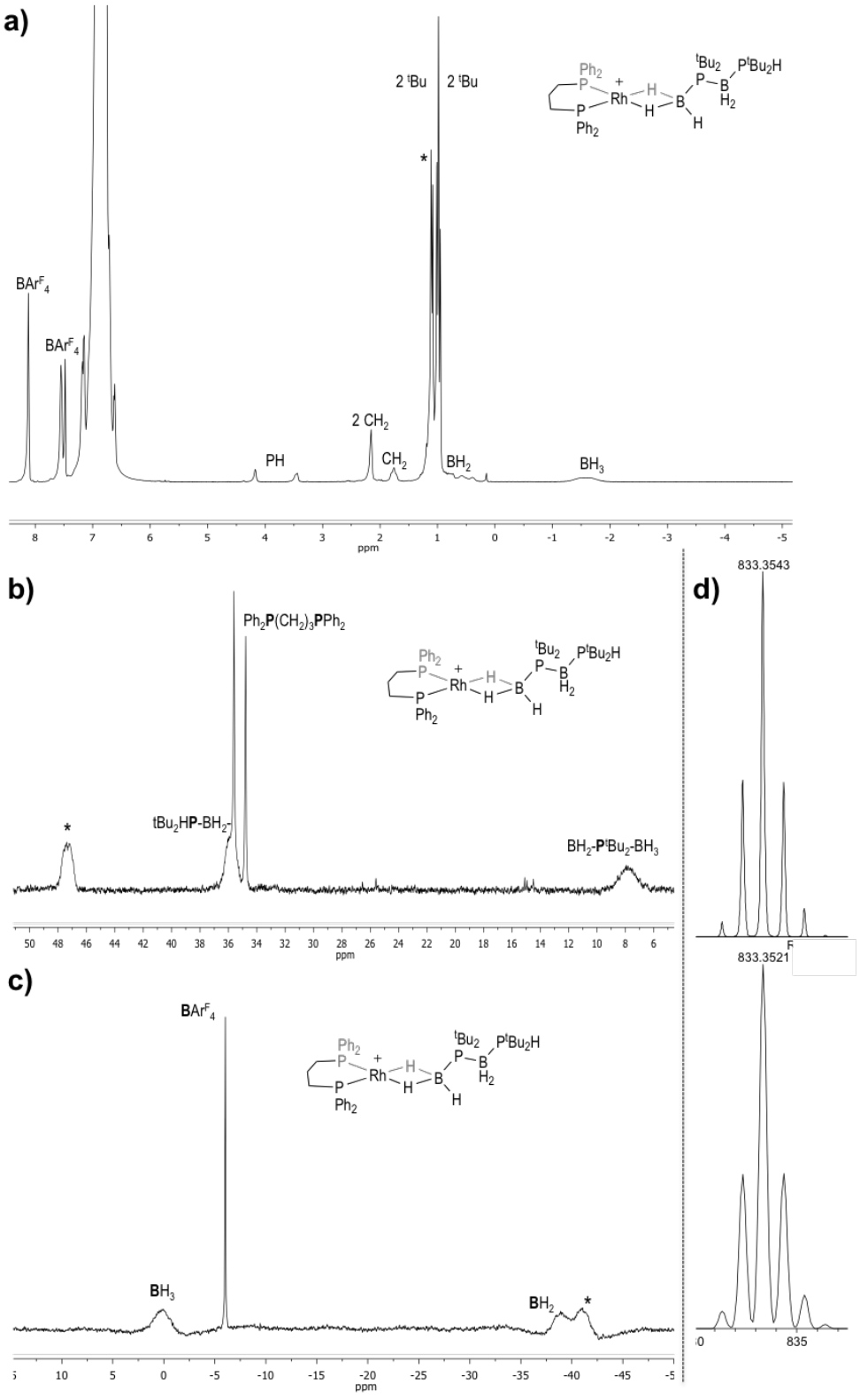

Figure S.2. a) ^{1}H NMR spectrum for complex **5**. **b)** $^{31}P\{^{1}H\}$ NMR spectrum for complex **5**. **c)** ^{11}B NMR spectrum for complex **5**. **d)** ESI.MS for compound $\mathbf{5^{+}}$, observed (top), simulated (bottom). In all NMR spectra (* = free $H_3B{\cdot}P^tBu_2H$ present in $H_3B{\cdot}P^tBu_2BH_2{\cdot}P^tBu_2H$, see main text)

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Synthesis of [Rh(dpp3)H(PPh_2·BH_3)(H_3B·PPh_2H)][BAr^F_4] (6)

To a Youngs flask charged with [Rh(dpp3)(C_6H_5F)][BAr^F_4] (50 mg, 0.034 mmol) and 2 equivalents of H_3B·PPh_2H (12 mg, 0.068 mmol) was added 1,2-$C_6H_4F_2$ (15 mL). The solution was stirred at room temperature 10 minutes and a change in the colour from pale orange to bright yellow was observed. Complex **6** was isolated as yellow oil, and characterised in situ by NMR and ESI-MS. Attempts to purify **6** lead to mixtures of **6** and **8** (vide infra).

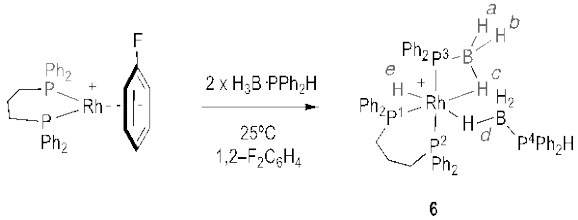
^{1}H NMR (500 MHz, $C_6H_4F_2$): δ 8.33 (s, 8H, BAr^F_4), 7.64 (s, 4H, BAr^F_4), 4.35 (d, 1H, $^1J_{H\text{-}P^4}$= 412, PH), 2.89 (m, 1H, CH), 2.70 (m, 2H 1+1 coincidence, 2CH), 2.45 (m, 1H, CH), 2.29 (m, 1H, CH), 1.42 (m, 1H, CH), 0.69 (br, 2H, Ha and Hb), -1.40 (br, 3H, 3Hd), -6.90 (d, 1H, $^2J_{H\text{-}P^2}$= 77, Hc), -16.68 (s, 1H, He). Signals from Ph not observed.

^{1}H{^{11}B} NMR (selected data, 500 MHz, $C_6H_4F_2$): δ 0.84 (s, 1H, Ha or Hb), 0.40 (s, 1H, Ha or Hb), -1.40 (s, 3H, 3Hd), -6.9 (d slightly sharper, 1H, $^2J_{H\text{-}P^2}$= 77, Hc)

^{31}P{^{1}H} NMR (202 MHz, $C_6H_4F_2$): δ 27.2 (ddd, 1P, $J_{Rh\text{-}P^1}$= 131, $J_{P^2\text{-}P^1(cis)}$= 32, $J_{P^3\text{-}P^1(cis)}$= 14, Ph_2***P*^{1}**-$(CH_2)_3$-P^2Ph_2), 10.5 (ddd, 1P, $J_{P^3\text{-}P^2(trans)}$= 232, $J_{Rh\text{-}P^2}$= 102, $J_{P^1\text{-}P^2(cis)}$= 32, Ph_2***P*^{2}**-$(CH_2)_3$-P^2Ph_2), 2.3 (dd, 1P, $J_{P^1\text{-}P^3(trans)}$= 232, $J_{Rh\text{-}P^3}$= 82, Rh-***P*^{3}**Ph_2BH_3), -8.1 (s, 1P, ***P*^{4}**Ph_2HBH_3).

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ -6.2 (BAr^F_4) -41.9 (br, 2 x BH_3).

ESI-MS ($C_6H_4F_2$, 60ºC): positive ion: *m/z*, 887.21 [M^+ - $2BH_3$] (calc. 887.17).



