Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Alkyl Dehydrogention in a Rh(I) Complex via an Isolated Agostic Intermediate.

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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. CH_2Cl_2, THF, MeCN and pentane were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.[i] CD_2Cl_2, C_6H_5F, 1,2-$C_6H_4F_2$ and 1,3-$C_6H_4(CH_3)F$ were distilled under vacuum from CaH_2 and stored over 3 Å molecular sieves. tert-butylethene was dried over sodium, vacuum distilled and stored over 3 Å molecular sieves. [Rh(BINOR-S)(P^iPr_3)][BAr^F_4],[ii] [Rh(P^iPr_3)$_2$Cl]$_2$,[iii] and Na[BAr^F_4][iv] were prepared by literature methods. All other chemicals are commercial products and were used as received. NMR spectra were recorded on a Varian Unity or a Bruker AVC 500 MHz spectrometer at room temperature, unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicroOTOF-Q instrument.[v] Microanalyses were performed by Elemental Microanalysis Ltd.

Synthesis of new complexes

[Rh(P^iPr_3)$_3$][BAr^F_4]*

To a solution of [Rh(BINOR-S)(P^iPr_3)]BAr^F_4 (0.30 g, 0.23 mmol) in C_6H_5F (15 mL) was added a solution of P^iPr_3 in pentane (0.86 mL, 0.56 M, 0.48 mmol). The mixture was stirred at room temperature for 10 minutes, during which time the solution became dark purple, then layered with pentane and held at 5ºC to give dark red crystals, which were isolated by decantation and washed with pentane (3 × 5 mL). Yield: 0.24 g. * Analysis of these crystals by ^{1}H NMR spectroscopy and X-ray diffraction indicated the presence of 20% [Rh(P^iPr_3)$_2$(P^iPr_2(C_3H_5))][BAr^F_4] as a cocrystalline impurity. Crystals could also be grown in a similar manor from CH_2Cl_2.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ7.71-7.75 (m, 8H, B<u>Ar</u>$^F_4$), 7.57 (br, 4H, B<u>Ar</u>$^F_4$), 1.89 (virtual sept, 9H, J = 7, PC<u>H</u>), 1.35-1.41 (m, 54H, PCH<u>Me</u>).

^{1}H NMR (CD_2Cl_2, 500 MHz, 200 K): 7.73 (br, 8H, B<u>Ar</u>$^F_4$), 7.56 (br, 4H, B<u>Ar</u>$^F_4$), 1.68-1.86 (m, 9H, PC<u>H</u>), 1.20-1.35 (m, 54H, PCH<u>Me</u>).

^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz): 162.1 (q, J_{BC} = 50, B<u>Ar</u>$^F_4$), 135.3 (s, B<u>Ar</u>$^F_4$),129.2 (qq, J_{FC} = 32 , J_{BC} = 3, B<u>Ar</u>$^F_4$), 125.1 (q, J_{FC} = 272, B<u>Ar</u>$^F_4$), 117.8 (virtual sept, J = 4, B<u>Ar</u>$^F_4$), 27.0 (dd, J = 14, J = 7, P<u>C</u>H), 20.7 (s, PCH<u>Me</u>).

^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz): δ47.1 (d, $^1J_{RhP}$ = 173).

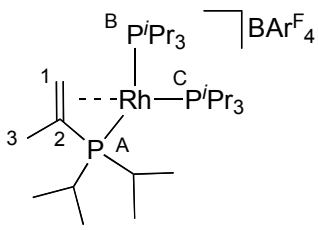
$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 202 MHz, 200 K): δ41 (br, fwhm = 4000 Hz).

ESI-MS (CH_2Cl_2, 100ºC, 4.5 kV) positive ion: *m/z*, 421.16 $[M\text{-}C_9H_{23}P]^+$ (58%, calc. 421.17), 581.30 $[M\text{-}H_2]^+$ (100%, calc. 583.30).

Anal. Calcd for $C_{59}H_{74.60}BF_{24}P_3Rh$ (1446.44 $gmol^{-1}$): C, 48.99; H, 5.20. Found: C, 49.19; H, 5.19.

$[Rh(P^iPr_3)_2(P^iPr_2(C_3H_5))][BAr^F_4]$

To a schlenk flask charged with $[Rh(P^iPr_3)_3][BAr^F_4]$* (0.050 g, 0.035 mmol) was added tert-butylethene (0.1 mL, excess) followed by 1,2-$C_6H_4F_2$ (1 mL). The resulting solution was stirred at room temperature for 72 h and then filtered. The filtrate was then concentrated in vacuo and the orange residue washed with pentane (3 × 4 mL) and dried in vacuo. Yield: 0.043 g (86%). Orange crystals suitable for X-Ray diffraction were obtained from a CH_2Cl_2 solution layered with pentane at 5ºC.



^{1}H NMR (CD_2Cl_2, 500 MHz): δ7.76-7.79 (m, 8H, B<u>Ar</u>$^F_4$), 7.60 (br, 4H, B<u>Ar</u>$^F_4$), 4.18-4.25 (m, 1H, H^1), 3.19-3.21 (m, 1H, $H^{1'}$), 2.30-2.45 (m, 8H, PC<u>H</u>+PC<u>H</u>'), 1.83-1.86 (m, 3H, H^3), 1.19-1.52 (m, 48H, PCH<u>Me</u>+PCH<u>Me</u>').

$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 126 MHz): 162.1 (q, J_{BC} = 50, B<u>Ar</u>$^F_4$), 135.2 (s, B<u>Ar</u>$^F_4$), 129.3 (qq, J_{FC} = 31, J_{BC} = 3, B<u>Ar</u>$^F_4$),125.0 (q, J_{FC} = 272, B<u>Ar</u>$^F_4$), 117.9 (virtual sept, J = 4, B<u>Ar</u>$^F_4$), 84.8 (C^2), 67.0 (C^1), 30.7 (d, J = 19, P<u>C</u>H'), 28.2 (t, J = 9, P<u>C</u>H), 23.6 (br), 22.7 (br), 21.3 (br, PCH<u>Me</u>), 20.9 (s, PCH<u>Me</u>').

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 202 MHz): δ55.8 (dt, J_{RhP} = 181, J_{PP} = 33, 1P, P^C), 41.9-42.7 (m, 2P, $P^{A,B}$).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 202 MHz, 250 K): δ55.8 (ddd, J_{RhP} = 188, J_{PPA} = 40, J_{PP2} = 27, 1P, P^C), 44.2 (ddd, J_{PPB} = 224, J_{RhP} = 93, J_{PPC} = 40, 1P, P^A), 41.3 (ddd, J_{PPA} = 224, J_{RhP} = 159, J_{PPC} = 27, 1P, P^B).

ESI-MS (CH_2Cl_2, 100ºC, 4.5 kV) positive ion: *m/z*, 421.17 $[M\text{-}C_9H_{21}P]^+$ (21%, calc. 421.17), 581.31 $[M]^+$ (100%, calc. 583.30).

Anal. Calcd for $C_{59}H_{73}BF_{24}P_3Rh$ (1444.83 $gmol^{-1}$): C, 49.05; H, 5.09. Found: C, 49.00; H, 4.86.

$[Rh(C_6H_5F)(P^iPr_3)_2][BAr^F_4]$

A suspension of $[Rh(P^iPr_3)_2Cl]_2$ (0.20 g, 0.22 mmol) and $Na[BAr^F_4]$ (0.39 g, 0.44 mmol) in C_6H_5F (12 mL) was stirred at room temperature for 1 h and then filtered. The filtrate was layered with pentane and held at room temperature to give the product as dark red crystals, which were isolated by decantation and washed with pentane (3 × 8 mL). Yield: 0.410 g (68%).

^{1}H NMR (C_6H_5F, 500 MHz): δ8.31 (br, 8H, B<u>Ar</u>$^F_4$), 7.62 (br, 4H, B<u>Ar</u>$^F_4$), 1.58-1.71 (m, 6H, PC<u>H</u>), 0.89-1.09 (m, 32H, PCH<u>Me</u>). Signals from η^6-C_6H_5F not observed.

