

Reduction of Dinitrogen to Ammonia and Hydrazine on Low-Valent Ruthenium Complexes

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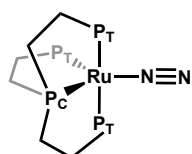
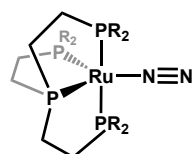
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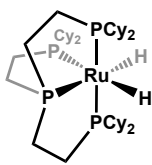
S 1. Compound numbers and labelling conventions



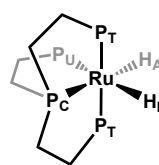
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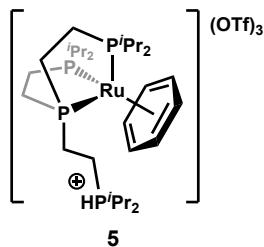
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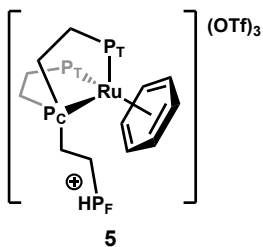
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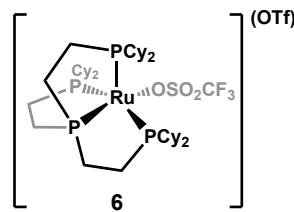
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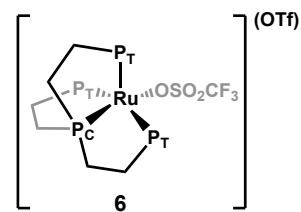
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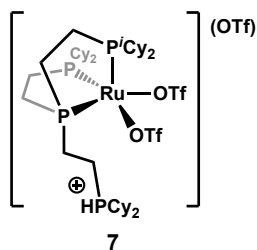
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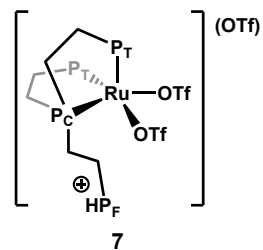
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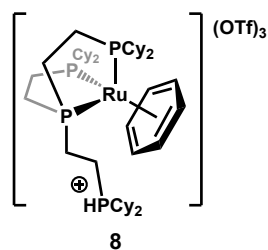
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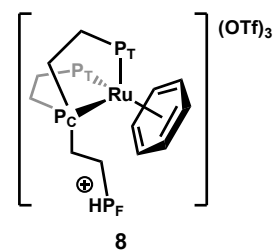
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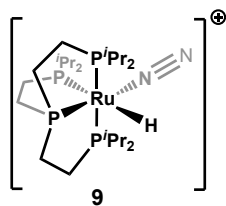
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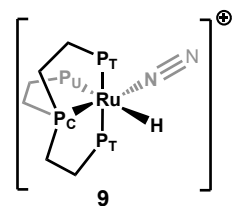
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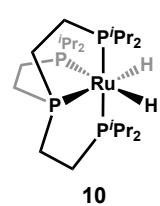
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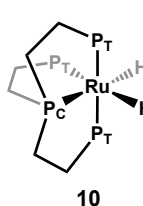
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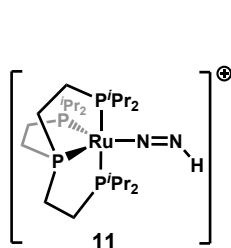
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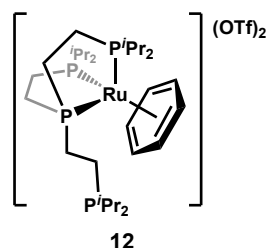
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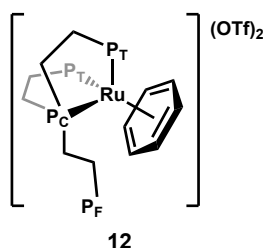
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S 2. EXPERIMENTAL

S 2.1 General Procedures

All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques or in nitrogen or argon filled glove boxes. Solvents were dried and distilled under nitrogen or argon from sodium/benzophenone (benzene, 1,4-dioxane). Tetrahydrofuran, diethyl ether, toluene and pentane were dried and deoxygenated using a Pure Solv 400-4-MD (Innovative Technology) solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Tetrahydrofuran- d_8 and benzene- d_6 was dried over and distilled from sodium/benzophenone ketyl. Dichloromethane- d_2 and methanol- d_4 were dried over, distilled from and stored over activated molecular sieves. Dimethyl sulfoxide- d_6 was dried over activated molecular sieves. ^{15}N -labeled dinitrogen was obtained from Cambridge Isotope Laboratories or Aldrich and used without further purification. Tris[2-(diphenylphosphino)ethyl]phosphine was purchased from Acros Organics and used without further purification. Hydrochloric acid (4M in dioxane or 2M in diethyl ether), trifluoroacetic acid, HBF_4 (54% solution in diethyl ether) and triflic acid were purchased commercially and degassed via three freeze-pump-thaw cycles before use. Lutidinium triflate was synthesized by reaction of equimolar amounts of 2,6-lutidine and triflic acid in diethyl ether. Oxonium acid $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ was synthesized by the literature method.¹ Potassium graphite was prepared by the literature method.²

Air-sensitive NMR samples were prepared in an argon- or nitrogen-filled glovebox or on a high vacuum line by vacuum transfer of solvent into an NMR tube fitted with a concentric Teflon valve. NMR spectra were recorded on Bruker Avance 300, 400, or 600 NMR spectrometers. ^1H NMR spectra were referenced to residual solvent resonances; ^{31}P NMR spectra were referenced to external neat trimethyl phosphite at δ 140.85 whilst ^{19}F spectra were referenced to external neat hexafluorobenzene at -164.9 ppm. ^{15}N and ^{14}N NMR spectra were referenced to external neat nitromethane at δ 0.00. In general, quantitative NMR experiments were conducted using the following parameters: 30° pulse, relaxation delay of 20 s, time domain size of 32k or 64k data points, (^1H); 90° pulse with inverse-gated proton decoupling, relaxation delay of 1 s, time domain size of 32k data points (^{14}N).

Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer as nujol mulls.

Microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. GC-MS analysis was carried out at the Bioanalytical Mass Spectrometry Facility, UNSW, using a Thermo DSQ II mass spectrometer interfaced to a ThermoTrace gas chromatograph and Triplus autosampler equipped with either Restek Rtx-Volatile Amine GC (ammonia analysis) or DB-624 (acetone azine analysis) columns.

Tris[2-(diisopropylphosphino)ethyl]phosphine ($\text{PP}_3^{i\text{Pr}}$), $[\text{RuCl}(\text{PP}_3^{i\text{Pr}})]^+\text{Cl}^-$, $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1**, $[\text{Ru}(^{15}\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1- $^{15}\text{N}_2$** , and $[\text{RuH}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]^+\text{BF}_4^-$ **9** were prepared by the literature method.³ The complexes $[\text{RuCl}_2(\text{PP}_3^{\text{Ph}})]$ **10**,⁴ and $[\text{RuCl}(\text{PP}_3^{\text{Cy}})]^+\text{BPh}_4^-$ **5** were prepared using literature methods.

X-ray crystallography for complexes **4** and **8** was carried out on a Bruker Nonius X8 Apex II CCD Diffractometer ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 100(2)\text{K}$) by Dr. S. J. Dalgarno and Dr. R. D. McIntosh at the Heriot-Watt University. Crystallographic analyses for complexes **5** and **6** were

performed by Dr M. Bhadbhade at the University of New South Wales on a Bruker Kappa APEXII area detector diffractometer (Mo K α radiation, λ = 0.71073 Å, T = 150K).

Crystallographic data are presented in Table S2.

S 2.2 Quantification of ammonium by ^1H and ^{14}N NMR spectroscopy. A known amount of 1,4-dioxane (10-140 mg) was added by vacuum transfer to the NMR solution of the sample in DMSO- d_6 . NH_4^+ was quantified by integration of the NH_4^+ and dioxane ^1H NMR signals.

Alternatively, a solution of 1,3,5-trimethoxybenzene (20 μL , 0.23 M) in DMSO- d_6 was added to the NMR solution of the sample in DMSO- d_6 . NH_4^+ was quantified by integration of the NH_4^+ and trimethoxybenzene ^1H NMR signals.

In cases where the region of the ^1H NMR spectrum near 7 ppm was obscured, a known amount of tetramethylammonium iodide (3-4 mg) was added and NH_4^+ was quantified by integration of the NH_4^+ and tetramethylammonium signals in the $^{14}\text{N}\{^1\text{H}\}$ NMR spectrum at -335.3 and -356.2 ppm respectively.

