Supporting Information

Tri(pyridylmethyl)phosphine: The Elusive Congener of TPA Shows Surprisingly Different Coordination Behaviour

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General Remarks

All manipulations of moisture and/or air sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques. Conventional nitrogen atmosphere glove boxes were used for the preparation of analytical and spectroscopic samples as well as for the weighing and storage of air sensitive compounds.

Solvents

All solvents used for air/ moisture sensitive manipulations were stored in sealed glass ampoules under an atmosphere of nitrogen. Pentane and toluene were dried by passing through a cylinder containing commercially available Q-5 reactant (13 wt. % copper(II) oxide on alumina and activated alumina (pellets, 3 mm) under nitrogen pressure. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were dried by prolonged reflux under a nitrogen atmosphere over sodium benzophenone ketyl. Dichloromethane (DCM) and acetonitrile (MeCN) were refluxed over calcium hydride. All solvents were freshly distilled under nitrogen and degassed by three freeze-thaw cycles prior to use. All NMR solvents, CD_2Cl_2, $CDCl_3$, C_6D_6 (benzene) and C_7D_8 (toluene) were degassed by three freeze-thaw cycles and dried over 4 Å molecular sieves and stored under nitrogen in sealed glass ampoules. Pyridine (Py), methanol (MeOH) and dimethylsulfoxide (DMSO) were purchased pre-dried from Sigma Aldrich and degassed by three freeze-thaw cycles prior to use and stored under nitrogen in sealed glass ampoules.

Starting Materials

$[RuCl_2(p\text{-cymene})]_2$ (*p*-cymene = 4-isopropyltoluene) was purchased from Sigma Aldrich and used without further purification. $P(SiMe_3)_3$ was kindly donated by Prof. G. Cloke, University of Sussex. 2-(Trimethylsilylmethyl)pyridine was prepared according to the method described by Kermagoret.[1] All other reagents were purchased from commercial sources and used without further purification unless stated.

Analytical Details

NMR spectra were recorded at ambient temperature on a Bruker AV-400 spectrometer unless stated. ^1H NMR spectra were referenced internally to the residual protio impurity of

the deuterated solvent and ^{13}C NMR spectra were referenced internally to the ^{13}C shift of the solvent. ^{19}F NMR spectra were referenced externally to $CFCl_3$ at 0 ppm. ^{31}P NMR spectra were referenced externally to 85 % H_3PO_4 in H_2O. The ^{13}C NMR spectra were all proton decoupled. The following abbreviations have been used to describe the multiplicities of the NMR signals: s (singlet), d (doublet), t (triplet), dd (double doublet), dt (double triplet), br (broad) and m (multiplet).

Elemental analyses were performed by Mr. S. Boyer of the microanalysis service of the London Metropolitan University.

Mass spectra were obtained using electrospray ionisation (ESI), chemical ionisation (CI) or liquid secondary ion mass spectrometry (LSIMS) on either a VG Autospec or VG Platform II spectrometer by Mr. J. Barton.

Crystallographic data were collected and solved by Dr. A. White of Imperial College London.

GC analysis was undertaken using an Agilent 6890 Series GC System equipped with a HP-5 column (30 m x 0.32 mm, film thickness 0.25 μm). Toluene was used as the internal standard for quantitative analysis.

Cyclic voltammetry studies were performed using an ADInstruments MacLab/2E potentiostat equipped with a platinum disc working electrode, a platinum wire ancillary electrode and an Ag/AgCl (1.0 M KCl) reference electrode. In all cases the electrolyte used was tetrabutylammonium hexafluorophosphate (0.1 M). All experiments were carried out under nitrogen, using distilled and degassed acetonitrile.

Synthesis of Ligands

Tetra(pyridylmethyl)phosphonium chloride

To a solution of freshly prepared picolyl choride (1.49 g, 11.7 mmol) in dichloromethane (25 mL) was slowly added tris(trimethylsilyl)phosphine (0.98 g, 3.9 mmol) at -78 ^{o}C. The

mixture was allowed to slowly warm to room temperature and stirred for a further 48 hours. The solvent was removed under vacuum to leave a red oil which was washed with diethyl ether. The resulting red solid was further washed with a mixture of dichloromethane and diethyl ether to yield a pale pink powder (396 mg, 33.0 %, based on picolyl chloride).
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.28 (t, 3H, $^{3}J_{HH}$ = 4.5, PyH), 7.51 (t, 3H, $^{3}J_{HH}$ = 7.1, PyH), 7.45 (d, 3H, $^{3}J_{HH}$ = 7.7, PyH), 7.08 (d, 3H, $^{3}J_{HH}$ = 6.1, PyH), 4.71 (d, 6H, $^{2}J_{HP}$ = 16.0, PCH_2). ^{31}P NMR (400 MHz, $CDCl_3$, 298 K): δ 32.55 (s). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K): δ 151.44 (d, $^{3}J_{CP}$ = 8.5), 148.87, 137.05, 125.53 (d, $^{2}J_{CP}$ = 7.8), 122.34 (Aromatic C), 30.50 (d, $^{1}J_{CP}$ = 48.4) (CH_2). ^{31}P NMR {^{1}H} (400 MHz, $CDCl_3$, 298 K): 32.55 (s). MS (ESI): *m/z* = 399, $[M -Cl]^+$, Elemental analysis for $C_{24}H_{24}ClN_4P$ (F.W. 434.9): C, 66.28; H, 5.58; N, 12.88%. Found C, 66.16; H, 5.47; N, 12.78 %.

Tri(pyridylmethyl)phosphine, (TPPh)

To a solution of phosphorus trichloride (1.41 ml, 16.1 mmol) in tetrahydrofuran (10 mL) at –78 ^{o}C was slowly added picolyltrimethylsilane (8.0g g, 48.4 mmol) in tetrahydrofuran (10 mL) and diethylether (10 mL). The solution was allowed to warm to room temperature and stirred overnight. After stirring, the resulting precipitate was filtered and the solvent removed from the filtrate. The resultant orange residue was triturated with diethylether (3 x 30 mL) and a yellow solid was extracted with boiling diethylether. After cooling large pale yellow crystals were obtained (3.76 g, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.51 (dd, 3H, $^{3}J_{HH}$ = 4.9, $^{4}J_{HH}$ = 1.8, PyH), 7.57 (td, 3H, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = 1.8, PyH), 7.26 (dd, 3H, $^{3}J_{HH}$ = 7.6, $^{4}J_{HH}$ = 0.8, PyH), 7.09 (m, 3H, PyH), 3.12 (d, 6H, $^{2}J_{HP}$ = 1.2, PCH_2). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K): δ 158.48 (d, $^{3}J_{CP}$ = 4.6), 149.20, 136.25, 123.90 (d, $^{2}J_{CP}$ = 4.8), 120.87 (Aromatic C), 35.81 (d, $^{1}J_{CP}$ = 20.8) (CH_2). ^{31}P NMR{^{1}H} (400 MHz, $CDCl_3$, 298 K): -13.03 (s). MS (CI): *m/z* = 308, $[M +H]^+$, Elemental analysis for $C_{18}H_{18}N_3P$ (F.W. 307.3): C, 70.35; H, 5.90; N, 13.67%. Found C, 70.21; H, 5.79; N, 13.59 %. Mp. 81 ˚C.

N,N',N''-Trimethyl-tri(pyridylamino)phosphine (**TPAMP**): To a solution of 2-(N-methylamino)pyridine (3.06 g, 28.3 mmol) in 20 ml THF was added KH (1.2 g, 30 mmol) and the mixture was stirred at room temperature overnight. The suspension was filtered to remove excess KH and to the clear solution was added a solution of PCl_3 (1.3 g, 9.4 mmol) in 10 ml THF. After the addition 20 ml of dichloromethane was added to dissolve the product.

The mixture was filtered through celite to remove KCl and after evaporation of the solvent in vacuum, the product was obtained as a white powder, which can be purified by precipitation from a dichloromethane/pentane mixture. Yield: 1.78 g (54 %). ^{1}H-NMR ($CDCl_3$): δ 8.18 (dd, 3H, PyrH_6), 7.49 (dt, 3H, PyrH_4), 6.88 (d, 3H, PyrH_5), 6.73 (dd, 3H, PyrH_3), 3.00 (d, 9H, J_{HP} = 2 Hz, CH_3). ^{13}C-NMR ($CDCl_3$): δ 158.9 (d, J = 31 Hz, C_{ipso}), 147.7, 137.1, 114.7, 108.9 (d, J = 20 Hz), 31.2 (d, J = 7 Hz). ^{31}P-NMR ($CDCl_3$): δ 96.8. MS (+FAB): m/z (%) 352 (15) $[M]^+$, 245 (100) $[M–PyrNMe]^+$. Elemental analysis for $C_{18}H_{21}N_6P$ (F.W. 352.4): C, 61.35; H, 6.01; N, 23.85%. Found C, 61.23; H, 5.95; N, 23.79 %.

Synthesis of Metal Complexes

[Cr(TPPh)Cl_3]

The ligand TPPh (135 mg, 0.43 mmol) and $CrCl_3$·3THF were combined in THF (20 mL) and stirred for 16 hours at room temperature. A navy blue precipitate had formed, which was filtered and dried under vacuum. Yield: 150 mg (75%). Single crystals were obtained by layering a solution of the complex in DMF with diethyl ether.

IR (KBr, cm^{-1}): 3447, 3067, 2942, 1604, 1590, 1565, 1473, 1435, 1385, 1310, 1263, 1160, 1105, 1059, 1020, 996, 903, 867, 833, 767, 668, 647, 472. MS (LSIMS): m/z 429 (M^+-Cl, 30 %) and 394 (M+ - 2Cl, 8%). Elem. Anal. calcd. for $C_{18}H_{18}Cl_3CrN_3P$: C, 46.42; 3.90; N, 9.02. Found: 46.49; H, 3.90; N; 8.96.

[Fe(TPPh)$_2$][$FeBr_4$]

To a solution of iron(II) bromide (281 mg, 1.3 mmol) in 10 mL of acetonitrile was added a solution of TPP (400 mg, 1.3 mmol) in 10 mL of acetonitrile. The solution was stirred overnight to yield an orange solution. The solvent was reduced by three quarters under vacuum and 30 mL of diethylether was added. The resulting orange precipitate was filtered and the resultant solid dried under vacuum to yield an orange powder (410 mg, 60 %). Crystals suitable for single crystal X-ray crystallography were obtained by slow diffusion of diethylether into a concentrated acetonitrile solution of the complex.

^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.58 (br s, 1H), 8.33 (br s, 1H), 7.87 (br s, 1H), 7.85 (br s, 1H), 7.29 (m, 5H), 6.88 (br s, 1H), 6.67 (br s, 1H), 4.14 (br s, 1H), 4.08 (br s, 1H), 3.59

(m, 3H), 3.32 (br s, 1H). ^{31}P NMR {^{1}H} (CD_3CN, 298 K): δ 96.38 (s). MS (LSIMS): *m/z* = 670, $[M]^+$. Elemental analysis for $C_{36}H_{36}N_6P_2Fe_2Br_4$ (F.W. 1046.0): C, 41.34; H, 3.47; N, 8.03 %. Found C, 41.43; H, 3.38; N, 7.92 %.

$[Fe(TPAMP)_2]OTf_2$

To a mixture of the ligand TPAMP (0.310 g, 0.88 mmol) and $Fe(OTf)_2 \cdot 2CH_3CN$ (0.383 g, 0.88 mmol) was added THF at room temperature. Immediately, a red solution is formed and a solid starts to precipitate after a few minutes. The solution is reduced to 5 mL and the solid is filtered and washed with diethyl ether. The product, an orange solid, is dried under vacuum. Yield: 0.25 g (54 %, based on TPAMP). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.21 (d, 1H), 8.09 (t, 1H), 7.76 (t, 1H), 7.69 (t, 1H), 7.24 (d, 1H), 7.19 (t, 1H), 7.10 (br s, 2H), 6.84-6.78 (m, 3H), 6.64 (br s, 1H), 3.00 (s, 6H, NMe), 2.93 (s, 3H, NMe). ^{31}P NMR {^{1}H} (CD_2Cl_2, 298 K): δ 196.3 (s). ^{19}F NMR (CD_2Cl_2, 298 K): δ -78.8 (s). Elemental analysis for $C_{38}H_{42}N_{12}P_2F_6O_6S_2Fe$ (F.W. 1058.74): C, 43.11; H, 4.00; N, 15.88 %. Found C, 43.22; H, 3.94; N, 15.79 %.

Attempted synthesis of $[Fe(TPAMP)Cl_3]$

A mixture of $FeCl_3$ (0.108 g, 0.67 mmol) and TPAMP (0.234 g, 0.66 mmol) in DCM was stirred at room temperature over night. The initially dark brown solution had turned bright red. The solution was filtered, reduced and the product precipitated with hexane, washed and dried under vacuum. Yield 0.20 g (58%). Elemental analysis for $C_{18}H_{21}N_6PCl_3Fe$ (F.W. 514.58): Calc.: C, 42.01; H, 4.11; N, 16.33 %. Found: C, 41.89; H, 4.15; N, 16.25 %. MS (FAB): *m/z* = 515 (10) $[M]^+$, 443 (30) $[M\text{-}2Cl]^+$.

