Supporting Information

Synthesis of Rh(III) thiophosphinito pincer complexes by base-free C-H bond activation at room temperature

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Experimental section

All manipulations were carried out under argon using standard Schlenk and glovebox techniques. All solvents were dispensed from a solvent purification system (PureSolv, Innovative Technology) or were freshly distilled prior to use. Subsequent removal of traces of oxygen from deuterated solvents was carried out through the six freeze-thaw cycle application. Chloro(1,5-cyclooctadiene)rhodium(I) dimer, chlorodiphenylphosphine, and 1,3-dimercaptobenzene were purchased from Sigma Aldrich and used as received. Ligands **1b** and **1c** were prepared according to published procedures.[1]

^{1}H NMR and ^{31}P{^{1}H} NMR spectra were obtained at room temperature on Bruker AV300 or AV400 spectrometers and were referenced internally to the deuterated solvent. All ^{1}H NMR spectra are referenced using the chemical shifts of residual protio solvent resonances (benzene-*d6*: δ_H 7.16, δ_C 128.06; toluene-*d8*: δ_H 2.08, 6.97, 7.01, 7.09, δ_C 20.4, 125.1, 127.9, 128.9, 137.5). Chemical shifts are reported in ppm (δ) relative to tetramethylsilane. For ^{31}P{^{1}H} NMR spectra, 85% H_3PO_4 was used as external standard. Mass spectra were recorded on a Finnigan MAT 95-XP (Thermo Electron) instrument using chemical or electronic ionisation. Mass spectra were recorded on a MAT 95XP Thermo Fisher Mass Spectrometer using chemical ionisation mode. X-Ray analysis was performed on a Bruker Kappa APEX II Duo diffractometer.

Synthesis of 1a: A suspension of NaH (0.180 g, 7.51 mmol) in THF (5 mL) was slowly added to a solution of 1,3-dimercaptobenzene (0.510 g, 3.58 mmol) in THF (50 mL) at room temperature. Residues of NaH were washed with additional 5 mL of THF. The reaction mixture was stirred for 1 h and Ph_2PCl (1.710 g, 7.73 mmol) was added. The resulting mixture was heated to reflux overnight before all volatile materials were removed in vacuo. Extraction with *n*-hexane (3 x 20 mL) and removal of the solvent in vacuo yielded the desired ligand (1.736 g, 95%). ^{1}H NMR (C_6D_6, 400 MHz, 297 K): δ 6.41 (t, J_{H-H} = 7.80 Hz, 1 H, *p-H*), 6.66-6.71 (m, 4 H, PCC(*p-H*)), 6.75-6.72 (m, 8 H, PCC(*m-H*), 7.01 (d, J_{H-H} = 8.00 Hz, 2 H, *m-H*), 7.25-7.29 (m, 8 H, PCC(*o-H*)) ppm; ^{31}P{^{1}H} NMR (C_6D_6, 400 MHz, 297 K): δ 32.2 (s) ppm; ^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 297 K): 128.4-129.1 (m, aromatic signals), 129.3 (s, p-C), 129.9 (d, J_{C-H}= 8 MHz, *m*-C), 132.6-133.0 (m, aromatic signals), 134.3 (s, *ipso*-C) ppm. MS (HR-ES(+), CH_3CN/0.1% HCOOH in H_2O 98:2): *m/z* 566 [(MOH)+CH_3CN]$^+$.

Synthesis of 2: To a toluene solution (2.0 mL) of [Rh(cod)(μ_2-Cl)]$_2$ (49 mg, 0.1 mmol) a toluene solution (2.0 mL) of ligand **1a** (51 mg, 0.1 mmol) was added dropwise and the reaction mixture was stirred at room temperature overnight. The colour of the solution changed from yellow-orange to dark red-orange. During reaction, a microcrystalline precipitate of complex **2** formed which was isolated by filtration. Additional material precipitated after layering this filtrate with *n*-hexane and storing at -78 °C overnight. Rhombic dark orange crystals suitable for X-ray analysis were precipitated from a xylene solution by layering with *n*-hexane (72 mg, 80%). ^{1}H NMR (300 MHz, C_6D_6, 297 K): δ -16.4 (dt, 1 H, J_{H-Rh}=27, J_{H-P}=12 Hz), 0.86-0.79 (m, 4 H, CH_2(COD)), 1.62-1.59 (m, 4 H, CH_2(COD)), 3.16 (d, J_{H-Rh}=39 Hz, 4 H, CH=(COD)), 6.20 (t, J_{H-H}=7.7 Hz, 1 H, *p-H*), 6.65 (d, J_{H-H}=7.6 Hz, 2 H, *m*-H), 7.04-6.66 (m, 12 H, aromatic signals), 7.93-7.77 (m, 8 H, PCC(*m-H*)) ppm; ^{31}P{^{1}H} NMR (300 MHz, C_6D_6, 297 K): δ 70.5 (d, J_{P-Rh}=123 Hz) ppm; ^{13}C{^{1}H} NMR (300 MHz, C_6D_6, 297 K): 30.0 (s, CH_2(COD)), 30.1 (s, CH_2(COD)), 77.0 (d, J_{C-Rh}=13.8 Hz, CH=(COD)), 77.6 (d, J_{C-Rh}=14.0 Hz, CH=(COD)), 120.4 (s, *m*-C), 123.9 (s, *p*-C), 129.8-124.4 (m, aromatic signals), 134.1 (d, J_{C-P}=22 Hz, Ar) ppm. MS (HR-ES(+), CH_3OH/0.1% HCOOH in H_2O 90:10): *m/z* 875 [(M-Cl)+OH]$^+$.

Synthesis of 3: Complex **2** (45 mg, 0.05 mmol) was dissolved in 1.0 mL of $CHCl_3$ and stirred for 20 min at room temperature. The solvent was then removed under high vacuum. The resulting residue was dissolved in 1.0 mL of THF and layered with *n*-pentane. After three days dark orange crystals suitable for X-ray analysis were precipitate (15 mg, 32%). ^{1}H NMR (300 MHz, C_6D_6, 297 K): δ 0.93-1.79 (m, 4 H, CH_2(COD)), 1.69-1.66 (m, 4 H, CH_2(COD)), 3.26 (d, J_{H-Rh}=39 Hz, 4 H, CH=(COD)), 6.19 (t, J_{H-H}=7.7 Hz, 1 H, *p-H*), 6.73 (d, J_{H-H}=7.6 Hz, 2 H, *m*-H), 7.01-6.75 (m, 12 H, aromatic signals), 7.92-7.71 (m, 8 H, PCC(*m-H*)) ppm; ^{31}P{^{1}H} NMR (300 MHz, C_6D_6, 25°C): δ 60.4 (d, J_{P-Rh} = 104 Hz) ppm.