^{13}C{^{1}H} NMR (C_6H_5F, 126 MHz): 135.7 (s, B<u>Ar</u>$^F_4$), 125.4 (q, J_{FC} = 276, B<u>Ar</u>$^F_4$), 118.0 (br, B<u>Ar</u>$^F_4$), 27.7 (t, J = 11, P<u>C</u>H), 18.5 (s, PCH<u>Me</u>). Signals from η^6-C_6H_5F not observed. Some signals from the anion are obscured by those of the solvent.

^{31}P{^{1}H} NMR (C_6H_5F, 202 MHz): δ55.5 (d, J_{RhP} = 210).

ESI-MS (C_6H_5F, 100ºC, 4.5 kV) positive ion: *m/z*, 423.18 $[M\text{-}C_6H_5F]^+$ (calc. 423.18).

Anal. Calcd for $C_{56}H_{59}BF_{25}P_2Rh$ (1382.7086 gmol^{-1}): C, 48.64; H, 4.30. Found: C, 48.47; H, 4.14.

[Rh(P^{i}Pr$_3$)$_3$H$_2$][BAr$^F_4$]

A solution of [Rh(P^{i}Pr$_3$)$_3$H$_2$][BAr$^F_4$], [Rh(P^{i}Pr$_3$)$_3$][BAr$^F_4$] and [Rh(P^{i}Pr$_3$)$_2$(P^{i}Pr$_2$(C_3H_5))][BAr$^F_4$] (0.4:1:1 ratio) in C_6H_5F was prepared by equilibration of [Rh(P^{i}Pr$_3$)$_3$][BAr$^F_4$]* (0.010 g, 0.007 mmol) at room temperature over 24 h. A small quantity of H_2 was passed over the solution until the solution remained yellow and ^{31}P NMR indicated reaction completion. The yellow solution was layered with pentane at room temperature to give the product as yellow crystals. Yield: 0.035 g (36%). Crystals grown in this manor were suitable for X-Ray diffraction (redissolving this material in C_6H_5F gave similar NMR data). Cooling in 1,3-$C_6H_4(CH_3)F$ did not resolve the hydride signal in the ^{1}H NMR spectrum; it broadened into the baseline at 200K. A broad resonance was also observed by ^{31}P{^{1}H} NMR at this temperature. The sample was not stable in CD_2Cl_2.

^{1}H NMR (C_6H_5F, 500 MHz): δ8.32 (br, 8H, B<u>Ar</u>$^F_4$), 7.63 (br, 4H, B<u>Ar</u>$^F_4$), 2.18 (br, 9H, PC<u>H</u>), 1.01 (br, 54H, PCH<u>Me</u>), -21.04 (d, J_{RhH} = 28, 2H, Rh<u>H</u>, T_1 = 0.38 $\pm$ 0.2 s)

^{13}C{^{1}H} NMR (C_6H_5F, 126 MHz): 135.8 (s, B<u>Ar</u>$^F_4$), 125.5 (q, J_{FC} = 276, B<u>Ar</u>$^F_4$), 118.0 (virtual sept, J = 4, B<u>Ar</u>$^F_4$), 27.0 (br, P<u>C</u>H), 18.6 (s, PCH<u>Me</u>). Some signals from the anion are obscured by those of the solvent.

^{31}P{^{1}H} NMR (C_6H_5F, 202 MHz): δ51.2 (d, J_{RhP} = 106).

ESI-MS (C_6H_5F, 100ºC, 4.5 kV) positive ion: *m/z*, 423.18 $[M\text{-}C_9H_{23}P]^+$ (54%, calc. 423.18),

425.20 $[M-C_9H_{21}P]^+$ (100%, calc. 425.20), 583.32 $[M-H_2]^+$ (3%, calc. 583.32), 585.34 $[M]^+$ (1%, calc. 585.34).

NMR experiments

1. Preparation of $[Rh(P^iPr_3)_3][BAr^F_4]$

From $[Rh(BINOR\text{-}S)(P^iPr_3)][BAr^F_4]$: To a solution of $[Rh(BINOR\text{-}S)(P^iPr_3)][BAr^F_4]$ (10 mg, 0.0076 mmol) in C_6H_5F (0.4 mL) was added a solution of P^iPr_3 in pentane (0.020 mL, 0.74 M, 2.0 eqv.). The resulting solution rapidly became purple and the products were immediately characterised in situ by NMR spectroscopy. Formation of $[Rh(P^iPr_3)_3][BAr^F_4]$ was quantitative by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S-2). An equilibrium mixture containing $[Rh(P^iPr_3)_3H_2][BAr^F_4]$, $[Rh(P^iPr_3)_3][BAr^F_4]$ and $[Rh(P^iPr_3)_2(P^iPr_2(C_3H_5))][BAr^F_4]$ (0.3:1:1 ratio) is observed after 24 h at RT.
From $[Rh(C_6H_5F)(P^iPr_3)_2][BAr^F_4]$:To a solution of $[Rh(C_6H_5F)(P^iPr_3)_2][BAr^F_4]$ (10 mg, 0.0072 mmol) in C_6H_6F (0.4 mL) was added a solution of P^iPr_3 in pentane (0.014 mL, 0.56 M, 1.1 eqv.). The resulting solution rapidly became purple and the products were immediately characterised in situ by NMR spectroscopy. Formation of $[Rh(P^iPr_3)_3][BAr^F_4]$ was quantitative by $^{31}P\{^1H\}$ NMR spectroscopy. An equilibrium mixture containing $[Rh(P^iPr_3)_3H_2][BAr^F_4]$, $[Rh(P^iPr_3)_3][BAr^F_4]$ and $[Rh(P^iPr_3)_2(P^iPr_2(C_3H_5))][BAr^F_4]$ (0.4:1:0.9 ratio) is observed after 24 h at RT.

2. Dehydrogenation of $[Rh(P^iPr_3)_3][BAr^F_4]$

Dehydrogenation reactions were carried out using isolated samples of $[Rh(P^iPr_3)_3][BAr^F_4]$*. In a typical experiment, a youngs type NMR tube (ca. 2.5 mL total volume) was charged with $[Rh(P^iPr_3)_3][BAr^F_4]$* (10 mg) and C_6H_5F (0.4 ml) and the reaction monitored in situ by NMR spectroscopy.

a. An equilibrium mixture containing $[Rh(P^iPr_3)_3H_2][BAr^F_4]$, $[Rh(P^iPr_3)_3][BAr^F_4]$ and $[Rh(P^iPr_3)_2(P^iPr_2(C_3H_5))][BAr^F_4]$ (0.4:1:1 ratio) is slowly established over 12 h at ambient temperature ($t_{1/2}$ ~ 1.5 h, see Figure S-2). Trace quantities of $[Rh(C_6H_5F)(P^iPr_3)_2]^+$ and P^iPr_3 can be observed during this equilibration process (< 3 % total by ^{31}P NMR, only when run in C_6H_5F).
b. Similar reactivity is observed in 1,2-$C_6H_4F_2$ and 1,3-$C_6H_4(CH_3)F$.
c. Addition of excess tert-butylethene (ca. 0.1 mL) to the equilibrium mixture results in the immediate disappearance of $[Rh(P^iPr_3)_3H_2][BAr^F_4]$ and gradual disappearance of $[Rh(P^iPr_3)_3][BAr^F_4]$ to afford only $[Rh(P^iPr_3)_2(P^iPr_2(C_3H_5))][BAr^F_4]$ after ca. 30 h (see Figure S-2).
d. Addition of 10 equivalents of P^iPr_3 does not halt the dehydrogenation process and a similar equilibrium distribution is found (0.3:1:1).

e. The equilibrium distribution of $[Rh(P^iPr_3)_3H_2][BAr^F_4]$, $[Rh(P^iPr_3)_3][BAr^F_4]$ and $[Rh(P^iPr_3)_2(P^iPr_2(C_3H_5))][BAr^F_4]$ is perturbed by repetitive freeze-pump-thaw cylces (ca. 20 over 2 days) from 0.4:1:1 to 0.3:1:1.2.

f. Addition of 1 equivalent of 1,8-Bis(dimethylamino)naphthalene did not inhibit dehydrogenation.

3. Hydrogenation of $[Rh(P^iPr_3)_2(P^iPr_2(C_3H_5))][BAr^F_4]$

H_2 was passed over a solution of $[Rh(P^iPr_3)_2(P^iPr_2(C_3H_5))][BAr^F_4]$ (0.008 g, 0.006 mmol) in C_6H_5F (0.5 mL) resulting in quantitative conversion to $[Rh(P^iPr_3)_3H_2][BAr^F_4]$ by NMR spectroscopy.