Crystals suitable for x-ray diffraction analysis were obtained from a DCM/pentane solution and analysed as a mixed iron(II/III) complex **$[Fe(TPAMP)_2][FeCl_4]_2$**.

Attempted synthesis of [Ru(TPA)(MeCN)Cl]Cl

To a suspension of $[RuCl_2(p\text{-cymene})]_2$ (316 mg, 0.52 mmol) in acetonitrile (10 mL) was added a solution of TPA (300 mg, 1.03 mmol) in acetonitrile (10 mL). The suspension was refluxed overnight resulting in a red solution. The solvent was removed under vacuum and the red oil was dissolved in dichloromethane (5 mL) and precipitated with pentane (30 mL) and filtered. The washing procedure was carried out three times and the solid was dried

under vacuum to yield a yellow powder (382 mg, 68 %). Due to the multiple species present in this sample we have been unable to characterise the product by ^{1}H NMR, elemental analysis or mass spectrometry. Crystals suitable for single crystal X-ray crystallography of a [Ru(TPA)Cl_2] were obtained from a concentrated dichloromethane solution of the complex.

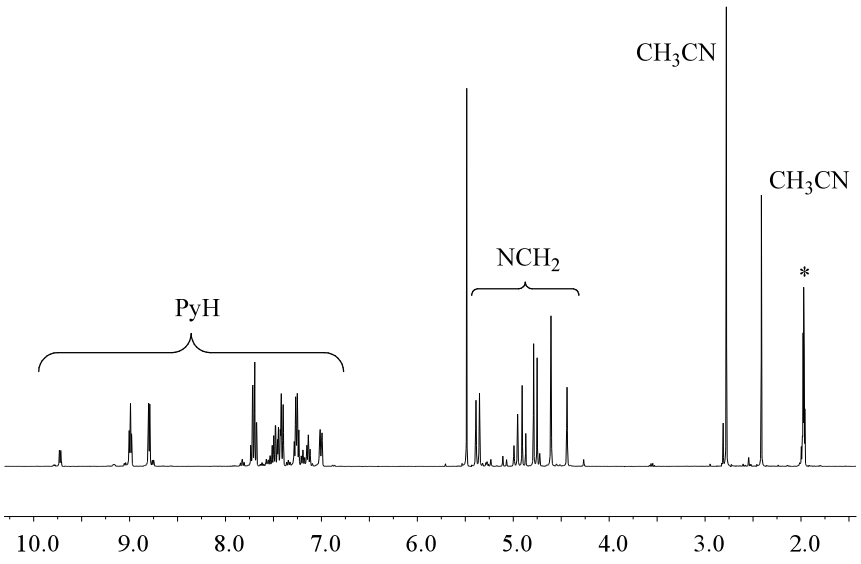

Figure S1. Initial ^{1}H NMR spectrum of the product from the attempted synthesis of [Ru(TPA)(MeCN)Cl]Cl in CD_3CN at 298 K (* residual protio impurity).

[Ru(TPA)(MeCN)$_2$](SbF$_6$)$_2$

To $AgSbF_6$ (710 mg, 2.07 mmol), TPA (300 mg, 103 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (316 mg, 0.52 mmol) was added acetonitrile (25 mL). The suspension was refluxed overnight in the dark. The suspension was filtered to remove most of the silver chloride formed overnight and the solvent removed. Dichloromethane (10 mL) was added followed by pentane (25 mL) and the mixture was filtered - this washing procedure was repeated 3 times. The solid was dissolved in acetonitrile (20 mL) and filtered to remove the remaining silver chloride. The solvent was removed from the filtrate and dichloromethane (10 mL) was added followed by pentane (25 mL). The precipitate was filtered and dried to yield a yellow powder (830 mg,

85 %). Crystals suitable for single crystal X-ray crystallography were obtained by slow diffusion of diethylether into a concentrated acetonitrile solution of the complex.

^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.99 (d, 1H, $^{3}J_{HH}$ = 5.7, PyH), 8.71 (d, 2H, $^{3}J_{HH}$ = 5.2, PyH), 7.83 (td, 2H, $^{3}J_{HH}$ = 6.4, $^{4}J_{HH}$ = 1.5, PyH), 7.63 (td, 1H, $^{3}J_{HH}$ = 7.8, $^{4}J_{HH}$ = 1.4, PyH), 7.51 (d, 2H, $^{3}J_{HH}$ = 7.8, PyH), 7.35 (t, 2H, $^{3}J_{HH}$ = 6.6, PyH), 7.26 (t, 1H, $^{3}J_{HH}$ = 6.0, PyH), 7.08, (d, 1H, $^{3}J_{HH}$ = 7.8, PyH), 5.02 (d, 2H, $^{2}J_{HH}$ = 15.5, NCH_2), 4.93 (d, 2H, $^{2}J_{HH}$ = 15.5, NCH_2), 4.60 (s, 2H, NCH_2), 2.75 (s, 3H, MeCN), 2.34 (s, 3H, MeCN). ^{13}C NMR (400 MHz, CD_3CN, 298 K): δ 162.89, 161.89 (CH_3CN), 153.26, 152.02, 137.84, 137.20, 124.89, 124.07, 123.05, 120.26 (Aromatic C), 69.70, 68.33 (CH_2), 4.16, 3.81 (CH_3CN). MS (LSIMS): *m/z* = 709, $[M - SbF_6]^+$, 668, $[M - SbF_6 - MeCN]^+$, 627, $[M - SbF_6 - 2MeCN]^+$. Elemental analysis for $C_{22}H_{24}N_6RuSb_2F_{12}$ (F.W. 945.0): C, 27.96; H, 2.56; N, 8.89%. Found C, 28.04; H, 2.51; N, 8.87 %.

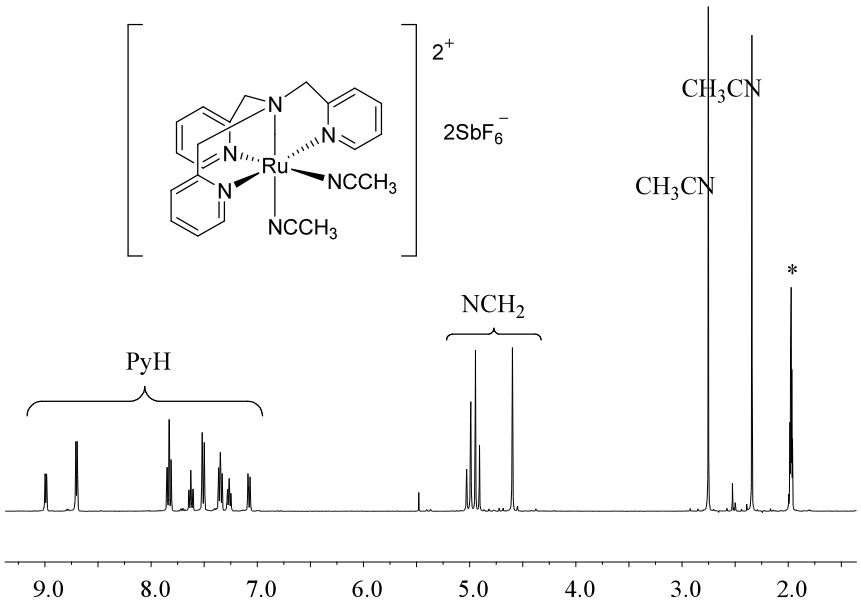

Figure S2. ^{1}H NMR spectrum of $[Ru(TPA)(MeCN)_2](SbF_6)_2$ in CD_3CN at 298 K.

[Ru(TPPh)(MeCN)$_2$Cl]Cl

To a suspension of $[RuCl_2(p\text{-cymene})]_2$ (339 mg, 0.55 mmol) in acetonitrile (10 mL) was added a solution of TPPh (340 mg, 1.11 mmol) in acetonitrile (10 mL). The suspension was refluxed overnight resulting in a yellow solution. The solvent was removed under vacuum and the orange oil was dissolved in dichloromethane (5 mL) and precipitated with pentane

(30 mL) and filtered. The washing procedure was carried out three times and the solid was dried under vacuum to yield a pale yellow powder (418 mg, 79 %).

^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 9.87 (dd, 2H, $^{3}J_{HH}$ = 5.8, $^{4}J_{HH}$ = 1.2, PyH), 8.62 (d, 1H, $^{3}J_{HH}$ = 4.1, PyH), 7.87 (br s, 1H, PyH), 7.62 (m, 3H, PyH), 7.44 (d, 2H, $^{3}J_{HH}$ = 7.8, PyH), 7.35 (br s, 1H, PyH), 7.14 (t, 2H, $^{3}J_{HH}$ = 6.6, PyH), 4.14 (br m, 4H, PCH_2), 3.80 (dd, 2H, $^{2}J_{HH}$ = 14.5, $^{2}J_{HP}$ = 18.3, PCH_2) 2.25 (s, 6H, MeCN). ^{13}C NMR (400 MHz, CD_3CN, 298 K): δ 163.67 (CH_3CN), 154.11, 136.71, 125.46, 123.59 ($^{2}J_{CP}$ = 12.0), 122.26 (Aromatic C), 38.62 ($^{1}J_{CP}$ = 27.4) (CH_2), 3.74 (CH_3CN) (the acetonitrile ligand *trans* to the phosphine donor has exchanged with the solvent during measurement). ^{31}P NMR {^{1}H} (400 MHz, CD_3CN, 298 K): δ 88.70 (s). MS (LSIMS): *m/z* = 526, $[M - Cl]^+$, 485, $[M - Cl - MeCN]^+$, 444, $[M - Cl - 2MeCN]^+$. Elemental analysis for $C_{22}H_{24}N_5PRuCl_2$ (F.W. 561.4): C, 47.07; H, 4.31; N, 12.47 %. Found C, 46.97; H, 4.22; N, 12.34 %.

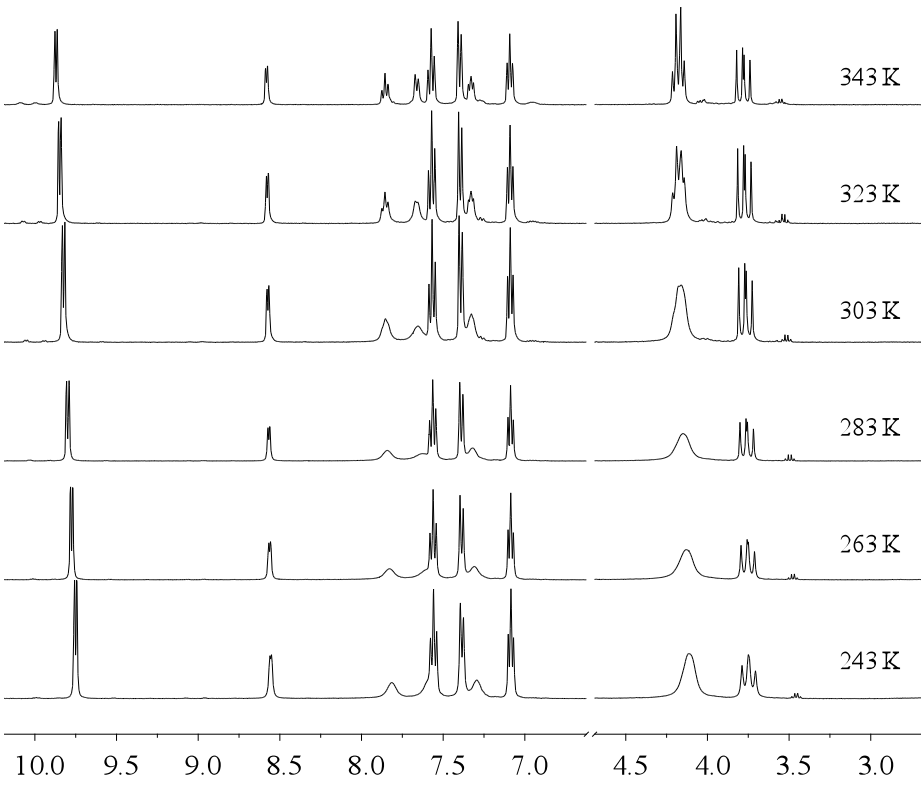

Figure S3. Variable temperature ^{1}H NMR study of $[Ru(TPPh)(MeCN)_2Cl]Cl$ in CD_3CN.

$[Ru(TPPh)(MeCN)_3](SbF_6)_2$

To $AgSbF_6$ (248 mg, 0.72 mmol) and $[Ru(TPPh)(MeCN)_2Cl]Cl$ (200 mg, 0.36 mmol) was added acetonitrile (25 mL). The suspension was stirred overnight in the dark. The solvent was removed, dichloromethane (10 mL) was added and the mixture was filtered. The product was precipitated from the filtrate by addition of pentane (20 mL) to yield a pale yellow powder (314 mg, 88 %). Crystals suitable for single crystal X-ray crystallography were obtained by slow diffusion of diethylether into a concentrated acetonitrile solution of the complex.