Synthesis of 4: To a toluene solution (2.0 mL) of [Rh(cod)(μ_2-Cl)]$_2$ (49 mg, 0.1 mmol) a toluene solution (2.0 mL) of ligand **1b** (37 mg, 0.1 mmol) was added dropwise and the reaction mixture was stirred at room temperature overnight. The resulting orange solution was layered with *n*-hexane and single crystals suitable for X-ray analysis were precipitated (67 mg, 75 %). ^{1}H NMR (300 MHz, C_6D_6, 297 K): δ 0.83 (dd, J_{C-H}=15.5 Hz, J_{H-H}=7.0 Hz, 12 H, PCH(CH_3)$_2$), 1.31 (dd, J_{C-H}=17.1 Hz, J_{H-H}=7.0 Hz, 12 H, PCH(CH_3)$_2$), 1.36-1.52 (m, 8 H, CH_2(COD)), 1.72-2.00 (m, 8 H, CH_2(COD)), 2.46-2.57 (m, 4 H, PCH(CH_3)$_2$), 3.76 (br, 4 H, CH=(COD)), 5.41 (br, 4 H, CH=(COD)), 6.35 (t, J_{H-H}=7.8 Hz, 1 H, *p*-H), 6.94 (s, 2 H, *m*-H), 7.43 (s, 1 H, CH(PSCSP)) ppm; ^{31}P{^{1}H} NMR (300 MHz, C_6D_6, 297 K): δ 92.6 (d, J_{P-Rh}=156 Hz) ppm; ^{13}C{^{1}H} NMR (300 MHz, C_6D_6, 297 K): 18.4 (s, PC(CH_3)$_2$), 19.1 (d, J_{C-P}=4.9 Hz, PC(CH_3)$_2$), 28.1 (d, J_{C-Rh}=10.9 Hz, CH_2(COD)), 28.5 (s, CH_2(COD)), 33.0 (s, CH_2(PCHP)), 71.0 (d, J_{C-Rh}=12.9 Hz, CH=(COD)), 104.6 (dd, J_{C-H}=7,2 Hz, J_{C-Rh}=12.2 Hz, CH=(COD)), 129.9 (s, *p*-C), 136.9 (s, *m*-C). MS (HR-ES(+),CH_3CN): *m/z* 822 [(M-(COD))+CH_3CN+Na]$^+$.

Synthesis of complex 5: Complex **4** (44 mg, 0.05 mmol) was dissolved in 1.0 mL of toluene and stirred at 55 °C for four hours. All volatiles were removed in high vacuum and a dark red-orange residue was obtained. For further purification, the residue was washed with *n*-hexane (3 x 3 ml). Analysis by ^{31}P{^{1}H} NMR indicates 45% of **5** and 55% of **4**. ^{31}P{^{1}H} NMR (300 MHz, C_6D_6, 297 K): δ 99.8 (d, J_{P-Rh}= 118 Hz), **5**) ppm.

Synthesis and spectroscopic data of complex 6: To a xylene solution (1.0 mL) of **2** (45 mg, 0.05 mmol) a xylene solution (1.0 mL) of ligand DPPP (21 mg, 0.05 mmol) was added dropwise and the reaction mixture was stirred at room temperature overnight. All volatiles were removed in high vacuum and a dark orange residue was obtained. For further purification, the residue was washed with *n*-hexane (3 x 3 mL). ^{1}H NMR (300 MHz, C_6D_6, 297 K): δ -16.9 ppm (d, J_{H-Rh}=27, J_{H-P}=15 Hz). Analysis by ^{31}P{^{1}H} NMR indicates 80% of **6**. ^{31}P{^{1}H} NMR (300 MHz, C_6D_6, 297 K): δ 64.9 (d, J_{P-Rh}=123 Hz), 31-33 (ddd, J_{Rh-P1} = 133 Hz, J_{P1-P2} = 71 Hz, J_{Rh-P2} = 125 Hz, J_{P2-P1} = 79 Hz) ppm.

Synthesis and spectroscopic data of complex 7: To a THF solution (1.0 mL) of **2** (45 mg, 0.05 mmol) a THF solution (1.0 mL) of ligand **1a** (25.5 mg, 0.05 mmol) was added dropwise and the reaction mixture was stirred at room temperature overnight. Removal of the solvent in vacuum led to precipitation of dark orange residue. For further purification, the residue was washed with *n*-hexane (3 x 3 mL). Analysis by ^{31}P{^{1}H} NMR indicates 63% of **7**. ^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 297 K): δ 65.0 (d, J_{P-Rh}=125 Hz); ^{1}H NMR (400 MHz, C_6D_6, 297 K): δ -20.3 (dt, J_{H-Rh}=27, J_{H-P}=15 Hz) ppm.

Synthesis of complex 8: To a toluene solution (2.0 mL) of [Rh(cod)(μ_2-Cl)]$_2$ (49 mg, 0.1 mmol) a toluene solution (2.0 mL) of ligand **1c** (^{iPr}POCOP^{iPr}) (34.2 mg, 0.1 mmol) was added dropwise and the reaction mixture was stirred at room temperature overnight. The solvent was then removed under high vacuum. The resulting yellow residue was dissolved in 1.0 mL of THF and layered with Et_2O. The day after, yellow single crystals suitable for X-ray analysis had precipitated (77 mg, 90%). ^{1}H NMR

(400 MHz, C_6D_6, 297 K): δ 0.88 (dd, $J_{C\text{-}H}$=14.3 Hz, $J_{H\text{-}H}$=7.1 Hz, 12 H, $PCH(CH_3)_2$), 1.27 (dd, $J_{C\text{-}H}$=16.3 Hz, $J_{H\text{-}H}$=7.2 Hz, 12 H, $PCH(CH_3)_2$), 1.40-1.54 (m, 8 H, CH_2(COD)), 1.88-1.97 (m, 8 H, CH_2(COD)), 2.35-2.43 (m, 4 H, $PCH(CH_3)_2$), 3.54 (br, 4 H, CH=(COD)), 5.48 (br, 4 H, CH=(COD)), 6.34 (dd, $J_{C\text{-}H}$=8.3 Hz, $J_{H\text{-}H}$=1.9 Hz, 2 H, *m*-H), 6.49 (t, $J_{H\text{-}H}$=7.6 Hz, 1 H, *p*-H), 6.65 (s, 1 H, CH(POCOP)) ppm; $^{31}P\{^1H\}$ NMR (400 MHz, C_6D_6, 297 K): δ 169.6 (d, $J_{P\text{-}Rh}$=178 Hz) ppm; $^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 297 K): 17.7 (s, $PC(CH_3)_2$), 18.2 (d, $J_{C\text{-}P}$=4.7 Hz, $PC(CH_3)_2$), 28.2 (s, CH_2(COD)), 29.4 (d, $J_{C\text{-}Rh}$=16.2 Hz, CH_2(COD)), 33.0 (s, CH_2(PCHP)), 69.1 (d, $J_{C\text{-}Rh}$=13.6 Hz, CH=(COD)), 107.8 (dd, $J_{C\text{-}H}$=6.1 Hz, $J_{C\text{-}Rh}$=13.0 Hz, CH=(COD)), 114.4 (s, *p*-C), 116.3 (s, *m*-C). MS (HR-ES(+),CH_3CN): *m/z* 771 $[(MOH\text{-}(COD))+CH_3CN+Na]^+$.