4. Reaction of $[Rh(P^iPr_3)_3H_2][BAr^F_4]$ with MeCN

To a solution of $[Rh(P^iPr_3)_3H_2][BAr^F_4]$ (0.007 mmol) in 1,3-$C_6H_4(CH_3)F$ prepared in situ similarly to as described above was added MeCN (ca. 0.05 mL). The solution rapidly become colourless and the products were immediately characterised in situ by NMR spectroscopy. Formation of $[Rh(P^iPr_3)_2(NCMe)_2H_2][BAr^F_4]$ (and 1 equivalent of P^iPr_3) was quantitative by $^{31}P\{^1H\}$ NMR spectroscopy.[vi]

Selected NMR spectra

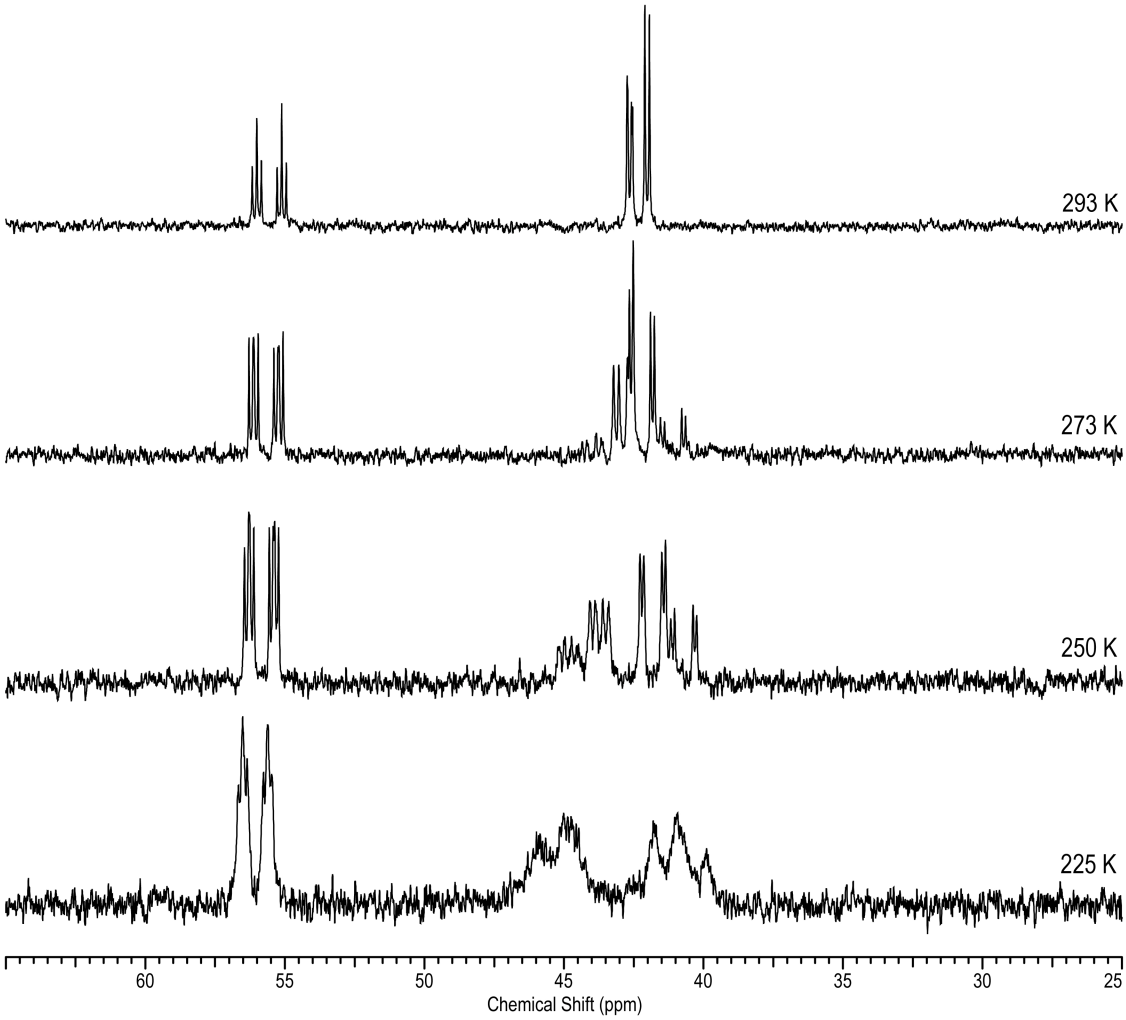


Figure S-1: Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of $[Rh(P^{i}Pr_3)_2(P^{i}Pr_2(C_3H_5))][BAr^{F}_4]$ (CD_2Cl_2, 202 MHz).

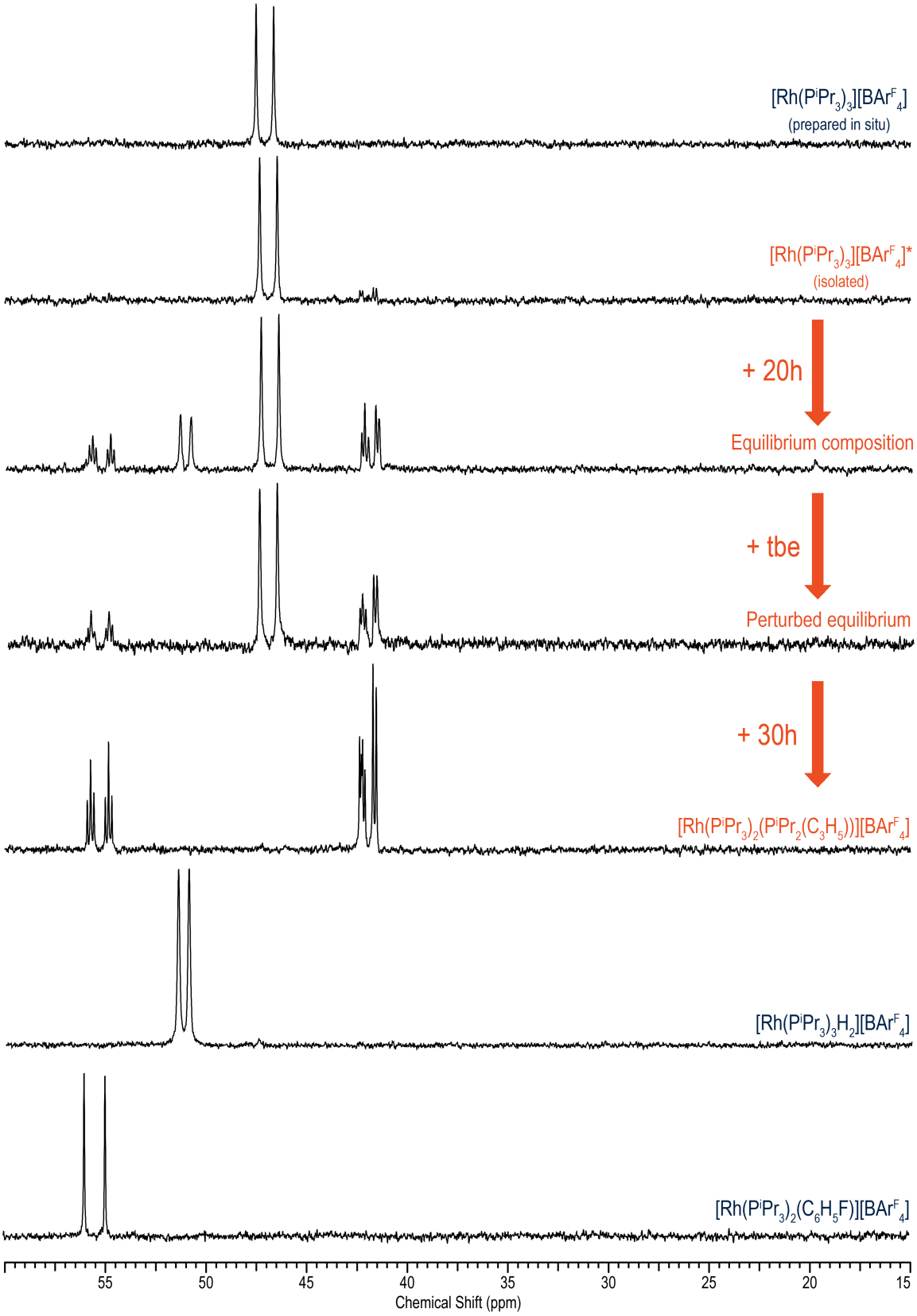


Figure S-2: Selected $^{31}P\{^{1}H\}$ NMR spectra (C_6H_5F, 202 MHz).

