Electronic Supplementary Information for Dalton Transactions


Supporting Information for:

# Reversible C-H activation of a $P^tBu^iBu_2$ ligand to reveal a masked 12 electron $[Rh(PR_3)_2]^+$ cation.

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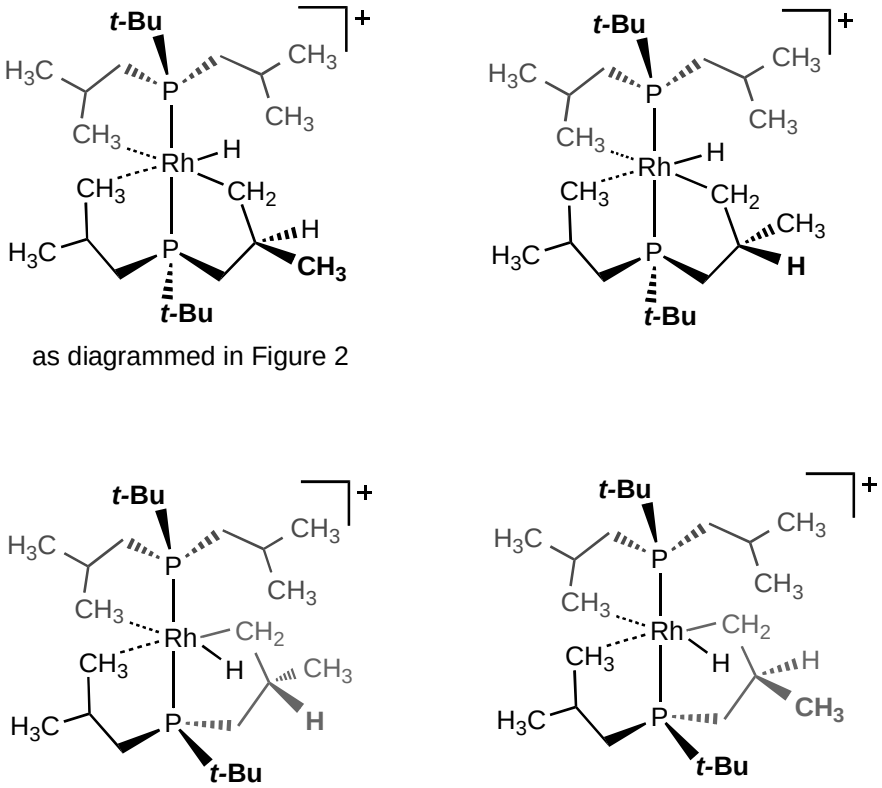
## *Possible isomers of 4*




as diagrammed in Figure 2

Figure S-1: Representations of four possible isomers of 4 present in solution, that arise from C-H activation of the diastereotopic $CH_3$ groups.

## *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. $CH_2Cl_2$, MeCN, $Et_2O$ and pentane were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.[1] *t*-butylethene (TBE) was dried over sodium, vacuum distilled and stored over 3 Å molecular sieves. $CD_2Cl_2$ and 1,2-$C_6H_4F_2$ were dried over $CaH_2$, vacuum distilled and stored over 3 Å molecular sieves. $CDCl_3$ was degassed by successive freeze-pump-thaw cycles and stored over 3 Å molecular sieves. $H_3B{\cdot}NMe_3$ was purchased from Aldrich and sublimed before use ($5 \times 10^{-2}$ Torr, 298 K). $[Rh(COE)_2Cl]_2$[2] and $Na[BAr^F{}_4]$[3] were prepared by literature methods. All other chemicals are commercial products and were used as received. NMR spectra were recorded on a Varian Mercury VX 300 MHz, Varian Unity Plus 500 MHz or Bruker AVC 500 MHz spectrometer at room temperature, unless otherwise stated. In

1,2-$C_6H_4F_2$, $^1$H NMR spectra were referenced to the centre of the downfield solvent multiplet ($\delta$ = 7.07). $^{31}$P spectra were referenced against 85% $H_3PO_4$ (external). $^{11}$B NMR spectra were referenced against $BF_3{\cdot}OEt_2$ (external). Chemical shifts are quoted in ppm and coupling constants in Hz. Infrared spectra were measured on a Nicolet 560 FTIR spectrometer. ESI-MS were recorded on a Bruker MicrOTOF-Q instrument interfaced with a glovebox.[4] Microanalyses were performed by Elemental Microanalysis Ltd.

## *Synthesis of new complexes*

### P$^i$Bu$_2$$^t$Bu

Isobutyl lithium (31.4 ml, 50.3 mmol) was added to 30 mL of $Et_2O$, in a large Schlenk equipped with a reflux condenser. The contents of the flask were cooled to 0 ºC in an ice bath. A solution of P$^t$BuCl$_2$ (2.00 g, 12.6 mmol) in $Et_2O$ (25 mL) was prepared and added to the isobutyl lithium solution dropwise over 15 minutes. An off-white suspension was formed, and the reaction mixture heated under reflux for 3 hours. The reaction mixture was cooled to room temperature and hydrolysed with 20 ml of degassed, deionised water. The ether layer was separated and dried over anhydrous magnesium sulphate. The solution was filtered and the solvent removed *in vacuo*. The resulting pale yellow liquid was purified by vacuum distillation; a colourless, viscous liquid was collected. Yield: 1.76 g (69 %).