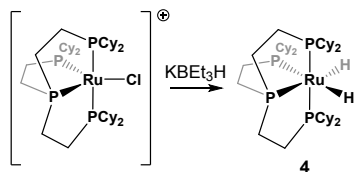
S 2.3 Quantification of ammonia by GC-MS. Reaction mixtures in DMSO- d_6 solution were diluted with DMSO to 10 mL in a volumetric flask. Alternatively, after evaporation of the reaction solvent, reaction mixtures were directly diluted with DMSO to 10 mL in a volumetric flask. Three aliquots of the resulting solution (2 mL each) were pipetted into individual 10 mL headspace vials. A solution of NaOH solution (250 μL , 2 M) was added to each vial and the vials immediately sealed with crimp septa. Head-space GC-MS analysis was performed, the ammonia peak was integrated against an ammonia calibration curve covering the concentration range of 100 μM to 1 mM.

S 2.4 Quantification of hydrazine by GC-MS. The literature method for derivatizing hydrazine as its acetone azine was used with minor modifications.⁷ The derivatization reagent was prepared by dissolving benzoic acid (0.5 g) and acetone (0.5 mL) in DMSO (9 mL). The sample was diluted with DMSO to 5 or 10 mL in a volumetric flask. Three aliquots of the resulting solution (10 μL each) were pipetted into individual 10 mL headspace vials. The derivatization reagent (100 μL) and a half-saturated solution of NaHCO_3 (10 μL , 45 g/L) were then added to each vial and the vials immediately sealed with crimp septa. Head-space GC-MS analysis was performed and the acetone azine peaks at both m/z 97 and 112 were integrated and compared against a hydrazine calibration curve covering the concentration range of 2 μM to 2 mM.

S 2.5 Preparation of $\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})$ 2. Complex 2 was prepared by a modification of the literature method.⁶ Potassium graphite (0.270 g, 2.00 mmol) was added to tetrahydrofuran (5 mL) and the suspension stirred for 5 min. $[\text{RuCl}(\text{PP}_3^{\text{Cy}})]^+\text{BPh}_4^-$ (0.253 g, 0.218 mmol) was added and the reaction mixture stirred until all orange solid had disappeared (2 min) then evaporated to dryness under reduced pressure. The residue was extracted with benzene (8 mL), filtered through diatomaceous earth and the clear yellow filtrate evaporated to dryness under reduced pressure with warming at 40°C. The residue was then washed with pentane to afford a yellow solid (89 mg, 0.11 mmol, 49%). NMR characterization corresponded with that reported in the literature.⁶

S 2.6 Preparation of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ 3. A mixture of $[\text{RuCl}_2(\text{PP}_3^{\text{Ph}})]$ (75 mg, 89 μmol) and KC_8 (38 mg, 0.28 mmol) in toluene (3 mL) was stirred overnight under nitrogen. The reaction mixture was filtered through diatomaceous earth and the dark brown filtrate was evaporated to dryness under reduced pressure to afford a maroon solid (58 mg, 73 μmol , 81% yield). NMR characterization corresponded with that reported in the literature.⁸

S 2.7 Synthesis and characterization of $[\text{RuH}_2(\text{PP}_3^{\text{Cy}})]$ **4** An authentic sample of $[\text{RuH}_2(\text{PP}_3^{\text{Cy}})]$ **4** was synthesized by treatment of the chloro precursor with KBET_3H in toluene under argon (Scheme S1).



Scheme S1

Toluene (30 mL) was added to a mixture of $[\text{RuCl}(\text{P}^2\text{P}_3^{\text{Cy}})]\text{BPh}_4$ (108 mg, 0.0929 mmol) and KBET_3H (69.9 mg, 0.506 mmol), and the resulting orange reaction mixture was then left stirring under argon overnight. The yellow/white reaction mixture was heated (313 K) and the solvent removed under a positive pressure of argon. The solid was extracted with pentane, filtered through diatomaceous earth to yield a dull yellow solution, and the solvent then removed under a positive pressure of argon to yield $[\text{RuH}_2(\text{PP}_3^{\text{Cy}})]$ **4** as a dull yellow solid (35 mg, 0.093 mmol, 46% yield). ^1H NMR (tetrahydrofuran- d_8 , 400 MHz, 298 K): δ 2.4–1.0 (m, 78H, CH_2 arm/CyH), –9.5 (br, 2H, RuH_2). ^1H NMR (tetrahydrofuran- d_8 , 400 MHz, 214 K): δ 2.6–1.0 (m, 78H, CH_2 arm/CyH), –6.0 (m, 1H, RuH), –13.0 (m, 1H, RuH). $^{31}\text{P}\{^1\text{H}\}$ NMR (tetrahydrofuran- d_8 , 162 MHz, 298 K): δ 153.0 (q, $^2J_{\text{P-P}} = 12$ Hz, 1P, P_C), 81.4 (br, 3P, P_T). $^{31}\text{P}\{^1\text{H}\}$ NMR (tetrahydrofuran- d_8 , 162 MHz, 228 K): δ 152.7 (br, 1P, P_C), 85.8 (v br, 2P, P_T), 72.1 (br, 1P, P_U). IR: 1952m $\nu(\text{Ru-H})$, 1704m, 1479w, 1449m, 1408w, 1340w, 1293w, 1261m, 1215w, 1191w, 1171w, 1100m, 1023m, 916w, 886w, 849w, 839w, 806m, 773w, 737w, 723w, 708w, 695w, 686m, 658w, 638w, 599m cm^{-1} . Crystals suitable for X-ray crystallography were grown by slow evaporation of a benzene- d_6 solution under argon (see Figure S1).

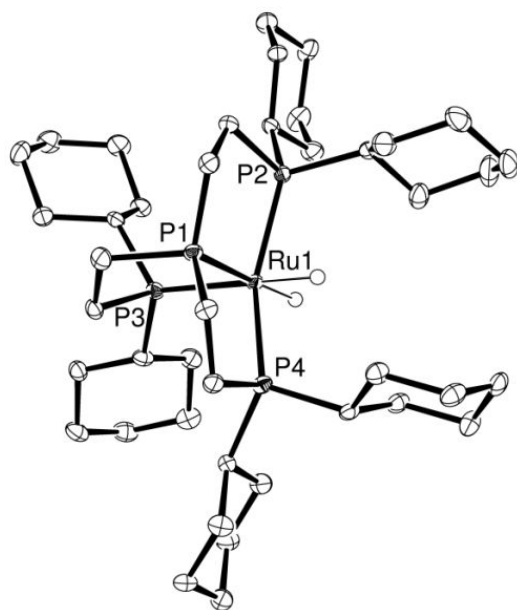


Figure S1. ORTEP plot of $[\text{RuH}_2(\text{PP}_3^{\text{Cy}})]$ **4**; 50% ellipsoid probability; benzene solvate, and carbon-bound hydrogen atoms excluded for clarity. Selected bond lengths (Å) and angles (deg): Ru1-P1 2.2478(11), Ru1-P2 2.3062(10), Ru1-P3 2.3768(11), Ru1-P4 2.3305(10), P1-Ru1-P2 85.65(4), P1-Ru1-P3 84.73(4), P1-Ru1-P4 84.55(4), P2-Ru1-P3 105.55(4), P2-Ru1-P4 150.01(4), P4-Ru1-P3 101.68(4).

The ^1H NMR spectrum of **4** at 298K in THF- d_8 exhibits a broad resonance at –9.5 ppm which, on cooling to 214K, splits into two resonances at –6.0 and –13.0 ppm integrating to 1 proton each (see Figure S3). At intermediate temperatures (see 251K in Figure S3), the signals are broadened into the baseline by exchange. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in THF- d_8 exhibits a quartet at 153.0 ppm integrating to 1P for the central P atom and a broad resonance at 81.4 ppm integrating to 3P for the terminal P atoms. On cooling to 228K, the ^{31}P signal at 81.4 ppm splits to 2 signals at 85.8 and

72.1 ppm (see Figure S4). At intermediate temperatures (see 251K in Figure S4), the signals are broadened into the baseline by exchange.

Note that the $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data for **4** do not match those previously reported for this compound (doublet at -59.5 ppm and quartet at 12.1 ppm in the ^{31}P NMR spectrum assigned to terminal and central P atoms respectively).⁵ It appears that the ^{31}P data previously reported for this compound have been referenced incorrectly.