6

Scheme S.3. Synthesis of complex **6**

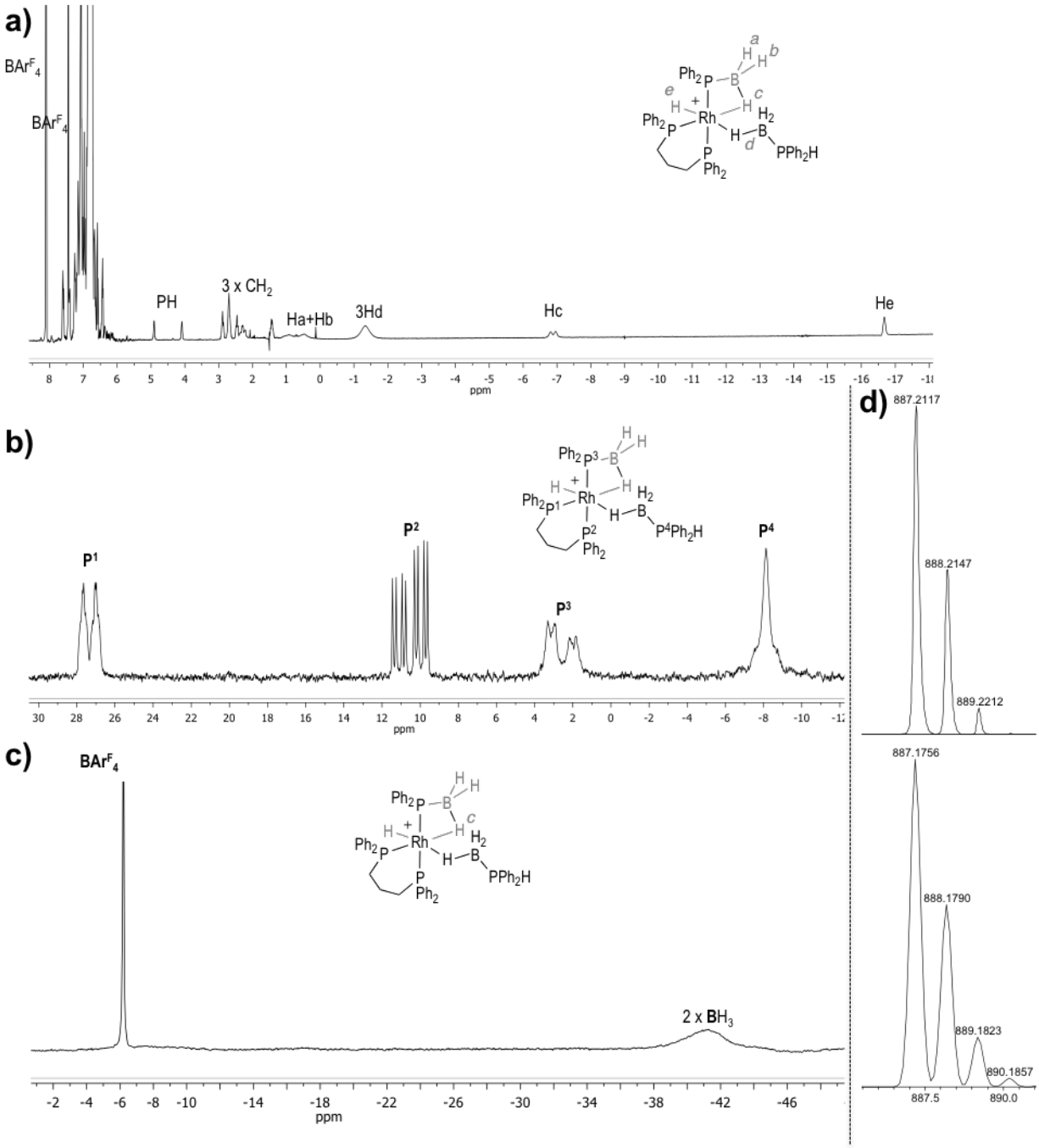


Figure S.3. a) ^{1}H NMR spectrum for complex **6**. **b)** $^{31}P\{^{1}H\}$ NMR spectrum for complex **6**. **c)** ^{11}B NMR spectrum for complex **6**. **d)** ESI.MS for compound **[6^{+} - $2BH_3$]**, observed (top), simulated (bottom).

Synthesis of [Rh(dpp3)H(PPh_2·BH_2· PPh_2·H_3B)][BAr^F_4] (8)

a) To a Youngs flask charged with [Rh(dpp3)(C_6H_5F)][BAr^F_4] (50 mg, 0.034 mmol) and 2 equivalents of H_3B·PPh_2H (12 mg, 0.068 mmol) was added 1,2-$C_6H_4F_2$ (15 mL). The solution was stirred at room temperature for 24 hours. The formation of H_2 is also observed. Complex **8** is isolated as a yellow solid (43 mg, 71%).

b) To a NMR tube charged with [Rh(dpp3)(C_6H_5F)][BAr^F_4] and 1 equivalent of $HPPh_2$·BH_2· PPh_2·H_3B was added 1,2-$C_6H_4F_2$ (4 mL). The solution was shaken at room temperature for 5 minutes and a change in the colour from pale orange to bright yellow was observed.

^{1}H NMR (500 MHz, $C_6H_4F_2$): δ 8.29 (s, 8H, BAr^F_4), 7.64 (s, 4H, BAr^F_4), 2.62 (m, 1H, CH), 2.48 (m, 1H, CH), 2.26 (m, 1H, CH), 2.10 (m, 1H, CH), 1.86 (m, 1H, CH), 1.26 (m, 1H, CH), -1.19 (vbr, 3H, BH_3), -14.55 (s, 1H, RhH). Signals from Ph not observed,being overlapped by $C_6H_4F_2$.

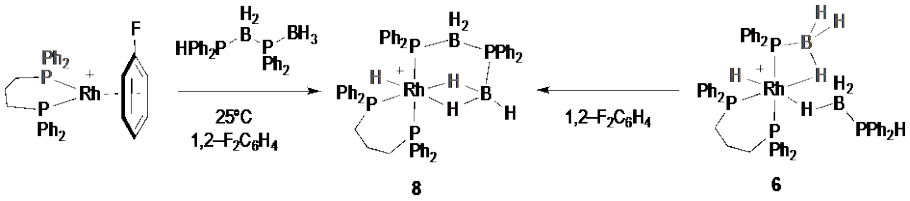
^{1}H NMR (selected data, 500 MHz, -3 ºC (270 K) $C_6H_4F_2$): δ 4.15 (br, 1H, BH), -1.69 (br, 1H, BH), -5.25 (br, 1H, BH)

^{1}H{^{11}B} NMR (selected data, 500 MHz, -3 ºC (270 K), $C_6H_4F_2$): δ 4.15 (br, 1H, BH), -1.69 (br, 1H, BH), -5,25 (br, 1H, BH)

^{31}P{^{1}H} NMR (202 MHz, $C_6H_4F_2$): δ 44.3 (dd, 1P, $J_{Rh\text{-}P^1}$= 111, $J_{P^2\text{-}P^1(cis)}$= 32, Ph_2***P*^{1}**-$(CH_2)_3$-P^2Ph_2), 31.9 (m, 1P, $J_{P^2\text{-}P^3(trans)}$= 284, Rh-***P*^{3}**$Ph_2BH_3P^4$ Ph_2HBH_3), 13.2 (ddd, 1P, $J_{P^3\text{-}P^2(trans)}$= 284, $J_{Rh\text{-}P^2}$= 91, $J_{P^1\text{-}P^2(cis)}$= 32, Ph_2P^1-$(CH_2)_3$-***P*^{2}**Ph_2), -6,5 (s, 1P, Rh-$P^3Ph_2BH_3$***P*^{4}**Ph_2HBH_3).

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ 3.2 (br), -6.2 (BAr^F_4), -27.2 (br).

ESI-MS ($C_6H_4F_2$, 60ºC): positive ion: *m/z*, 913.23 $[M]^+$ (calc. 913.23).



8 **6**

Scheme S.4. Synthesis of complex **8**

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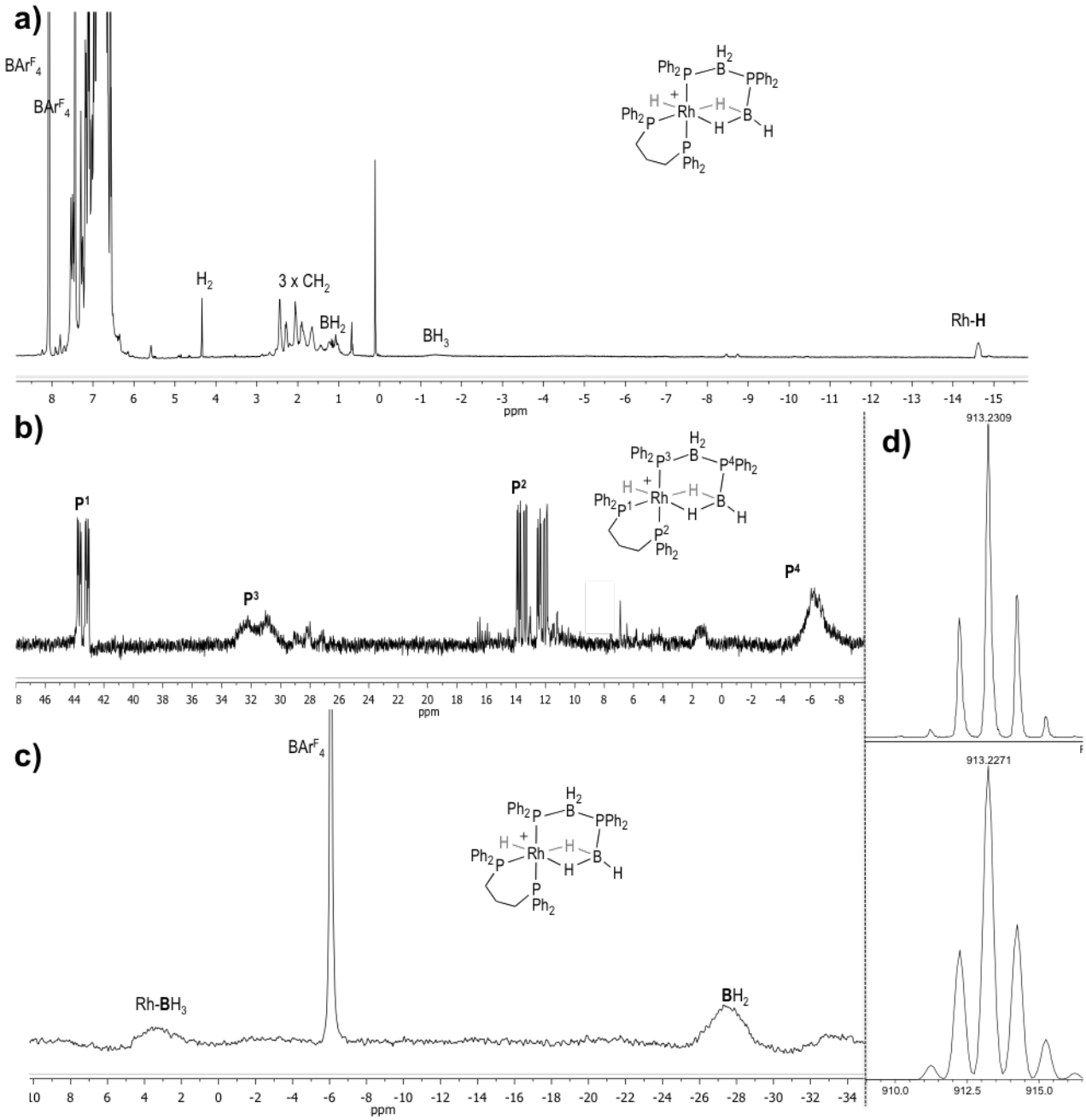