Synthesis of complex 10: To a toluene solution (1.0 mL) of $[Rh(cod)(\mu_2\text{-}Cl)]_2$ (49 mg, 0.1 mmol) a toluene solution (2.0 mL) of ligand **1d** (^{Ph}POCOP^{Ph}) (41 mg, 0.1 mmol) was added dropwise and the reaction mixture was stirred at room temperature overnight. During reaction, a microcrystalline precipitate of complex **10** formed which was isolated by filtration. Orange crystals suitable for X-ray analysis were precipitated from a 1,2-dichloroethane solution layered with Et_2O (105 mg, 60%). Analysis by $^{31}P\{^1H\}$ NMR in C_6D_6 indicates approximately 49% and 51% of two species evidenced by a doublet in $^{31}P\{^1H\}$ NMR spectrum at 134.3 ppm with a coupling constant of $J_{Rh\text{-}P}$ = 231 Hz, as well as a doublet in $^{31}P\{^1H\}$ NMR spectrum at 125.8 ppm with a coupling constant of $J_{Rh\text{-}P}$ = 221 Hz, respectively. MS (HR-ES(+),CH_3CN): *m/z* 1044 $[(M\text{-}[Rh(COD)(POCOP)Cl])+CH_3CN+Na]^+$, 640 $[Rh(POCOP)Cl +Na]^+$.

Crystallographic details

Diffraction data were collected at low temperature on a Bruker Kappa APEX II Duo diffractometer using Mo-Kα radiation (**2** and **8**) or Cu-Kα radiation (**3**, **4** and **10**). The structures were solved by direct methods (SHELXS-97[2]) and refined by full matrix least square techniques against F^2 (SHELXL-97[2] or SHELXL-2014[3]). XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed into theoretical positions (except the hydrogen atoms of the hydride in **2**) and were refined by using the riding model.

*Crystal data for **2***: $C_{38}H_{36}Cl_2P_2Rh_2S_2$, triclinic space group $P\bar{1}$, a = 10.7617(13), b = 17.854(2), c = 19.459(2) Å, α = 78.973(2), β = 84.819(2), γ = 78.382(2)°, V = 3589.5(8) Å^3, T = 150.(2) K, Z = 2, ρcalcd = 1.657 g cm^{-3}, μ(Mo Kα) = 1.302 mm^{-1}. 48210 total data, Θ_{max} = 27.103. R = 0.0347 for 12245 data with $I > 2\sigma(I)$ of 15834 unique data and 866 refined parameters. The final $wR(F^2)$ values were 0.0752 ($I > 2\sigma(I)$). The final R_1 values were 0.0545 (all data). The final $wR(F^2)$ values were 0.0857 (all data). The goodness of fit on F^2 was 1.023.

*Crystal data for **3***: $C_{38}H_{35}Cl_3P_2Rh_2S_2$, monoclinic space group $P2_1/c$, a = 12.0429(3), b = 13.0157(3), c = 45.0034(12) Å, 90.9850(10)°, V = 7053.1(3) Å^3, T = 150(2) K, Z = 4, ρcalcd = 1.751 g cm^{-3}, μ(Cu Kα) = 11.848 mm^{-1}. 38252 total data, Θ_{max} = 61.165. R = 0.0398 for 9315 data with $I > 2\sigma(I)$ of 10806 unique data and 294 refined parameters. The final $wR(F^2)$ values were 0.0990 ($I > 2\sigma(I)$). The final R_1 values were 0.0486 (all data). The final $wR(F^2)$ values were 0.1040 (all data). The goodness of fit on F^2 was 1.069.

*Crystal data for **4***: $C_{34}H_{56}Cl_2P_2Rh_2S_2$, orthorhombic space group $P2_12_12_1$, a = 14.1210(5), b = 14.5253(5), c = 18.8086(6) Å, °, V = 3857.9(2) Å^3, T = 150(2) K, Z = 4, ρcalcd = 1.494 g cm^{-3}, μ(Cu Kα) = 10.148 mm^{-1}. 24056 total data, Θ_{max} = 66.595. R = 0.0357 for 6377 data with $I > 2\sigma(I)$ of 6590 unique data and 377 refined parameters. The final $wR(F^2)$ values were 0.0947 ($I > 2\sigma(I)$). The final R_1 values were 0.0369 (all data). The final $wR(F^2)$ values were 0.0958 (all data). The goodness of fit on F^2 was 1.029.

*Crystal data for **8**:* $C_{34}H_{56}Cl_2O_2P_2Rh_2$, orthorhombic space group Pbca, a = 16.0812(7), b = 15.1354(7), c = 29.4358(13) Å, °, V = 7164.5(6) Å^3, T = 150(2) K, Z = 8, ρcalcd = 1.549 g cm^{-3}, μ(Mo Kα) = 1.189 mm^{-1}. 68470 total data, Θ_{max} = 27.996. R = 0.0327 for 6882 data with $I > 2\sigma(I)$ of 8637 unique data and 387 refined parameters. The final $wR(F^2)$ values were 0.0744 ($I > 2\sigma(I)$). The final R_1 values were 0.0467 (all data). The final $wR(F^2)$ values were 0.0826 (all data). The goodness of fit on F^2 was 1.037.

*Crystal data for **10** (2 DCM)*: $C_{76}H_{72}Cl_4O_4P_4Rh_4 * 2(CH_2Cl_2)$, triclinic space group $P\bar{1}$, a = 12.2267(3), b = 13.3049(4), c = 13.5035(4) Å, α = 73.9060(10), β = 69.5690(10), γ = 68.3040(10)°, V = 1884.77(9) Å^3, T = 150.(2) K, Z = 1, ρcalcd = 1.671 g cm^{-3}, μ(Cu Kα) = 10.766 mm^{-1}. 28462 total data, Θ_{max} = 65.082. R = 0.0292 for 5895 data with $I > 2\sigma(I)$ of 6417 unique data and 500 refined parameters. The final $wR(F^2)$ values were 0.0754 ($I > 2\sigma(I)$). The final R_1 values were 0.0321 (all data). The final $wR(F^2)$ values were 0.0776 (all data). The goodness of fit on F^2 was 1.044.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-

1816555 for **2**, CCDC-1816556 for **3**, CCDC-1816554 for **4,** CCDC-1837751 for **8** and CCDC-1842313 for **10**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk.

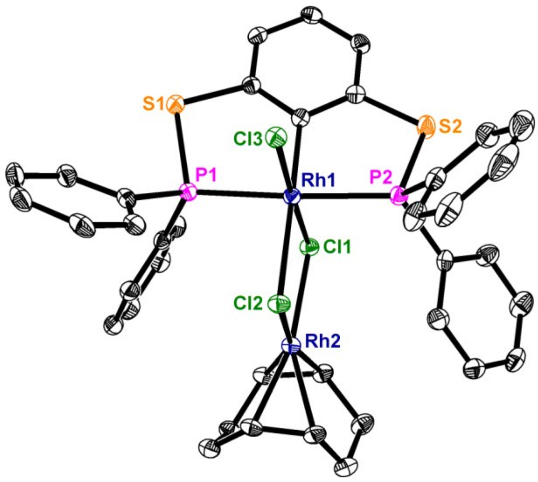


Figure S1. Molecular structure of complex **3**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

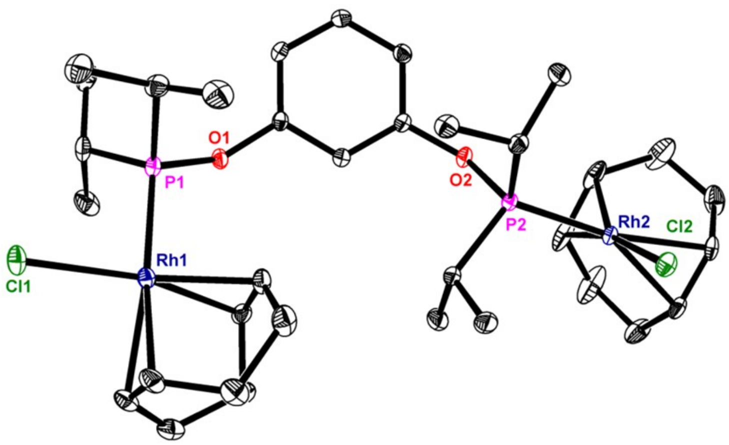


Figure S2. Molecular structure of complex **8**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms and the second molecule of the asymmetric unit are omitted for clarity.

