

Water-soluble transition metal complexes of Ruthenium(II), Osmium(II), Rhodium (III) and Iridium (III) with chelating *N*-heterocyclic carbene ligands in hydrogenation and transfer hydrogenation catalysis

Supporting Information

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1. ^1H and ^{13}C NMR spectra.

Figure S1. ^1H (MeOD- d_4 , 400MHz) and ^{13}C (MeOD- d_4 , 100 MHz) NMR spectra of **2a**.

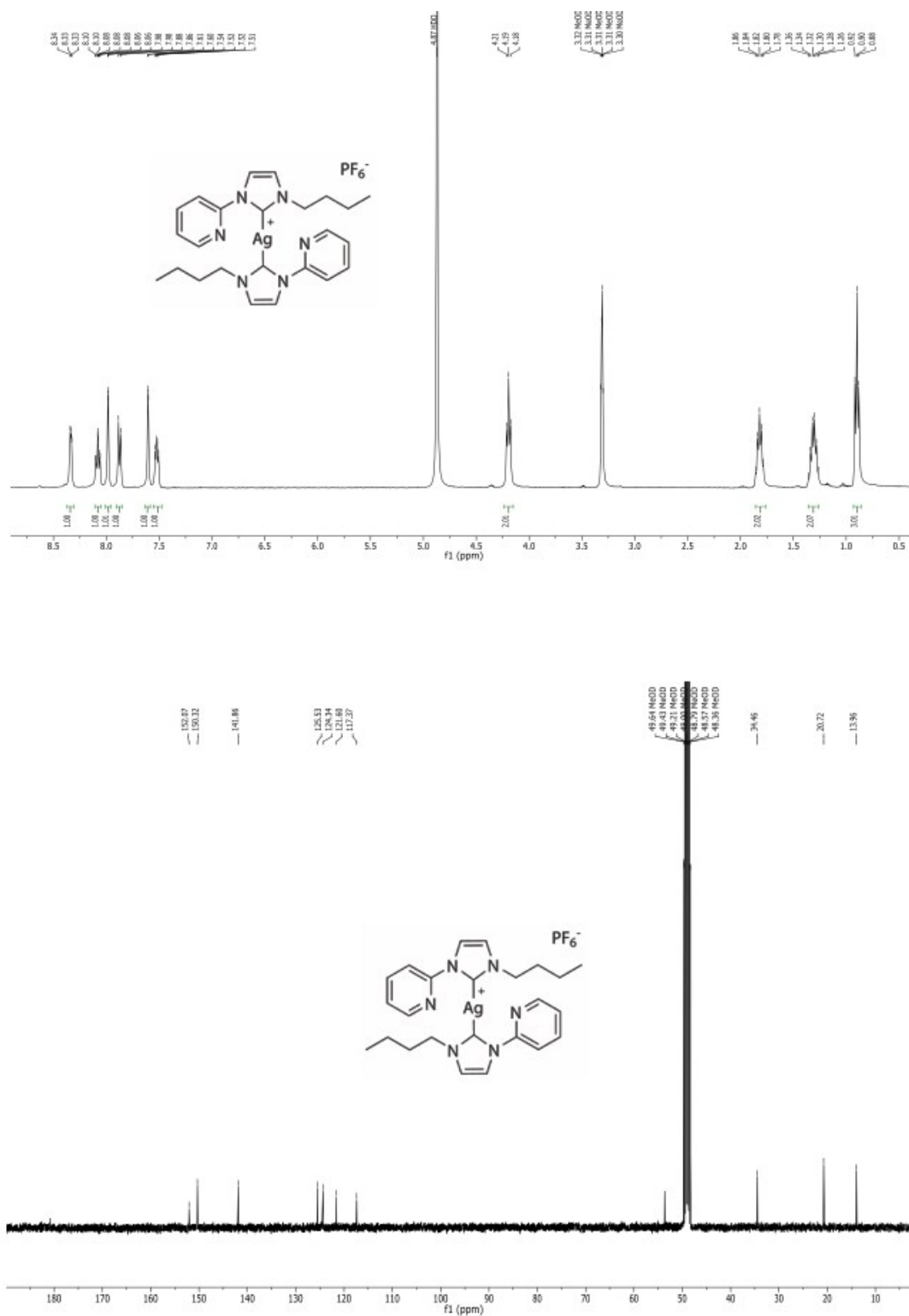


Figure S2. ^1H (DMSO- d_6 , 400MHz) and ^{13}C (DMSO- d_6 , 100MHz) NMR spectra of **2b**.