Figure S.4. a) ^{1}H NMR spectrum for complex **8** formed insitu. **b)** ^{31}P{^{1}H} NMR spectrum for complex **8** formed insitu. **c)** ^{11}B NMR spectrum for complex **8** . **d)** ESI.MS for compound **8^{+}**, observed (top), simulated (bottom).

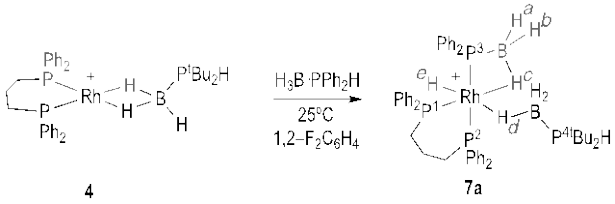
Synthesis of [Rh(dpp3)H(PPh$_2$·BH$_3$)(H$_3$B·P^{t}Bu$_2$H)][BAr^F$_4$] (7)

A blue solution of **4** (0.34 mmol) in 1,2-$C_6H_4F_2$ (15 mL) was added into a Youngs flask charged with the equimolar amount of $H_3B{\cdot}PPh_2H$ (5.5 mg, 0.34 mmol). The solution was stirred at room temperature, and instantaneously is observed a change in the colour from blue to yellow. Compound **7** was isolated as yellow oil, which was best characterised in situ by NMR and ESI-MS. Attempts to purify **7** lead to rapid decomposition.

^{1}H NMR (500 MHz, $C_6H_4F_2$): δ 8.33 (s, 8H, BAr^F$_4$), 7.64 (s, 4H, BAr^F$_4$), 3.15 (m, 1H, CH), 2.90 (m, 1H, CH), 2.76 (m, 1H, CH), 2.40 (m, 2H 1+1 coincidence, 2CH), 1.88 (d, 1H, $^1J_{H\text{-}P}$= 352, PH),1.10 (m, 1H, CH), 0.89 (d, 9H, $^3J_{H\text{-}P}$= 13.7, ^{t}Bu), 0.55 (d, 9H, $^3J_{H\text{-}P}$= 13.7, ^{t}Bu), -1.88 (br, 3H, 3Hd), -6.90 (d, 1H, $^2J_{H\text{-}P}$= 77, Hc), -16.88 (s, 1H, RHe). Signals from Ph were not observed and signals for BH_2 are overlapped by ^{t}Bu groups.

^{31}P{^{1}H} NMR (202 MHz, $C_6H_4F_2$): δ 34.8 (s, 1P, ***P^4***^{t}Bu$_2$HBH$_3$), 27.6 (ddd, 1P, $J_{Rh\text{-}P^1}$= 134, $J_{P^2\text{-}P^1(cis)}$= 39, $J_{P^3\text{-}P^1(cis)}$= 15, Ph$_2$***P^1***-(CH$_2$)$_3$-P^{2}Ph$_2$), 9.2 (ddd, 1P, $J_{P^3\text{-}P^2(trans)}$= 234, $J_{Rh\text{-}P^2}$= 102, $J_{P^1\text{-}P^2(cis)}$= 39, Ph$_2$P^1-(CH$_2$)$_3$-***P^2***Ph$_2$), 1.9 (dm, 1P, $J_{P^2\text{-}P^3(trans)}$= 232, $J_{P^1\text{-}P^3(cis)}$= 15, Rh-***P^3***Ph$_2$BH$_3$).

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ -6.2 (BAr^F$_4$) -41.9 (br, 2 x BH_3).



Scheme S.5. Synthesis of complex **7**

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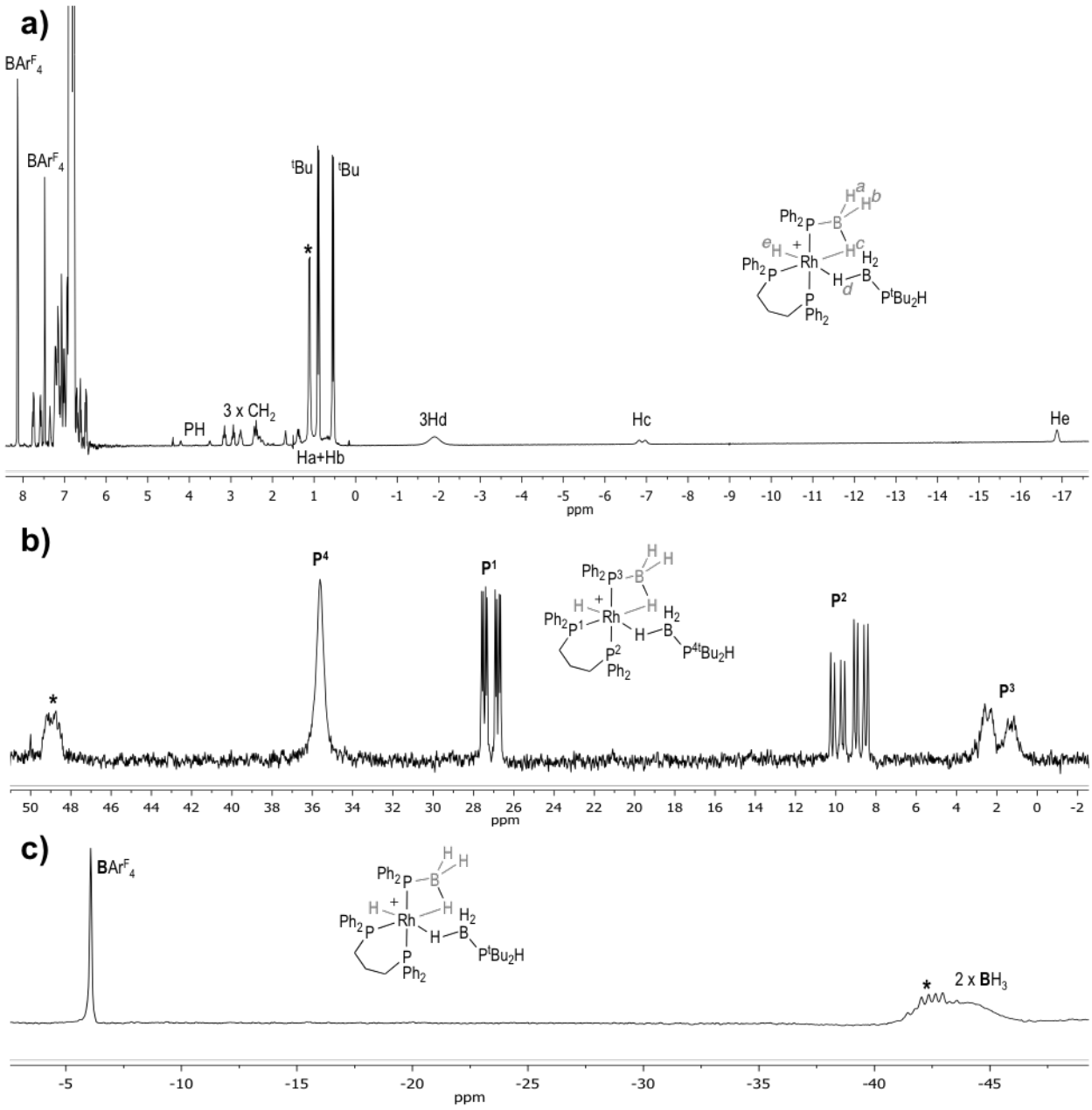

Figure S.5. a) ^{1}H NMR spectrum for complex **7**. **b)** $^{31}P\{^{1}H\}$ NMR for for complex **7**. **c)** ^{11}B NMR spectrum for complex **7**. In all NMR spectra (* = free $H_3B{\cdot}P^tBu_2H$).

Synthesis of ($D_3B{\cdot}P^tBu_2H$)

$D_3B{\cdot}THF$ (4.6 mL of a 1M solution in THF, 4.6 mmol) was added to a solution of $^tBu_2HP$ (0.74 mL, 4 mmol) in THF (10 mL) cooled to 0 ºC. The reaction mixture was stirred 10 hours at room temperature. The solution was concentrated under reduced pressure to a volume of 2 mL. The addition of hexane (10 mL) caused precipitation of a white solid, which was washed with hexane (3 x 10 mL) and dried under vacuum. Yield: 567 mg (987 %).