S 2.8 Reaction of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1 with TfOH.** (i) In a typical reaction, a solution of TfOH (20 μL , 0.23 mmol, 6 equiv) in pentane (3 mL) was added to the yellow solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (23 mg, 39 μmol) in pentane (4 mL) under nitrogen. The solution turned nearly colorless and an oily maroon-brown precipitate formed. The reaction mixture was stirred overnight and the volatiles were removed under reduced pressure. The residue was dissolved in $\text{DMSO}-d_6$ and analyzed by ^1H and/or ^{14}N NMR spectroscopy before being analyzed by GC-MS or alternatively, the residue was dissolved in DMSO and analyzed by GC-MS only.

(ii) In a typical reaction, TfOH (28 μL , 0.20 mmol) was added to a solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (17 mg, 29 μmol) in benzene (4 mL) under nitrogen. The solution turned green then pale yellow. The reaction mixture was stirred overnight and the volatiles were removed under reduced pressure. The residue was dissolved in $\text{DMSO}-d_6$ and analyzed by ^1H and/or ^{14}N NMR spectroscopy before being analyzed by GC-MS or alternatively, the residue was dissolved in DMSO and analyzed by GC-MS only.

S 2.9 Reaction of $[\text{Ru}(^{15}\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1- $^{15}\text{N}_2$ with TfOH.** A solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (40 mg, 67 μmol) in benzene (0.6 mL) was degassed with three freeze-pump-thaw cycles then placed under an atmosphere of $^{15}\text{N}_2$ and left to stand for a month to allow exchange of the dinitrogen ligand to take place. The $^{15}\text{N}_2$ atmosphere was refreshed and the solution left for 3 days to allow for further exchange (approximately 88% enrichment). TfOH (56 μL , 0.63 mmol) was added and the reaction mixture was left to stand for 3 d. The volatiles were removed under reduced pressure and the residue dissolved in $\text{DMSO}-d_6$. ^1H NMR ($\text{DMSO}-d_6$, 600 MHz): δ 7.04 (d, $^2J_{\text{HN}} = 72$ Hz, $^{15}\text{NH}_4^+$). $^{15}\text{N}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 61 MHz): δ -328.7 ($^{15}\text{N}_2\text{H}_5^+$) -358.8 ($^{15}\text{NH}_4^+$).

S 2.10 Reaction of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2 with TfOH.** In a typical reaction, TfOH (39 mg, 0.26 mmol) was added to a yellow suspension of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2** (26 mg, 30 μmol) in benzene (2 mL) under nitrogen. The reaction mixture was stirred at room temperature overnight and the volatiles removed under reduced pressure. The residue was dissolved in DMSO and analyzed by GC-MS for NH_4^+ and N_2H_5^+ .

S 2.11 Preparation of $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{i\text{Pr}}\text{H})]^{3+}$ **5** TfOH (89 μL , 0.63 mmol) was added to the yellow solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (54 mg, 91 μmol) in benzene (4 mL) under nitrogen and the color of the reaction mixture turned green then orange. The reaction mixture was stirred for 3 days and the volatiles were removed under reduced pressure to afford an oily yellow residue. ^1H NMR (600 MHz, acetone- d_6): δ 6.83 (s, 6H, C_6H_6), 3.21 (m, 2H, CH_2), 3.09 (m, 2H, $2\times\text{CH}$), 2.99-2.86 (m, 4H, $2\times\text{CH}_2$), 2.74-2.57, 4H, CH_2 , $2\times\text{CH}$), 2.23 (m, 2H, $2\times\text{CH}$), 2.10 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.50-1.44 (m, 18H, $6\times\text{CH}_3$), 1.41 (m, 6H, $2\times\text{CH}_3$), 1.37 (m, 6H, $2\times\text{CH}_3$), 1.16 (m, 6H, $2\times\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, acetone- d_6 , from ^1H - ^{13}C HSQC): δ 97.9 (C_6H_6) 33.5 (CH), 31.5 (CH), 28.2 ($2\times\text{CH}_2$), 25.6 (CH_2), 21.7 (CH_2), 21.4 (CH_2), 20.6 ($2\times\text{CH}_3$), 19.7 ($2\times\text{CH}_3$), 19.3 (CH), 18.8 ($2\times\text{CH}_3$), 18.7 ($2\times\text{CH}_3$),

17.0 (4×CH₃), 10.5 (CH₂). ³¹P{¹H} NMR (243 MHz, acetone-*d*₆): δ 105.0 (dt, ³J_{PP} = 35 Hz, ²J_{PP} = 27 Hz, 1P, **P_C**), 86.9 (d, ²J_{PP} = 27 Hz, 2P, **P_T**), 35.3 (dt, ³J_{PP} = 35 Hz, ¹J_{PD} = 74 Hz, 1P, **P_FD⁺**). ¹⁹F NMR (565 MHz, acetone-*d*₆): δ -76.3. See Figures S14, S15 and S16. Crystals suitable for X-ray crystallography were grown from a solution of Ru(benzene)(κ³-PP₃^{iPr}H)]³⁺ **5** in dichloromethane / diethyl ether.

S 2.12 Preparation of [Ru(OTf)(PP₃^{Cy})]⁺OTf **6.** TfOH (42 mg, 0.28 mmol) was added to a suspension of [Ru(N₂)(PP₃^{Cy})] **2** (23 mg, 28 μmol) in pentane (4 mL) under nitrogen. The reaction mixture was stirred at room temperature overnight, the volatiles removed under reduced pressure and the residue dissolved in methanol-*d*₄ (0.5 mL). Layering the solution with diethyl ether (1.5 mL) afforded orange crystals of [Ru(OTf)(PP₃^{Cy})]⁺OTf **6** (0.16 g, 14 μmol, 52%) which were suitable for X-ray crystallography. Anal. Calcd for C₄₄H₇₈F₆O₆P₄RuS₂ (1106.18): C, 47.78; H, 7.11. Found: C, 47.79; H, 6.86. ¹H NMR (400 MHz, methanol-*d*₄): δ 2.43-1.41 (m, 78H **CH** and **CH₂**), 0.74 (m, 2H, **CH₂**); ³¹P{¹H} NMR (162 MHz, methanol-*d*₄): δ 144.5 (q, ²J_{PP} = 14 Hz, 1P, **P_C**), 64.5 (br, 3P, **P_T**). ¹⁹F NMR (376 MHz, methanol-*d*₄): δ -77.8 (s, OSO₂CF₃). For ¹H, ³¹P and ¹⁹F spectra see Figures S5, S6 and S7.

S 2.13 Preparation of [Ru(OTf)₂(κ³-PP₃^{Cy}H)]⁺OTf **7.** TfOH (0.131 g, 0.872 mmol) was added to a suspension of [Ru(N₂)(PP₃^{Cy})] **2** (58 mg, 69 μmol) in pentane (5 mL) under nitrogen. The reaction mixture was stirred at room temperature for 2 days and the colorless pentane supernatant was decanted off. The orange gummy residue was washed with diethyl ether then dried *in vacuo* to afford a complex whose spectra are consistent with the formulation [Ru(OTf)₂(κ³-PP₃^{Cy}H)]⁺OTf **7** as an orange solid (22 mg, 25%). ¹H NMR (400 MHz, dichloromethane-*d*₂): δ 5.86 (dm, ¹J_{PH} = 472 Hz, 1H, **HP_F**), 2.82 (m, 2H, **CH₂**), 2.70-1.12 (m, 74H, **CH** and **CH₂**), 0.74 (m, 2H, **CH₂**). ³¹P{¹H} NMR (162 MHz, dichloromethane-*d*₂): δ 109.5 (dt, ²J_{PP} = 38 Hz, ²J_{PP} = 23 Hz, 1P, **P_C**), 78.0 (d, ²J_{PP} = 23 Hz, 2P, **P_T**), 28.5 (d, ²J_{PP} = 23 Hz, 1P, **P_FH⁺**). ¹⁹F NMR (376 MHz, dichloromethane-*d*₂): δ -76.8 (s, OSO₂CF₃). For ¹H, ³¹P and ¹⁹F spectra see Figures S8, S9 and S10.