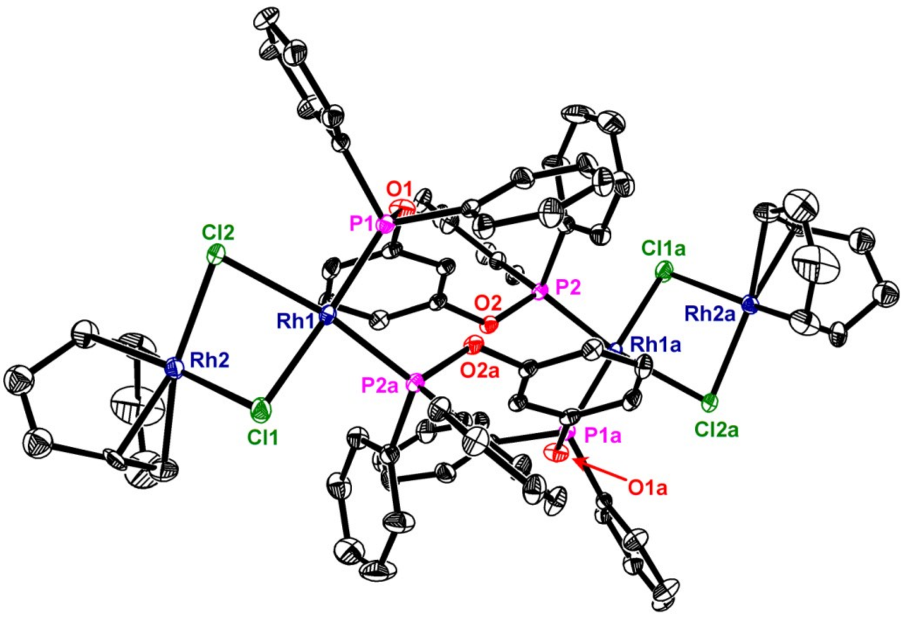


Figure S3. Molecular structure of complex **10**. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms, DCM solvent molecule and the second part of the disordered COD are omitted for clarity.

NMR spectra

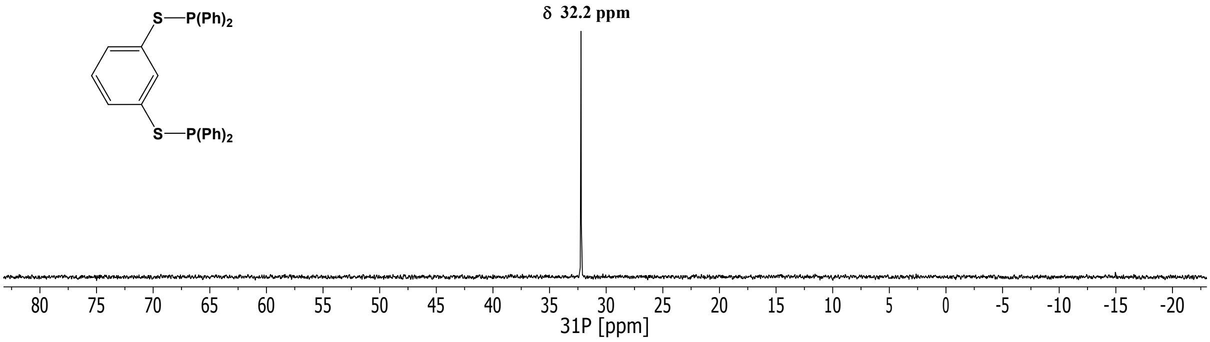


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of ligand **1a** (C_6D_6, 161 MHz).

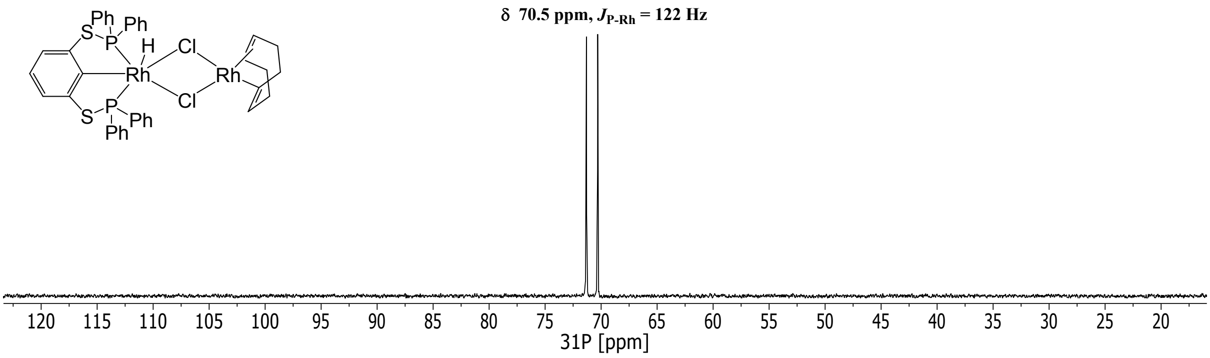


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** (toluene, 161 MHz).

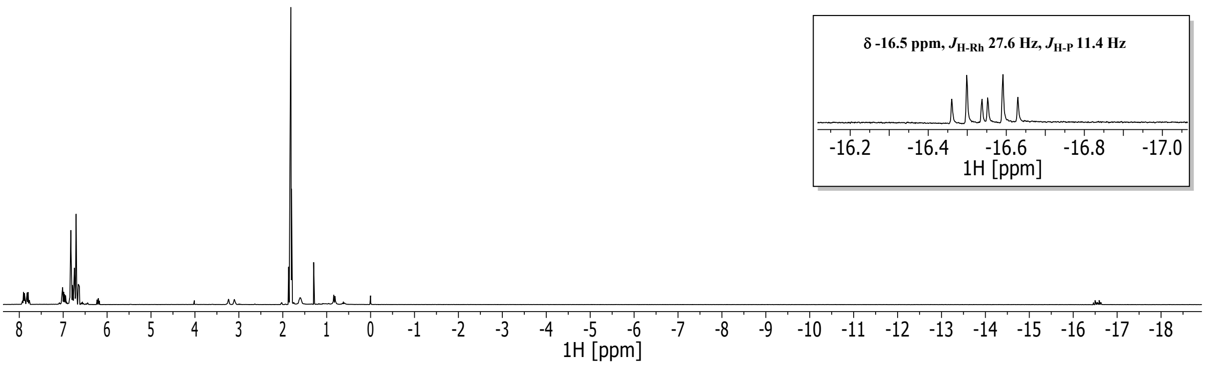


Figure S6. ^{1}H NMR spectrum of complex **2** (toluene, 400 MHz). The inset shows a magnification of the hydride region.