^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.95 (dd, 2H, $^3J_{HH}$ = 5.8, $^4J_{HH}$ = 0.9, PyH), 8.62 (d, 1H, $^3J_{HH}$ = 4.6, PyH), 7.87 (td, 1H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.7, PyH), 7.73 (m, 2H, PyH), 7.50 (d, 3H, $^3J_{HH}$ = 7.8, PyH), 7.37 (m, 1H, PyH), 7.22 (t, 2H, $^3J_{HH}$ = 6.6, PyH), 4.14 (dd, 2H, $^2J_{HH}$ = 18.4, $^2J_{HP}$ = 10.9, PCH_2), 4.05 (d, 2H, $^2J_{HP}$ = 12.6, PCH_2), 3.87 (dd, 2H, $^2J_{HH}$ = 18.4, $^2J_{HP}$ = 14.7, PCH_2), 2.53 (s, 3H, MeCN), 2.23 (s, 6H, MeCN). ^{13}C NMR (400 MHz, CD_3CN, 298 K): δ 163.34 (CH_3CN), 153.61, 149.64, 137.86, 137.49, 126.34, 124.78 ($^2J_{CP}$ = 4.8), 124.48 ($^2J_{CP}$ = 12.1), 122.63 (Aromatic C), 38.34 ($^1J_{CP}$ = 29.4), 32.84 ($^1J_{CP}$ = 29.0) (CH_2), 3.42 (CH_3CN) (the acetonitrile ligand *trans* to the phosphine donor has partially exchanged with the solvent during measurement). ^{31}P NMR {^{1}H} (CD_3CN, 298 K): δ 86.2. MS (LSIMS): *m/z* = 726, $[M - SbF_6]^+$, 685, $[M - SbF_6 - MeCN]^+$, 644, $[M - SbF_6 - 2MeCN]^+$. Elemental analysis for $C_{24}H_{27}N_6PRuSb_2F_{12}$ (F.W. 1003.1): C, 28.74; H, 2.71; N, 8.38 %. Found C, 28.65; H, 2.62; N, 8.23 %.

[Ru(TPAMP)(MeCN)$_2$Cl]Cl

To a suspension of $[RuCl_2(p\text{-cymene})]_2$ (609 mg, 0.99 mmol) in acetonitrile (10 mL) was added a solution of TPAMP (700 mg, 1.99 mmol) in acetonitrile (10 mL). The suspension was refluxed overnight resulting in a brown solution. The solvent was removed under vacuum and the orange oil was dissolved in dichloromethane (5 mL) and precipitated with pentane (30 mL) and filtered. The washing procedure was carried out three times and the solid was dried under vacuum to yield a yellow powder (746 mg, 62 %).

^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 9.73 (dd, 2H, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 1.4, PyH), 8.21 (dd, 1H, $^3J_{HH}$ = 4.8, $^4J_{HH}$ = 1.6, PyH), 7.83 (td, 1H, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.7, PyH PyH), 7.77-7.67 (m, 2H, PyH), 7.35 (d, 1H, $^3J_{HH}$ = 8.4, PyH), 7.11 (m, 1H, PyH), 6.93-6.81 (m, 4H, PyH), 3.50 (d, 3H, $^3J_{HP}$ = 9.3, NCH_3), 3.15 (d, 6H, $^3J_{HP}$ = 5.7, NCH_3) 2.15 (s, 6H, MeCN). ^{13}C NMR (400 MHz, CD_3CN, 298 K): δ 161.33 (CH_3CN), 152.35, 147.83, 138.70, 138.51,

124.12, 124.00, 118.86, 115.70, 114.32 ($^2J_{CP}$ = 2.6), 109.13 ($^2J_{CP}$ = 9.9) (Aromatic C), 35.29 ($^2J_{CP}$ = 7.2), 31.98 ($^2J_{CP}$ = 5.2) (NCH_3), 3.05 (CH_3CN) (the acetonitrile ligand *trans* to the phosphine donor has exchanged with the solvent during measurement). ^{31}P NMR $\{^1H\}$ (400 MHz, CD_3CN, 298 K): δ 164.45 (s). MS (LSIMS): *m/z* = 571, $[M - Cl]^+$, 530, $[M - Cl - MeCN]^+$, 489, $[M - Cl - 2MeCN]^+$. Elemental analysis for $C_{22}H_{27}N_8PRuCl_2$ (F.W. 606.5): C, 43.57; H, 4.49; N, 18.48 %. Found C, 43.86; H, 4.43; N, 18.23 %.

$[Ru(TPAMP)(MeCN)_3](SbF_6)_2$

To $AgSbF_6$ (453 mg, 1.32 mmol) and $[Ru(TPAMP)(MeCN)_2Cl]Cl$ (400 mg, 0.66 mmol) was added acetonitrile (25 mL). The suspension was stirred overnight in the dark. The solvent was removed, dichloromethane (10 mL) was added and the mixture was filtered. The solvent was removed to yield a pale yellow powder (548 mg, 70 %).

^1H NMR (400 MHz, CD_3CN, 298 K): δ 8.75 (dd, 2H, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 1.3, PyH), 8.16 (dd, 1H, $^3J_{HH}$ = 4.7, $^4J_{HH}$ = 1.5, PyH), 7.92-7.84 (m, 1H, PyH), 7.83-7.77 (m, 2H, PyH), 7.38 (d, 1H, $^3J_{HH}$ = 8.4, PyH), 7.37 (qd, 1H, , $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 4.9, $^4J_{HP}$ = 0.7 PyH), 6.97 (m, 2H, PyH), 6.90 (d, 2H, $^3J_{HH}$ = 8.6, PyH), 3.50 (d, 3H, $^3J_{HP}$ = 9.5, NCH_3), 3.15 (d, 6H, $^3J_{HP}$ = 5.9, NCH_3), 2.17 (s, 3H, MeCN), 1.94 (s, 6H, MeCN (substituted by solvent)). ^{13}C NMR (400 MHz, CD_3CN, 298 K): δ 161.12 (CH_3CN), 151.95, 147.70, 139.56, 138.76, 124.95, 124.87, 119.30, 116.72, 114.56 ($^2J_{CP}$ = 3.4), 110.05 ($^2J_{CP}$ = 9.8) (Aromatic C), 35.46 ($^2J_{CP}$ = 6.5), 31.90 ($^2J_{CP}$ = 5.1) (NCH_3), 2.98 (CH_3CN) (the acetonitrile ligand *trans* to the phosphine donor has exchanged with the solvent during measurement). ^{31}P NMR $\{^1H\}$ (400 MHz, CD_3CN, 298 K): δ 165.10. MS (LSIMS): *m/z* = 771, $[M - SbF_6 - MeCN]^+$, 689, $[M - SbF_6 - 3MeCN]^+$. Elemental analysis for $C_{25}H_{30}N_9PRuSb_2F_{12}$ (F.W. 1048.1): C, 27.50; H, 2.89; N, 12.03 %. Found C, 27.56; H, 3.12; N, 12.01 %.

Oxidation Reactions

Oxidation of Ruthenium complexes using *meta*-chloroperoxybenzoic acid

To the complex (50 μmol) in acetonitrile (5 mL) was added 5 mL of an acetonitrile solution of *m*-CPBA (180 mg, 0.80 mmol, 8 mL). The reaction was stirred at room temperature and

followed by UV-Vis spectroscopy every 3 minutes in the case of $[Ru(TPA)(MeCN)_2](SbF_6)_2$, every 6 minutes in the case of $[Ru(TPPh)(MeCN)_3](SbF_6)_2$ and every 15 minutes in the case of $[Ru(TPAMP)(MeCN)_3](SbF_6)_2$.

Oxidation of cyclohexene

Oxidation of cyclohexene was carried out by the method described by Masuda and co-workers.[2] Cyclohexene (41 mg, 0.5 mmol) was mixed with either acetonitrile or chloroform (5 mL). To the solution was added freshly prepared iodosylbenzene (110 mg, 0.5 mmol) and complex (5 μmol) under a nitrogen atmosphere. The reaction mixture was heated to 40 ^{o}C for 4 hours and the products were then identified by GC-MS analysis using authentic samples to confirm identity.

Additional NMR Spectra

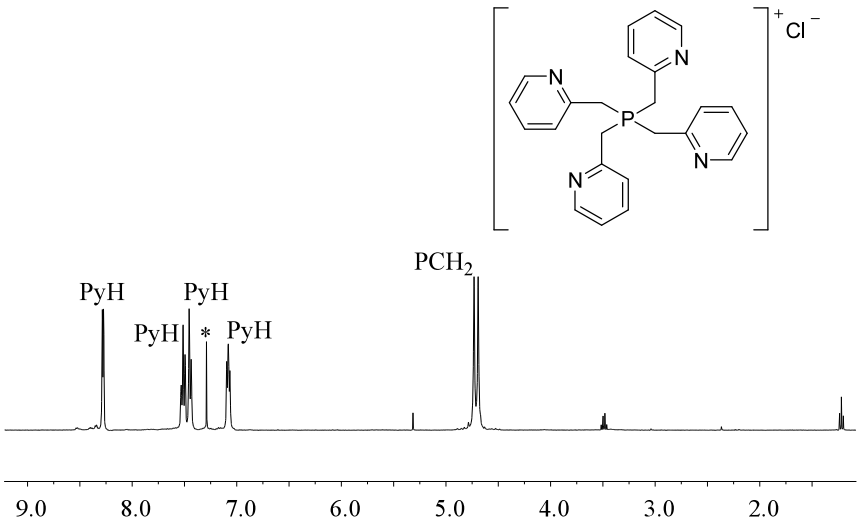

Figure S4. ^{1}H NMR spectrum of tetra(pyridylmethyl)phosphonium chloride in $CDCl_3$ (* residual protio impurity).

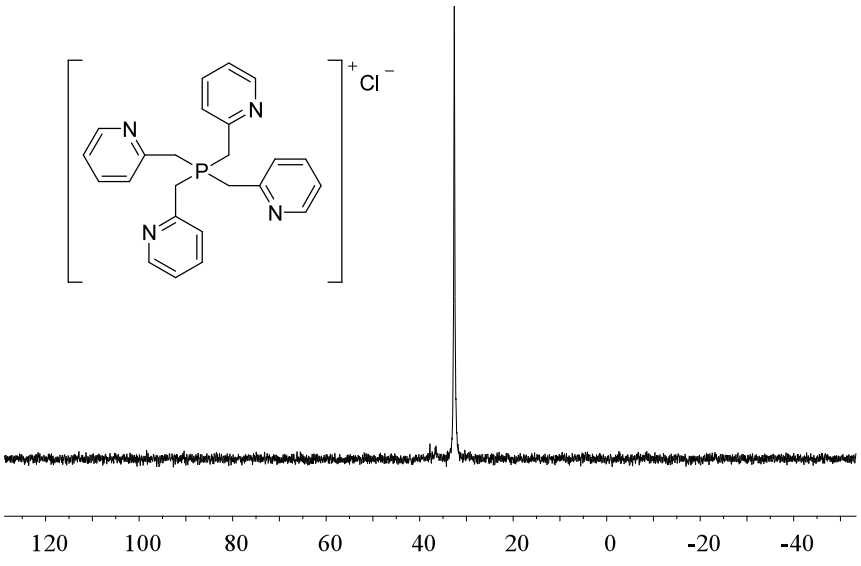

Figure S5. ^{31}P $\{^{1}H\}$ NMR spectrum of tetra(pyridylmethyl)phosphonium chloride in $CDCl_3$.

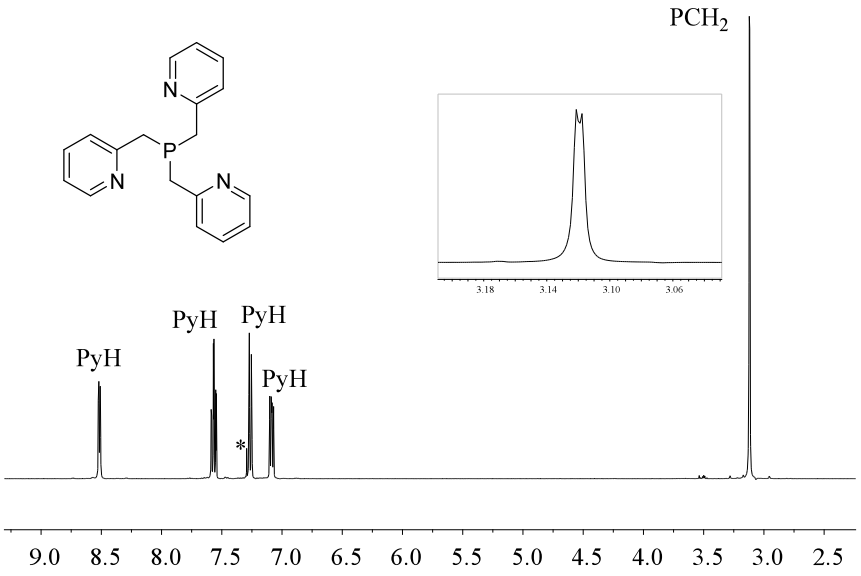

Figure S6. ^{1}H NMR spectrum of TPPh in $CDCl_3$ (* residual protio impurity).