S 2.14 Preparation of [Ru(benzene)(κ³-PP₃^{Cy}H)]³⁺ **8.** TfOH (70 mg, 0.47 mmol) was added to a suspension of [Ru(N₂)(PP₃^{Cy})] **2** (50 mg, 60 μmol) in benzene (5 mL) under nitrogen. The volatiles were removed under reduced pressure to afford an orange oily gum. The gum was triturated with diethyl ether (10 mL) until an orange-yellow solid formed (68 mg). The solid contained a mixture of [Ru(OTf)(PP₃^{Cy})]⁺OTf **6** (42%) and [Ru(benzene)(κ³-PP₃^{Cy}H)]³⁺ **8** (58%). Crystals of **8** suitable for X-ray crystallography preferentially crystallized from a solution of the mixture of **6** and **8** in dichloromethane/diethyl ether (see Figure S3). Anal. Calcd for C₅₁H₈₅F₉O₉P₄RuS₃ (1334.36): C, 45.91; H, 6.42. Found: C, 45.82; H, 6.59. ¹H NMR (400 MHz, methanol-*d*₄): δ 6.68 (s, C₆H₆), 3.01-1.21 (m, **CH** and **CH₂**). ¹³C{¹H} NMR (101 MHz, methanol-*d*₄, from ¹H-¹³C HSQC, low field only): δ 97.3 (C₆H₆). ³¹P{¹H} NMR (162 MHz, methanol-*d*₄): δ 104.0 (dt, ²J_{PP} = 34 Hz, ²J_{PP} = 28 Hz, 1P, **P_C**), 79.9 (d, ²J_{PP} = 28 Hz, 2P, **P_T**), 27.8 (br, 1P, **P_FH⁺**). ¹⁹F NMR (565 MHz, methanol-*d*₄): δ -77.7 (s, OSO₂CF₃). For ¹H, ³¹P and ¹⁹F spectra see Figures S11, S12 and S13.

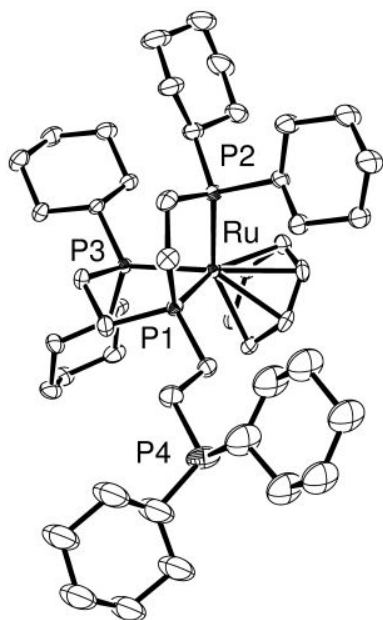


Figure S2. ORTEP plot of $[\text{Ru}(\eta^6\text{-benzene})(\kappa^3\text{-PP}_3\text{CyH})]^{3+}$ **8**; 50% ellipsoid probability; triflate counterions, 12 partially occupied carbon atoms on disordered cyclohexyl groups, and hydrogen atoms excluded for clarity. Selected bond lengths (Å) and angles (deg): Ru-P3 2.3901(7), Ru-P1 2.2960(8), Ru-P2 2.3655(8), Ru-C 2.273(3) to 2.330(3), C-C (benzene) 1.396(5) to 1.422(4), P1-Ru-P3 81.14(3), P1-Ru-P2 82.57(3), P2-Ru-P3 96.86(3).

S 2.15 Reaction of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1 with TfOH and CoCp^*_2 .** In a typical reaction, TfOH (42.3 μL , 0.302 mmol) was added to a suspension of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (30 mg, 50 μmol) and decamethylcobaltocene (99.5 mg, 0.302 mmol) in pentane (4 mL) under nitrogen. The reaction mixture was left to stir overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed by GC-MS for NH_4^+ and N_2H_5^+ .

S 2.16 Reaction of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1 with $\text{LutH}^+\text{OTf}^-$.** Lutidinium triflate (20 mg, 79 μmol) was added to a solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (47 mg, 79 μmol) in THF (8 mL) under nitrogen. The yellow solution turned green after a couple of minutes and then turned back to yellow. The reaction mixture was left to stir for 5 days and the volatiles were removed under reduced pressure. Multiple products were formed including $[\text{RuH}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]^+$ **9**. The residue was dissolved in DMSO- d_6 or DMSO and analyzed by GC-MS for NH_4^+ and N_2H_5^+ .

S 2.17 Reaction of $[\text{RuH}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]^+\text{BF}_4^-$ **9 with TfOH.** TfOH (26 μL , 29 mmol) was added to a suspension of $[\text{RuH}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]^+\text{BF}_4^-$ **9** (34 mg, 49 μmol) in pentane (4 mL) under nitrogen. The reaction mixture was left to stir overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO and analyzed by GC-MS for NH_4^+ and N_2H_5^+ .

S 2.18 Reaction of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1 with HCl.** (i) A solution of HCl (2 M in diethyl ether, 75 μL , 0.15 mmol) was added to a solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (15 mg, 25 μmol) in pentane (4 mL) under nitrogen. The reaction mixture was left to stir overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed by GC-MS for NH_4^+ and N_2H_5^+ .

(ii) A solution of HCl (2 M in diethyl ether, 75 μ L, 0.15 mmol) was added to a solution of [Ru(N₂)(PP₃^{*i*Pr})] (15 mg, 25 μ mol) in benzene (4 mL) under nitrogen. The reaction mixture was left to stir overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO and analyzed by GC-MS for NH₄⁺ and N₂H₅⁺.

S 2.19 Reaction of [Ru(N₂)(PP₃^{*i*Pr})] 1 with HBF₄. A solution of HBF₄ (54% in diethyl ether, 10 μ L, 0.15 mmol) was added to a solution of [Ru(N₂)(PP₃^{*i*Pr})] (15 mg, 25 μ mol) in pentane (4 mL) under nitrogen. The reaction mixture was left to stir for 2 days and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO-*d*₆ or DMSO and analyzed by GC-MS for NH₄⁺ and N₂H₅⁺.

S 2.20 Reaction of [Ru(N₂)(PP₃^{*i*Pr})] 1 with CF₃COOH. (i) In a typical reaction, CF₃COOH (22 μ L, 0.29 mmol) was added to a solution of [Ru(N₂)(PP₃^{*i*Pr})] (29 mg, 48 μ mol) in pentane (4 mL) under nitrogen. The reaction mixture was left to stir overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO-*d*₆ or DMSO and analyzed by GC-MS for NH₄⁺ and N₂H₅⁺.

(ii) CF₃COOH (12 μ L, 0.15 mmol) was added to a solution of [Ru(N₂)(PP₃^{*i*Pr})] (15 mg, 25 μ mol) in benzene (4 mL) under nitrogen. The reaction mixture was left to stir overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO and analyzed by GC-MS for NH₄⁺ and N₂H₅⁺.

S 2.21 Reaction of [Ru(N₂)(PP₃^{*i*Pr})] 1 with [H(OEt₂)₂][B(C₆F₅)₄]. (i) In a typical reaction, [H(OEt₂)₂][B(C₆F₅)₄] (334 mg, 0.403 mmol) was added to a solution of [Ru(N₂)(PP₃^{*i*Pr})] (30 mg, 50 μ mol) in pentane (4 mL) under nitrogen. The reaction mixture was left to stir overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO-*d*₆ or DMSO and analyzed by GC-MS for NH₄⁺ and N₂H₅⁺.

(ii) In a typical reaction, [H(OEt₂)₂][B(C₆F₅)₄] (146 mg, 0.176 mmol) was added to a solution of [Ru(N₂)(PP₃^{*i*Pr})] (15 mg, 25 μ mol) in benzene (4 mL) under nitrogen. The reaction mixture was left to stir overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO-*d*₆ or DMSO and analyzed by GC-MS for NH₄⁺ and N₂H₅⁺.

S 2.22 Reaction of [Ru(N₂)(PP₃^{*i*Pr})] 1 with H₂ gas. A solution of [Ru(N₂)(PP₃^{*i*Pr})] (15 mg, 25 μ mol) in pentane (0.5 mL) was degassed with three freeze-pump-thaw cycles then placed under an atmosphere of H₂ gas. After 5 days, the solution was once again degassed with three freeze-pump-thaw cycles then placed under an atmosphere of H₂ gas. ¹H NMR (pentane, 300 MHz, high field only): δ -9.35 (br, Ru-H). ³¹P{¹H} NMR (pentane, 122 MHz): δ 155.2 (q, ³J_{PP} = 12 Hz, 1P, P_C), 92.4 (br, 3P, P_T). TfOH (21 μ L, 0.23 mmol) was added to the reaction mixture and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO-*d*₆ or DMSO and analyzed by GC-MS for NH₄⁺ and N₂H₅⁺.

S 2.23 Reaction of [Ru(N₂)(PP₃^{Ph})] 4 with TfOH. (i) TfOH (35 μ L, 0.25 mmol) was added to a suspension of [Ru(N₂)(PP₃^{Ph})] (34 mg, 42 μ mol) in pentane (4 mL) under nitrogen. Gas evolution was observed, and an oily brown residue with a pale yellow supernatant formed. The reaction mixture was stirred for 3 days and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO-*d*₆ or DMSO and analyzed by GC-MS for NH₄⁺ and N₂H₅⁺.