Crystallography

Relevant details about the structure refinements are given in Table S-1. The structures of **4** and **5** are depicted in Figure S-3 and Figure S-4. Data were collected on a Bruker 1000 CCD diffractometer (**1**) and an Enraf Nonius Kappa CCD (**4**, **5**) diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryostream low-temperature device.[vii] Structures were solved by direct methods using SHELXS-97 (**1**),[viii] SIR92 (**4**)[ix] and SIR2004 (**5**),[x] and refined by full-matrix least squares on F^2 using SHELXL-97.[viii] The structure of **4** was refined with a twin scale factor of 0.064(15). All non-hydrogen atoms were refined anisotropically. H1A in **1** was located on the Fourier difference map and its position refined freely. The alkene protons in **4** were located on the Fourier difference map and the 1,2 and 1,3 bond lengths restrained. All other hydrogen atoms were placed in calculated positions using the riding model. The hydride ligands in **5** were not located. CCDC 705127 – 705129 contain the supplementary crystallographic data for this paper (see Table S-1).

Table S-1: Crystallographic data for **1**, **4** and **5**.

	1	**4**	**5**
CCDC	705127	705128	705129
Formula	$C_{59}H_{74.60}BF_{24}P_3Rh$	$C_{59}H_{73}BF_{24}P_3Rh$	$C_{59}H_{75}BF_{24}P_3Rh$
M	1446.42	1444.80	1446.82
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$	$P2_1/n$
T [K]	120(2)	150(2)	150(2)
a [Å]	13.1039(6)	19.3219(2)	19.1792(2)
b [Å]	28.6518(12)	17.7292(2)	27.4349(3)
c [Å]	17.9634(8)	29.0445(3)	26.6460(3)
β [deg]	106.228(1)	96.6182(4)	105.5035(5)
V [Å^3]	6475.6(5)	9883.2(2)	13510.4(3)
Z	4 (*Z*' = 1)	6 (*Z*' = 3)	8 (*Z*' = 2)
Density [gcm^{-3}]	1.484	1.456	1.423
μ (mm^{-1})	0.444	0.436	0.426
θ range [deg]	$1.38 \leq \theta \leq 26.37°$	$5.12 \leq \theta \leq 26.37$	$5.11 \leq \theta \leq 26.37$
Reflns collected	63360	31319	44330
R_{int}	0.0395	0.0396	0.0337
No. of data/restr/ param	13255 / 500 / 1037	31319 / 442 / 2558	26498 / 480 / 1789
R_1, wR_2 [$I > 2\sigma(I)$]	0.0455, 0.1070	0.0506, 0.0882	0.0591, 0.1480
GoF	1.071	1.043	1.024
Largest diff. pk	0.964, -0.897	0.671, -0.385	2.015, -1.194

and hole [eÅ^{-3}]

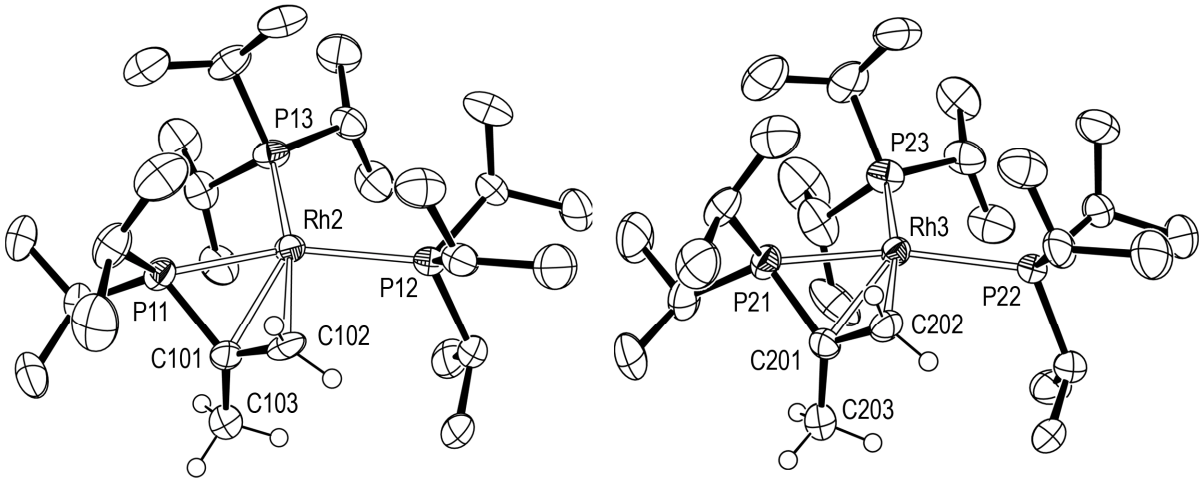


Figure S-3: Complex **4**; ellipsoids are depicted at the 50% probability level. Independent molecules in the asymmetric unit (Z'=3, see Figure 2 in the main text for the other independent molecule) - the anions and most H atoms are omitted for clarity. Key bond lengths [Å] and angles [º]: Rh2-P11, 2.303(2); Rh2-P12, 2.397(2); Rh2-P13, 2.344(2); P11-Rh2-P12, 154.56(5); P11-Rh2-P13, 99.12(6); P12-Rh2-P13, 106.07(6); Rh2-C101, 2.193(5); Rh2-C102, 2.242(5); Rh2-P11-C101, 63.5(2); C101-C102, 1.389(7); C101-C103, 1.496(8); Rh3-P21, 2.303(2);Rh3-P22, 2.392(2); Rh3-P23, 2.347(2); P21-Rh3-P22, 154.19(6); P21-Rh3-P23, 99.53(6); P22-Rh3-P23, 105.95(6); Rh3-C201, 2.201(5); Rh3-C202, 2.239(5); Rh3-P21-C201, 63.8(2); C201-C202, 1.405(7); C201-C203, 1.505(8).

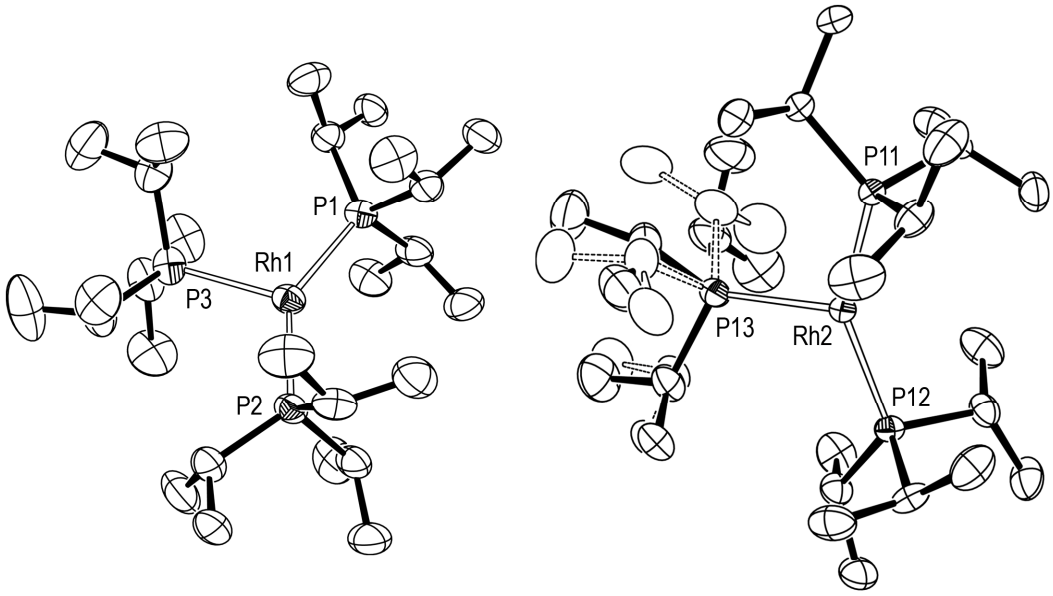


Figure S-4: Complex **5**; ellipsoids are depicted at the 50% probability level. Independent molecules in

the asymmetric unit (Z'=2) - the anion and H atoms are omitted for clarity; the minor disordered component in one of the independent molecules is shown with dashed bonds. Key bond lengths [Å] and angles [º]: Rh1-P1, 2.3612(12); Rh1-P2, 2.3564(12); Rh1-P3, 2.4508(14); P1-Rh1-P2, 141.95(5); P1-Rh1-P3, 108.38(4); P2-Rh1-P3, 109.67(4), Rh2-P11, 2.3557(10); Rh2-P12, 2.3444(10); Rh2-P13, 2.4184(12); P12-Rh2-P12, 144.95(4); P11-Rh2-P13, 106.39(4); P12-Rh2-P13, 108.66(4).