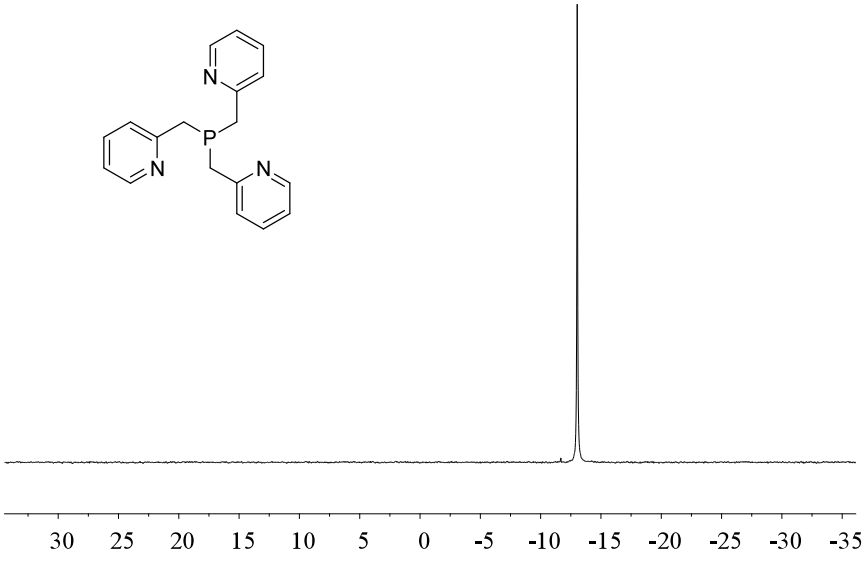

Figure S7. ^{31}P $\{^{1}H\}$ NMR spectrum of TPPh in $CDCl_3$.

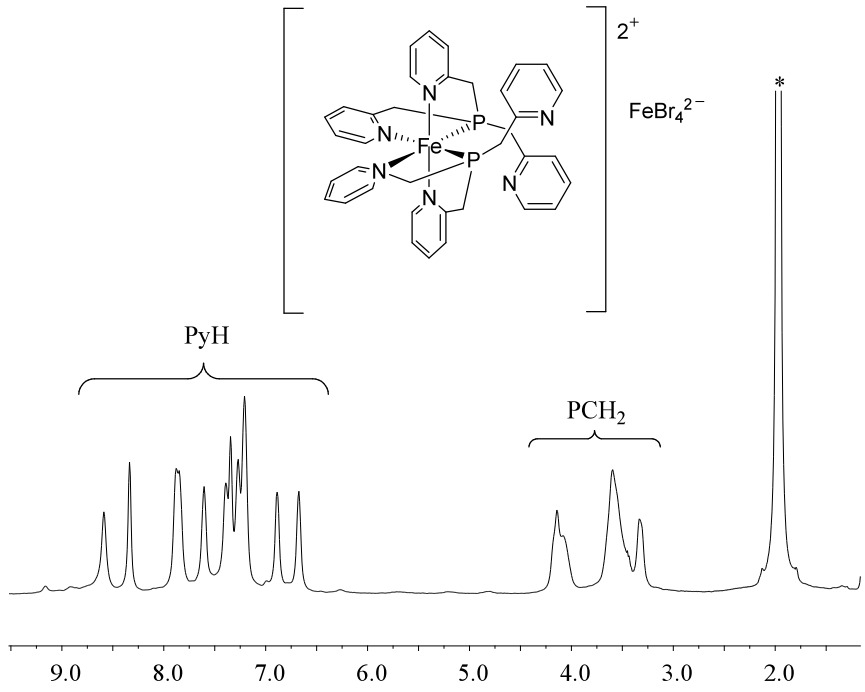

Figure S8. ^{1}H NMR spectrum of $[Fe(TPPh)_2][FeBr_4]$ in CD_3CN.

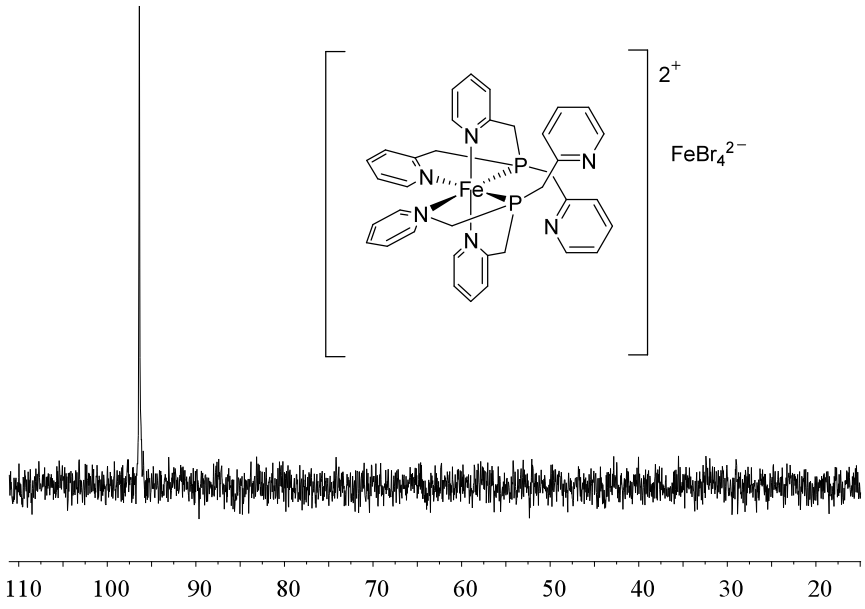

Figure S9. ^{31}P $\{^{1}H\}$ NMR spectrum of $[Fe(TPPh)_2][FeBr_4]$ in CD_3CN.

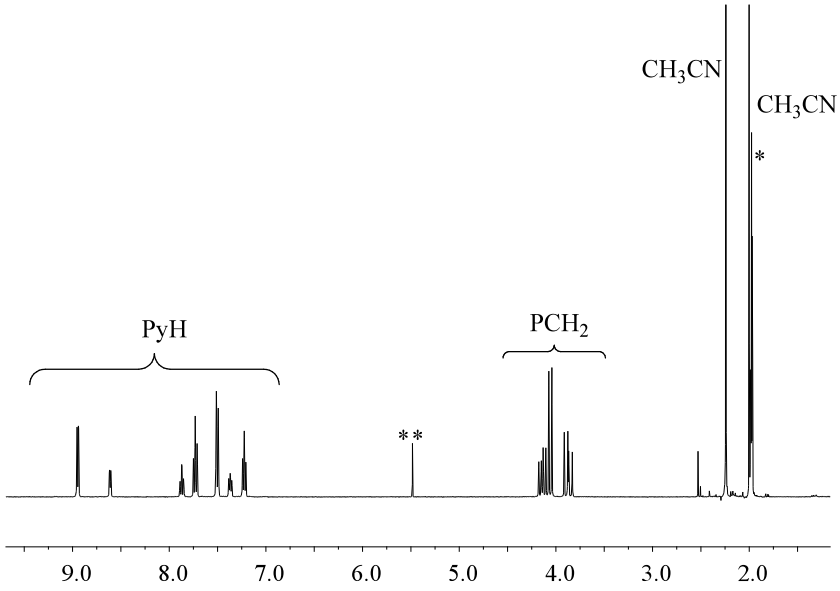

Figure S10. ^{1}H NMR spectrum of $[Ru(MeCN)_3(TPPh)](SbF_6)_2$ in CD_3CN at 298 K (* residual protio impurity, ** residual CH_2Cl_2 from synthesis).

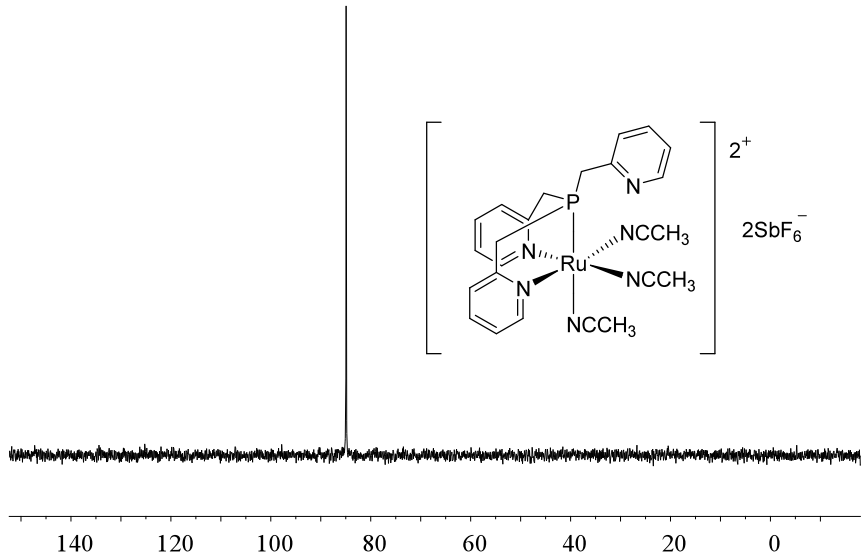

Figure S11. ^{31}P NMR spectrum of $[Ru(MeCN)_3(TPPh)](SbF_6)_2$ in CD_3CN at 298 K.

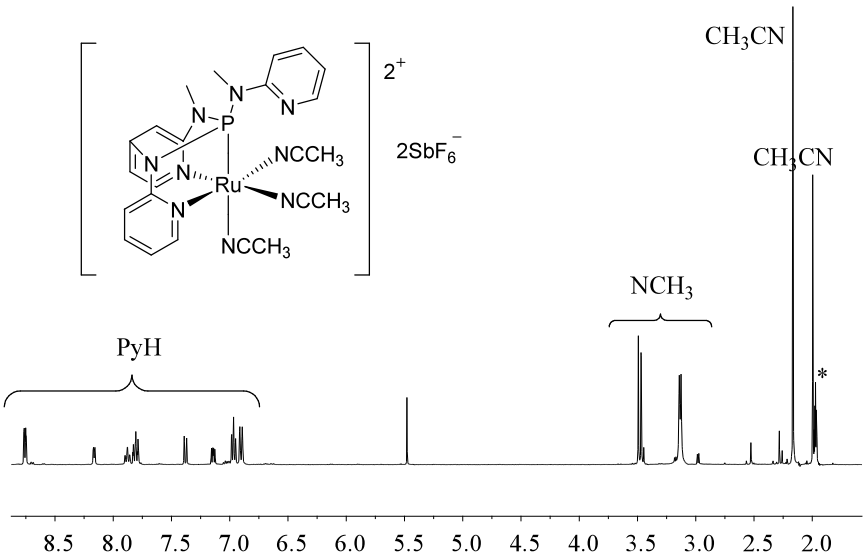

Figure S12. ^{1}H NMR spectrum of [Ru(TPAMP)(MeCN)$_3$](SbF$_6$)$_2$ in CD$_3$CN at 298 K (* residual protio impurity).

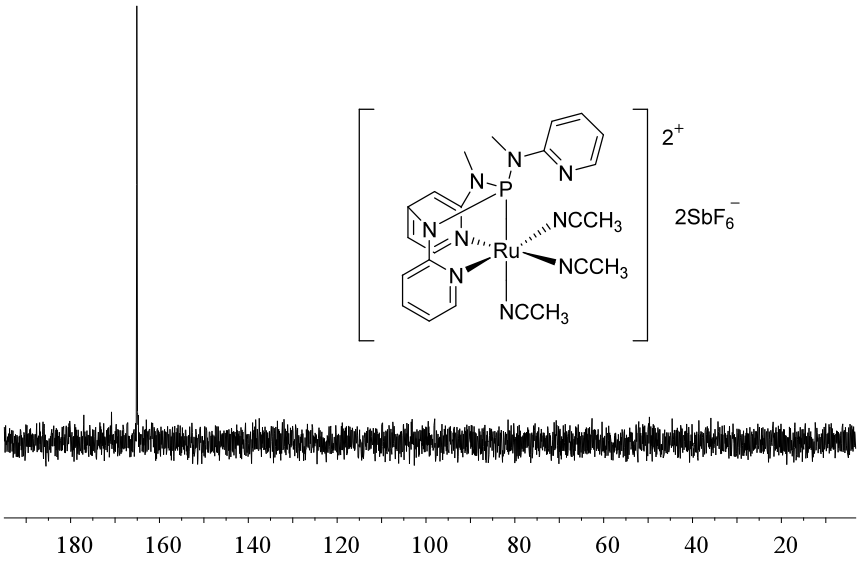

Figure S13. ^{31}P {^{1}H} NMR spectrum of [Ru(TPAMP)(MeCN)$_3$](SbF$_6$)$_2$ in CD$_3$CN at 298 K.