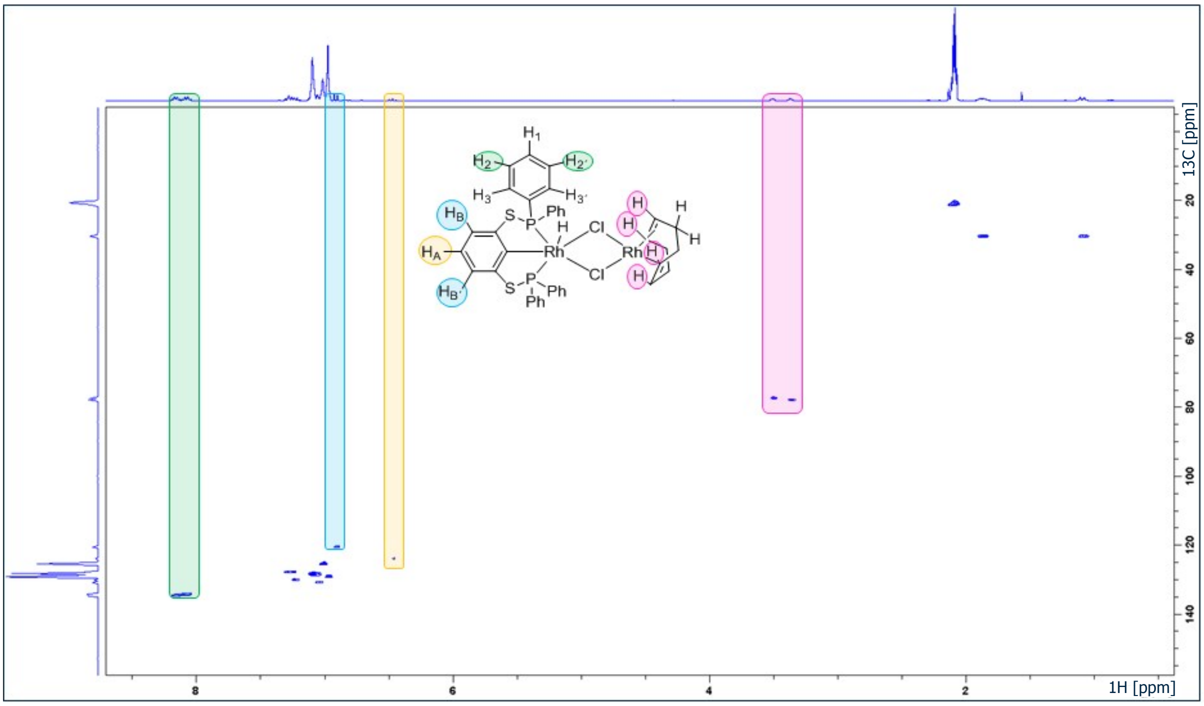


Figure S7. ^{1}H-^{13}C HSQC NMR spectrum of complex **2**.

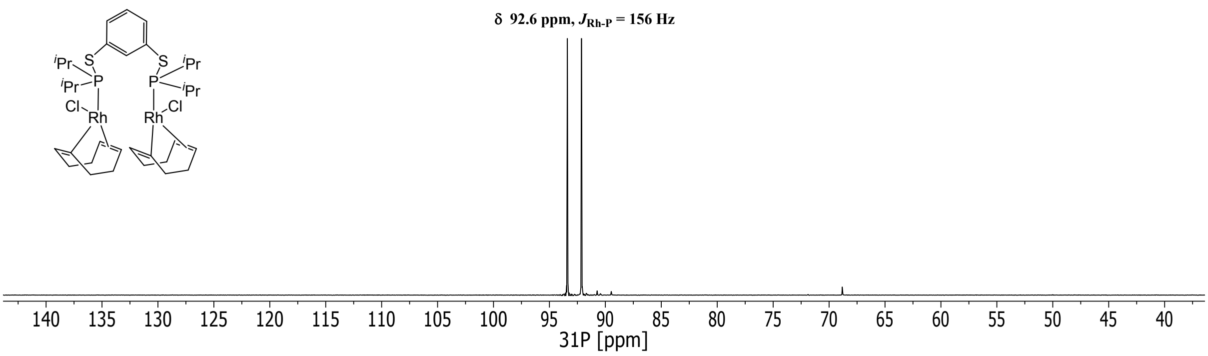


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** (C_6D_6, 121 MHz).

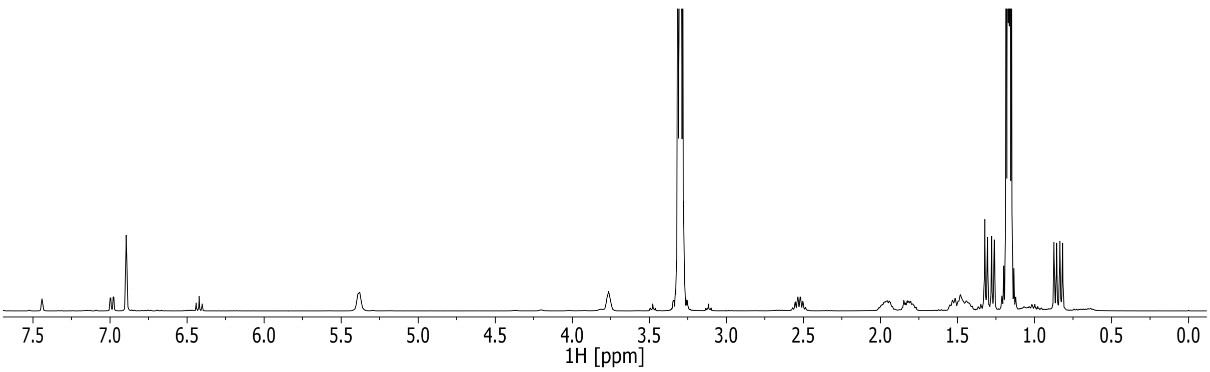


Figure S9. ^{1}H NMR spectrum of complex **4** (C_6D_6, 300 MHz).

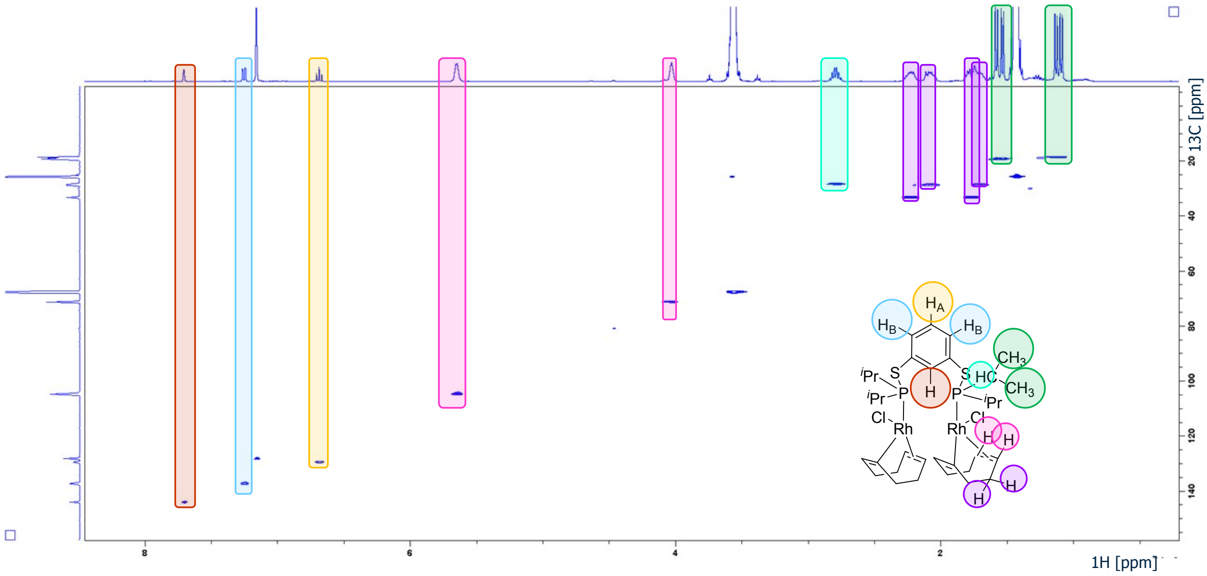


Figure S10. ^{1}H-^{13}C HSQC NMR spectrum of complex **4**.