Along with **1** some of the dehydrogenation product (**4**) had co-crystallised (20% occupancy; C3b-C1b-C2b), however, the presence of **4** did not distort the orientation or location of the rest of the molecule, see Figure S-5.

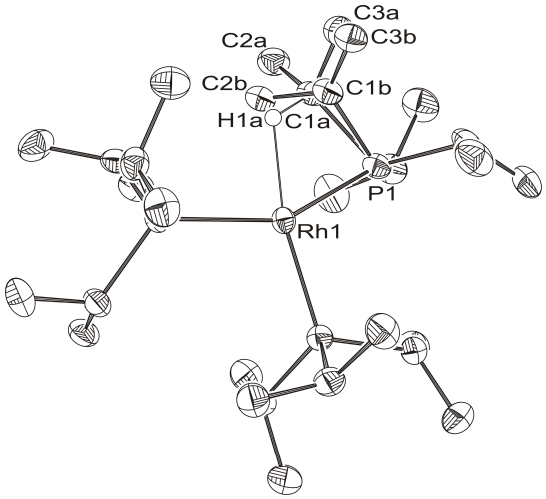


Figure S-5: Crystal structure of **1** (C1a-C2a-C3a), showing the presence of around 20% of the dehydrogentaiton product **4** (C1b-C2b-C4b) which had co-crystallised with **1**. Ellipsoids are depicted at the 50% probability level. All of the hydrogens, apart from H1a, and the anion are omitted for clarity.

The structure of **5** exhibits a significantly disordered phosphine ligand. This disorder was treated by modelling the appropriate phosphine substituents over two sites and restraining their geometry. In the absence of locating the hydride ligands, we note the lack of any significant agostic interactions (all Rh-C_{iPr} distances > 3.36 Å) and acute Rh-P-C_{iPr} angles (all > 105º) in this structure as seen in **1** [Rh1-C1a = 2.494(12) Å; Rh1-P1-C1a = 73.8(4)º]. The presence of relatively large Fourier peaks (6 peaks > 1.0 eÅ^{-3}) near the two metal centers in this structure is attributed to Fourier truncation errors.

Rotational disorder of the CF_3 groups on the anions was present in all of the structures. The relevant fluorine atoms, or in some cases the entire CF_3, were modelled over two or more sites and the

geometries restrained where necessary.

Graphical representations of the structures were made with ORTEP3[xi] or XP.[viii]

Computational details

Calculations were carried out using Gaussian 03, Revision C.02[xii] and employed the BP86 functional.[xiii] Rh and P were described using the Stuttgart RECPs and the associated basis sets[xiv] and a polarisation function was added for P (ζ = 0.387).[xv] 6-31G** basis sets were used for C and H atoms.[xvi] All stationary points were characterized via analytical frequency calculations, which furnished the zero-point energy corrections that are included in the figures quoted in the text. IRC calculations showed the local minima to which transition states connected, as reported in the text.[xvii]

Optimised geometries and energies

1. Interconversion between 1' isomers and C-H activation processes of 1'.

1'γ

BP86 Energy = -253.551779083
Enthalpy 0K= -253.388225
Enthalpy 298K= -253.374108
Free Energy 298K= -253.430844

Rh	0.45989	-0.06565	-0.02026
P	2.22069	-1.58378	0.03292
P	1.81275	1.69056	0.07544
H	2.38419	-2.38105	1.21324
H	2.24387	-2.63311	-0.94285
H	3.57444	-1.13735	-0.10832
H	3.23295	1.51086	0.00591
H	1.66096	2.69956	-0.92999
H	1.74290	2.51111	1.24899
P	-1.50766	1.15093	-0.08766
H	-1.85671	2.13605	-1.06700
H	-2.02245	1.79132	1.08721
C	-2.62444	-0.34693	-0.38583
C	-1.68222	-1.52534	-0.03001
H	-0.74217	-1.51620	-0.68200
H	-2.11419	-2.50823	-0.29222
C	-3.95079	-0.35623	0.37916
H	-4.58742	0.49666	0.09316
H	-4.51180	-1.27960	0.15148
H	-3.79233	-0.31916	1.47048
H	-2.81105	-0.35204	-1.47494
H	-1.43831	-1.55945	1.04815

TS 1'γ-6'γ

BP86 Energy = -253.529217650
Enthalpy 0K= -253.369854
Enthalpy 298K= -253.356167
Free Energy 298K= -253.411113
Frequency= -727.0274cm-1

Rh	-0.38981	0.04791	-0.03374
P	-1.95934	1.76166	0.02529
P	-2.01224	-1.66766	0.15386
H	-2.57791	2.06597	1.28200
H	-1.54273	3.07956	-0.34295
H	-3.13883	1.66825	-0.78079
H	-3.41060	-1.41498	-0.02784
H	-1.88376	-2.77914	-0.73638
H	-2.10356	-2.39633	1.38595
P	1.53706	-1.25420	-0.16968
H	1.87100	-2.15476	-1.23045
H	2.02912	-1.98644	0.95977
C	2.55484	0.32251	-0.34751
C	1.39767	1.30658	-0.03554
H	0.25661	0.86191	-1.20297
H	1.47128	2.26473	-0.57545
C	3.80867	0.46853	0.51779
H	4.57299	-0.27861	0.24730
H	4.25233	1.46846	0.37167
H	3.57740	0.35673	1.59078
H	2.81587	0.38235	-1.41992
H	1.30300	1.52382	1.04717

6'γ

BP86 Energy = -253.539637421
Enthalpy 0K= -253.379559
Enthalpy 298K= -253.365483
Free Energy 298K= -253.420961

Rh	0.38560	0.03024	-0.04927
P	1.77448	1.90697	0.03907
P	2.16393	-1.61484	-0.06173
H	2.35656	2.37367	-1.18540
H	1.21187	3.13630	0.50498
H	2.95742	1.87391	0.84326
H	3.51957	-1.29541	0.28161
H	2.02248	-2.75597	0.79136
H	2.44923	-2.32395	-1.27640
P	-1.52295	-1.29785	0.09158
H	-1.78223	-2.28952	1.08934
H	-2.02798	-1.94677	-1.08228
C	-2.50979	0.27173	0.39205
C	-1.36919	1.21824	-0.07497
H	0.32906	0.08678	1.46869
H	-1.31609	2.14477	0.51894
C	-3.87555	0.42351	-0.27892
H	-4.60067	-0.31577	0.10046
H	-4.28149	1.42872	-0.07137
H	-3.80408	0.31053	-1.37402
H	-2.60733	0.33143	1.49173
H	-1.48299	1.48568	-1.14671

1'β

BP86 Energy = -253.542544812
Enthalpy 0K= -253.379373
Enthalpy 298K= -253.364985
Free Energy 298K= -253.422429

Rh	-0.44321	0.00343	0.02078
P	-1.78484	1.89191	-0.00711
P	-2.15419	-1.40994	-0.01992
H	-2.04863	-2.55057	-0.87817
H	-2.48002	-2.06039	1.21510
H	-3.46090	-0.95793	-0.39752
H	-1.27899	3.05916	-0.66587
H	-3.08582	1.86001	-0.60643
H	-2.14316	2.48671	1.24672
P	1.37567	-1.35665	-0.00533
C	2.18824	0.34352	-0.00717
H	1.90729	-2.07816	-1.12112
H	1.94445	-2.08391	1.08844
C	2.94733	0.65739	-1.31027
H	2.34323	0.45119	-2.20806
H	3.86849	0.05353	-1.36221
C	2.98408	0.63853	1.27852
H	3.27120	1.70292	1.30730
H	2.40809	0.41561	2.19078
H	3.90861	0.03782	1.29390
H	1.28527	1.07224	0.01077
H	3.23792	1.72104	-1.32983