^1H NMR (500 MHz, $C_6H_4F_2$): δ 3.84 (dm, 1H, $J_{P\text{-}H}$= 352, P-*H*), 1.11 (d, 18H, $^3J_{H\text{-}P}$= 13, ^{t}Bu)

^{2}H NMR (500 MHz, $C_6H_4F_2$): δ 1.3 (br, 3D).

^{31}P{^{1}H} NMR (202 MHz, $C_6H_4F_2$): δ 49.0 (br)

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ -41.9 (br)

Synthesis of ($D_3B{\cdot}PPh_2H$)

$D_3B{\cdot}THF$ (4.6 mL of a 1M solution in THF, 4.6 mmol) was added to a solution of Ph_2HP (0.44 mL, 4 mmol) in THF (10 mL) cooled to 0 ºC. The reaction mixture was stirred 10 hours at room temperature. The solution was concentrated under reduced pressure to a volume of 2 mL. The addition of hexane (10 mL) caused precipitation of a white solid, which was washed with hexane (3 x 10 mL) and dried under vacuum. Yield: 666 mg (82 %).

^{1}H NMR (500 MHz, $C_6H_4F_2$): δ 7.74-6.50 (10 H, 2 x Ph, partially overlapped by $C_6H_4F_2$), 5.97 (dm, 1H, $J_{P\text{-}H}$= 376, P-*H*).

^{2}H NMR (500 MHz, $C_6H_4F_2$): δ 1.31 (br, 3D).

^{31}P{^{1}H} NMR (202 MHz, $C_6H_4F_2$): δ 1.5 (br).

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ -40.1 (br)

Synthesis of ($D_3B{\cdot}PPh_2D$)

^{n}BuLi (3.5 mL of a 1.6 M solution in hexane, 5.6 mmol) was added to a solution of Ph_2HP (1 mL, 5.4 mmol) at -78 ºC, and the colour of the solution changed immediately from colourless to orange. The mixture was allowed to reach room temperature and the solvent was removed under vacuum. D_2O (5 mL) was added to the residue and a change in the colour from orange to colourless was observed. The Ph_2DP formed was extracted with CH_2Cl_2 and evaporated to dryness. The residue was dissolved in THF (10 mL) and $D_3B{\cdot}THF$ (5.6 mL of a 1M solution in THF, 5.6 mmol) was added at 0 ºC. The reaction mixture was stirred 10 hours at room temperature. The solution was concentrated under reduced pressure to a volume of 2 mL. The addition of hexane (10 mL) caused precipitation of a white solid, which was washed with hexane (3 x 10 mL) and dried under vacuum. Yield: 836 mg (76 %).

^{1}H NMR (500 MHz, $C_6H_4F_2$): δ 7.74-6.50 (10 H, 2 x Ph, partially overlapped by $C_6H_4F_2$).

^{2}H NMR (500 MHz, $C_6H_4F_2$): δ 5.8 (d, 1D, $J_{P\text{-}H}$= 370, P-*D*), 1.3 (br, 3D).

^{31}P{^{1}H} NMR (202 MHz, $C_6H_4F_2$): δ 0.65 (br).

^{11}B NMR (160 MHz, $C_6H_4F_2$): δ -40.2 (br)

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Synthesis of $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(Ph_2PCH_2CH_2PPh_2)][BAr^F{}_4]$

To a NMR tube charged with **3** (20 mg, 0.014 mmol) and $Ph_2PCH_2CH_2PPh_2$ (5 mg, 0.014 mmol) was added 1,2-$C_6H_4F_2$ (0,4 mL). The solution was stirred at room temperature for minutes and checked by NMR and ESI-MS.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.86 (s, 8H, $BAr^F{}_4$), 7.64 (s, 4H, $BAr^F{}_4$), 7.43-7.19 (40H, 4 Ph dpp3 + dppe), 2.28 (m, 4H, 2 CH_2 dpp3), 2.00 (m, 2H, CH_2 dpp3), 2.28 (m, 4H, 2 CH_2 dppe),

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 55.9 (d, 1P, $J_{P\text{-}P(trans)}$= 226, $J_{Rh\text{-}P}$= 133, dppe), 10.3 (d, 1P, $J_{P\text{-}P(trans)}$= 226, $J_{Rh\text{-}P}$= 133, dpp3)

ESI-MS ($C_6H_4F_2$, 60ºC): positive ion: *m/z* = 913.19 (calc. 913.19).

Preliminary Catalytic Studies

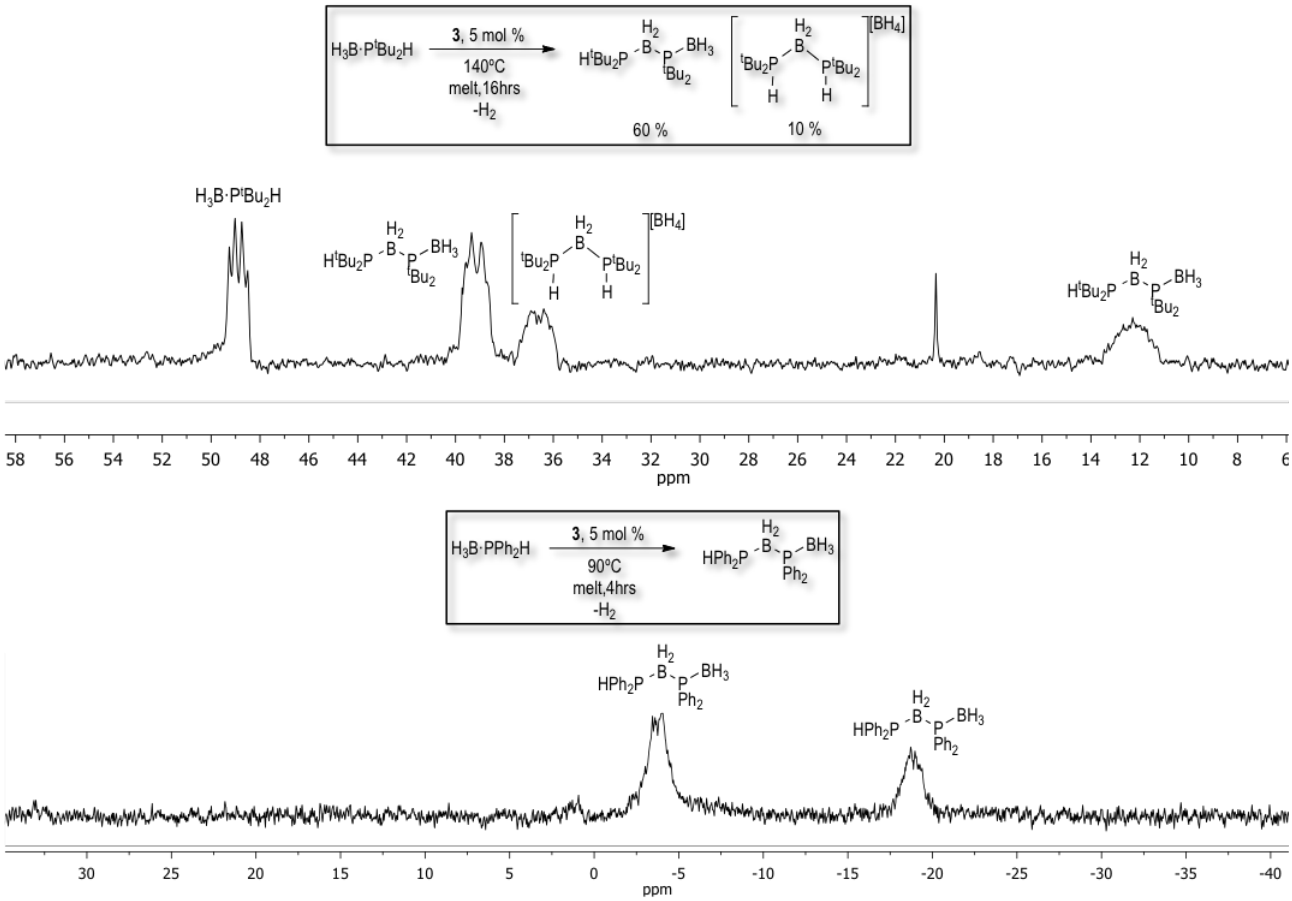

Figure S.6. ^{31}P{^{1}H} NMR spectra for the initial catalytic reactions

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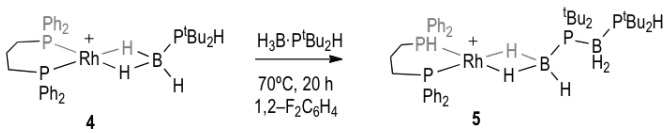
Formation of 5 from 4

To a blue solution of **4** in 1,2-$C_6H_4F_2$ was added into a NMR tube charged with the equimolar amount of $H_3B{\cdot}P^tBu_2H$. The solution was heated at 70 ºC for 20 h. $^{31}P\{^1H\}$ NMR spectroscopy (Figure S.7) showed the partial formation of **5.** However, this was not clean and there was significant decomposition observed to unidentified products.