(ii) TfOH (35 μ L, 0.25 mmol) was added to a solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ (33 mg, 41 μ mol) in benzene (4 mL) under nitrogen. Gas evolution was observed, and an oily brown residue with a pale yellow supernatant formed. The reaction mixture was stirred for 3 days and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO and analyzed by GC-MS for NH_4^+ and N_2H_5^+ .

S 2.24 Reaction cycle converting $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** to $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{i\text{Pr}}\text{H})]^{3+}$ **5** to $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{i\text{Pr}})]^{2+}$ **12** then back to $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1**

TfOH (28 μ L, 0.20 mmol) was added to a solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (20 mg, 33 μ mol) in benzene (4 mL) under nitrogen and the reaction mixture was stirred for 3 h. The volatiles were removed under reduced pressure to afford $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{i\text{Pr}}\text{H})]^{3+}$ quantitatively as determined by ^{31}P NMR spectroscopy. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, acetone): δ 105.7 (dt, $^2J_{\text{PP}} = 35$ Hz, $^2J_{\text{PP}} = 27$ Hz, 1P, P_C), 87.0 (d, $^2J_{\text{PP}} = 27$ Hz, 2P, P_T), 36.2 (d, $^2J_{\text{PP}} = 35$ Hz, $\text{P}_\text{F}\text{H}^+$). The residue was extracted with acetone (4 mL), filtered, then treated with sodium bicarbonate (45 mg, 0.53 mmol) and stirred overnight to afford $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{i\text{Pr}})]^{2+}$ **12** quantitatively as determined by ^{31}P NMR spectroscopy (Figure S17). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, acetone): δ 105.9 (dt, $^2J_{\text{PP}} = 31$ Hz, $^2J_{\text{PP}} = 26$ Hz, 1P, P_C), 87.7 (d, $^2J_{\text{PP}} = 26$ Hz, 2P, P_T), 10.7 (d, $^2J_{\text{PP}} = 31$ Hz, P_F). One quarter of the solution was evaporated to dryness under reduced pressure then redissolved in tetrahydrofuran (3 mL) and treated with Cp^*Co (18 equiv) for 15 min to afford $[\text{Ru}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]$ **1** (approximately 60% yield by NMR) and $[\text{RuH}(\text{N}_2)(\text{PP}_3^{i\text{Pr}})]^+$ **9** (approximately 40% yield by NMR). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, tetrahydrofuran): δ 162.1 (q, $^2J_{\text{PP}} = 22$ Hz, 1P, P_C **1**), 142.1 (m, 1P, P_C **9**), 88.3 (d, $^2J_{\text{PP}} = 22$ Hz, 3P, P_T **1**), 73.6 (m, 2P, P_T **9**), 61.8 (m, 1P, P_U **9**).

S 2.25 Reaction cycle converting $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2** to $[\text{Ru}(\text{OTf})(\text{PP}_3^{\text{Cy}})]^+$ **6** and $[\text{Ru}(\text{OTf})_2(\kappa^3\text{-PP}_3^{\text{Cy}}\text{H})]^+$ **7** then back to $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2**

TfOH (57 mg, 0.38 mmol) was added to a solution of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2** (34 mg, 41 μ mol) in pentane (4 mL) under nitrogen and the reaction mixture was stirred at room temperature overnight. The volatiles were removed under reduced pressure and the gum washed several times with diethyl ether to afford 50 mg of a mixture of $[\text{Ru}(\text{OTf})(\eta^3\text{-PP}_3^{\text{Cy}})]^+$ **6** (approximately 10% yield by NMR) and $[\text{Ru}(\text{OTf})_2(\kappa^3\text{-PP}_3^{\text{Cy}})]^+$ **7** (approximately 90% yield by NMR). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ 143.1 (q, $^2J_{\text{PP}} = 15$ Hz, 1P, P_C **6**), 109.5 (dt, $^2J_{\text{PP}} = 40$ Hz, $^2J_{\text{PP}} = 23$ Hz, 1P, P_C **7**), 80.6 (br, 2P, P_T **7**), 60.2 (br, 3P, P_T **6**), 28.9 (d, $^2J_{\text{PP}} = 40$ Hz, 1P, $\text{P}_\text{F}\text{H}^+$ **7**). The mixture of **6** and **7** (23 mg) was added to a suspension of potassium graphite (50 mg, 0.37 mmol) in tetrahydrofuran (3 mL) then stirred for 5 min to afford $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2** in approximately 70 % yield by NMR. $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, tetrahydrofuran): δ 161.6 (q, $^2J_{\text{PP}} = 21$ Hz, 1P, P_C), 74.5 (d, $^2J_{\text{PP}} = 21$ Hz, 3P, P_T).

Table S1. Yields of ammonia and hydrazine from reactions of $[M(N_2)(PP_3^R)]$ with acids.

Entry	M	R	Cpd No	Acid / Electrophile / Additive	Solvent	% Yield of NH_4^+ [a]	Std Dev	% Yield of $N_2H_5^+$ [a]	Std Dev	% N_2 converted [b]
1	Ru	ⁱ Pr	1	TfOH	pentane	3 [c]	<1	18 [c]	7	20
2	Ru	ⁱ Pr	1	TfOH	benzene	2 [d]	<1	18 [d]	7	19
3	Ru	Cy	2 [e]	TfOH	pentane	4 [d]	<1	5 [d]	<1	7
4	Ru	Cy	2 [e]	TfOH	benzene	<1 [d]	<1	2 [d]	<1	2
5	Ru	Ph	3	TfOH	pentane	0 [f]	-	0 [f]	-	0
6	Ru	Ph	3	TfOH	benzene	0 [f]	-	0 [f]	-	0
7	Ru	ⁱ Pr	1	TfOH, Cp* ₂ Co	pentane	7 [g]	<1	17 [g]	3	21
8	Ru	ⁱ Pr	1	LutHOTf	THF	0 [f]	-	0 [f]	-	0
9	Ru	ⁱ Pr	1	HCl	pentane / Et ₂ O	0 [d]	<1	0 [d]	<1	0
10	Ru	ⁱ Pr	1	HCl	benzene / Et ₂ O	0 [d]	<1	0 [d]	<1	0
11	Ru	ⁱ Pr	1	HBF ₄	pentane / Et ₂ O	<1 [f]	-	0 [f]	-	<1
12	Ru	ⁱ Pr	1	CF ₃ COOH	pentane	<1 [f]	-	0 [f]	-	<1
13	Ru	ⁱ Pr	1	CF ₃ COOH	benzene	<1 [f]	-	0 [f]	-	<1
14	Ru	ⁱ Pr	1	[H(OEt ₂) ₂][B(C ₆ F ₅) ₄]	pentane	2 [d]	<1	0 [d]	<1	1
15	Ru	ⁱ Pr	1	[H(OEt ₂) ₂][B(C ₆ F ₅) ₄]	benzene	5 [f]	-	3 [f]	-	6
16	Ru	ⁱ Pr	1	H ₂	pentane	0 [f]	-	0 [f]	-	0

[a] Yield = moles of NH_4^+ or $N_2H_5^+$ per mole of metal complex as quantified by GC; [b] Percentage of complexed dinitrogen from the starting material which ends up as NH_4^+ or $N_2H_5^+$ (calculated as half % yield NH_4^+ + % yield of $N_2H_5^+$). [c] Average of 3 runs. [d] Average of 2 runs. [e] sample contained approximately 5% $[RuH_2(PP_3^{Cy})]$. [f] Analysis from 1 run only. [g] Average of 4 runs.