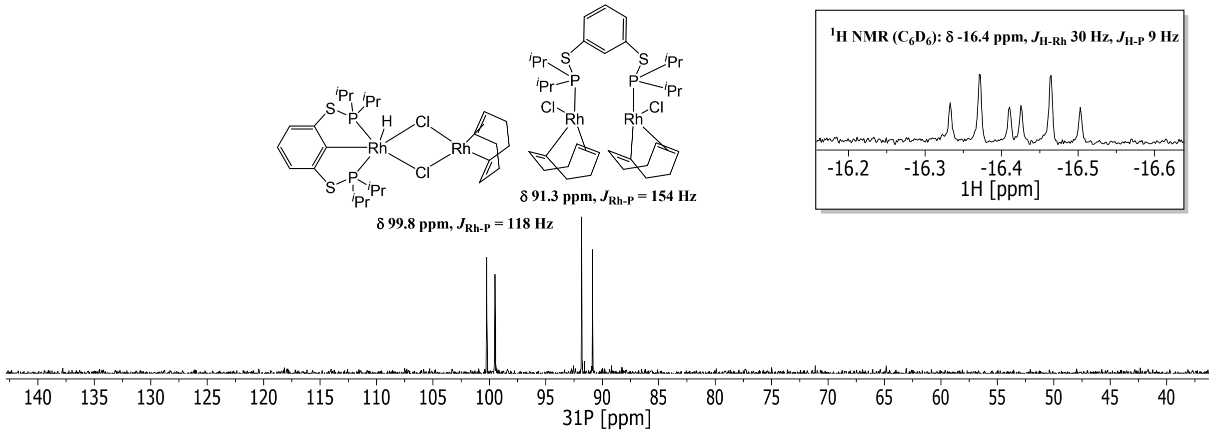


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of complexes **4** and **5** (C_6D_6, 121 MHz). The inset shows the hydride region of ^{1}H NMR spectrum of complex **5** (C_6D_6, 300 MHz).

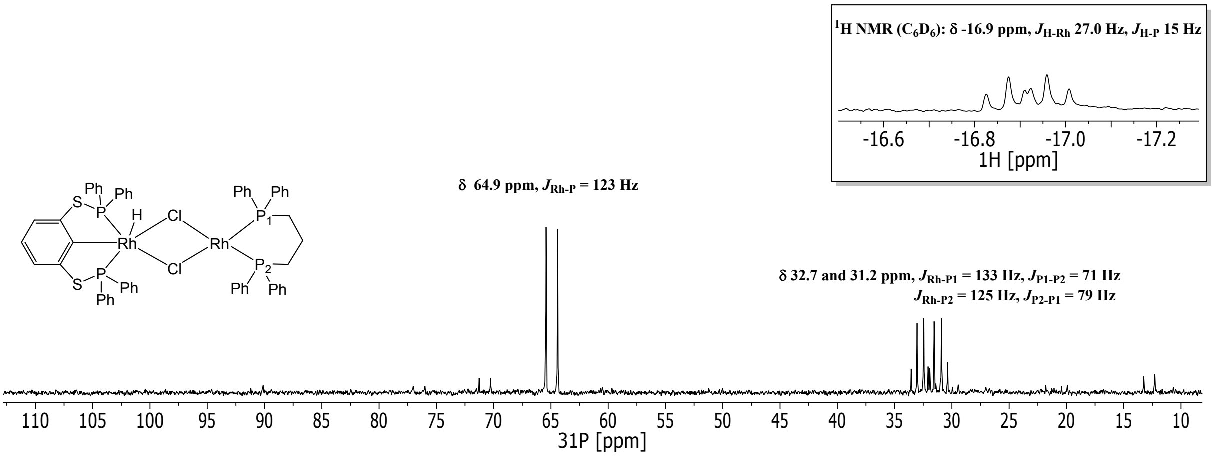
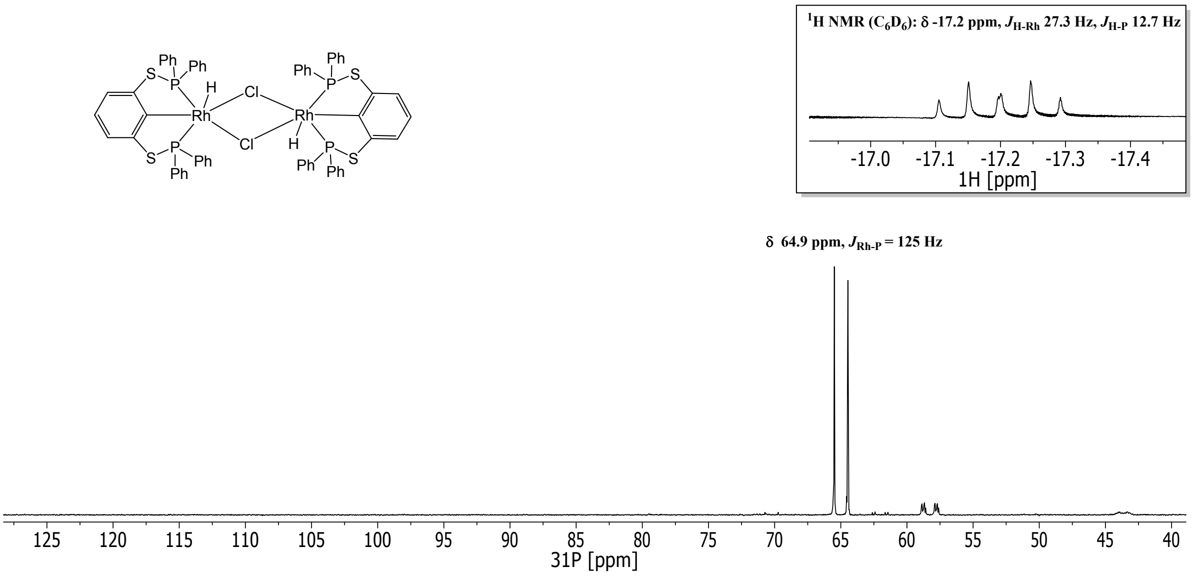


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6** (C_6D_6, 121 MHz). The inset shows the hydride region of the ^{1}H NMR spectrum (C_6D_6, 300 MHz).



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igure S13. $^{31}P\{^{1}H\}$ NMR spectrum of complex **7** (C_6D_6, 161 MHz). The inset shows the hydride region of the ^{1}H NMR spectrum (C_6D_6, 400 MHz).