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.70 – 1.55 (m, 2H, $^i$Bu{CH}), 1.20 (dd, 2H, $^2J_{HH}$ = 13.8, $J$ = 8.0, $^i$Bu{CH$_2$}), 1.11 (doublet of apparent triplets, 2H, $^2J_{HH}$ = 13.8, $J$ = 5.8, $^i$Bu{CH$_2$}), 0.98 (dd, $J$ = 6.5, $J$ = 3.9, 12H, $^i$Bu{Me}), 0.97 (d, $^3J_{PH}$ = 11.3, 9H, $^t$Bu{Me}).
$^{31}$P {$^1$H} NMR (122 MHz, $CDCl_3$): $\delta$ -12.7 (s).

### Rh(H)$_2$(P$^i$Bu$_2$$^t$Bu)$_2$Cl

To a J. Youngs' flask charged with [Rh(COE)$_2$Cl]$_2$ (0.146 g, 0.72 mmol) was added a solution of P$^i$Bu$_2$$^t$Bu (0.115 g, 0.16 mmol) in $CH_2Cl_2$ (5 mL) at -78 ºC. The flask was sealed and immediately frozen in liquid nitrogen. The argon atmosphere was removed and replaced with hydrogen (4 atm). The solution was stirred at room temperature for 30 minutes before removal of the solvent *in vacuo*. Recrystallisation from pentane at -80 ºC yielded the product as yellow crystals. Yield: 0.122 g (70%).

$^1$H NMR ($CD_2Cl_2$, 500 MHz): $\delta$ 2.10 (apparent nonet, 4H, $J$ = 6, $^i$Bu{CH}), 1.83 – 1.77 (m, 4H, $^i$Bu{CH$_2$}), 1.64 – 1.59 (m, 4H, $^i$Bu{CH$_2$}), 1.17 (apparent t, 18H, $J$ = 6, $^t$Bu{Me}), 1.03, (d, $^3J_{HH}$ = 1.2, 12H, $^i$Bu{Me}),1.02, (d, $^3J_{HH}$ = 1.2, 12H, $^i$Bu{Me}), -22.84 (dt, 2H, $^1J_{RhH}$ = 27.7, $^2J_{PH}$ = 15.5, RhH).

$^{1}$H {$^{31}$P @ 44.9 ppm} NMR ($CD_2Cl_2$, 500 MHz): δ 2.10 (nonet, 4H, $^{3}J_{HH}$ = 6.4, $^{i}$Bu{CH}), 1.79 (dd, $^{2}J_{HH}$ = 14.3, $^{3}J_{HH}$ = 5.7, 4H, $^{i}$Bu{$CH_2$}), 1.61 (dd, $^{2}J_{HH}$ = 14.3, $^{3}J_{HH}$ = 7.0, 4H, $^{i}$Bu{$CH_2$}), 1.17 (s, 18, $^{t}$Bu{Me}), 1.03, (d, $^{3}J_{HH}$ = 1.2, 12H, $^{i}$Bu{Me}),1.02, (d, $^{3}J_{HH}$ = 1.2, 12H, $^{i}$Bu{Me}), -22.84 (d, 2H, $^{1}J_{RhH}$ = 27.9, RhH).
$^{31}$P {$^{1}$H} NMR ($CD_2Cl_2$, 202 MHz): δ 44.9 (d, $^{1}J_{RhP}$ = 115).
$^{13}$C {$^{1}$H} NMR ($CD_2Cl_2$, 126 MHz): 34.9 (apparent t, *J* = 10, $^{i}$Bu{$CH_2$}), 31.8 (apparent td, *J* = 13, J = 1, $^{t}$Bu{C}), 28.1 (apparent t, *J* = 3, $^{t}$Bu{Me}), 26.5 (s, $^{i}$Bu{CH}), 26.0 (apparent t, *J* = 4, iBu{Me}), 25.6 (apparent t, *J* = 3, $^{i}$Bu{Me}).
Anal. Calcd for $C_{24}H_{56}ClP_2Rh$ (545.01 gmol$^{-1}$): C, 52.89; H, 10.36. Found: C, 52.88; H, 10.35.

$[Rh(H)_2(P^{i}Bu_2{}^{t}Bu)_2][BAr^{F}{}_4]$ (3)
To a J. Youngs' flask charged with $Rh(H)_2(P^{i}Bu{}^{t}Bu_2)_2Cl$ (0.015 g, 0.028 mmol) and $Na[BAr^{F}{}_4]$ (0.026 g, 0.029 mmol) was added $CH_2Cl_2$ (1 mL). The solution was sonnicated for 10 minutes and then filtered. The solution was layered with pentane and held at 5 ºC affording 3 as pale yellow crystals. Yield: 0.027 g (71%).