Table S2. Crystallographic data for [RuH₂(PP₃Cy)₃] **4**,^[a] [Ru(η⁶-benzene)(κ³-PP₃ⁱPrH)]³⁺(OTf)₃ **5**,^[b] [Ru(OTf)(PP₃Cy)]⁺(OTf) **6**,^[b] and [Ru(η⁶-benzene)(κ³-PP₃CyH)]³⁺(OTf)₃ **8**.^[a]

	4	5	6	8
CCDC Number	1570095	1570098	1570096	1570097
Formula	C ₄₅ H ₈₃ P ₄ Ru	C ₃₄ H ₆₃ Cl ₂ F ₉ O ₉ P ₄ RuS ₃	C ₄₄ H ₇₈ F ₆ O ₆ P ₄ RuS ₂	C ₅₁ H ₈₅ F ₉ O ₉ P ₄ RuS ₃
M (g mol ⁻¹)	849.06	1178.87	1106.13	1334.31
Size (mm ³)	0.2 × 0.2 × 0.2	0.263 × 0.109 × 0.053	0.294 × 0.146 × 0.108	0.33 × 0.25 × 0.18
Crystal morphology	Clear light yellow block	Light colorless plate	Dark red block	Colorless block
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	C2/c	P2 ₁ /n	P-1
a (Å)	13.802(3)	37.16(3)	9.7219(6)	14.8341(12)
b (Å)	13.827(2)	10.661(8)	38.657(2)	15.4287(13)
c (Å)	13.847(3)	26.19(2)	13.2588(8)	18.7251(16)
α (°)	92.166(11)	90	90	112.190(4)
β (°)	99.126(11)	100.35(4)	97.990(2)	102.921(4)
γ (°)	118.955(10)	90	90	100.365(4)
V (Å ³)	2263.0(7)	10206(14)	4934.6(5)	3698.1(5)
Z	2	8	4	2
D _c (g/cm ³)	1.246	1.534	1.489	1.198
μ (mm ⁻¹)	0.517	0.738	0.600	0.447
F(000)	914	4848	2320	1392
2θ _{max} (°)	54.04	49.996	54.316	58.26
N	35930	170043	155195	76013
N _{ind}	9433	8989	10927	19804
	(R _{int} = 0.0898)	(R _{int} = 0.1399)	(R _{int} = 0.0417)	(R _{int} = 0.0380)
Goodness of fit	1.027	1.082	1.078	1.044
Final R indexes	R _i = 0.0510	R _i = 0.0567	R _i = 0.0311	R _i = 0.0596
(I > 2σ(I))	wR ₂ = 0.0854	wR ₂ = 0.1118	wR ₂ = 0.0682	wR ₂ = 0.1608
Final R indexes	R _i = 0.0935	R _i = 0.0912	R _i = 0.0347	R _i = 0.0788
(all data)	wR ₂ = 0.0986	wR ₂ = 0.1295	wR ₂ = 0.0703	wR ₂ = 0.1726

[a] Crystallographic analyses for complexes **4** and **8** were carried out on a Bruker Nonius X8 Apex II CCD Diffractometer (MoKα radiation, λ = 0.71073 Å, T = 100(2)K) by Dr. S. J. Dalgarno and Dr. R. D. McIntosh at the Heriot-Watt University.

[b] Crystallographic analyses for complexes **5** and **6** were performed by Dr M. Bhadbhade at the University of New South Wales on a Bruker Kappa APEXII area detector diffractometer (Mo Kα radiation, λ = 0.71073 Å, T = 150K).

Figure S3. Low temperature ^1H NMR spectra for $[\text{RuH}_2(\text{PP}_3^{\text{Cy}})]$ **4** ($\text{C}_4\text{D}_8\text{O}$, 400 MHz, high field region only).

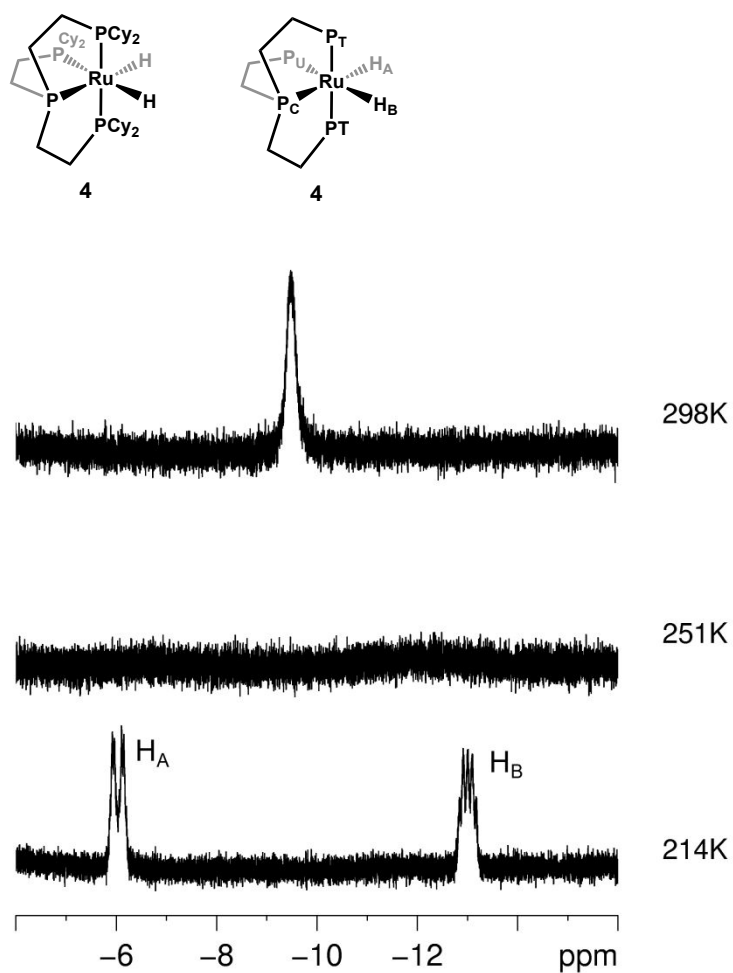


Figure S4. Low temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for $[\text{RuH}_2(\text{PP}_3^{\text{Cy}})]$ **4** ($\text{C}_4\text{D}_8\text{O}$, 162 MHz).

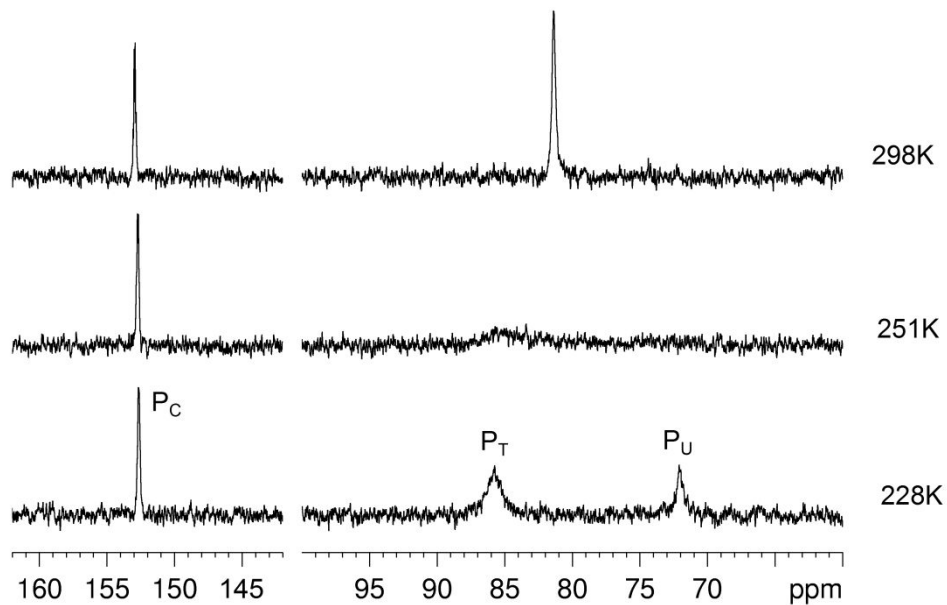


Figure S5. ^1H NMR spectrum of $[\text{Ru}(\text{OTf})(\text{PP}_3^{\text{Cy}})]^+\text{OTf}$ **6** (CD_3OD , 400 MHz).

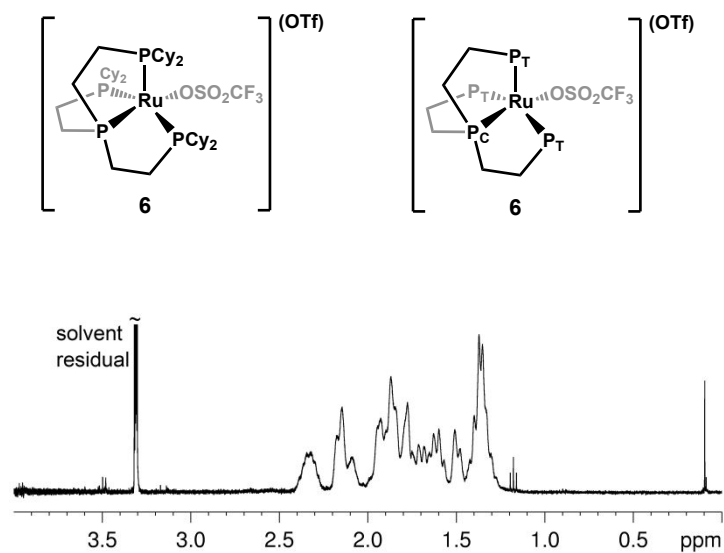


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ru}(\text{OTf})(\text{PP}_3^{\text{Cy}})]^+\text{OTf}$ **6** (CD_3OD , 162 MHz).