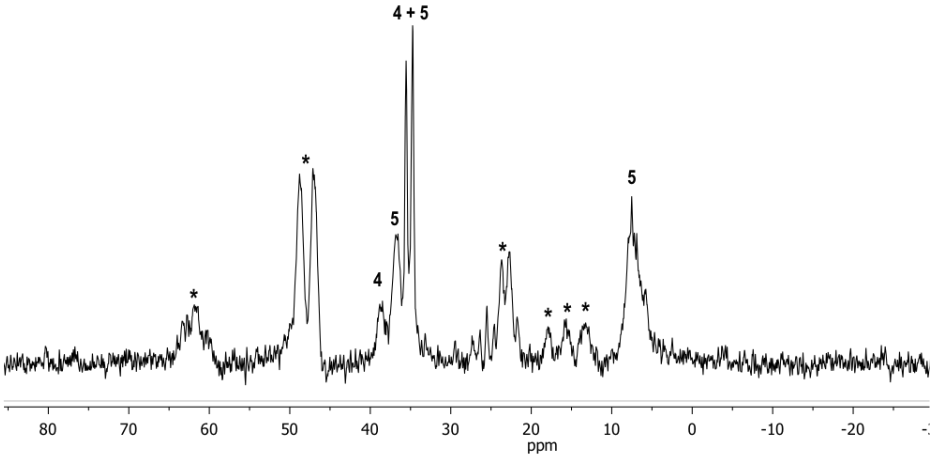
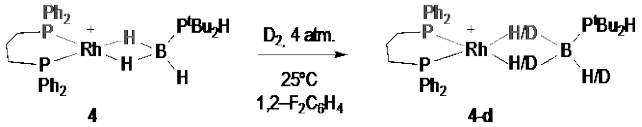


Figure S.7. $^{31}P\{^1H\}$ NMR spectrum for the reaction of **4** and $H_3B{\cdot}P^tBu_2H$ after 20 h at 70 ºC. (*) unidentified products.

Deuterium experiments to 4

A high pressure NMR tube charged with a solution of **4** in 1,2-$C_6H_4F_2$ was placed under D_2 (4 atm) and the resulting mixture was characterised *in situ* by ^1H and ^2H NMR experiments after 10 minutes and ESI-MS after 40 minutes. ^2H NMR spectroscopy shows a peak for Rh-D-B (Figure S.8). ESI-MS shows isotopic distribution consistent with sequential H/D interchange into the borane (Figure S.9).



Scheme S.6. Synthesis of complex **4-d**

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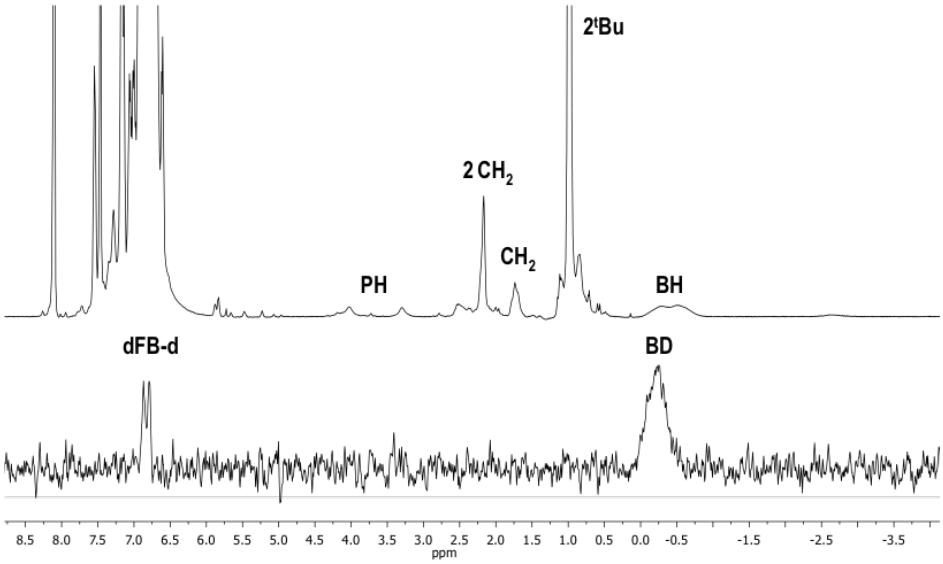

Figure S.8. ^{1}H NMR spectrum for **4** on exposure to D_2 (top), ^{2}H NMR spectrum (bottom).

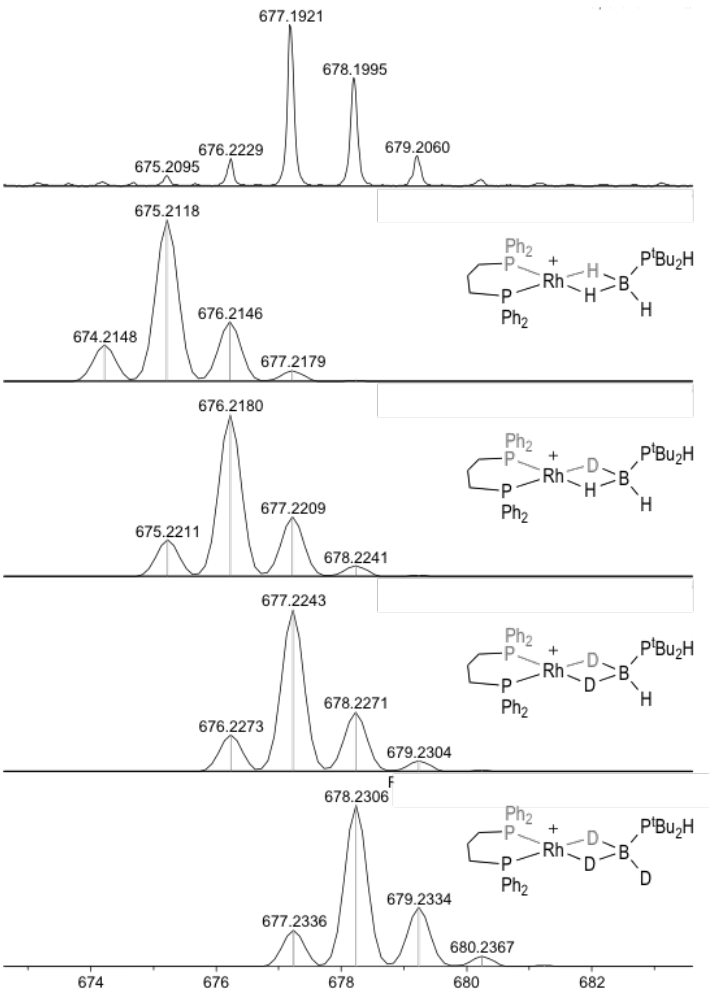

Figure S.9. ESI-MS for compound **4** on exposure to D_2 , observed (top), simulated in different levels of H/D exchange (botton)

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Kinetic studies 6 ⊙ 8

a) Eyring analysis

The reaction from **6** to **8** is a first order process, and following this process using ^{1}H NMR at different temperatures allowed for Eryng analysis. Figure S.10 shows the change in the ^{1}H NMR going from **6** to **8**. Figure S.11 shows the Eyring analysis and the combined first order plots . Figure S.12 shows the plots (concentration of **6** *vs* time and ln[6] *vs* time) at different temperatures..

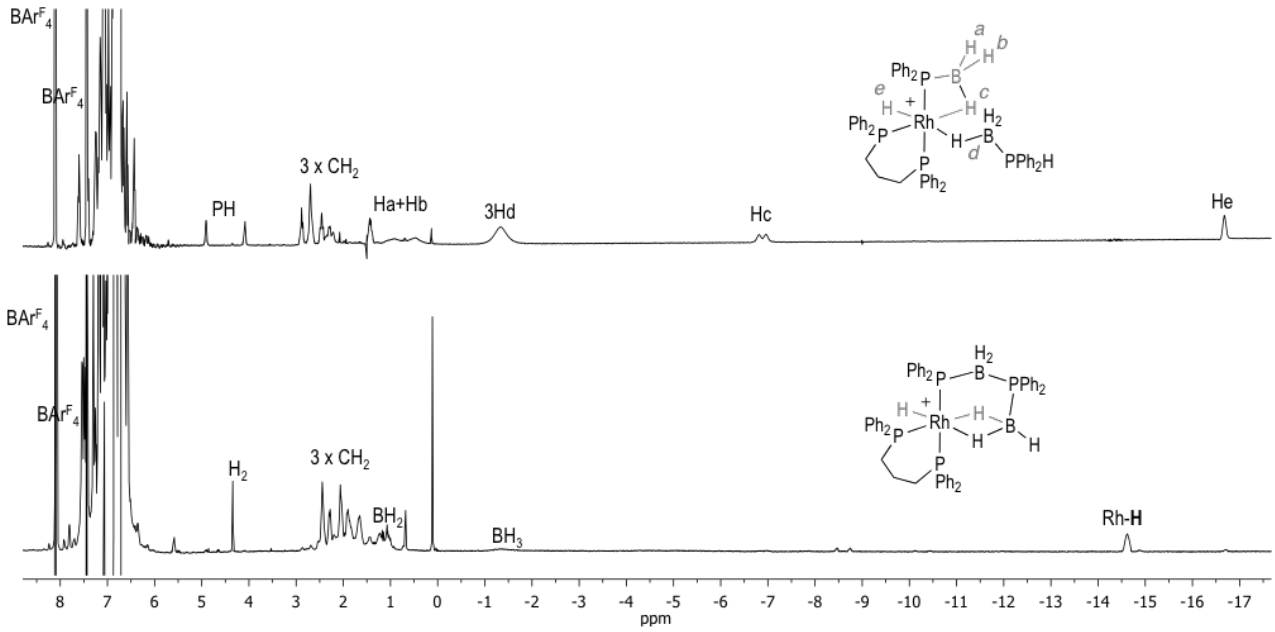

Figure S.10. ^{1}H NMR for **6** (top), and **8** (botton).