$^{1}$H NMR ($CD_2Cl_2$, 500 MHz): δ 7.72 (br, 8H, $BAr^{F}{}_4$), 7.56 (br, 4H, $BAr^{F}{}_4$), 1.95 – 1.79 (m, 8H, $^{i}$Bu{CH/$CH_2$}), 1.73 – 1.67 (m, 4H, $^{i}$Bu{$CH_2$}), 1.16 (apparent t, 18H, J = 7, $^{t}$Bu{Me}), 0.89 (d, 12H, $^{3}J_{HH}$ = 6.5, $^{i}$Bu{Me}), 0.81 (d, 12H, $^{3}J_{HH}$ = 6.5, $^{i}$Bu{Me}), -22.03 (dt, 2H, $^{1}J_{RhH}$ = 47.1, $^{2}J_{PH}$ = 13.3, RhH).
$^{1}$H {$^{31}$P @ 56.9 ppm} NMR ($CD_2Cl_2$, 500 MHz): δ 7.72 (br, 8H, $BAr^{F}{}_4$), 7.56 (br, 4H, $BAr^{F}{}_4$), 1.95 – 1.79 (m, 8H, $^{i}$Bu{CH/$CH_2$}), 1.69 (dd, 4H, J = 6.9, J = 14.5, $^{i}$Bu{$CH_2$}), 1.16 (s, 18H, $^{t}$Bu{Me}), 0.89 (d, 12H, $^{3}J_{HH}$ = 6.5, $^{i}$Bu{Me}), 0.81 (d, 12H, $^{3}J_{HH}$ = 6.5, $^{i}$Bu{Me}), -22.03 (d, 2H, $^{1}J_{RhH}$ = 47.3, RhH).
$^{31}$P {$^{1}$H} NMR ($CD_2Cl_2$, 202 MHz): δ 56.9 (d, $^{1}J_{RhP}$ = 109).
$^{13}$C {$^{1}$H} NMR ($CD_2Cl_2$, 126 MHz): δ 162.3 (q, $^{1}J_{BC}$ = 50, $BAr^{F}{}_4$), 135.4 (s, $BAr^{F}{}_4$), 129.4 (qq, $^{2}J_{FC}$ = 32, $^{3}J_{BC}$ = 3, $BAr^{F}{}_4$), 125.2 (q, $^{1}J_{FC}$ = 272, $BAr^{F}{}_4$), 118.0 (sept, $^{3}J_{FC}$ = 4, $BAr^{F}{}_4$), 35.7 (apparent t, J = 11, $^{i}$Bu{$CH_2$}), 31.3 (apparent td, J = 15, J = 2, $^{t}$Bu{C}), 28.0 (apparent t, J = 2, $^{i}$Bu{CH}), 27.5 (apparent t, J = 3, $^{t}$Bu{Me}), 25.2 (apparent t, J = 2, $^{i}$Bu{Me}), 24.9 (apparent t, J = 3, $^{i}$Bu{Me}).
$^{1}$H NMR ($CD_2Cl_2$, 500 MHz, 190 K): δ 7.71 (br, 8H, $BAr^{F}{}_4$), 7.53 (br, 4H, $BAr^{F}{}_4$), 1.76 (br, 8H, $^{i}$Bu{$CH_2$}), 1.54 (br, 4H, , $^{i}$Bu{CH}), 1.04 (br, 18H, $^{t}$Bu{Me}), 0.75 (d, J = 4.6, 12H, $^{i}$Bu{Me}), 0.67 (d, $^{3}J_{HH}$ = 4.2, 12H, $^{i}$Bu{Me}), -21.48 (dt (br), $^{1}J_{RhH}$ = 44.9, $^{2}J_{PH}$ = 11.7, 2H, RhH).
$^{31}$P {$^{1}$H} NMR ($CD_2Cl_2$, 202 MHz, 190 K): δ 57.2 (br d, $^{1}J_{RhP}$ = 105).
Anal. Calcd for $C_{56}H_{68}BF_{24}P_2Rh$ (1372.77 gmol$^{-1}$): C, 49.00; H, 4.99. Found: C, 48.87; H, 4.92.
ESI-MS ($C_6H_5F$, 60ºC) positive ion: *m/z,* 509.2859 [$M^+$] (calc. 509.2907).
IR ($CH_2Cl_2$, cm$^{-1}$): $\nu$($CH_{agostic}$) 2671 (br).

$[Rh(P^iBu_2{}^tBu)_2][BAr^F{}_4]$ (4)

To a J. Youngs' flask charged with $Rh(H)_2(P^iBu{}^tBu_2)_2Cl$ (0.015 g, 0.028 mmol) and $Na[BAr^F{}_4]$ (0.026 g, 0.029 mmol) was added $CH_2Cl_2$ (1 mL). The solution was sonnicated for 10 minutes and then filtered before the addition of TBE (9 µL, 0.069 mmol). The solution was left for 1 hour before layering with pentane and then held at 5 ºC affording 4 as yellow crystals. Yield: 0.021 g (56%).

$^1H$ NMR ($CD_2Cl_2$, 500 MHz): δ 7.73 (br, 8H, $BAr^F{}_4$), 7.57 (br, 4H, $BAr^F{}_4$), 1.90 – 1.74 (m, 8H, $^i$Bu{CH/$CH_2$}), 1.72 – 1.63 (m, 4H, $^i$Bu{$CH_2$}), 1.14 (dd, 18H, J = 7.5, J = 7.3, $^t$Bu{Me}), 1.00 – (–0.80) (br, 24H, $^i$Bu{Me}).

$^1H$ {$^{31}P$} NMR ($CD_2Cl_2$, 500 MHz): δ 7.73 (br, 8H, $BAr^F{}_4$), 7.57 (br, 4H, $BAr^F{}_4$), ), 1.89 – 1.76 (m, 8H, $^i$Bu{CH/$CH_2$}), 1.67 (dd, 4H, J = 14, J = 7, $^i$Bu{CH/$CH_2$}), 1.00 – (-0.80) (br, 24H, $^i$Bu{Me}), 1.14 (s, 18H, $^t$Bu{Me}).