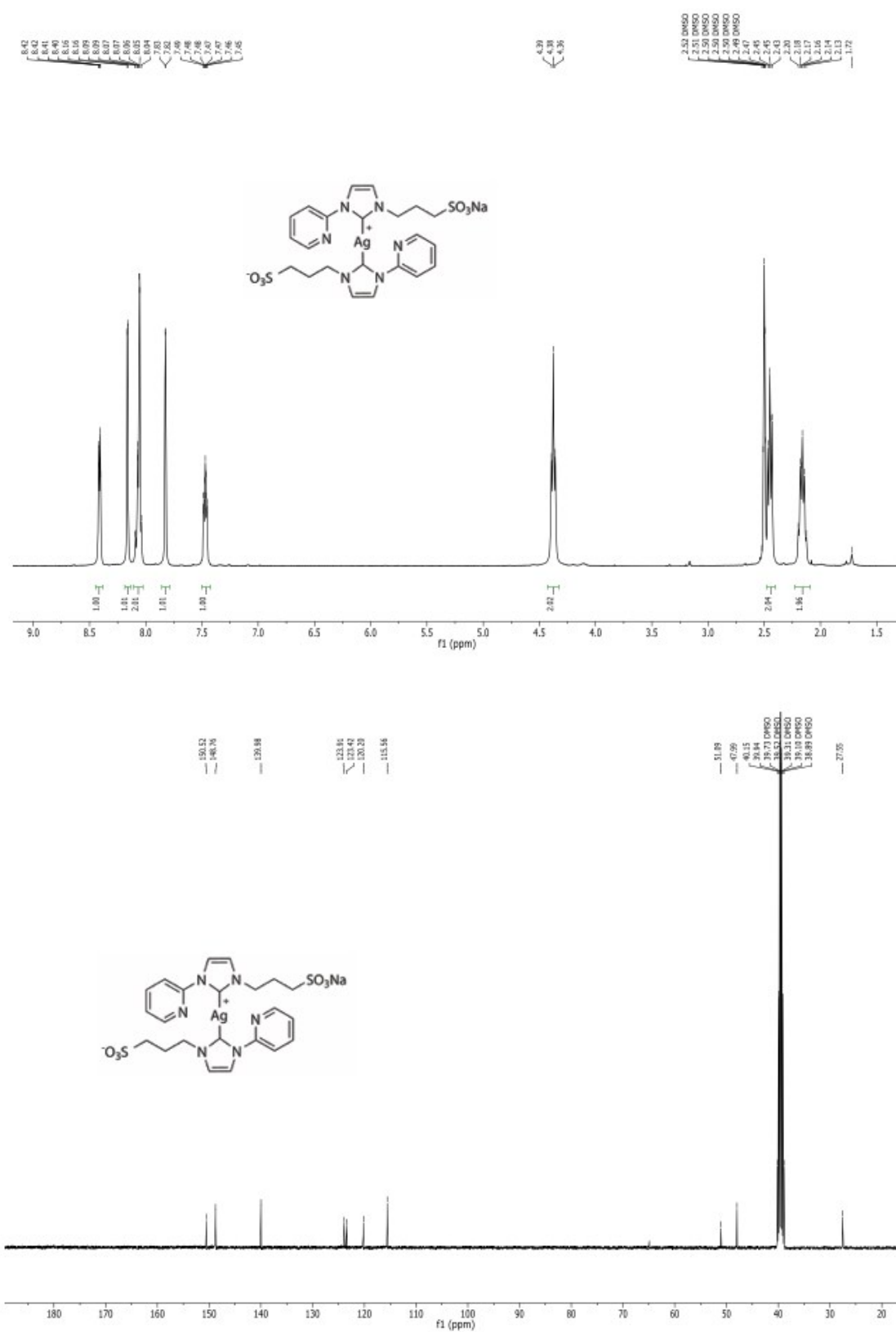


Figure S3. ^1H (MeOD- d_4 , 400MHz) and ^{13}C (MeOD- d_4 , 100MHz) NMR spectra of **3a**.