Cyclic Voltammetry Measurements

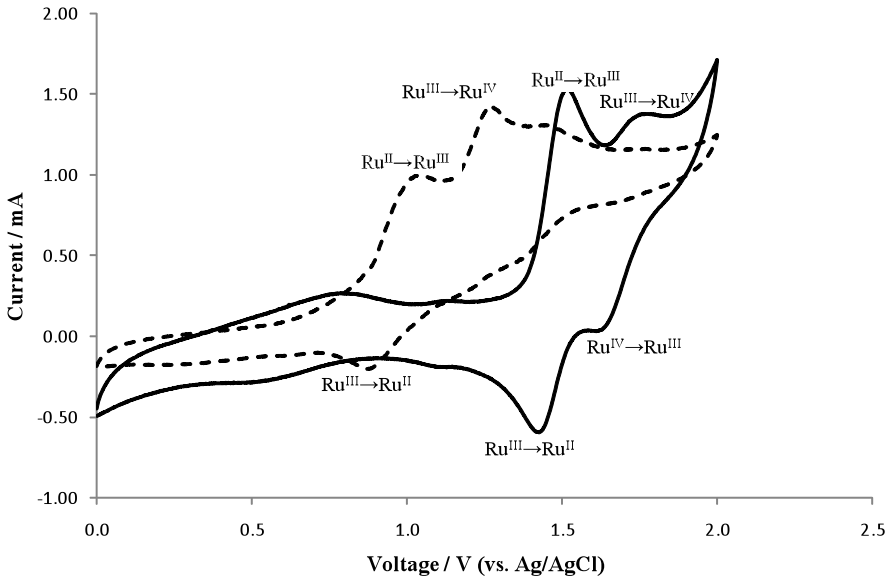

Figure S14. Cyclic voltammograms of $[RuCl(TPAMP)(MeCN)_2]Cl$ (- - -) and $[Ru(TPAMP)(MeCN)_3](SbF_6)_2$ (——) (1 mM in CH_3CN, 0.1 M $[NBu_4][PF_6]$ vs. Ag/AgCl).

UV-Vis Spectroscopy

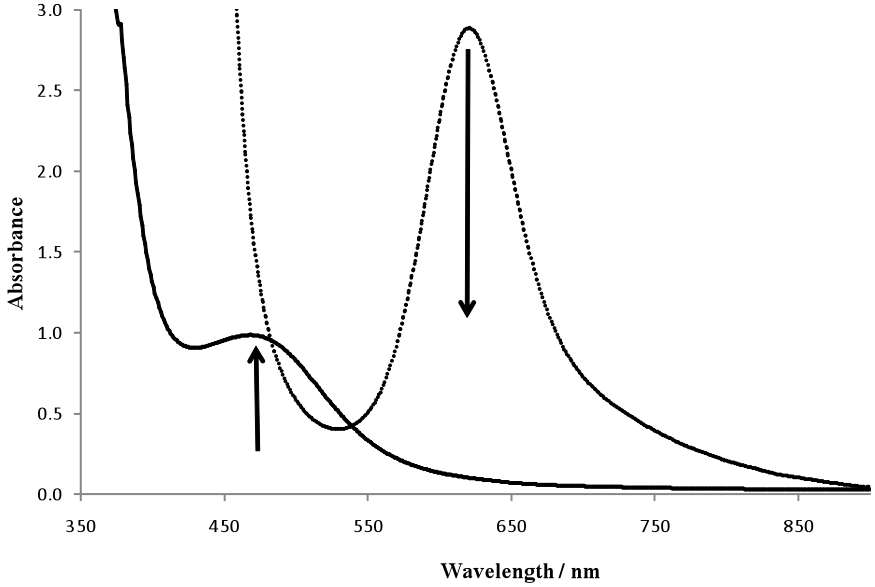

Figure S15. UV-Visible spectrum of complex $[Ru(TPA)(H_2O)_2](SbF_6)_2$ (c = 10 mM) before and after the addition of cerium(IV) ammonium nitrate in water (c=100 mM).

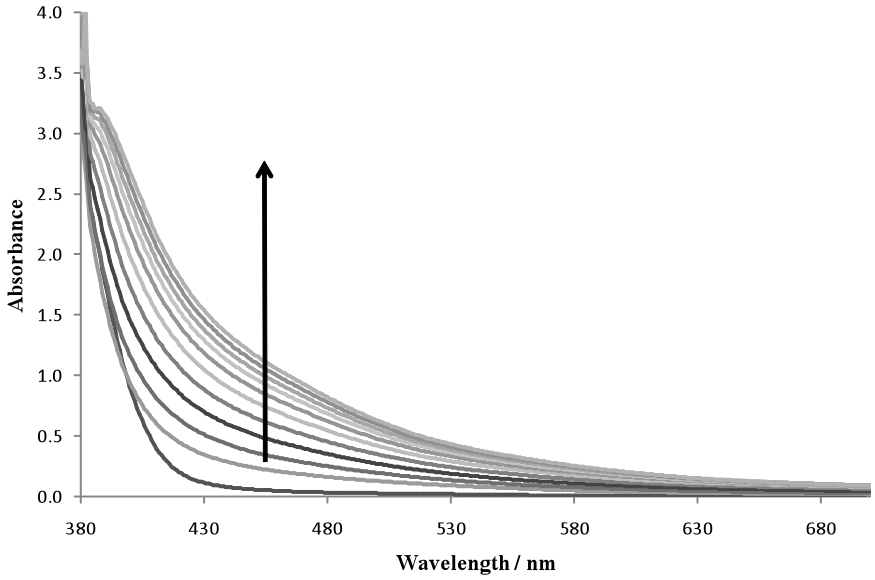

Figure S16. UV-Visible spectrum of $[Ru(MeCN)_3(TPPh)](SbF_6)_2$ (c = 5 mM) after addition of 10 equiv. of *m*-CPBA in acetonitrile. Readings taken every 6 minutes.

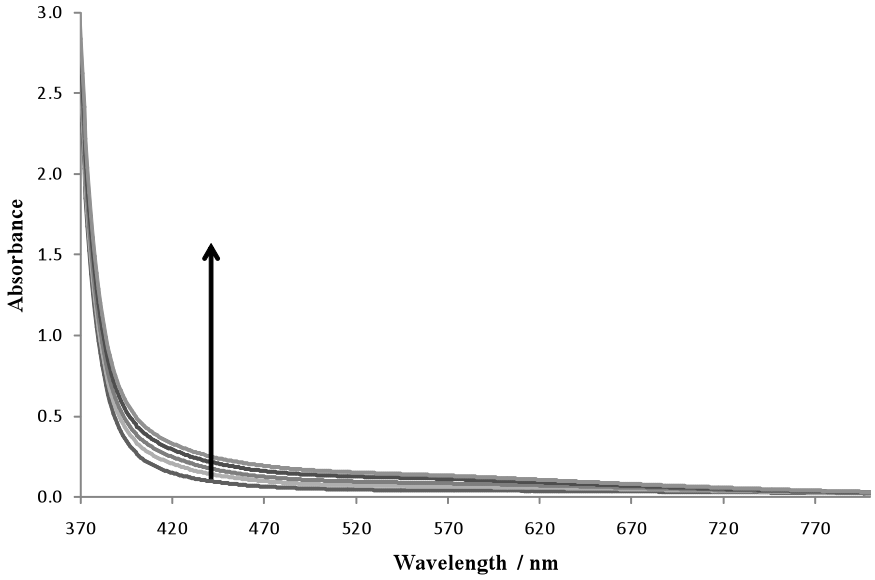

Figure S17. UV-Visible spectrum of $[Ru(MeCN)_3(TPAMP)](SbF_6)_2$ (c = 5 mM) after addition of 10 equiv. of *m*-CPBA in acetonitrile at 298K. Readings taken every 15 minutes.

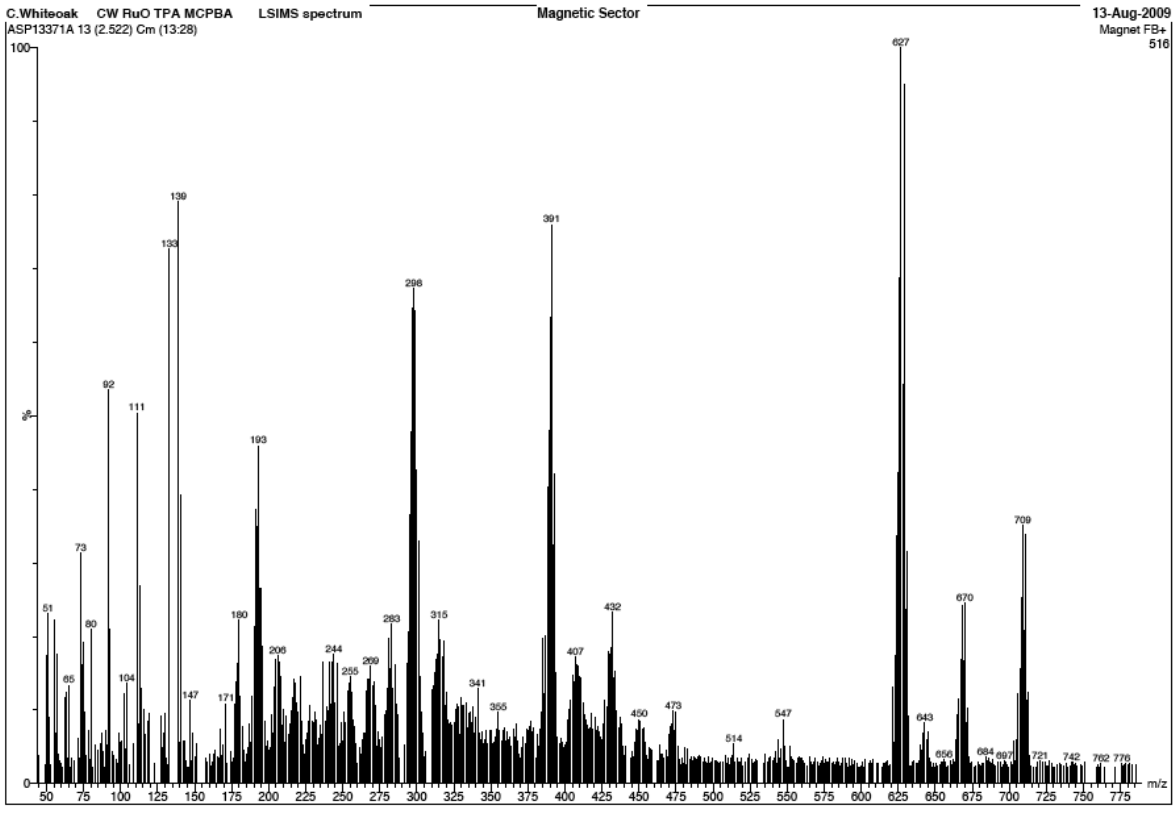

Figure S18: MS (LSIMS) of the product from the reaction of $[Ru(MeCN)_2(TPA)](SbF_6)_2$ with *m*-CPBA in CH_3CN. MS (LSIMS): *m/z* = 391 $[Ru(TPA)]^+$, 407 $[Ru(O)(TPA)]^+$, 432

$[Ru(MeCN)TPA]^+$, 473 $[Ru(MeCN)_2TPA]^+$,627 $[Ru(TPA)(SbF_6)]^+$, 643 $[Ru(O)(TPA)(SbF_6)]^+$, 670 $[Ru(MeCN)(TPA)(SbF_6)]^+$, 709 $[Ru(MeCN)_2(TPA)(SbF_6)]^+$.

X-Ray Crystallography

The X-ray crystal structure of $[CrCl_3(TPPh)]$

The position of the nitrogen atom of the non-coordinated pyridyl ring, [*i.e.* N(18)] in the structure of $[CrCl_3(TPPh)]$ was determined by its lower thermal parameter when both N(18) and C(22) were refined as carbon atoms, its shorter bond lengths, and by the location from a ΔF map of a hydrogen atom bound to C(22).

The X-ray crystal structure of $[Fe(TPPh)_2][FeBr_4]$

The $[Fe(TPPh)_2]^{2+}$ cation, the $[FeBr_4]^{2-}$ anion and the included acetonitrile molecule in the structure of $[Fe(TPPh)_2][FeBr_4]$ were all found to situated on C_2 axes. For the cation, the axis passes through the iron centre and bisects the P(1)–Fe(1)–P(1A), N(3)–Fe(1)–N(3A) and N(13)–Fe(1)–N(13A) angles.

The non-coordinated CH_2–C_5H_4N side arm of the ligand was found to be disordered, and two orientations of *ca*. 78 and 22% occupancy were identified. The geometries of the two orientations were optimised (including the pyridyl rings being refined as idealised hexagons with a side length of 1.39 Å), and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the remainder were refined isotropically). The position of the nitrogen atom for both orientations of the pyridyl ring was determined by comparison of the thermal parameters when both possible *ortho* sites in each case were refined as carbon atoms; due to the disorder it was not possible to rely upon either the bond lengths or the location of hydrogen atoms from a ΔF map.