$^{13}C$ {$^1H$} NMR ($CD_2Cl_2$, 126 MHz): δ 162.3 (q, $^1J_{BC}$ = 50, $BAr^F{}_4$), 135.4 (s, $BAr^F{}_4$), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, $BAr^F{}_4$), 125.2 (q, $^1J_{FC}$ = 272, $BAr^F{}_4$), 118.0 (sept, $^3J_{FC}$ = 4, $BAr^F{}_4$), 32.5 (vbr, $^i$Bu{$CH_2$}), 31.7 (vbr, $^i$Bu{CH}), 31.4 (apparent t, J = 14, $^t$Bu{C}), 27.2 (apparent t, J = 2, $^t$Bu{Me}), 26.6 – 26.0 (vbr overlapping multiplet, $^i$Bu{Me}).

$^{31}P$ {$^1H$} NMR ($CD_2Cl_2$, 202 MHz): δ 64.5 (br).

$^1H$ NMR ($CD_2Cl_2$, 500 MHz, 173 K): δ 7.74 (br, 8H, $BAr^F{}_4$), 7.55 (br, 4H, $BAr^F{}_4$), 2.39 – 1.30 (multiple peaks, 12H, $^i$Bu{CH/ $CH_2$}), 1.21 - 0.30 (multiple peaks, 35H, $^i$Bu/$^t$Bu{Me}), 0.25 – (-0.38) (at least 4 broad peaks @ 0.05, -0.04, -0.14, -0.25, 6H, $^i$Bu{Me-agostic}), -22.00 (br d, J = 54.4, 0.63H, RhH), -22.15 (br d, J ~ 50, 0.03H, RhH), -22.83 (br d, J = 55.8, 0.06H, RhH), -23.04 (br d, J = 56.9, 0.28H, RhH).

$^1H$ {$^{31}P$} NMR ($CD_2Cl_2$, 500 MHz, 173 K): δ 7.74 (br, 8H, $BAr^F{}_4$), 7.55 (br, 4H, $BAr^F{}_4$), 2.39 – 1.30 (multiple peaks, 12H, $^i$Bu{CH/ $CH_2$}), 1.21 - 0.30 (multiple peaks, 35H, $^i$Bu/$^t$Bu{Me}), 0.25 - -0.38 (4 broad peaks @ 0.05, -0.04, -0.14, -0.25, 6H, $^i$Bu{Me-agostic}), -22.00 (d, J = 54.6, 0.63H, RhH), -22.15 (d, J ~ 50, 0.03H, RhH), -22.83 (d, J = 55.7, 0.06H, RhH), -23.04 (d, J = 56.9, 0.28H, RhH).

$^{31}P$ {$^1H$} NMR ($CD_2Cl_2$, 202 MHz, 173 K): δ 85.7 (dd, $^2J_{PP}$ = 295, $^1J_{RhP}$ = 115, C-H activated P -isomer 1), 83.9 (dd, $^2J_{PP}$ = 296, $^1J_{RhP}$ = 114, C-H activated P - isomer 2),78.6 (dd, $^2J_{PP}$ = 299, $^1J_{RhP}$ = 114, C-H activated P – isomer 3), 69.8 (dd, $^2J_{PP}$ = 298, $^1J_{RhP}$ = 116, C-H activated P - isomer 4), 56.2 2 (dd, $^2J_{PP}$ = 295, $^1J_{RhP}$ = 115, non C-H activated P – isomer 4), ~49.8 (assumed dd, obscured by isomers at 49.2 and 48.9, outer lines only visible, non C-H activated P – isomer 3), 49.2 (dd, $^2J_{PP}$ = 296, $^1J_{RhP}$ = 114, non C-H activated P – isomer 2), 48.9 (dd, $^2J_{PP}$ = 296, $^1J_{RhP}$ = 116, non C-H activated P – isomer 1).

Peaks assigned by relative integrals and coupling constants. Approximate percentage of the 4 isomers by relative $^{31}P$ integrals; 1, 55%; 2, 34%; 3, 8%; 4, 3%.

Anal. Calcd for $C_{56}H_{66}BF_{24}P_2Rh$ (1370.75 gmol$^{-1}$): C, 49.07; H, 4.85. Found: C, 48.99 H, 4.80.

ESI-MS ($C_6H_5F$, 60ºC,) positive ion: *m/z,* 507.2760 [M$^+$] (calc. 507.2750).

IR ($CH_2Cl_2$, cm$^{-1}$): $\nu(CH_{agostic})$ 2684 (vbr).

$[Rh(P^iBu_2{}^tBu)_2(MeCN)_2][BAr^F{}_4]$ (5)

MeCN (4 µL, 0.073 mmol) was added to a solution of 4 (0.010 g, 0.0073 mmol) in $CH_2Cl_2$ (1 mL). The yellow solution was layered with pentane and held at 5 ºC yielding 5 as yellow crystals. Yield: 0.006 g (56%).