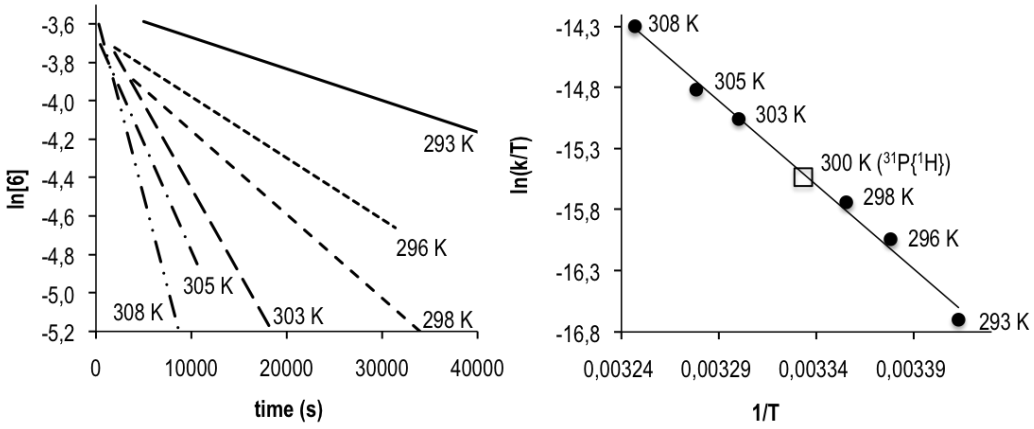

Figure S.11. First order plots and Eyring analysis.

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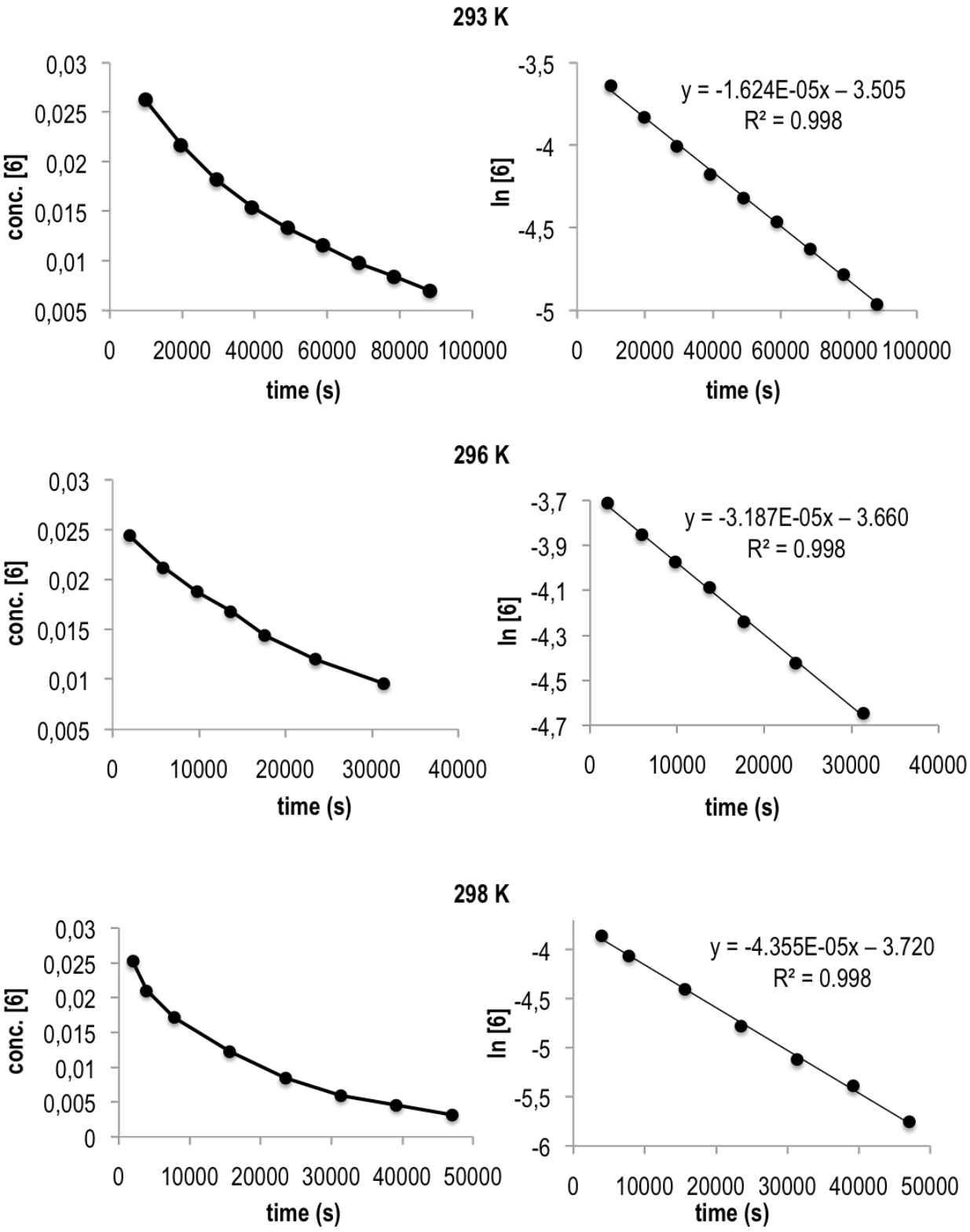

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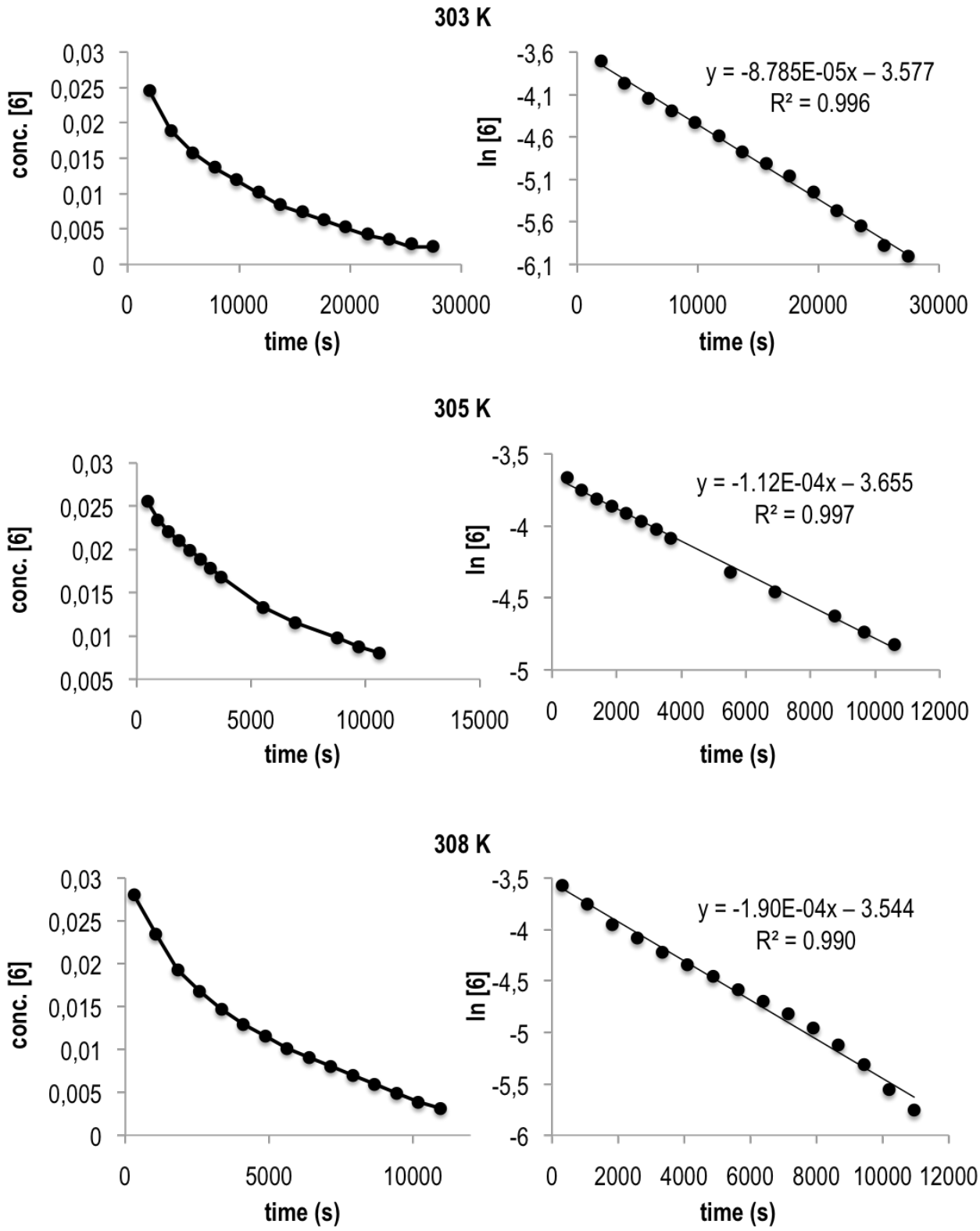

Figure S.12. Conc.[6] *vs*. time and first order plots for **6** ⊙ **8** process at different temperatures.