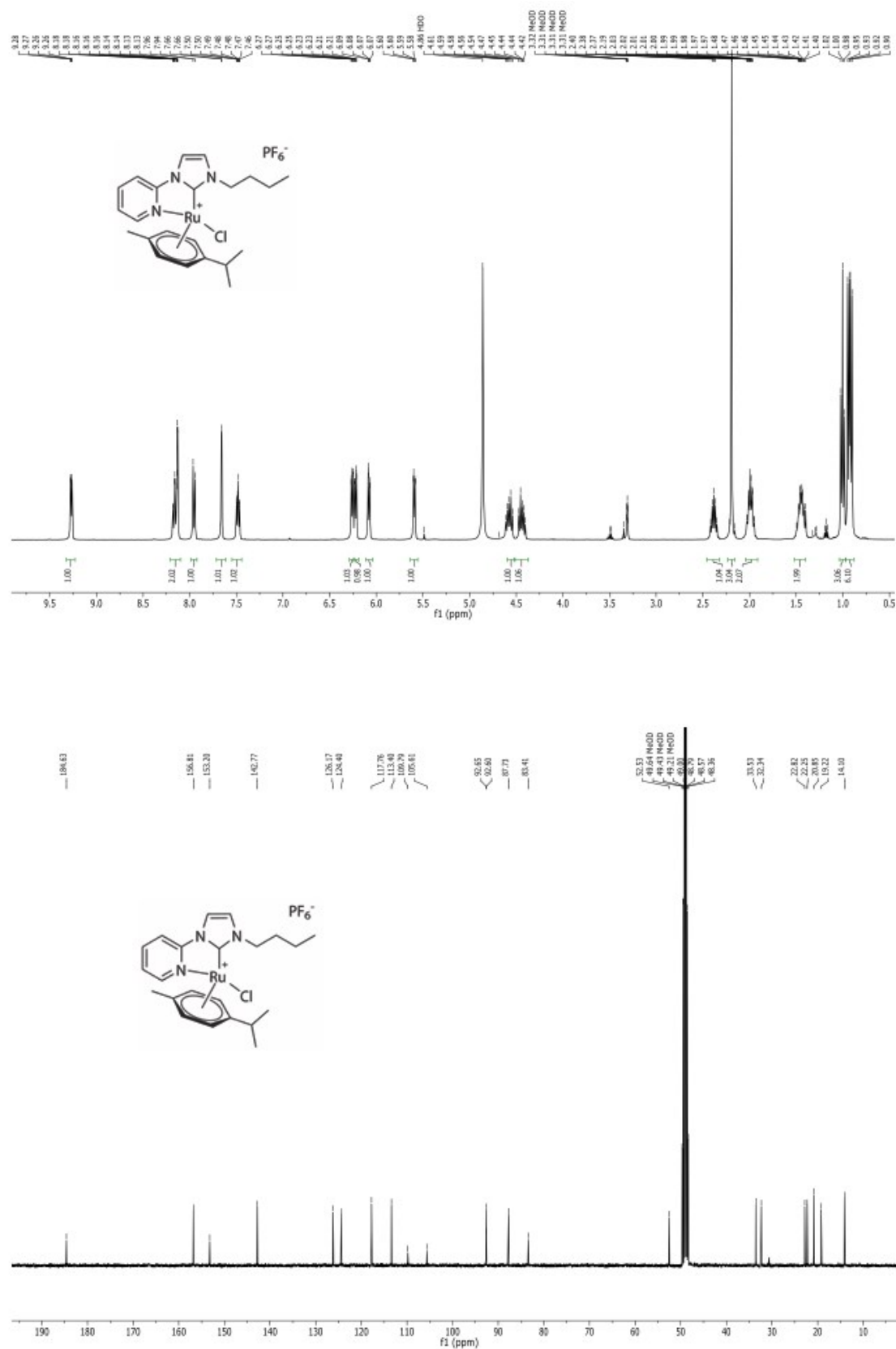


Figure S4. ^1H (MeOD- d_4 , 400MHz) and ^{13}C (MeOD- d_4 , 100MHz) NMR spectra of **4a**.