TS 1'β-6'β

BP86 Energy = -253.518736806
Enthalpy 0K= -253.360324
Enthalpy 298K= -253.345986
Free Energy 298K= -253.402730
Frequency= -468.3463cm-1

Rh	-0.31764	-0.01554	-0.15037
P	-1.39601	2.01408	-0.01128
P	-2.28446	-1.31095	0.12419
H	-2.70290	-2.01918	-1.04599
H	-2.26736	-2.40356	1.04837
H	-3.54672	-0.74691	0.50017
H	-1.98612	2.55173	-1.20033
H	-2.51382	2.15400	0.87312
H	-0.64618	3.16177	0.39494
P	1.36786	-1.57138	0.02093
C	1.91982	0.16906	0.09083
H	2.09221	-2.25766	-1.00074
H	1.71453	-2.27244	1.21515
C	2.89296	0.62765	-0.99919
H	2.67207	0.19370	-1.98716
H	3.91849	0.33010	-0.71341
C	2.17558	0.78653	1.45884
H	2.08550	1.88485	1.40609
H	1.49404	0.41919	2.24155
H	3.21444	0.56017	1.77015
H	0.64005	0.94124	-0.94922
H	2.88436	1.72677	-1.09660

6'β

BP86 Energy = -253.533809141
Enthalpy 0K= -253.374490
Enthalpy 298K= -253.359879
Free Energy 298K= -253.416219

Rh	0.33391	-0.07117	0.00467
P	2.56087	-0.96394	0.07505
H	0.38388	-0.01232	-1.51283
H	3.71608	-0.20068	-0.29812
H	3.06269	-1.45537	1.32626
H	2.84133	-2.12607	-0.71201
P	-1.28025	-1.70650	-0.23109
H	-1.75131	-2.65638	0.72836
H	-1.75339	-2.19090	-1.48361
C	-1.83139	0.00074	0.07443
C	-2.19205	0.32439	1.52345
H	-1.49828	-0.12437	2.26154
H	-3.20344	-0.04976	1.77633
C	-2.65139	0.72034	-0.98411
H	-3.72850	0.50078	-0.86069
H	-2.53185	1.81354	-0.88305
H	-2.36274	0.44344	-2.01065
H	-2.19834	1.41645	1.68379
P	0.80140	2.19984	-0.08461
H	1.92773	2.65933	-0.83863
H	-0.18800	3.09246	-0.60793
H	1.07697	2.87861	1.14831

TS 1'β-1'an

BP86 Energy = -253.542230280
Enthalpy 0K= -253.378857
Enthalpy 298K= -253.365205
Free Energy 298K= -253.421259
Frequency= -46.2322cm-1

Rh	0.50291	0.05136	-0.02809
P	2.04129	1.79810	0.00864
P	2.02348	-1.54129	0.03036
H	2.45150	2.38275	-1.23403
H	1.65803	2.99567	0.69663
H	3.33550	1.62457	0.59771
H	3.37001	-1.22487	0.40615
H	1.79465	-2.65632	0.89894
H	2.27505	-2.23346	-1.19982
P	-1.38787	-1.21123	-0.00713
H	-1.86676	-1.98784	1.09674
H	-1.90101	-1.97787	-1.10291
C	-2.35313	0.41318	0.01059
C	-3.19730	0.60986	-1.26316
H	-2.60644	0.47800	-2.18405
H	-3.62041	1.62825	-1.27436
C	-3.13182	0.61913	1.32376
H	-2.49524	0.48952	2.21394
H	-3.55078	1.63890	1.35111
H	-3.97087	-0.09357	1.38824
H	-1.52787	1.19412	-0.01298
H	-4.03604	-0.10579	-1.28248

1'an

BP86 Energy = -253.547862259
Enthalpy 0K= -253.383659
Enthalpy 298K= -253.369075
Free Energy 298K= -253.428348

Rh	-0.69581	-0.18692	-0.20599
P	-2.79305	-1.19819	-0.04026
P	-1.42928	1.76333	0.46869
H	-3.62022	-1.30835	-1.20578
H	-2.79485	-2.57498	0.36188
H	-3.77957	-0.71159	0.87644
H	-2.64046	1.81120	1.23279
H	-0.58859	2.56694	1.30555
H	-1.74559	2.72092	-0.55199
P	1.46744	0.63604	-0.37391
H	1.86055	1.71960	0.48121
H	1.79906	1.23661	-1.63526
C	2.87116	-0.60382	-0.10191
C	4.22696	0.04839	-0.42513
H	4.28103	0.41843	-1.46178
H	5.02806	-0.70019	-0.29616
C	2.79482	-1.16466	1.33050
H	1.82085	-1.63482	1.54745
H	3.57744	-1.92964	1.46723
H	2.96963	-0.37453	2.08100
H	2.66700	-1.41274	-0.82955
H	4.44301	0.88735	0.25825

2. H-transfer: Pathway 1.

TS 6'β-7'trans

BP86 Energy = -253.506166272
Enthalpy 0K= -253.350564
Enthalpy 298K= -253.337000
Free Energy 298K= -253.390940
Frequency= -482.6061cm-1

Rh	0.25474	-0.06843	0.03527
P	0.94491	2.13134	-0.20881

```
P    2.36972 -1.09402 -0.00850
H    0.12441  3.01261 -0.98084
H    1.11845  2.94739  0.95514
H    2.19870  2.38051 -0.84951
H    3.49092 -0.35543 -0.50600
H    2.96284 -1.60405  1.18721
H    2.49638 -2.25145 -0.83705
P   -1.43594 -1.61660 -0.37296
H   -1.95578 -2.64418  0.48219
H   -2.04283 -1.87927 -1.63380
C   -1.92163  0.04280  0.20234
C   -1.39476  0.23971  1.53584
H    0.43861 -0.10251  1.66886
H   -1.45993 -0.55990  2.28166
C   -2.81404  1.01249 -0.53110
H   -3.87055  0.82290 -0.26689
H   -2.58518  2.05185 -0.23967
H   -2.71646  0.92507 -1.62437
H   -1.47548  1.24572  1.96713
H    0.41486  0.00942 -1.57985
```

7'trans

```
BP86 Energy = -253.510506493
Enthalpy 0K= -253.352773
Enthalpy 298K= -253.339256
Free Energy 298K= -253.393194

Rh   0.24483 -0.05575  0.11438
P    1.31948  1.97262 -0.08079
P    2.12268 -1.35402 -0.25594
H    0.55934  3.05640 -0.62108
H    1.84095  2.60518  1.09065
H    2.46845  2.05070 -0.92863
H    3.30013 -0.71844 -0.76311
H    2.69406 -2.07828  0.83284
H    2.00086 -2.40361 -1.21671
P   -1.54637 -1.52536  0.10421
H   -2.13483 -2.16811  1.23911
H   -2.12721 -2.19111 -1.01432
C   -1.97853  0.24728  0.02950
C   -1.51373  0.93212  1.18096
H    0.67519 -0.22768  1.68576
H   -1.51378  0.47924  2.17422
C   -2.69387  0.89281 -1.13095
H   -3.77942  0.89612 -0.92067
H   -2.37487  1.94082 -1.25277
H   -2.52842  0.36334 -2.08073
H   -1.55527  2.02899  1.17167
H    0.13717  0.04328 -1.53269
```

TS 7'trans-7'cis

```
BP86 Energy = -253.495298096
Enthalpy 0K= -253.339300
Enthalpy 298K= -253.326018
Free Energy 298K= -253.378280
Frequency= -163.9905cm-1

Rh  -0.27297 -0.14487  0.02122
P   -2.42599 -1.02220 -0.02670
P    1.63567  0.13971  1.33442
H   -3.24388 -1.03455  1.14531
H   -2.57649 -2.38551 -0.42725
H   -3.34260 -0.40961 -0.93795
H    2.09350 -0.71488  2.38427
H    2.41587  1.32328  1.49853
C    1.94625 -0.52324 -0.33373
C    1.26909 -1.74652 -0.56986
C    2.74428  0.23232 -1.37078
H    3.80400 -0.07637 -1.31208
H    2.37803 -0.00257 -2.38340
H    2.70831  1.32435 -1.23121
H    1.15983 -2.50929  0.20524
H    1.24199 -2.12284 -1.59866
H   -0.50392 -1.15460  1.25547
H   -0.53376 -0.05764 -1.55385
P   -0.92174  2.10095 -0.20810
H   -2.12041  2.37190 -0.93998
H   -1.20522  2.87404  0.96395
H   -0.06815  3.04126 -0.87143
```