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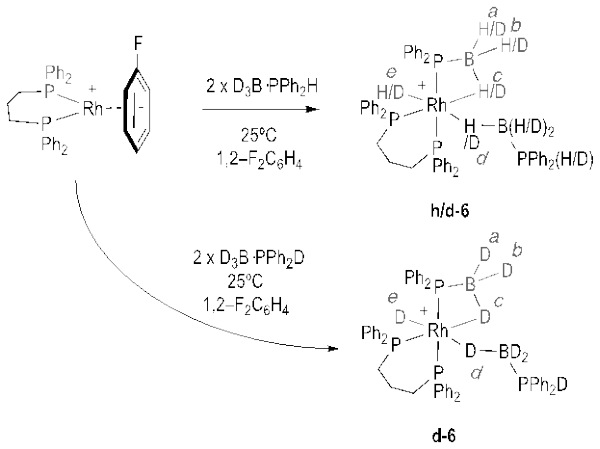
b) Kinetic Isotopic Effect (KIE)

Addition of two equivalents of $D_3B{\cdot}PPh_2H$ to **3** resulting in incorporation of D into all the B–H/P–H and Rh–H positions of **6** as measured by ^1H and ^2H NMR spectroscopy after 10 minutes. The H/D incorporation into the B and P sites was equitable, i.e. 1:3 H : D. (Figure S.13)



Scheme S.7. Synthesis of complexes **h/d-6** and **d-6**.

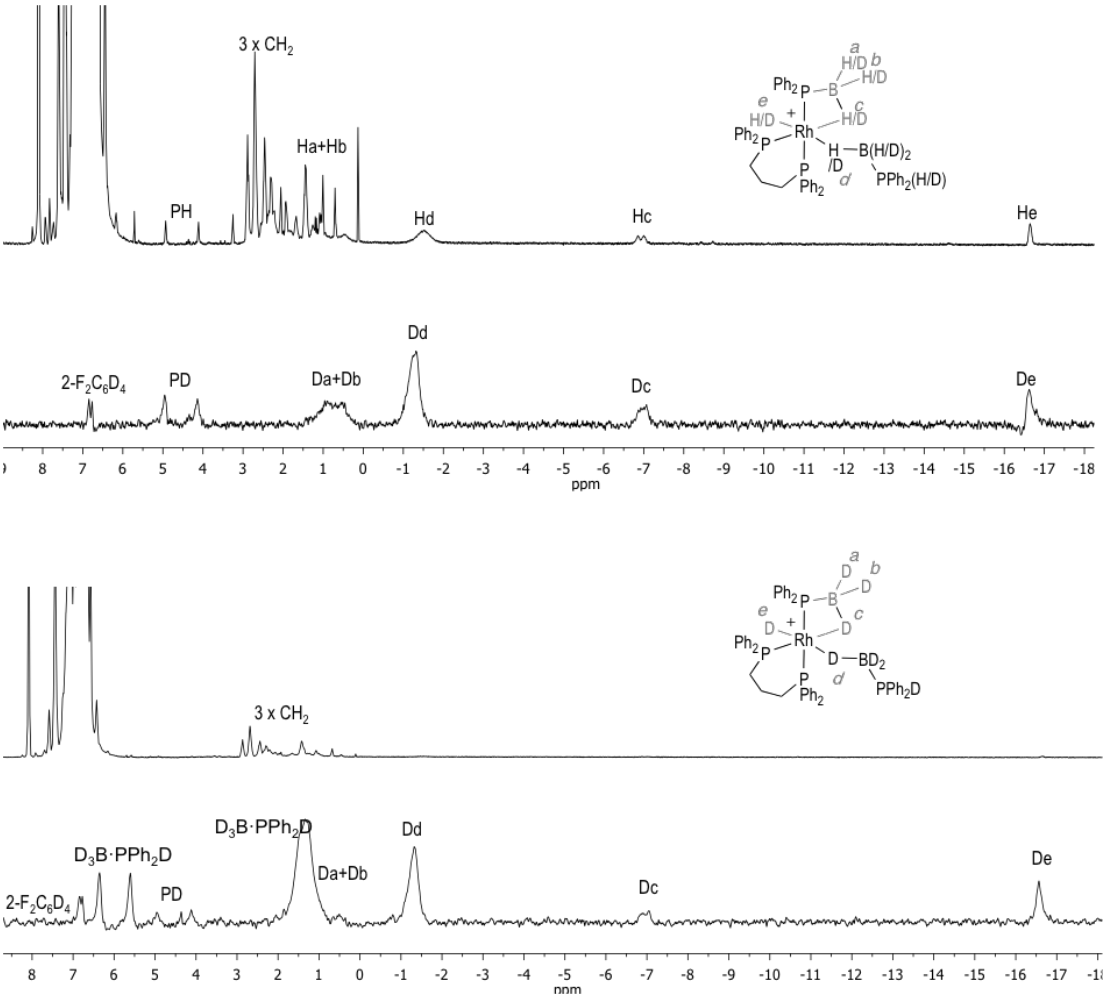


Figure S.13. ^1H NMR spectrum for **h/d-6** and ^2H NMR spectrum for **h/d-6** (top two), ^1H NMR for **d-6** and ^2H NMR for **d-6** (free $D_3B{\cdot}PPh_2H$ is observed) (bottom two).

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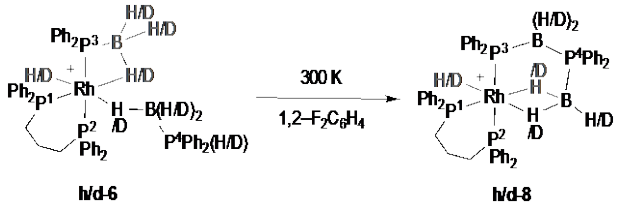
Heating ***h/d*–6** for 8 hours at 300 K results in incorporation of D into all the B–H/P–H and Rh–H positions in ***h/d*–8** (Scheme S.8). The kinetics of this process were followed using $^{31}P\{^{1}H\}$ NMR spectroscopy. (Figure S.14)



Scheme S.8. Synthesis of complex **h/d-8**

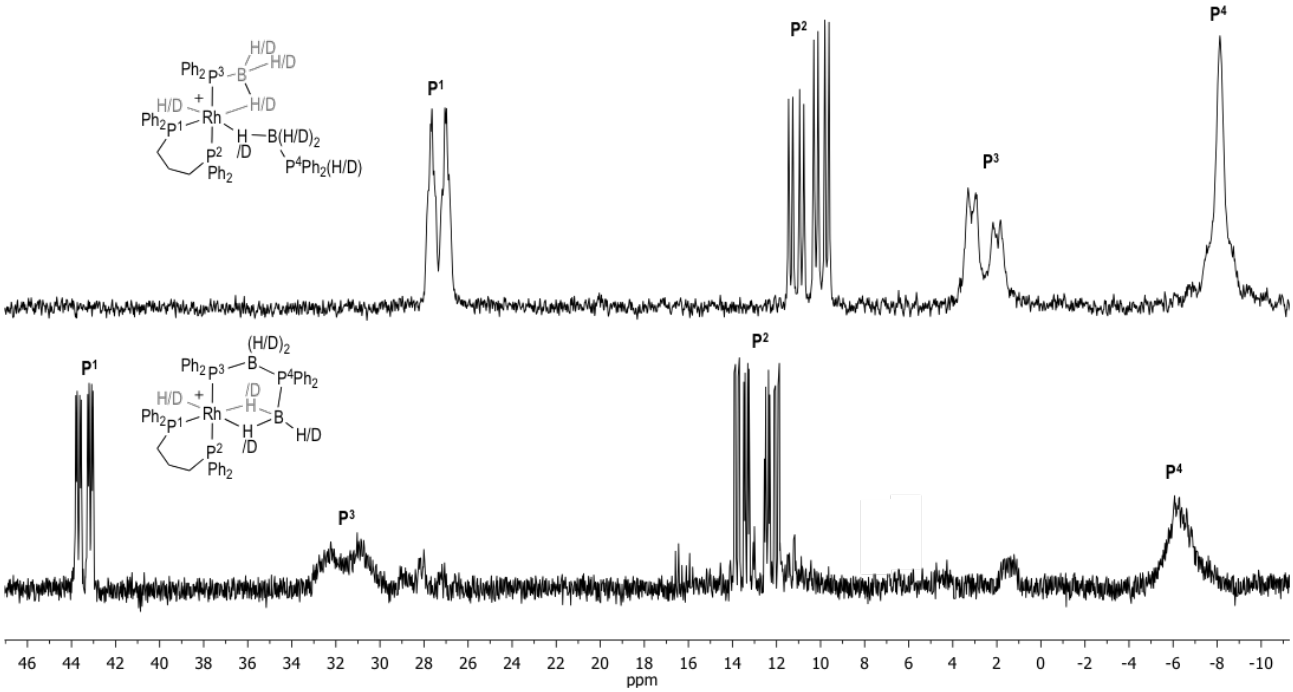


Figure S.14. $^{31}P\{^{1}H\}$ NMR for **h/d-6** (top), $^{31}P\{^{1}H\}$ NMR for **h/d-8** (botton).