$^1H$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ 7.72 (br, 8H, $BAr^F{}_4$), 7.56 (br, 4H, $BAr^F{}_4$), 2.21 (td, $^4J_{PH}$ = 1.6, $^5J_{RhH}$ = 0.6, 6H, MeCN), 2.07 (br, 4H, $^i$Bu{CH}), 1.67 – 1.62 (m, 4H, $^i$Bu{$CH_2$}), 1.58 – 1.52 (m, 4H, $^i$Bu{$CH_2$}),1.25 (apparent t, J = 7, 18H, $^t$Bu{Me}), 1.21 (d, $^3J_{HH}$ = 6.6, 12H, $^i$Bu{Me}), 1.14 (d, $^3J_{HH}$ = 6.6, 12H, $^i$Bu{Me}).

$^1H$ {$^{31}P$ @ 21.9 ppm} NMR ($CD_2Cl_2$, 500 MHz): $\delta$ 7.72 (br, 8H, $BAr^F{}_4$), 7.56 (br, 4H, $BAr^F{}_4$), 2.21 (d, $^4J_{RhH}$ = 0.6, 6H, MeCN), 2.07 (nonet, $^3J_{HH}$ = 6.6, 4H, $^i$Bu{CH}), 1.64 (dd, $^2J_{HH}$ = 14.6, $^3J_{HH}$ = 5.6, 4H, $^i$Bu{$CH_2$}), 1.55 (dd, $^2J_{HH}$ = 14.6, $^3J_{HH}$ = 8.0, 4H, $^i$Bu{$CH_2$}), 1.25 (s, 18H, $^t$Bu{Me}), 1.21 (d, $^3J_{HH}$ = 6.7, 12H, $^i$Bu{Me}), 1.14 (d, $^3J_{HH}$ = 6.6, 12H, $^i$Bu{Me}).

$^{31}P$ {$^1H$} NMR ($CD_2Cl_2$, 202 MHz): $\delta$ 21.9 (d, $^1J_{RhP}$ = 128).

$^{13}C$ {$^1H$} NMR ($CD_2Cl_2$, 126 MHz): $\delta$ 162.3 (q, $^1J_{BC}$ = 50, $BAr^F{}_4$), 135.4 (s, $BAr^F{}_4$), 129.4 (qq, $^2J_{FC}$ = 32, $^3J_{BC}$ = 3, $BAr^F{}_4$), 125.1 (q, $^1J_{FC}$ = 272, $BAr^F{}_4$), 125.1 (d, J = 14, Me<u>C</u>N), 118.0 (sept, $^3J_{FC}$ = 4, $BAr^F{}_4$), 33.6 (apparent t, J = 11, $^t$Bu{C}), 31.3 (apparent t, J = 8, $^i$Bu{$CH_2$}), 28.2 (apparent t, J = 3, $^t$Bu{Me}), 26.3 (apparent t, J = 4, $^i$Bu{Me}), 25.9 (s, $^i$Bu{CH}), 25.4 (apparent t, J = 3, $^i$Bu{Me}), 4.99 (s, <u>Me</u>CN).

Anal. Calcd for $C_{60}H_{72}BF_{24}N_2P_2Rh$ (1452.85 gmol$^{-1}$): C, 49.60; H, 5.00; N, 1.93. Found: C, 49.48; H, 4.95; N, 1.77.

ESI-MS (1,2-$C_6H_4F_2$, 60ºC) positive ion: *m/z,* 589.3280 [M$^+$] (calc. 589.3281).

$[Rh((P^iBu_2{}^tBu)_2(\eta^2\text{-}H_3B.NMe_3)][BAr^F{}_4]$ (6)

1,2-$C_6H_4F_2$ (1 mL) was added to a J. Youngs' crystallisation tube containing 4 (0.017 g, 0.012 mmol) and $H_3B.NMe_3$ (0.0009 g, 0.012 mmol). Recrystallisation from 1,2-$C_6H_4F_2$ and pentane at 5 ºC yielded 6 as blue crystals. Yield: 0.009 g (50%).

$^{1}$H NMR (1,2-$C_6H_4F_2$, 500 MHz): $\delta$ 8.34 (br, 8H, $BAr^F_4$), 7.69 (br, 4H, $BAr^F_4$),2.88 (s, 9H, $H_3B.N\underline{Me}_3$), 2.17 (m, 4H, , $^{i}$Bu{CH}), 1.95 (m, 4H, $^{i}$Bu{$CH_2$}), 1.72 (m, 4H, $^{i}$Bu{$CH_2$}), 1.35 (d, $^{3}J_{PH}$ =13.2, 18H, $^{t}$Bu{Me}), 1.27 (d, $^{3}J_{HH}$ = 6.5, 12H, $^{i}$Bu{Me}), 1.23 (d, $^{3}J_{HH}$ = 6.7, 12H, $^{i}$Bu{Me}), -2.80 (br, 3H, $\underline{H}_3B.NMe_3$).

$^{31}$P {$^{1}$H} NMR (1,2-$C_6H_4F_2$, 202 MHz): $\delta$ 56.2 (d, $^{1}J_{RhP}$ = 183).

$^{11}$B NMR (1,2-$C_6H_4F_2$, 160 MHz): $\delta$ 26.8 (br).

Anal. Calcd for $C_{59}H_{78}B_2F_{24}NP_2Rh.2(SiOMe_2)$ (1592.00 gmol$^{-1}$): C, 47.53; H, 5.70; N, 0.88. Found: C, 47.26; H, 5.29; N, 0.84.