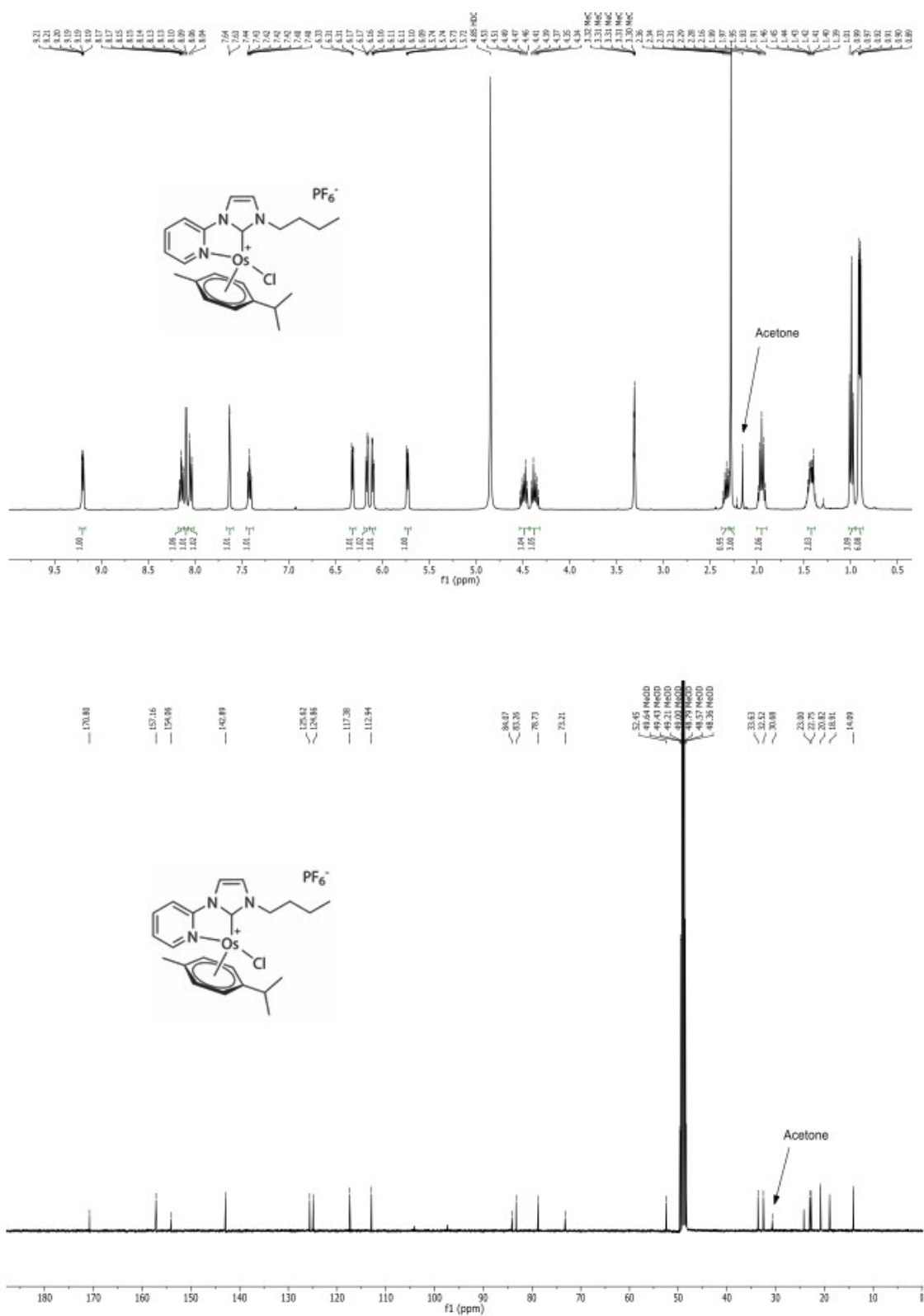


Figure S5. ^1H (DMSO- d_6 , 400MHz) and ^{13}C (DMSO- d_6 , 100MHz) NMR spectra of **5a**.