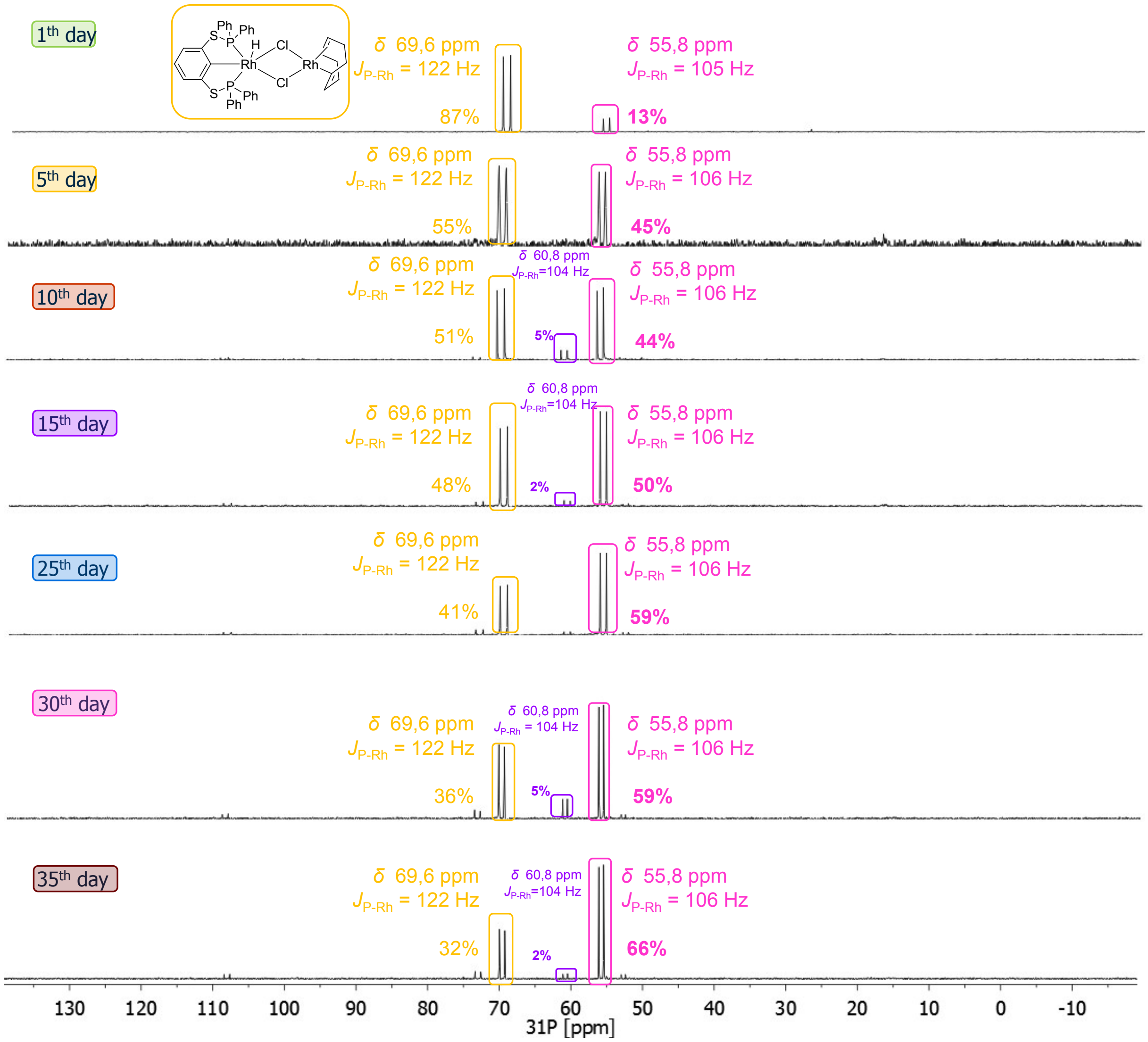

Figure S14. $^{31}P\{^1H\}$ NMR spectra of the reaction of complex **2** with pyridine (C_6D_6, 121 MHz).

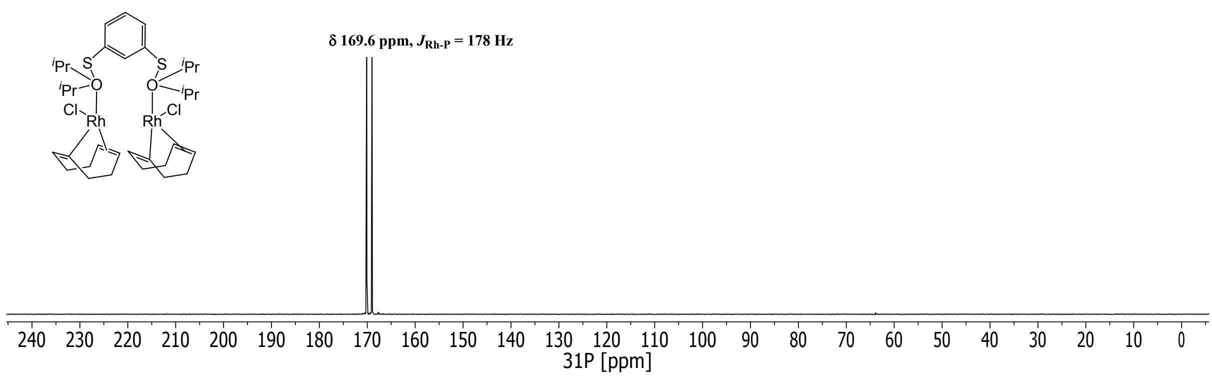

Figure S15. $^{31}P\{^1H\}$ NMR spectrum of complex **8** (C_6D_6, 121 MHz).

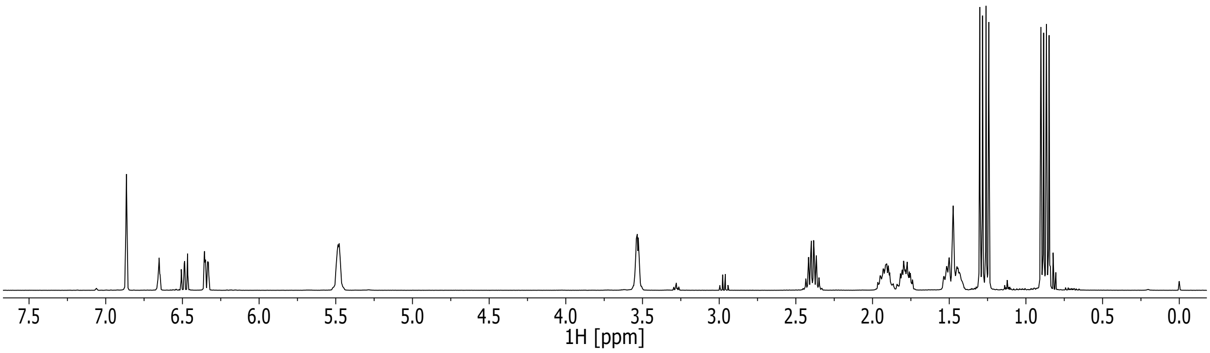

Figure S16. ^{1}H NMR spectrum of complex **8** (C_6D_6, 300 MHz).