ESI-MS (1,2-$C_6H_4F_2$, 60ºC) positive ion: *m/z,* 580.3796 [$M^+$] (calc. 580.3818), 507.2736 [$M^+$ - $H_3B.NMe_3$] (calc. 507.2750).

3 + vacuum

A solid sample of 3 (0.008 g, 0.0058 mmol) was placed under a vacuum of 6 x 10$^{-2}$ mbar for 15 hours. $CD_2Cl_2$ (0.5 mL) was added, after which analysis by $^{1}$H NMR spectroscopy showed a 60% conversion to 4.

4 + $H_2$

A sample of 4 (0.008 g, 0.0058 mmol) in $CD_2Cl_2$ (0.5 mL) was placed under 1 atm of hydrogen. Quantitative formation of 3 was seen by $^{31}$P and $^{1}$H NMR spectroscopy (in situ).

4 + $C_6H_6$

$C_6H_6$ (0.1 mL, 1.119 mmol) was added to a solution of 4 (0.020 g, 0.0146 mmol) in $CD_2Cl_2$ (0.5 mL). No reaction was seen by $^{1}$H or $^{31}$P NMR spectroscopy.

4 + $C_6H_5Br$

$C_6H_5Br$ (6.2 µL, 0.058 mmol) was added to a solution of 4 (0.008 g, 0.0058 mmol) in $CD_2Cl_2$ (0.5 mL). No reaction was seen by $^{1}$H or $^{31}$P NMR spectroscopy.

*Selected NMR Spectra*

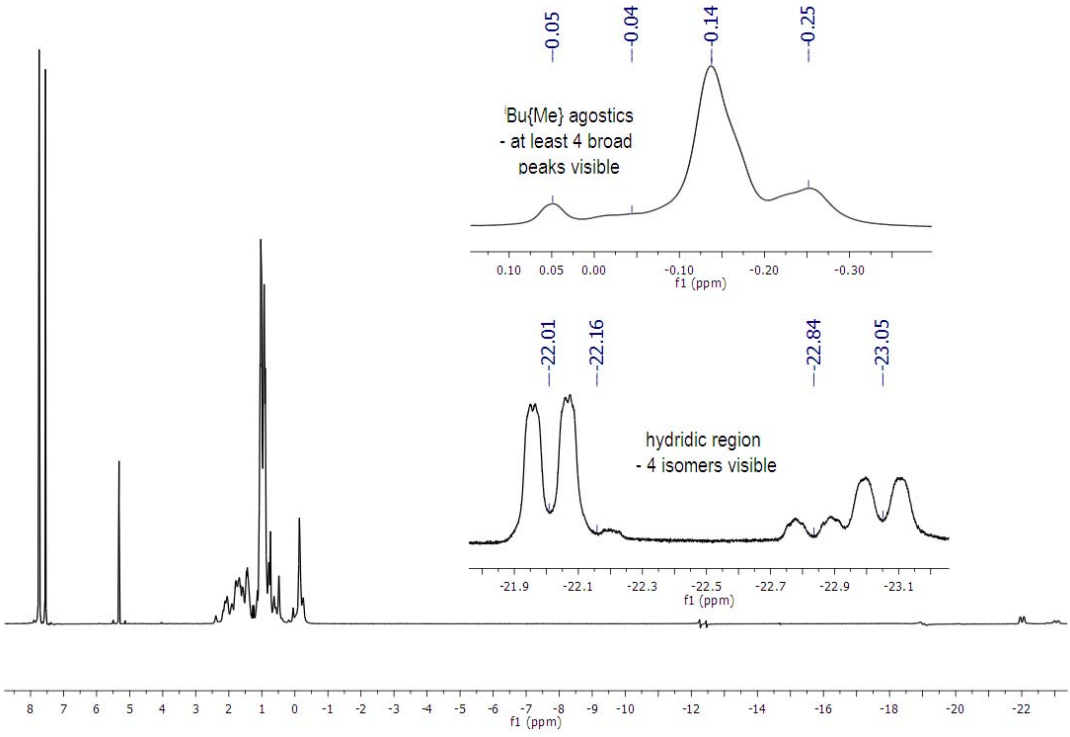



Figure S-2: $^{1}H$ NMR ($CD_2Cl_2$) spectra of 4 at 173K.