7'cis

```
BP86 Energy = -253.525255650
Enthalpy 0K= -253.367068
Enthalpy 298K= -253.353302
Free Energy 298K= -253.407252

Rh   0.36079 -0.16961  0.33784
P    2.55700 -0.54528 -0.22128
P   -1.21389 -1.35043 -1.09611
H    2.82577 -1.59642 -1.15074
H    3.43991 -0.91627  0.83540
H    3.32668  0.50626 -0.81461
H   -1.59425 -2.69831 -0.81100
H   -2.01933 -1.06817 -2.24657
C   -1.94172 -0.29022  0.22370
C   -1.56139 -0.56862  1.54507
C   -2.79622  0.89941 -0.14920
H   -3.85071  0.56782 -0.17870
H   -2.72673  1.69923  0.60658
H   -2.56402  1.31276 -1.14408
H   -1.37056 -1.58255  1.90283
H   -1.80985  0.16503  2.32086
H    0.64313 -1.55878  1.03358
H    0.90390  0.37406  1.70113
P    0.33895  2.14204 -0.37248
H    1.61185  2.79496 -0.41906
H   -0.14445  2.58962 -1.64716
H   -0.34173  3.10519  0.43945
```

Alternative trans-cis Isomerisation.

TS 7'trans-7'cis (2)

```
BP86 Energy = -253.501466110
Enthalpy 0K= -253.345239
Enthalpy 298K= -253.332110
Free Energy 298K= -253.384172
Frequency= -128.9859cm-1

Rh   0.28439 -0.00823 -0.06169
P    2.14894 -1.40343  0.01580
P    1.02815  2.19194  0.30458
H    2.33675 -2.17637  1.20287
H    2.28116 -2.43977 -0.95913
H    3.45152 -0.82425 -0.09083
H    2.31554  2.37158  0.90058
```

```
H   1.18694  3.07126 -0.81276
H   0.28456  3.06532  1.15975
P  -1.68355  0.26925 -1.25114
H  -2.11087 -0.53527 -2.35413
H  -2.55099  1.40153 -1.28668
C  -1.84008 -0.58791  0.33872
C  -1.05365 -1.78201  0.29931
H   1.03764  0.06107 -1.49663
H  -1.00647 -2.40056 -0.60374
C  -2.66252 -0.10565  1.50725
H  -3.68553 -0.51697  1.42743
H  -2.22684 -0.45880  2.45589
H  -2.74274  0.99183  1.54586
H  -0.90641 -2.32412  1.24125
H   0.47272  0.07090  1.53605
```

7'cis (2)

```
BP86 Energy = -253.526697527
Enthalpy 0K= -253.368574
Enthalpy 298K= -253.354686
Free Energy 298K= -253.409042

Rh  0.36445  0.43390  0.01082
P   2.61663 -0.14923  0.13050
P  -1.35341  1.98207 -0.15466
H   3.05135 -1.34732  0.78829
H   3.31952 -0.30151 -1.10418
H   3.47502  0.78811  0.77736
H  -0.94764  3.34472 -0.05870
H  -2.14059  2.05989 -1.34769
H  -2.40649  1.97998  0.81525
P  -0.46598 -1.47574 -1.25330
H   0.18866 -2.74535 -1.35915
H  -1.61315 -1.70752 -2.07694
C  -1.15261 -1.38061  0.46092
C  -0.23993 -1.40847  1.50492
H   1.02948  1.50833 -0.91073
H   0.71660 -1.93200  1.43546
C  -2.62779 -1.12299  0.66800
H  -3.14739 -2.09754  0.71497
H  -2.81513 -0.60159  1.62111
H  -3.09598 -0.55544 -0.15350
H  -0.58098 -1.17178  2.51915
H   0.72997  1.36927  1.21114
```

3. H-transfer: Pathway 2.

TS 6'β-6'β(PH_3)

```
BP86 Energy = -253.515538632
Enthalpy 0K= -253.356575
Enthalpy 298K= -253.342667
Free Energy 298K= -253.397391
Frequency= -110.9702cm-1

Rh  0.44433  0.08328  0.15048
P   2.64242 -0.61430 -0.11534
P  -0.78115 -1.91048 -0.23614
H   2.88977 -1.41308 -1.27655
H   3.27800 -1.43696  0.87005
H   3.67631  0.35920 -0.27982
H  -1.09479 -2.86518  0.77335
H  -1.11047 -2.54657 -1.46920
C  -1.72681 -0.38177 -0.01239
C  -2.35741 -0.18742  1.36630
C  -2.54184  0.14658 -1.18675
H  -3.52152 -0.36536 -1.23094
H  -2.75636  1.22322 -1.06387
H  -2.04244  0.00684 -2.15908
H  -3.32093 -0.73070  1.41949
H  -2.57269  0.87979  1.54576
H  -1.72163 -0.54465  2.19334
H   1.34393  0.80276  1.19496
P  -0.04118  2.29569 -0.14747
H   0.98310  3.28039  0.00813
H  -0.50730  2.65164 -1.45385
H  -1.06286  2.92326  0.63782
```

6'β(PH_3)

```
BP86 Energy = -253.523882887
Enthalpy 0K= -253.365192
Enthalpy 298K= -253.351121
Free Energy 298K= -253.405995

Rh -0.31501 -0.09520 -0.23221
P  -2.55149 -0.85323  0.07518
P   1.33506 -0.65662  1.49670
H  -2.99157 -1.24174  1.38155
H  -3.00197 -2.00985 -0.63950
H  -3.64714  0.00717 -0.25772
H   1.97595 -1.88154  1.88643
H   2.07404  0.29492  2.26542
C   1.80416 -0.29820 -0.25603
C   1.45032 -1.45047 -1.15189
C   2.85263  0.70233 -0.67392
H   3.86249  0.25317 -0.61992
H   2.68857  1.02805 -1.71609
H   2.85822  1.59291 -0.02496
H   1.78385 -2.44338 -0.79992
H   1.73734 -1.28570 -2.20046
H   0.28216 -1.64547 -1.18442
H  -0.74295  0.42455 -1.64594
P  -0.60097  2.11843  0.14378
H  -1.83706  2.70204 -0.27315
H  -0.55733  2.59367  1.49415
H   0.30913  3.04430 -0.45971
```

TS 6'β(PH_3)-7'cis

```
BP86 Energy = -253.514092714
Enthalpy 0K= -253.358174
Enthalpy 298K= -253.344292
Free Energy 298K= -253.399388
Frequency= -654.4997cm-1

Rh -0.31812 -0.15534 -0.27459
P  -2.55334 -0.72602  0.11804
P   1.33360 -0.77976  1.46438
H  -2.85866 -1.44343  1.31776
H  -3.22209 -1.56705 -0.82333
H  -3.54824  0.29972  0.22010
H   1.95676 -2.03578  1.77430
H   2.08288  0.10216  2.30480
C   1.86844 -0.33152 -0.25094
C   1.41307 -1.30409 -1.20769
C   2.80702  0.79830 -0.60216
H   3.85288  0.44438 -0.54456
H   2.62890  1.15105 -1.63231
H   2.71365  1.65434  0.08519
H   1.45566 -2.37387 -0.96253
H   1.57934 -1.08934 -2.27062
```

H -0.20120 -1.56852 -1.06062
H -0.77109 0.33001 -1.68575
P -0.52029 2.14675 0.21782
H -1.79819 2.75267 0.00407
H -0.26195 2.67501 1.52540
H 0.27608 3.06818 -0.53434

4. H-transfer: Pathway 3.

TS 6'β-6'β(PH2)

BP86 Energy = -253.517388670
Enthalpy 0K= -253.358536
Enthalpy 298K= -253.343557
Free Energy 298K= -253.399577