The C_2 axis through the three non-hydrogen atoms of the included acetonitrile molecule mean that the hydrogen atoms of the methyl group are inherently disordered. This was modelled using one 50% occupancy orientation, with the C_2 axis generating a second 50% occupancy orientation. Initially, the hydrogen atoms were placed in idealised positions and the group was allowed to rotate about the C_2 axis so as to find the position that gave the best fit (the SHELX HFIX/AFIX 137 command). Unfortunately, no clear "best-fit" orientation was found, and the group continued to rotate no matter how many refinement cycles were employed. So, in order to allow the refinements to converge, the group was fixed in an arbitrary position (using the SHELX HFIX/AFIX 3 command).

The X-ray crystal structure of $[Fe(TPAMP)_2](OTf)_2$

The positions of the nitrogen atoms of the non-coordinated pyridyl rings, [*i.e.* N(21) and N(51)] in the structure of $[Fe(TPAMP)_2](OTf)_2$ were determined by comparison of the thermal parameters and bond lengths when both possible *ortho* sites in each ring were refined as carbon atoms, and by the location from a ΔF map of hydrogen atoms bound to C(23) and C(53).

The S(70)-based triflate group was found to be disordered. Two orientations were identified of *ca*. 95 and 5% occupancy, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the remainder were refined isotropically).

The C(80)-based included dichloromethane solvent molecule was found to be disordered. Two orientations were identified of *ca*. 90 and 10% occupancy, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the remainder were refined isotropically).

The X-ray crystal structure of $[Fe(TPAMP)_2][FeCl_4]_2$

The structure of $[Fe(TPAMP)_2][FeCl_4]_2$ was found to contain four crystallographically independent complexes (**A**, **B**, **C** and **D**) in the asymmetric unit. The positions of the nitrogen atoms of the non-coordinated pyridyl rings, [*i.e.* N(23) and N(53)] were determined by comparison of the thermal parameters and bond lengths when both possible *ortho* sites in each ring were refined as carbon atoms. Unfortunately the less than perfect quality of the structure meant that it was not possible to locate a hydrogen atom bound to one of these *ortho* sites from a ΔF map.

The Fe(8)- and Fe(9)-based $FeCl_4$ anions were found to the disordered, and in each case two orientations were identified, of *ca*. 83 and 17%, and 74 and 26% occupancy respectively. The geometries of all four orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all the atoms of the major occupancy orientations, and the iron centres of the minor occupancy orientations, were refined anisotropically (the remainder were refined isotropically).

The general background noise of this structure is quite high, the ten largest residual electron density peaks in the final ΔF map being *ca*. 3.07, 1.94, 1.91, 1.84, 1.58, 1.55, 1.52, 1.25, 1.22 and 1.22 $eÅ^{-3}$ respectively. The largest peak (Q1), which stands out somewhat from the rest, is situated *ca*. 1.61 Å away from Fe(1C), between P(1C) and P(2C), the distances to these two phosphorus centres being *ca*. 1.23 and 2.05 Å respectively. The fifth and seventh largest peaks in the residual electron density list (Q5 and Q7 at 1.58 and 1.52 $eÅ^{-3}$ respectively) are also around the Fe(1C) centre, and the arrangement of the three peaks closely matches that of the FeP_2 unit with Q1 being an alternative iron position and Q5 and Q7 alternative phosphorus sites; the Fe(1C)–P(1C) and Fe(1C)–P(2C) distances are both *ca*. 2.11 Å, with an P–Fe–P angle of *ca*. 102°, whilst the Q1–Q5 and Q1–Q7 distances are *ca*. 2.12 and 2.10 Å respectively, the Q5–Q1–Q7 angle being *ca*. 100°. The two V-shapes have their concave "faces" towards each other, the Fe–P bonds crossing forming a shape resembling two Xs placed one above the other. Refinement of these two FeP_2 units as partial occupancy alternatives suggested an occupancy ratio of *ca*. 95:5. As the estimated occupancy of the second orientation is low (*ca*. 5%), it was considered not to be worthwhile to try and model the whole of the second orientation, and so for simplicity and consistency none of the second orientation was included.

The X-ray crystal structure of $[RuCl_2(TPA)]$

The C(40)- and C(50)-based included dichloromethane solvent molecules in the structure of $[RuCl_2(TPA)]$ were found to be disordered, and in each case three orientations were identified, of *ca*. 81, 11 and 8%, and 71, 16 and 13% occupancy respectively. The geometries of all six orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation in each case were refined anisotropically (the remainder were refined isotropically).

The X-ray crystal structure of $[Ru(MeCN)_2(TPA)](SbF_6)_2$

nothing to say

The X-ray crystal structure of $[Ru(MeCN)_3(TPPh)](SbF_6)_2$

The structure of $[Ru(MeCN)_3(TPPh)](SbF_6)_2$ was found to contain two crystallographically independent complexes (**A** and **B**) in the asymmetric unit. The positions of the nitrogen atoms of the non-coordinated pyridyl rings, [*i.e.* N(23A) and N(23B)] were determined by comparison of the thermal parameters and bond lengths when both possible *ortho* sites in each ring were refined as carbon atoms. Unfortunately the less than perfect quality of the structure meant that it was not possible to locate a hydrogen atom bound to one of these *ortho* sites from a ΔF map.

The Sb(3)- and Sb(4)-based SbF_6 anions were found to be disordered, and in each case two orientations with common antimony positions were identified, of *ca*. 59 and 41%, and 74 and 26% occupancy respectively. The geometries of all four orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the atoms of the major occupancy orientation in each case were refined anisotropically (the remainder were refined isotropically).

Both the O(60)- and O(70)-based included diethylether solvent molecules were found to be disordered across centres of symmetry. In each case this was modelled by using one complete, geometry optimised, 50% occupancy molecule, with the action of the centre of symmetry generating an adjacent 50% occupancy orientation. The non-hydrogen atoms of the unique orientations were refined anisotropically.

Though situated in general positions, the N(80)- and N(90)-based included acetonitrile solvent molecules were both refined at 50% occupancy based on their thermal parameters in comparison with the rest of the structure.

Figures

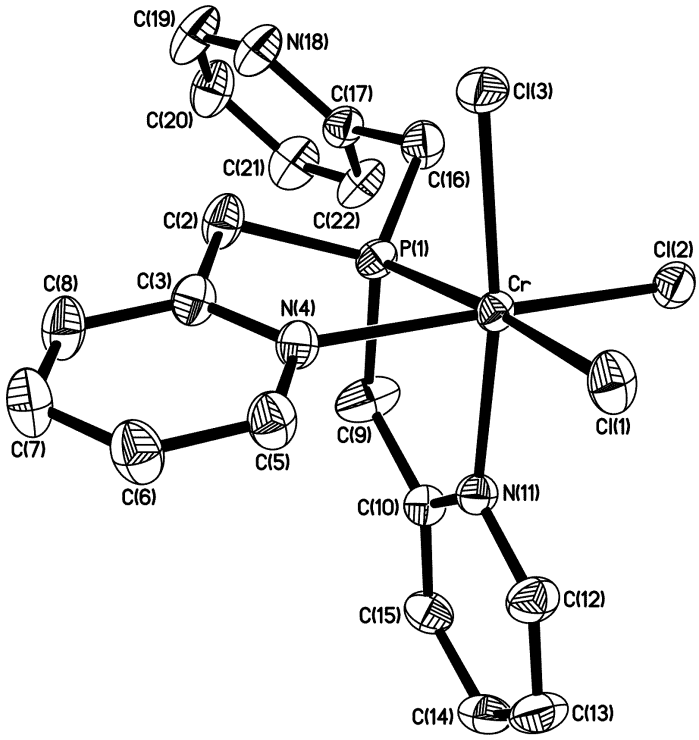

Figure S19. The crystal structure of $[CrCl_3(TPPh)]$ (50% probability ellipsoids).

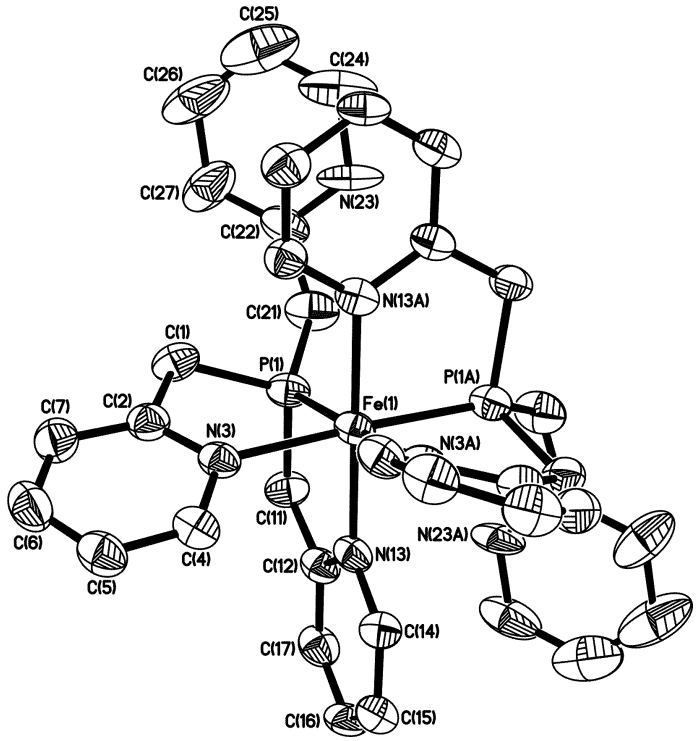

Figure S20. The structure of the C_2-symmetric cation present in the crystals of $[Fe(TPPh)_2][FeBr_4]$ (50% probability ellipsoids).

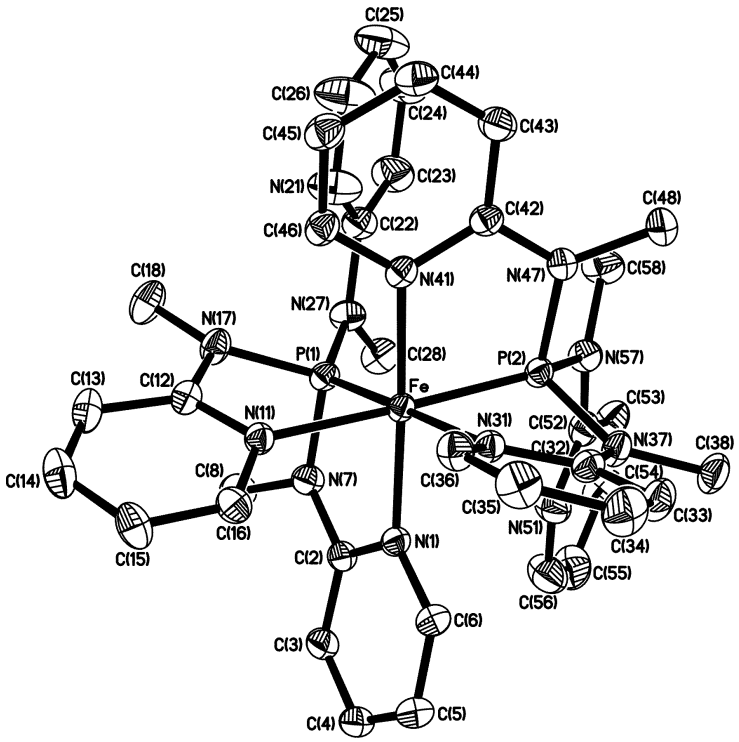

Figure S21. The structure of the cation present in the crystals of $[Fe(TPAMP)_2](OTf)_2$ (50% probability ellipsoids).

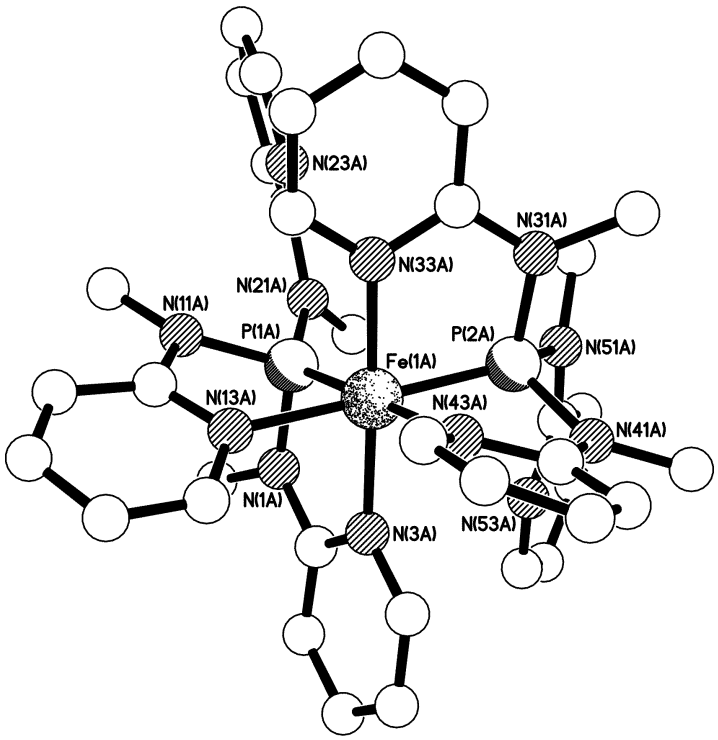

Figure S22. The structure of one (A) of the four independent cations present in the crystals of $[Fe(TPAMP)_2][FeCl_4]_2$.