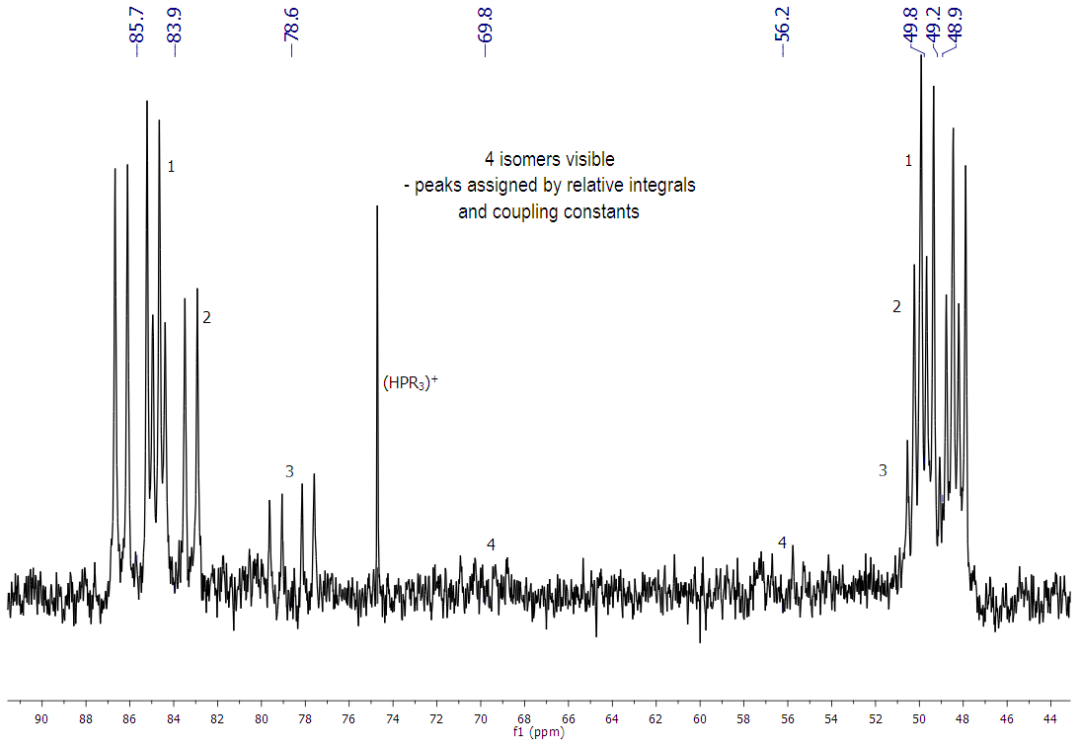



Figure S-3: $^{31}P$ NMR ($CD_2Cl_2$) spectra of 4 at 173K.

## *Crystallography*

Relevant details about the structure refinements are given in Table S-1. Data were collected on an Enraf Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) and a low-temperature device;[5] data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK.[6] The structures were solved by direct methods using SIR2004[7] and refined full-matrix least squares on $F^2$ using SHELXL-97. [8] In both solutions, the asymmetric units contain two independent cations that lie on special positions and are disordered across these points. All non-hydrogen atoms were refined anisotropically. The hydride ligands were only located in one of the unique molecules of in 3 (H0A, H0B) – their isotropic displacement parameters were fixed to ride on the parent atoms. All other hydrogen atoms were placed in calculated positions using the riding model. Restraints were applied to the geometry of the hydride ligands and phosphine ligands – further details of disorder modelling are documented in the crystallographic information files under the heading _refine_special_details. Restraints to thermal parameters were applied were necessary in order to maintain sensible values. Graphical representations of the structures were made using ORTEP3.[9]

Table S-1: Crystallographic data.

| | 3 | 4 |
|---|---|---|
| CCDC | 776219 | 776220 |

| | | |
|---|---|---|
| formula | $C_{56}H_{68}BF_{24}P_2Rh$ | $C_{56}H_{66}BF_{24}P_2Rh$ |
| *M* | 1372.76 | 1370.75 |
| cryst syst | Triclinic | Triclinic |
| space group | *P*-1 | *P*-1 |
| *a* [Å] | 12.88050(10) | 12.9373(2) |
| *b* [Å] | 13.05280(10) | 13.0919(2) |
| *c* [Å] | 22.3154(2) | 22.2056(3) |
| $\alpha$ [deg] | 103.1981(3) | 72.9625(7) |
| $\beta$ [deg] | 94.4213(4) | 85.6901(6) |
| $\gamma$ [deg] | 118.4125(4) | 60.4717(6) |
| *V* [Å$^3$] | 3136.24(4) | 3118.05(8) |
| *Z* | 2 | 2 |
| density [gcm$^{-3}$] | 1.454 | 1.460 |
| $\mu$ (mm$^{-1}$) | 0.430 | 0.432 |
| $\theta$ range [deg] | $5.11 \leq \theta \leq 27.88$ | $5.10 \leq \theta \leq 26.37$ |
| Reflns collected | 26387 [$R_{int}$ = 0.0193] | 22967 [$R_{int}$ = 0.0252] |
| no. of data/restr/param | 14829 / 1704 / 1244 | 12605 / 1802 / 1214 |
| *R*1 [$I > 2\sigma(I)$] | 0.0560 | 0.0722 |
| *wR*2 [all data] | 0.1669 | 0.2276 |
| GoF | 1.032 | 1.042 |
| Largest diff. pk and hole [eÅ$^{-3}$] | 1.236, -0.550 | 0.857, -0.605 |