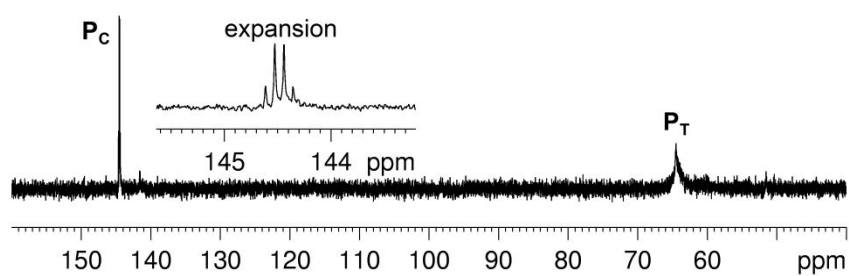


Figure S7. Low temperature ^{19}F NMR spectra of $[\text{Ru}(\text{OTf})(\text{PP}_3^{\text{Cy}})]^+\text{OTf}$ **6** (CD_3OD , 376 MHz).

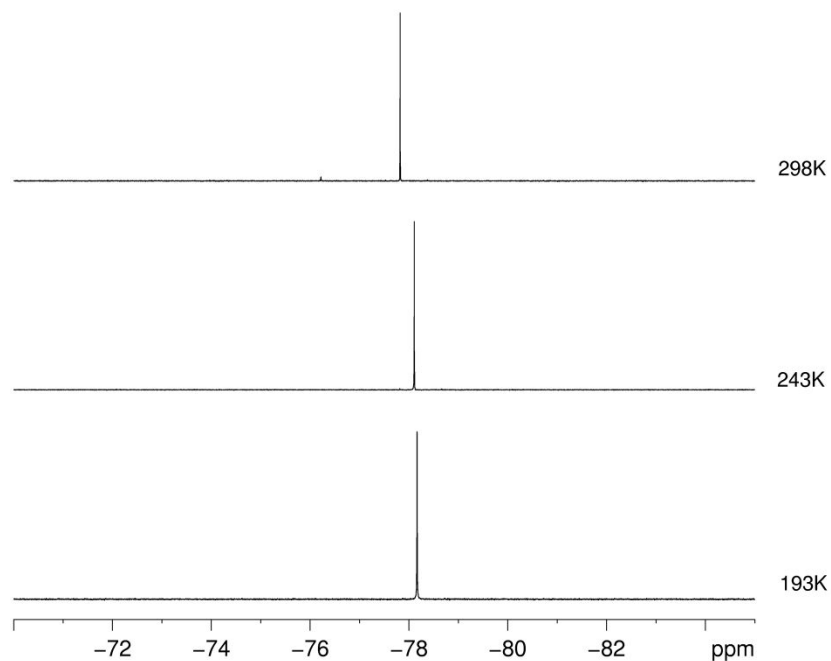


Figure S8. ^1H NMR spectrum of $[\text{Ru}(\text{OTf})_2(\kappa^3\text{-PP}_3^{\text{CyH}})]^+\text{OTf}^-$ **7** (CD_2Cl_2 , 400 MHz).

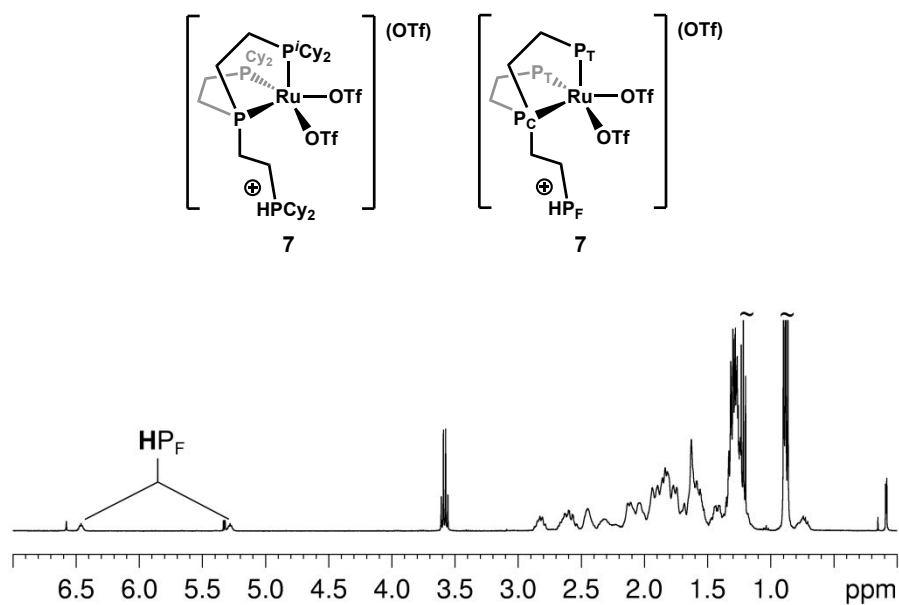


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ru}(\text{OTf})_2(\kappa^3\text{-PP}_3^{\text{CyH}})]^+\text{OTf}^-$ **7** (CD_2Cl_2 , 162 MHz).

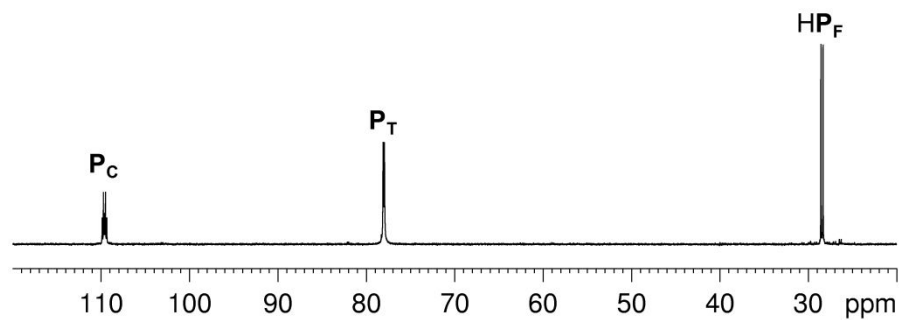


Figure S10. ^{19}F NMR spectra of $[\text{Ru}(\text{OTf})_2(\kappa^3\text{-PP}_3^{\text{CyH}})]^+\text{OTf}^-$ **7** (CD_2Cl_2 , 376 MHz).

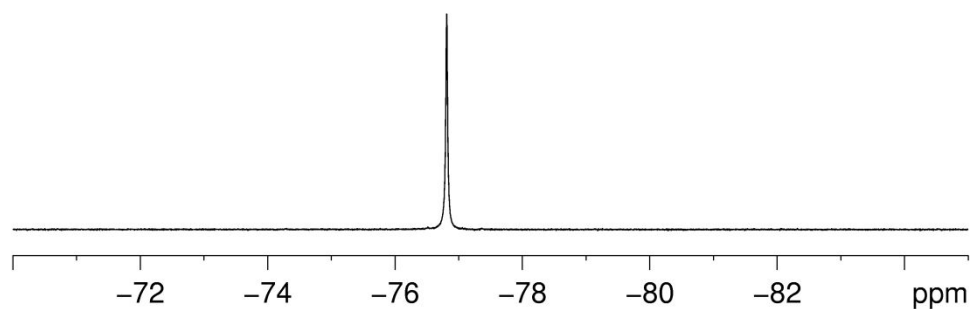


Figure S11. Reaction of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2** with TfOH in benzene. ^1H NMR spectrum of mixture of $[\text{Ru}(\text{OTf})(\text{PP}_3^{\text{Cy}})]^+\text{OTf}^-$ **6** and $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{\text{Cy}}\text{H})]^{3+}(\text{OTf})_3^-$ **8** (CD_3OD , 400 MHz).