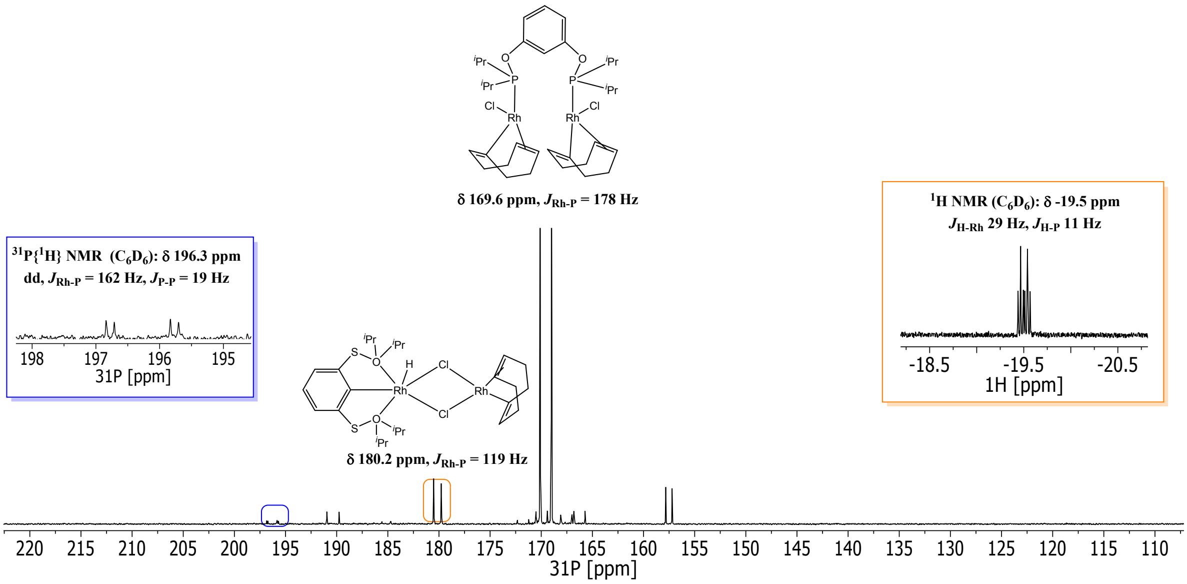

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of conversion of complex **8** into **9** (C_6D_6, 121 MHz).

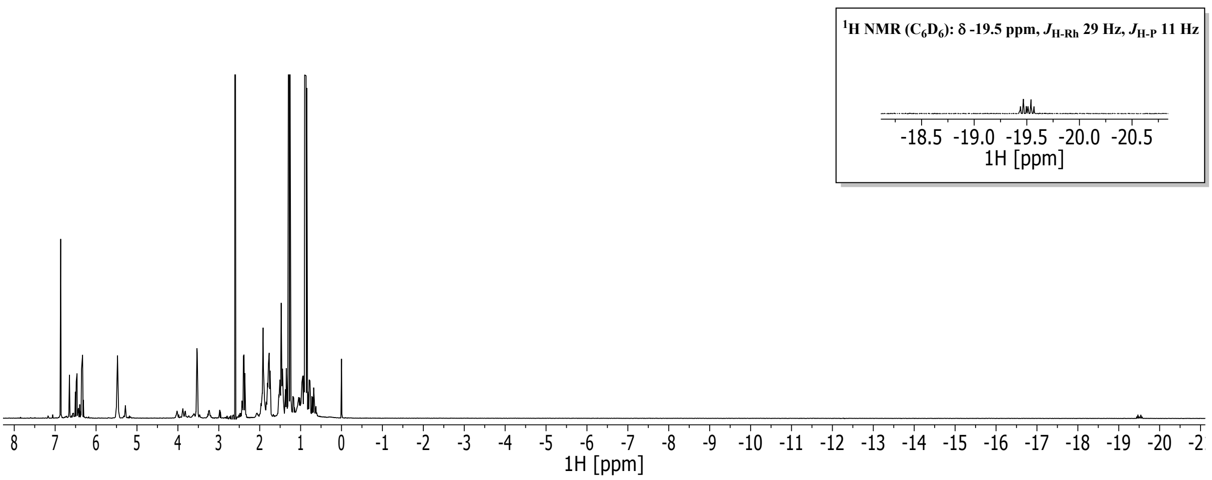

Figure S18. ^{1}H NMR spectrum (C_6D_6, 300 MHz) of conversion of complex **8** into **9**.

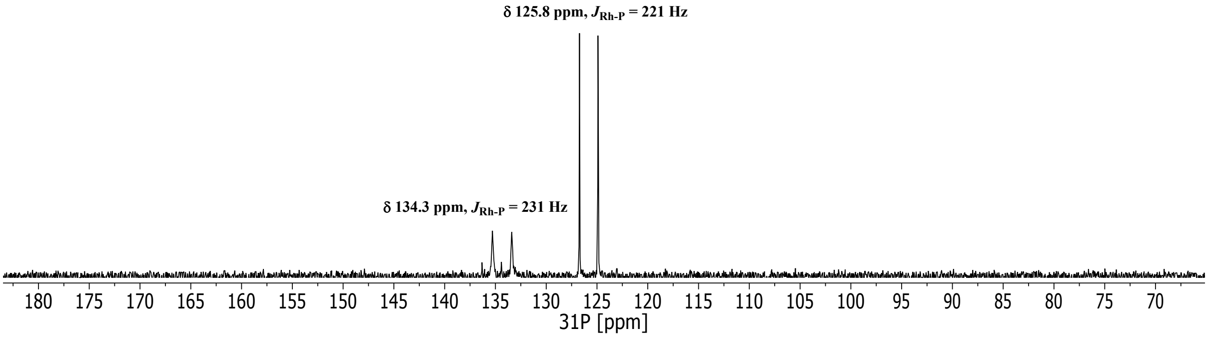

Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of crystals reported in Figure S3 (complex **10**) dissolved in C_6D_6 (121 MHz). The two signals observed are related to two unknown Rh(POCOP) complexes.

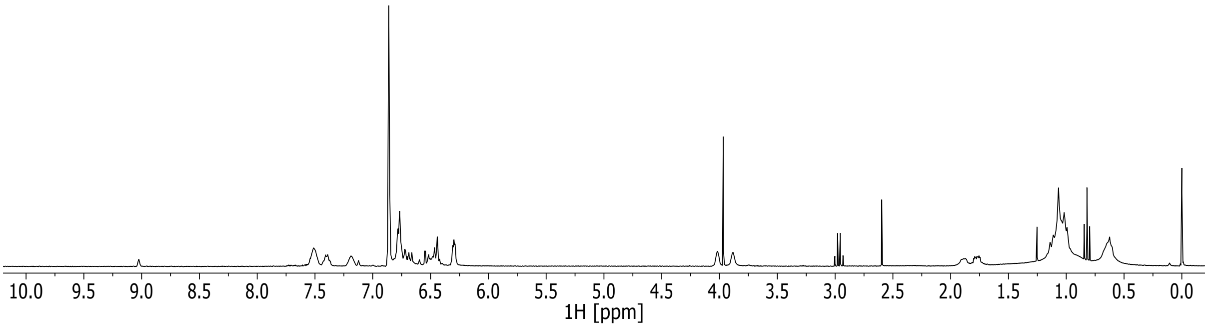

Figure S20. ^{1}H NMR spectrum of crystals reported in Figure S3 (complex **10**) dissolved in C_6D_6 (300 MHz).

References for Supporting Information

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