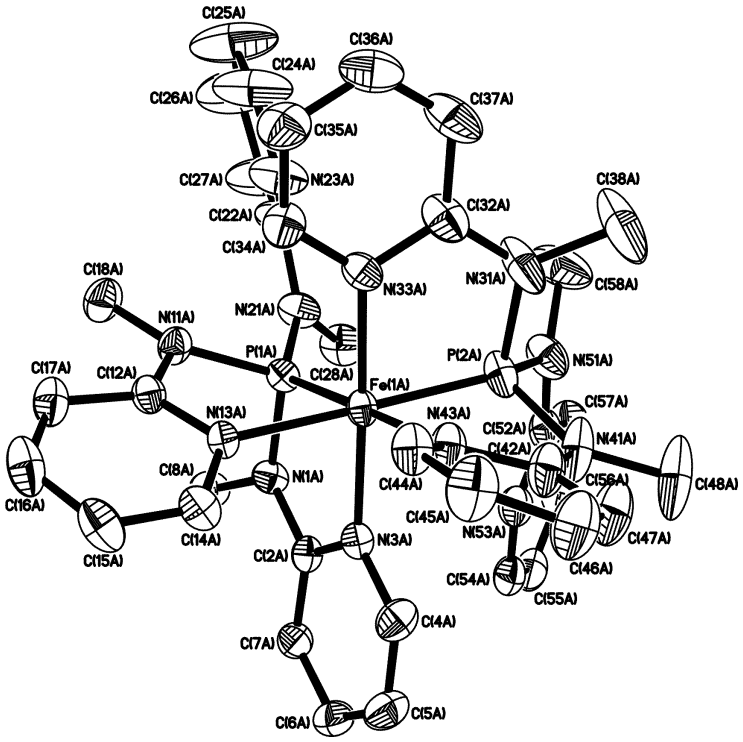

Figure S23. The structure of one (A) of the four independent cations present in the crystals of $[Fe(TPAMP)_2][FeCl_4]_2$ (50% probability ellipsoids).

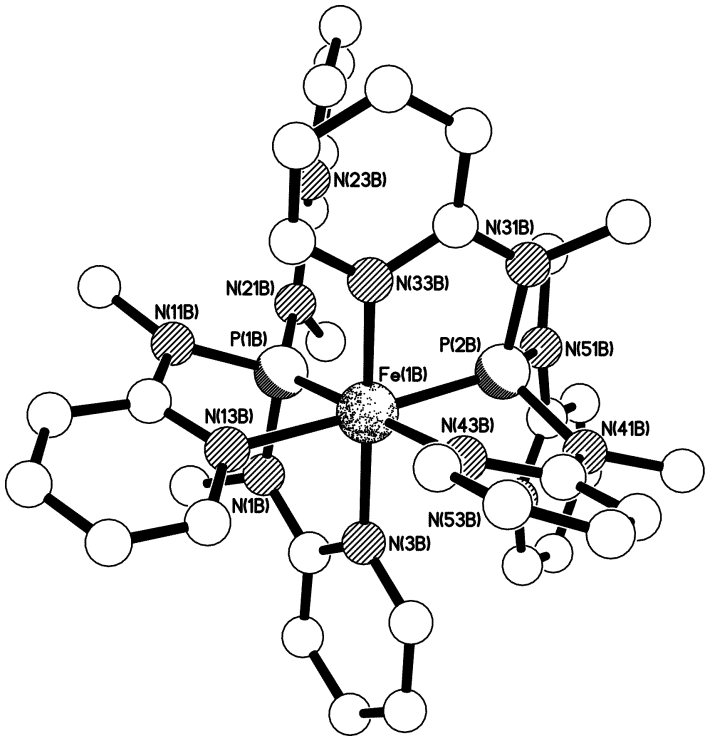

Figure S24. The structure of one (B) of the four independent cations present in the crystals of $[Fe(TPAMP)_2][FeCl_4]_2$.

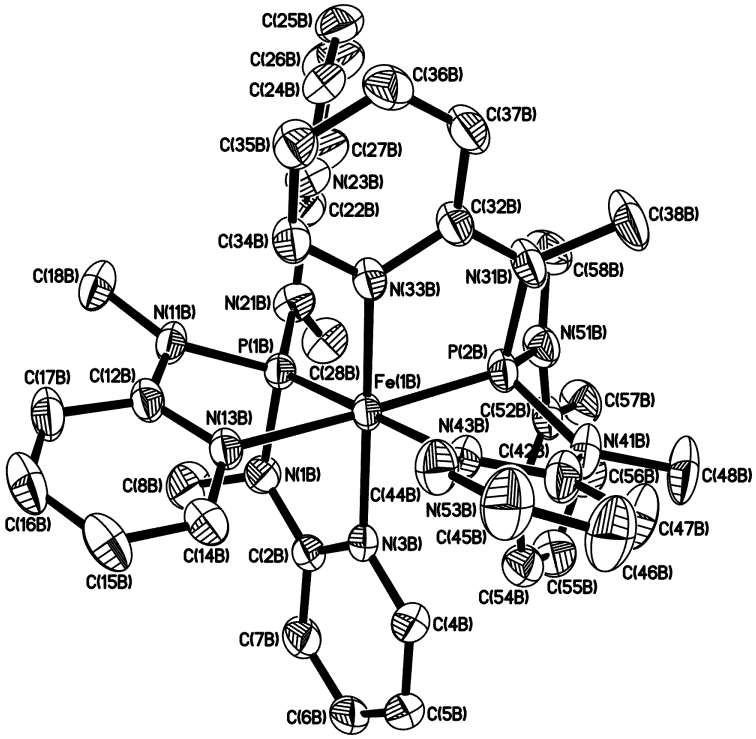

Figure S25. The structure of one (B) of the four independent cations present in the crystals of $[Fe(TPAMP)_2][FeCl_4]_2$ (50% probability ellipsoids).

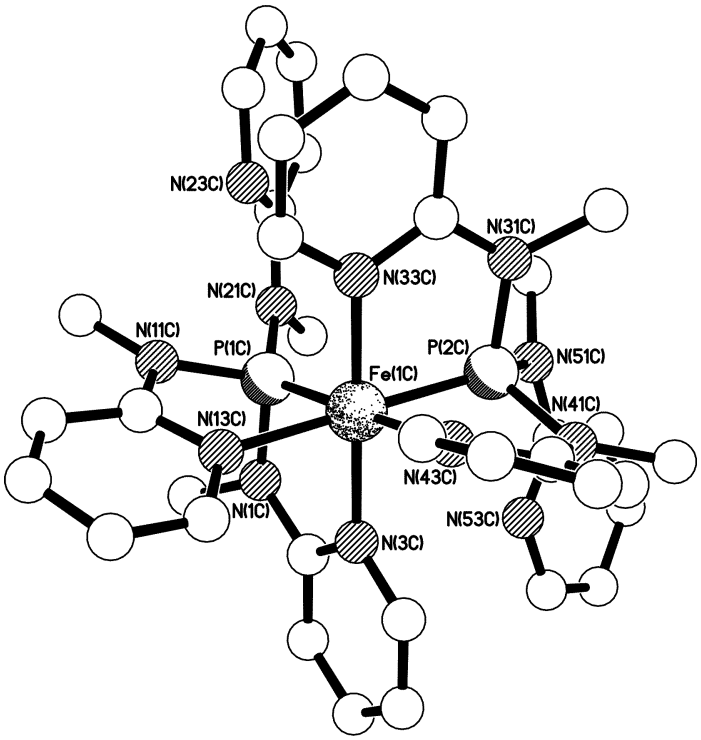

Figure S26. The structure of one (C) of the four independent cations present in the crystals of $[Fe(TPAMP)_2][FeCl_4]_2$.

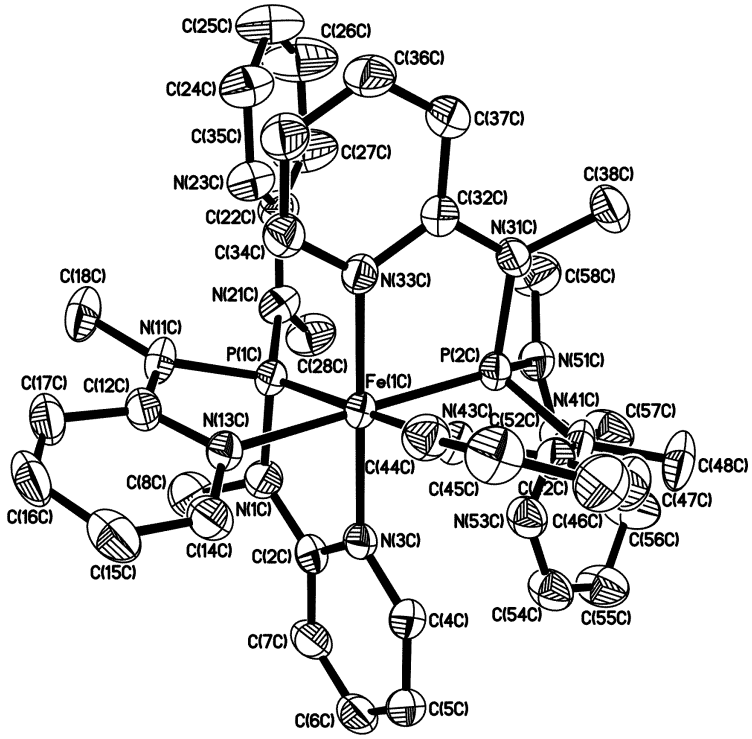

Figure S27. The structure of one (C) of the four independent cations present in the crystals of $[Fe(TPAMP)_2][FeCl_4]_2$ (50% probability ellipsoids).

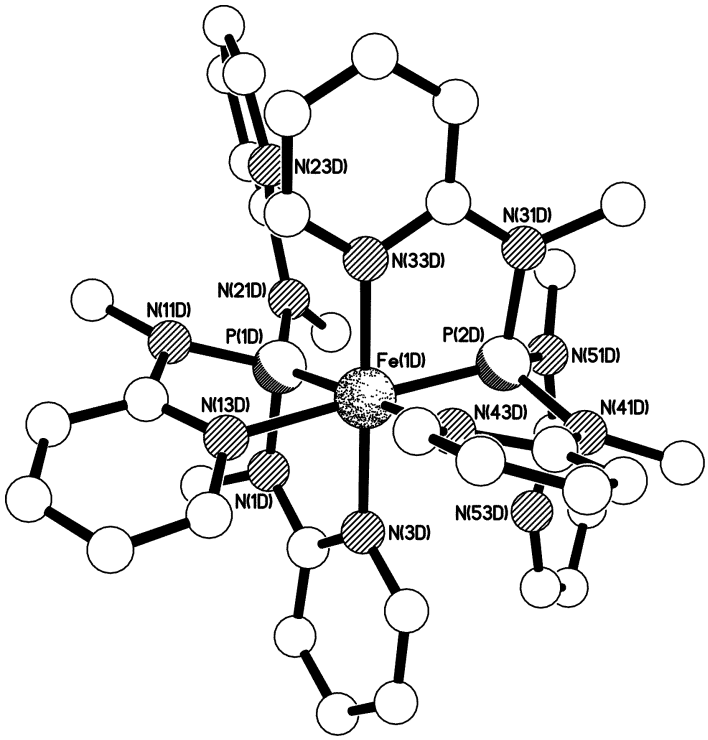

Figure S28. The structure of one (D) of the four independent cations present in the crystals of $[Fe(TPAMP)_2][FeCl_4]_2$.

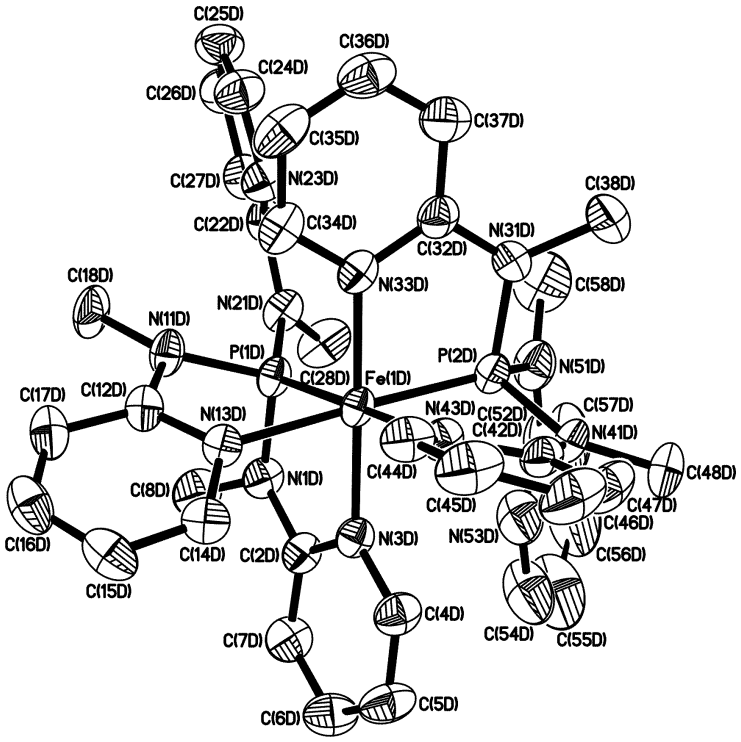

Figure S29. The structure of one (D) of the four independent cations present in the crystals of $[Fe(TPAMP)_2][FeCl_4]_2$ (50% probability ellipsoids).