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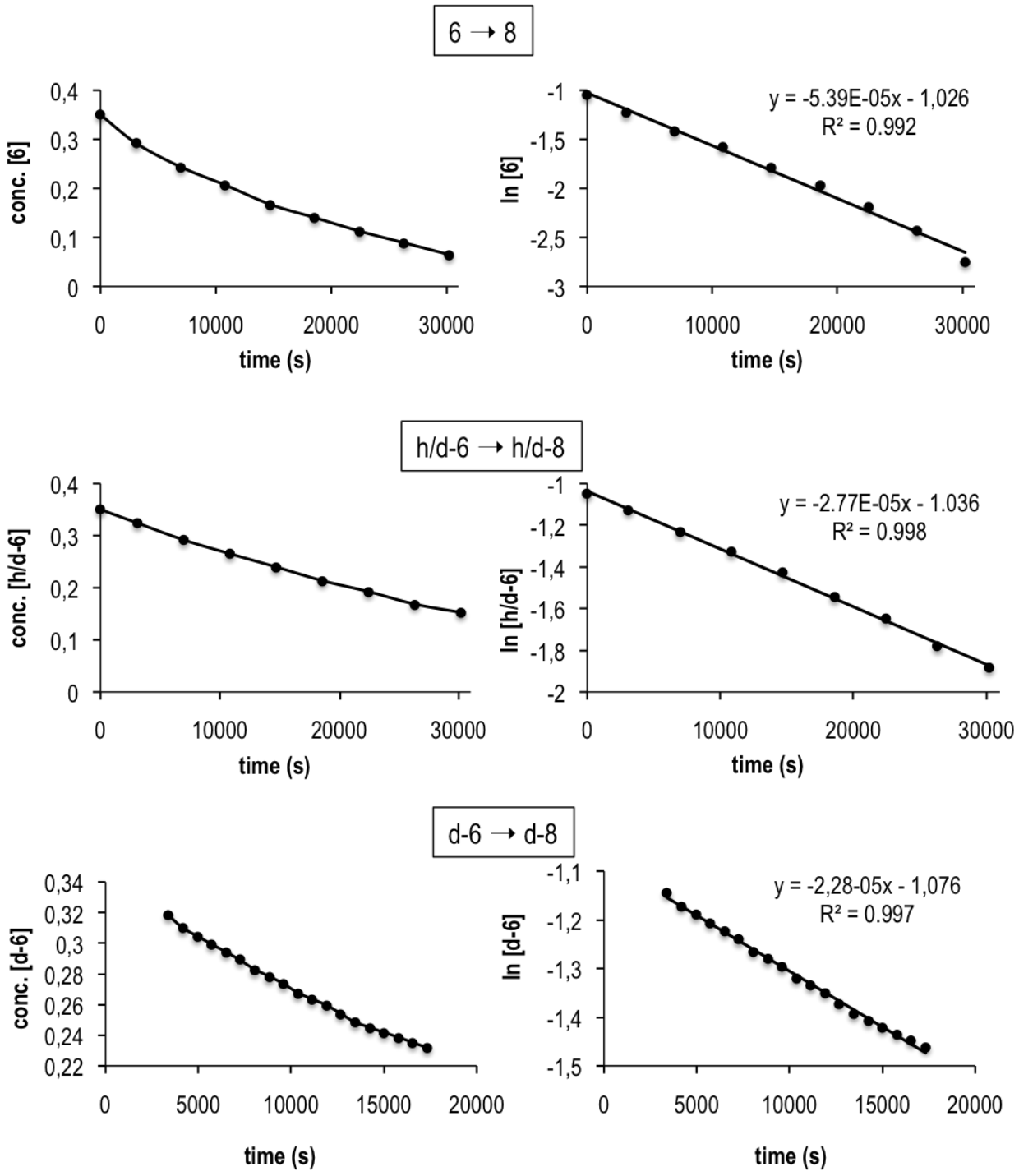

$$\text{KIE} = \frac{k(6)}{k(\text{h/d-6})} = \frac{\text{-5.4(2)E-05}}{\text{-2.81(4)E-05}} = 1.9(1) \qquad \text{KIE} = \frac{k(6)}{k(\text{d-6})} = \frac{\text{-5.4(2)E-05}}{\text{-2.26(3)E-05}} = 2.3(2)$$

Figure S.15. conc. *vs.* time and first order plots for **6** ⊙ **8** process, conc. *vs.* time and first order plots for **h/d-6** ⊙ **h/d-8** process, conc. *vs.* time and first order plots for **d-6** ⊙ **d-8** process, and KIEs calculated as calculated using ^{31}P NMR data.

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Reactivity of 8

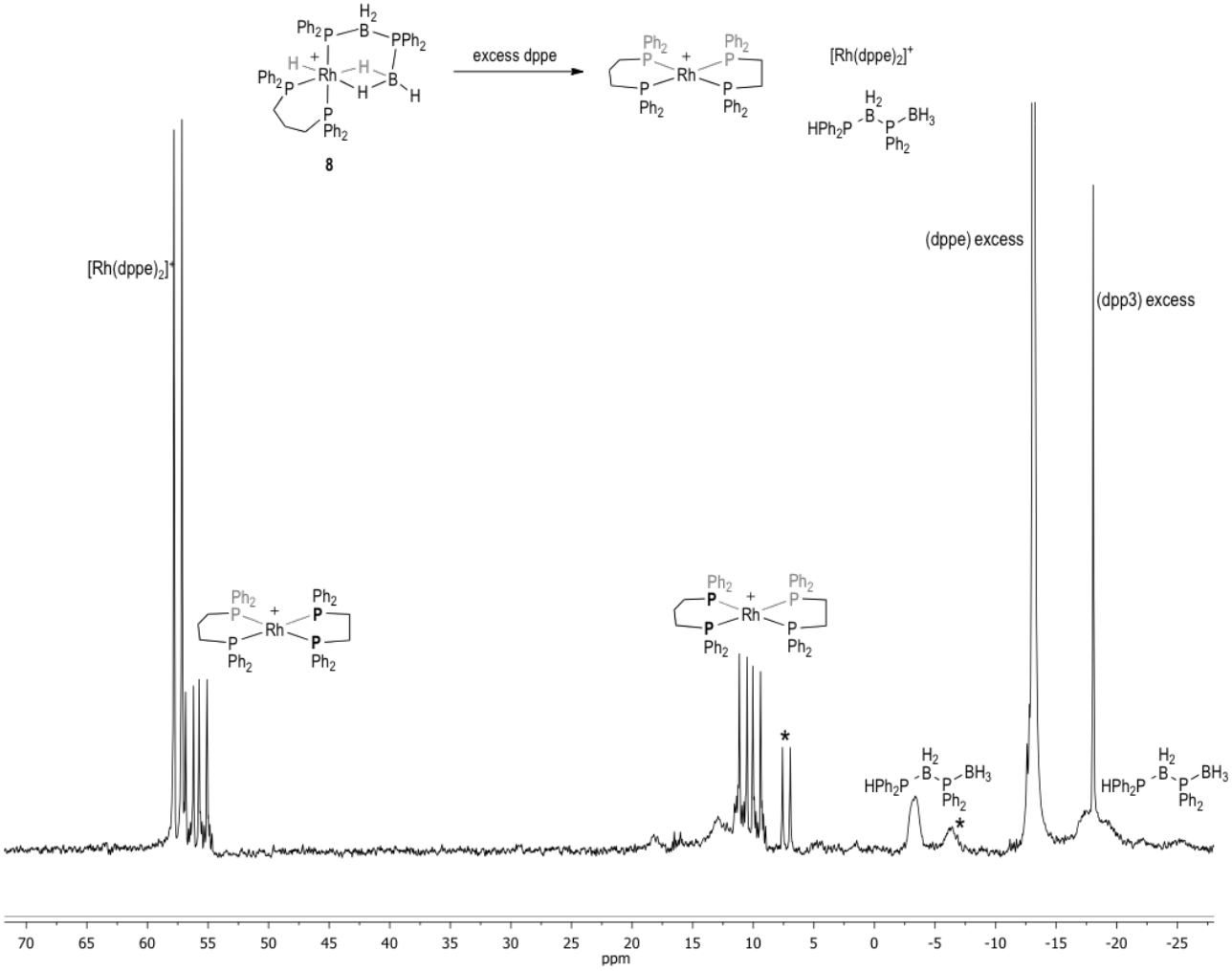

Figure S.16. $^{31}P\{^{1}H\}$ NMR spectrum for the reaction of **8** and dppe in excess after 5 minutes at room temperature. $[Rh(dppe)_2]^+$ (δ 57.5, $J_{Rh\text{-}P}$ = 133, dppe).[6] (*) Unidentified products.

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