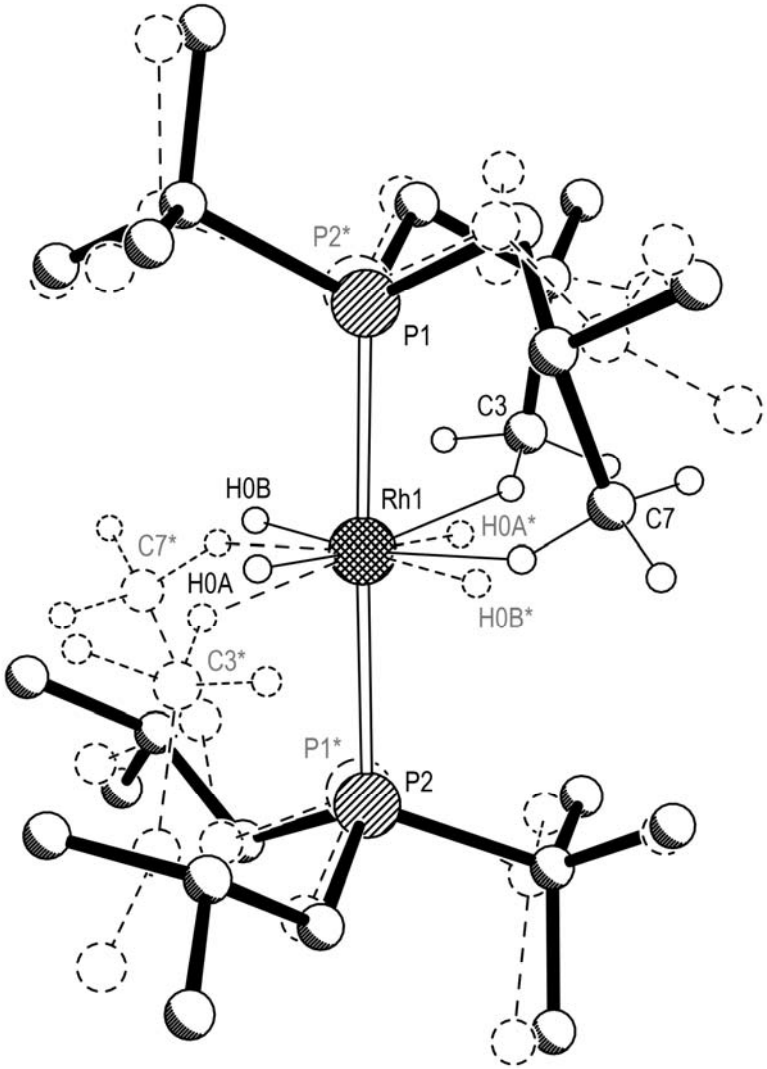



Figure S-4: Ball and stick representation of the cationic portion of 3; only one unique molecule shown and most H atoms are omitted for clarity. Both independent cations are disordered equally across special positions. In the molecule shown the disordered component (generated using the symmetry operation –*x*+2, -*y*+2, -*z*+1) is shown with dashed atoms and bonds.

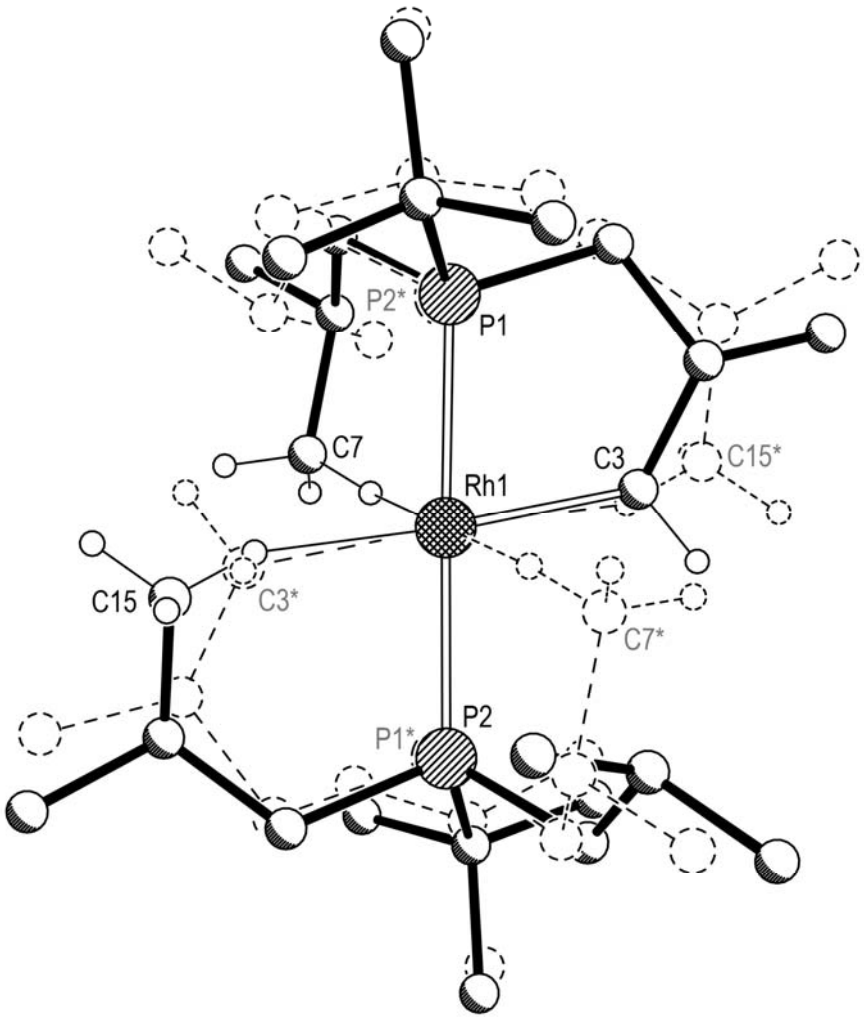



Figure S-5: Ball and stick representation of the cationic portion of 4; only one unique molecule shown and most H atoms are omitted for clarity. Both independent cations are disordered equally across special positions. In the molecule shown the disordered component (generated using the symmetry operation –*x*+2, -*y*+1, -*z*) is shown with dashed atoms and bonds.

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