Rh 0.36966 -0.18850 0.13663
P 2.62872 -0.74601 -0.04592
P -1.27074 -1.59274 -0.44372
H 2.95933 -2.09516 -0.38435
H 3.52552 -0.58910 1.06202
H 3.41067 -0.07469 -1.04137
H -1.70483 -2.69460 0.34774
H -1.48659 -1.96717 -1.80402
C -1.90417 0.00239 0.02654
C -2.49941 0.16484 1.41932
C -2.49285 0.89989 -1.05279
H -3.57355 0.69377 -1.16925
H -2.40432 1.96261 -0.76558
H -2.01482 0.77070 -2.03728
H -2.06951 -0.52475 2.16319
H -3.59405 0.00077 1.38994
H 0.55130 -1.41722 1.06685
H -2.33780 1.19437 1.78391
P 0.71585 2.21212 -0.10024
H 1.92911 2.79115 -0.59403
H -0.21043 3.02541 -0.82821
H 0.65622 2.90300 1.15204

6'β(PH$_2$)

BP86 Energy = -253.520587139
Enthalpy 0K= -253.360883
Enthalpy 298K= -253.346347
Free Energy 298K= -253.402836

Rh -0.36266 -0.20799 -0.18182
P -2.62862 -0.81553 -0.09045
P 1.19311 -0.84825 1.27042
H -2.95775 -1.92742 0.74388
H -3.26954 -1.26171 -1.29229
H -3.64191 0.09557 0.35460
H 1.44755 -2.21916 1.56233
H 1.46666 -0.12696 2.47191
C 1.96804 -0.16919 -0.16894
C 2.44171 -1.07569 -1.28941
C 2.64488 1.18659 -0.08911
H 3.73681 1.05102 0.02955
H 2.49476 1.75029 -1.02708
H 2.29704 1.80687 0.75195
H 2.00838 -2.08663 -1.25399
H 3.54475 -1.16842 -1.25684
H -0.26945 -1.76159 -0.45296
H 2.18908 -0.63174 -2.26994
P -0.73046 2.16880 0.06994
H -1.97918 2.63477 0.59554
H 0.12595 2.99273 0.87092
H -0.71151 2.98654 -1.10917

TS 6'β(PH$_2$)-7'cis (2)

BP86 Energy = -253.505336805
Enthalpy 0K= -253.349095
Enthalpy 298K= -253.335650
Free Energy 298K= -253.388723
Frequency= -755.4400cm-1

Rh 0.33942 -0.22994 0.17015
P 2.60148 -0.59272 -0.05135
P -1.45437 -1.26637 -1.07207
H 3.04328 -1.53821 -1.02979
H 3.32690 -1.08408 1.07759
H 3.44749 0.50840 -0.40178
H -1.84901 -2.59320 -0.71599
H -2.46876 -0.93947 -2.03770
C -1.89755 -0.17267 0.33665
C -1.40341 -0.45624 1.66368
C -2.72162 1.06872 0.07266
H -3.78780 0.82473 0.23840
H -2.46474 1.88658 0.76747
H -2.63467 1.43382 -0.96364
H -1.34581 -1.48800 2.02309
H -1.70602 0.26220 2.43905
H 0.54110 -1.74753 0.55721
H 0.06687 -0.07982 1.79245
P 0.51243 2.11522 -0.36372
H 1.82801 2.62921 -0.59826
H -0.11840 2.68586 -1.51814
H 0.09021 3.10606 0.58251

5. Final Product Formation from 7'cis.

TS cis-7'- 4'(η^2-H$_2$)

BP86 Energy = -253.510224310
Enthalpy 0K= -253.355258
Enthalpy 298K= -253.341434
Free Energy 298K= -253.395763
Frequency= -720.1921cm-1

Rh 0.31843 -0.13486 0.40554
P 2.42477 -0.68104 -0.37765
P -1.17219 -1.58756 -0.74910
H 2.51382 -1.57155 -1.49137
H 3.30755 -1.34369 0.52903
H 3.30409 0.35296 -0.83488
H -1.70321 -2.77565 -0.15488
H -1.76373 -1.63260 -2.05320
C -1.93814 -0.14126 0.06323
C -1.70608 -0.04388 1.45333
C -2.65779 0.91834 -0.73578
H -3.72708 0.64165 -0.79077
H -2.60433 1.90198 -0.23967
H -2.28990 1.00933 -1.77012
H -1.66441 -0.92815 2.09395
H -1.96798 0.89253 1.96015
H 0.68297 -1.03583 1.72858
H 0.91003 0.03877 1.91888
P 0.52473 2.11636 -0.35428

```
H    1.83967  2.68047 -0.41436
H    0.07076  2.57894 -1.63636
H   -0.08529  3.14390  0.43646
```

4′ (η^2-H_2)

```
BP86 Energy = -253.519434587
Enthalpy 0K= -253.363236
Enthalpy 298K= -253.348895
Free Energy 298K= -253.403900

Rh -0.23884 -0.05836 -0.44600
P  -1.49672 -1.72282  0.65939
P   1.81295 -1.12523 -0.32126
H  -1.06264 -2.20027  1.93962
H  -1.70246 -2.99810  0.04077
H  -2.85943 -1.45437  1.01311
H   2.80216 -1.24405 -1.35101
H   2.25970 -2.03174  0.68580
C   1.72034  0.55676  0.35678
C   1.36488  1.44513 -0.71349
C   2.01726  0.94966  1.78120
H   3.09179  1.18902  1.88484
H   1.45039  1.85275  2.06238
H   1.77976  0.14904  2.49918
H   1.77408  1.31694 -1.72227
H   1.15396  2.49067 -0.45338
H  -1.15308 -0.58061 -2.00136
H  -0.70145  0.06658 -2.23257
P  -1.67808  1.63990  0.19602
H  -2.88485  1.34562  0.91091
H  -1.15706  2.65694  1.05835
H  -2.23027  2.48081 -0.82328
```

TS H2 loss

```
BP86 Energy = -253.515529336
Enthalpy 0K= -253.362103
Enthalpy 298K= -253.347044
Free Energy 298K= -253.403268
Frequency= -230.1714cm-1

Rh -0.23608 -0.06275 -0.30422
P  -1.88856 -1.45777  0.56460
P   1.62346 -1.41595 -0.15415
H  -1.50231 -2.54161  1.41518
H  -2.71945 -2.19848 -0.33926
H  -2.92603 -0.91383  1.39059
H   2.47695 -1.87404 -1.21042
H   2.06829 -2.16692  0.97467
C   1.89131  0.35786  0.16969
C   1.53682  1.12661 -0.96970
C   2.34616  0.91639  1.49287
H   3.45099  0.97015  1.50270
H   1.96351  1.93979  1.63940
H   2.03334  0.29519  2.34669
H   1.69955  0.75983 -1.99026
H   1.53083  2.21944 -0.87321
H  -0.75037 -0.51331 -2.28776
H  -1.31969 -0.15750 -2.66488
P  -1.39316  1.88395  0.16943
H  -2.57925  1.85887  0.97342
H  -0.68493  2.90966  0.87320
H  -1.88955  2.67791 -0.91572
```

4′

```
BP86 Energy = -252.339734907
Enthalpy 0K= -252.198560
Enthalpy 298K= -252.185004
Free Energy 298K= -252.239780

Rh -0.23508 -0.05435 -0.16329
P  -1.98952 -1.47459  0.33043
P   1.61975 -1.42657 -0.23698
H  -1.72092 -2.67189  1.06415
H  -2.67711 -2.05164 -0.78689
H  -3.12973 -1.02142  1.07066
H   2.29711 -1.88344 -1.41250
H   2.24961 -2.16925  0.80678
C   1.95954  0.34939  0.03325
C   1.45958  1.14686 -1.01537
C   2.54574  0.87820  1.31694
H   3.64942  0.85363  1.24848
H   2.24244  1.92382  1.48753
H   2.25410  0.27733  2.19329
H   1.40619  0.79185 -2.05267
H   1.49029  2.23701 -0.89664
P  -1.48099  1.86979  0.05924
H  -2.77748  1.85251  0.66912
H  -0.91575  2.95628  0.79981
H  -1.81733  2.57474 -1.14247
```

H2

```
BP86 Energy = -1.17646509080
Enthalpy 0K= -1.166537
Enthalpy 298K= -1.163232
Free Energy 298K= -1.178044

H   0.00000  0.00000  0.37519
H   0.00000  0.00000 -0.37519
```

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