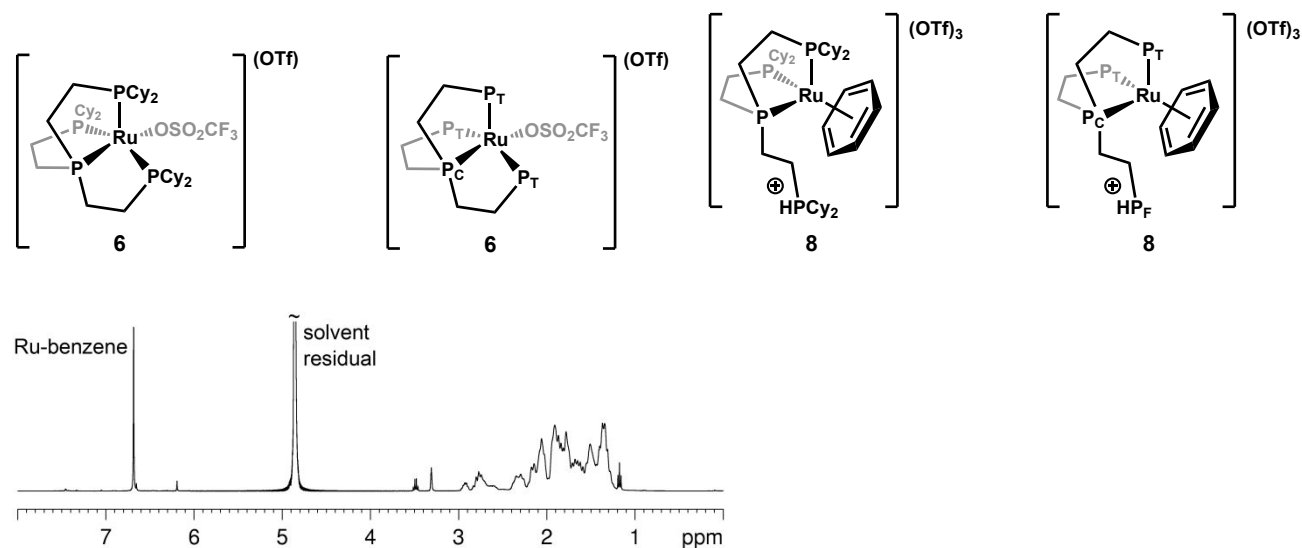


Figure S12. Reaction of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2** with TfOH in benzene. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of mixture of $[\text{Ru}(\text{OTf})(\text{PP}_3^{\text{Cy}})]^+\text{OTf}^-$ **6** and $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{\text{Cy}}\text{H})]^{3+}(\text{OTf})_3^-$ **8** (CD_3OD , 162 MHz).

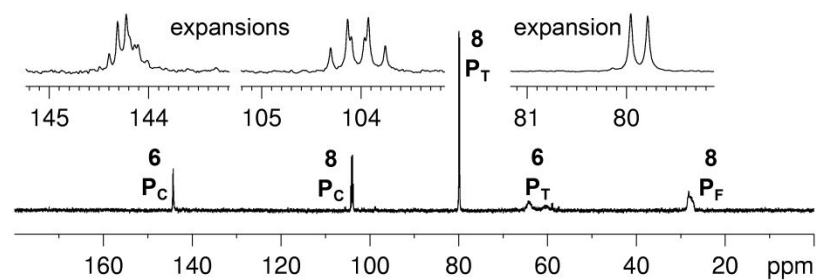


Figure S13. Reaction of $[\text{Ru}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **2** with TfOH in benzene. ^{19}F NMR spectrum of mixture of $[\text{Ru}(\text{OTf})(\text{PP}_3^{\text{Cy}})]^+\text{OTf}^-$ **6** and $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{\text{Cy}}\text{H})]^{3+}(\text{OTf})_3^-$ **8** (CD_3OD , 565 MHz).

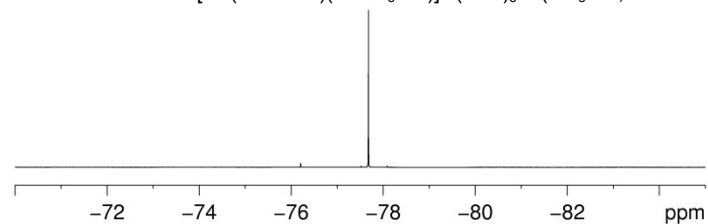


Figure S14. ^1H NMR spectrum of $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{\text{P}^{\text{r}}\text{H}})]^{3+}(\text{OTf})_3$ **5** (CD_3COCD_3 , 400 MHz).

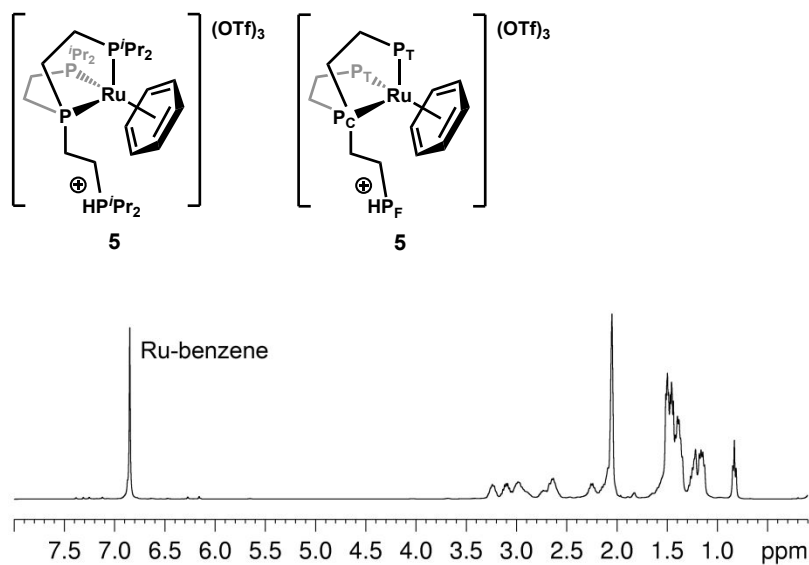


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{\text{P}^{\text{r}}\text{H}})]^{3+}(\text{OTf})_3$ **5** (CD_3COCD_3 , 162 MHz).

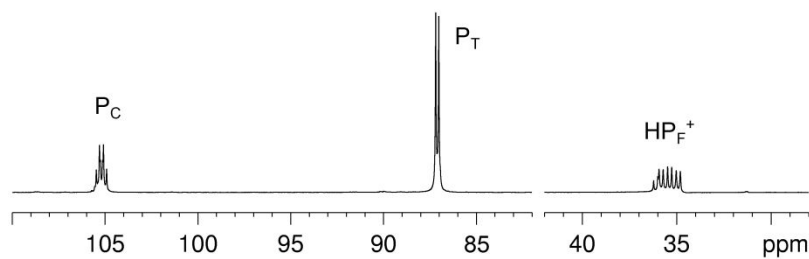


Figure S16. ^{19}F NMR spectrum of $[\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{\text{P}^{\text{r}}\text{H}})]^{3+}(\text{OTf})_3$ **5** (CD_3COCD_3 , 565 MHz).

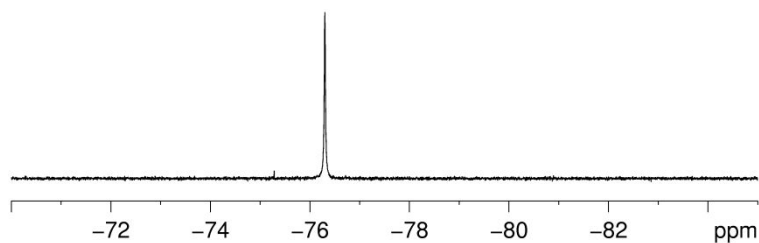
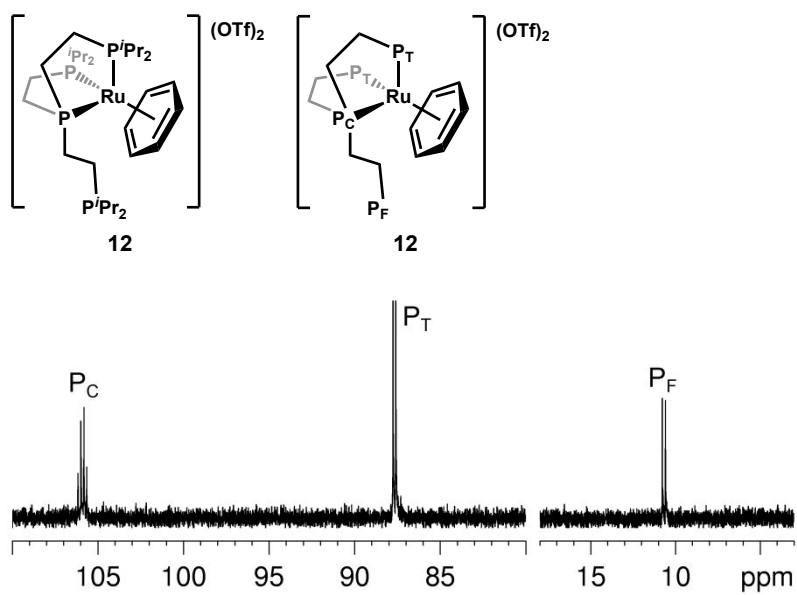


Figure S17. ^{31}P NMR spectrum of $\text{Ru}(\text{benzene})(\kappa^3\text{-PP}_3^{\text{iPr}})]^{2+}(\text{OTf})_2$ **12** (CH_3COCH_3 , 162 MHz).



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