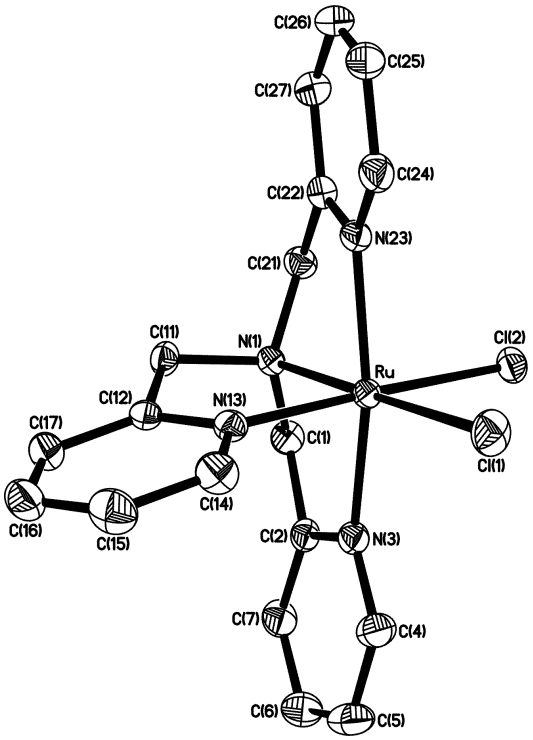

Figure S30. The crystal structure of $[RuCl_2(TPA)]$ (50% probability ellipsoids).

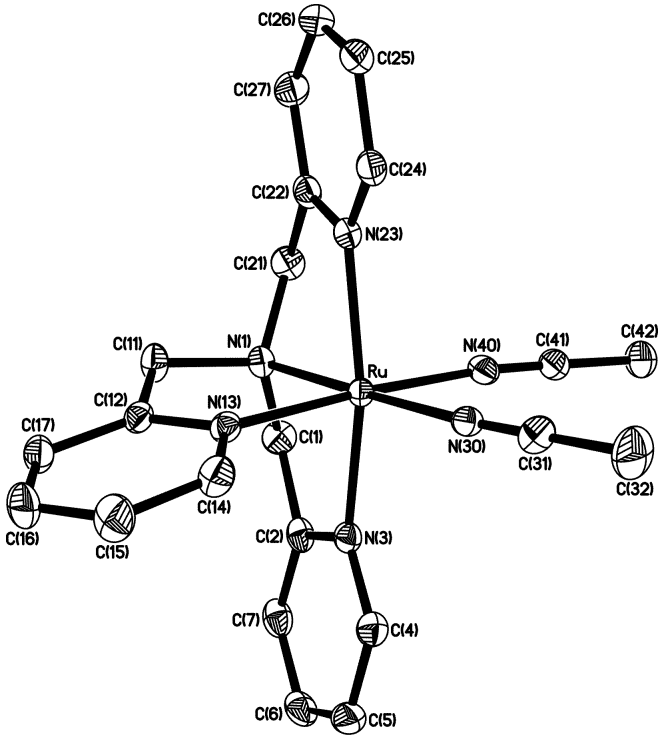

Figure S31. The structure of the cation present in the crystals of $[Ru(MeCN)_2(TPA)](SbF_6)_2$ (50% probability ellipsoids).

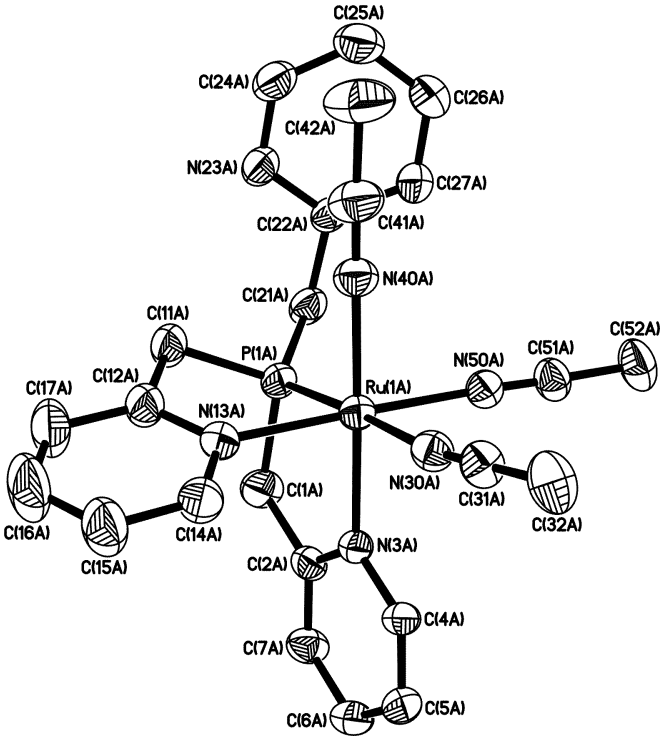

Figure S32. The structure of one (A) of the two independent cations present in the crystals of $[Ru(MeCN)_3(TPPh)](SbF_6)_2$ (30% probability ellipsoids).

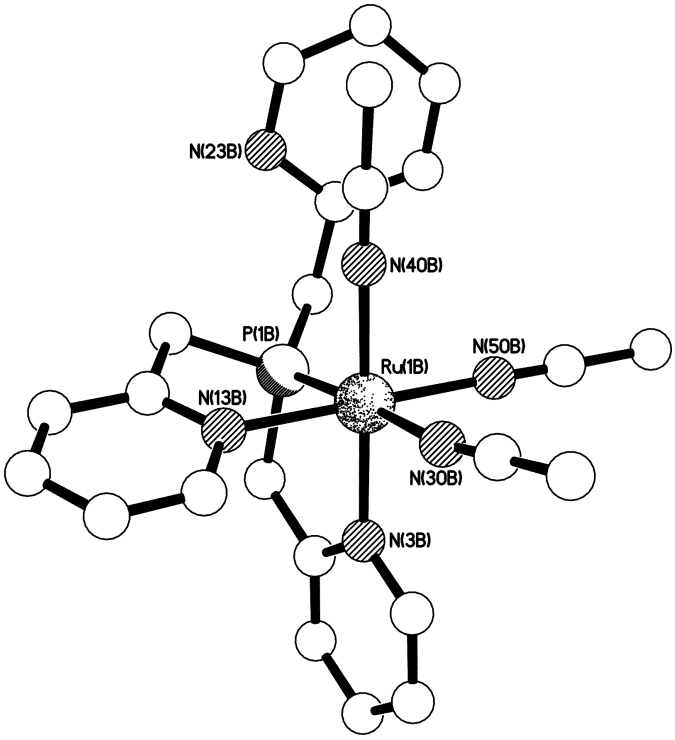

Figure S33. The structure of one (B) of the two independent cations present in the crystals of $[Ru(MeCN)_3(TPPh)](SbF_6)_2$.

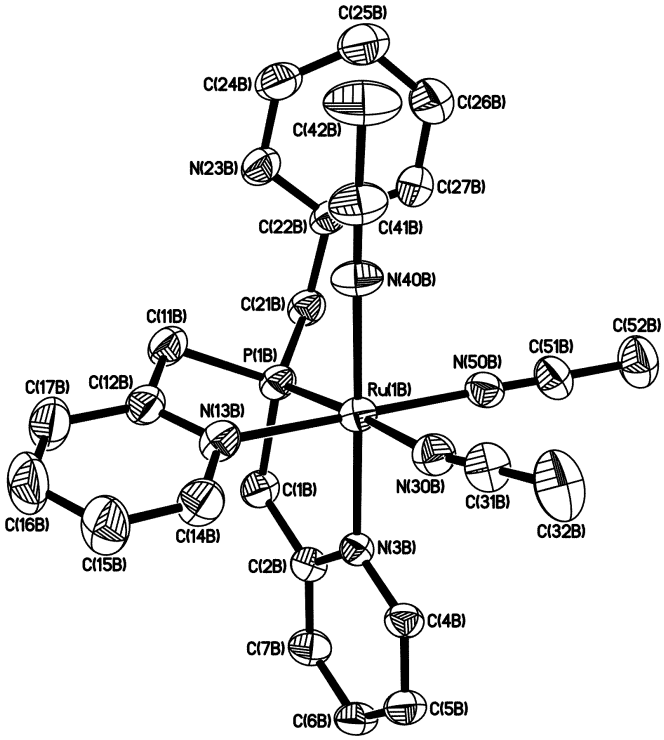

Figure S34. The structure of one (B) of the two independent cations present in the crystals of $[Ru(MeCN)_3(TPPh)](SbF_6)_2$ (30% probability ellipsoids).

Table S1. Selected bond distance and angles for various TPA, TPPh and TPAMP complexes.

	M	X[a]	Y[b]	M–X Å	M–N(py) Å	M–X–Y (coord) degrees	M–X–Y (non-coord) degrees
$[CrCl_3(TPPh)]$	Cr^{III}	P	CH_2	2.3333(4)	2.1256(11), 2.1486(11)	102.97(5), 103.72(5)	122.25(5)
$[CrCl_2(TPA)]$	Cr^{II}	N	CH_2	2.152(5), 2.164(5)	2.105(5) – 2.123(5), 2.474(6),[c] 2.633(6)[c]	105.3 – 107.1	112.6, 113.7[c]
$[CrCl_2(TPA)](BPh_4)$	Cr^{III}	N	CH_2	2.082(3)	2.053(3) – 2.074(3)	106.7, 107.2, 109.7	n/a
$[Fe(TPPh)_2][FeBr_4]$	Fe^{II}	P	CH_2	2.1547(11)	2.021(3), 2.085(3)	102.66(13), 103.84(14)	133.12(17)
$[Fe(TPA)_2](OTf)_2$	Fe^{II}	N	CH_2	2.317(5), 2.330(5)	2.134(5) – 2.215(5)	103.7 – 107.9	111.6, 115.3
$[Fe(TPA)_2](BPh_4)_2$	Fe^{II}	N	CH_2	2.389(3)	2.426(3) – 2.540(3)	108.9 – 110.6	n/a
$[Fe(TPAMP)_2](OTf)_2$	Fe^{II}	P	NMe	2.1050(4), 2.1154(4)	2.0077(14) – 2.0963(13)	102.61(5) – 104.62(5)	133.45(6), 136.36(6)
$[Fe(TPAMP)_2][FeCl_4]_2$	Fe^{II}	P	NMe	2.0972(9) – 2.1122(9)	1.990(3) – 2.084(3)	102.17(11) – 104.90(12)	133.98(12) – 136.01(12)
$[RuCl_2(TPA)]$	Ru^{II}	N	CH_2	2.0529(17)	2.0279(18) – 2.0534(18)	105.69(12), 106.23(12), 110.05(12)	n/a
$[RuCl_2(TPA)](ClO_4)$	Ru^{III}	N	CH_2	2.068(5)	2.073(5) – 2.087(6)	105.8(4), 106.4(4), 110.0(4)	n/a
$[RuCl(TPA)]_2(ClO_4)_2$	Ru^{II}	N	CH_2	2.062(4)	2.066(4) – 2.104(5)	106.2, 106.5, 107.8	n/a
$[RuCl(S\text{-}DMSO)(TPA)](PF_6)$	Ru^{II}	N	CH_2	2.093(3)	2.062(3) – 2.091(3)	105.2, 106.1, 111.4	n/a
$[Ru(MeCN)_2(TPA)](SbF_6)_2$	Ru^{II}	N	CH_2	2.0628(18)	2.0427(18) – 2.0693(17)	105.43(12), 106.31(13), 110.19(13)	n/a
$[Ru(MeCN)_3(TPPh)](SbF_6)_2$	Ru^{II}	P	CH_2	2.208(2), 2.210(2)	2.085(7) – 2.098(6)	101.7(4) – 105.1(3)	128.1(3), 128.3(3)

[a] X is the central atom of the ligand (N for TPA, P for TPPh and TPAMP).
[b] Y is the group directly bonded to the central atom X (CH_2 for TPA and TPPh, NMe for TPAMP)
[c] The associated pyridyl rings are loosely coordinated; see text.

References

(1) Kermagoret, A.; Tomicki, F.; Braunstein, P. *Dalton Trans.* **2008**, 2945-2955.

(2) Jitsukawa, K.; Oka, Y.; Yamaguchi, S.; Masuda, H. *Inorg. Chem.* **2004**, *43*, 8119-8129.