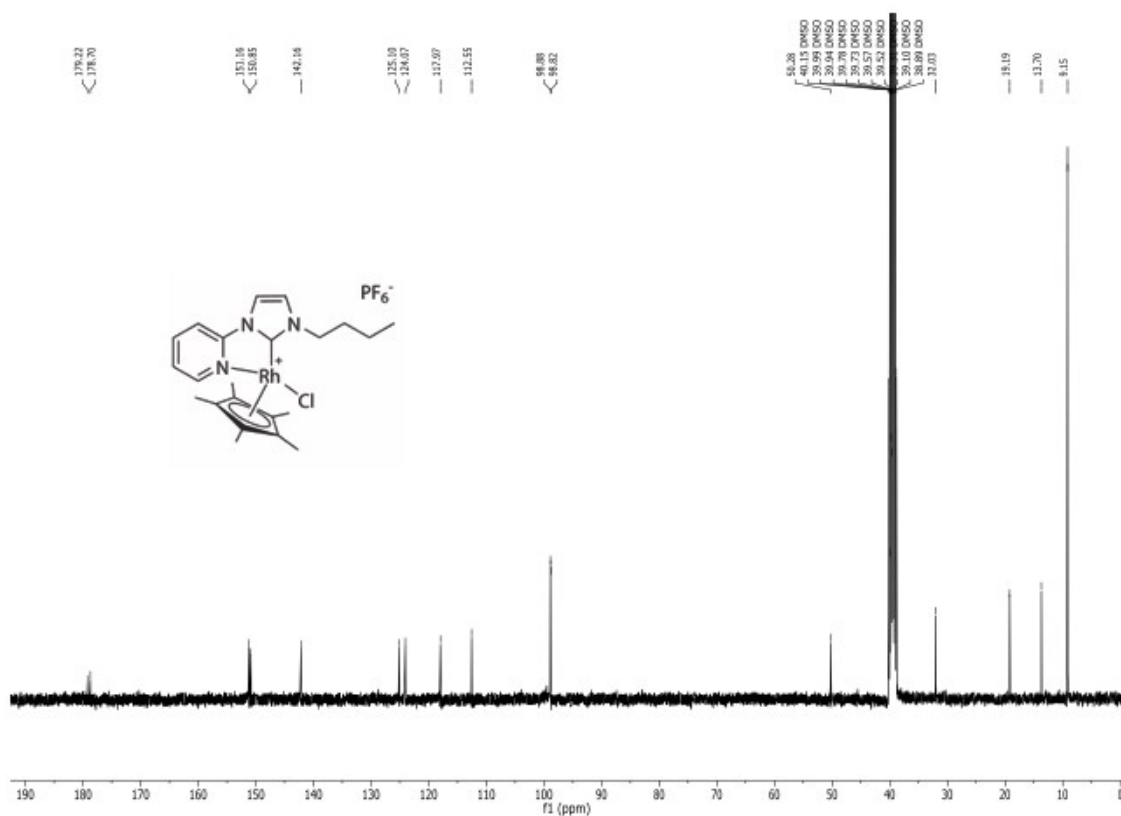
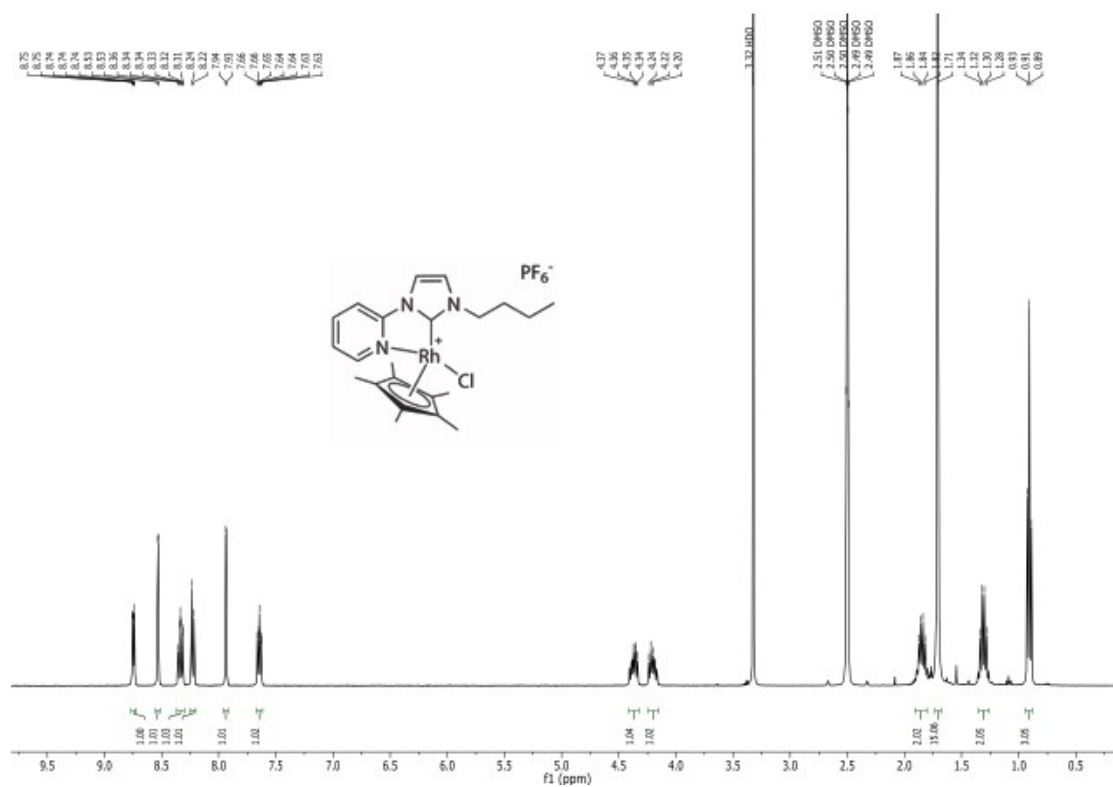


Figure S6. ^1H (DMSO- d_6 , 400MHz) and ^{13}C (DMSO- d_6 , 100MHz) NMR spectra of **6a**.

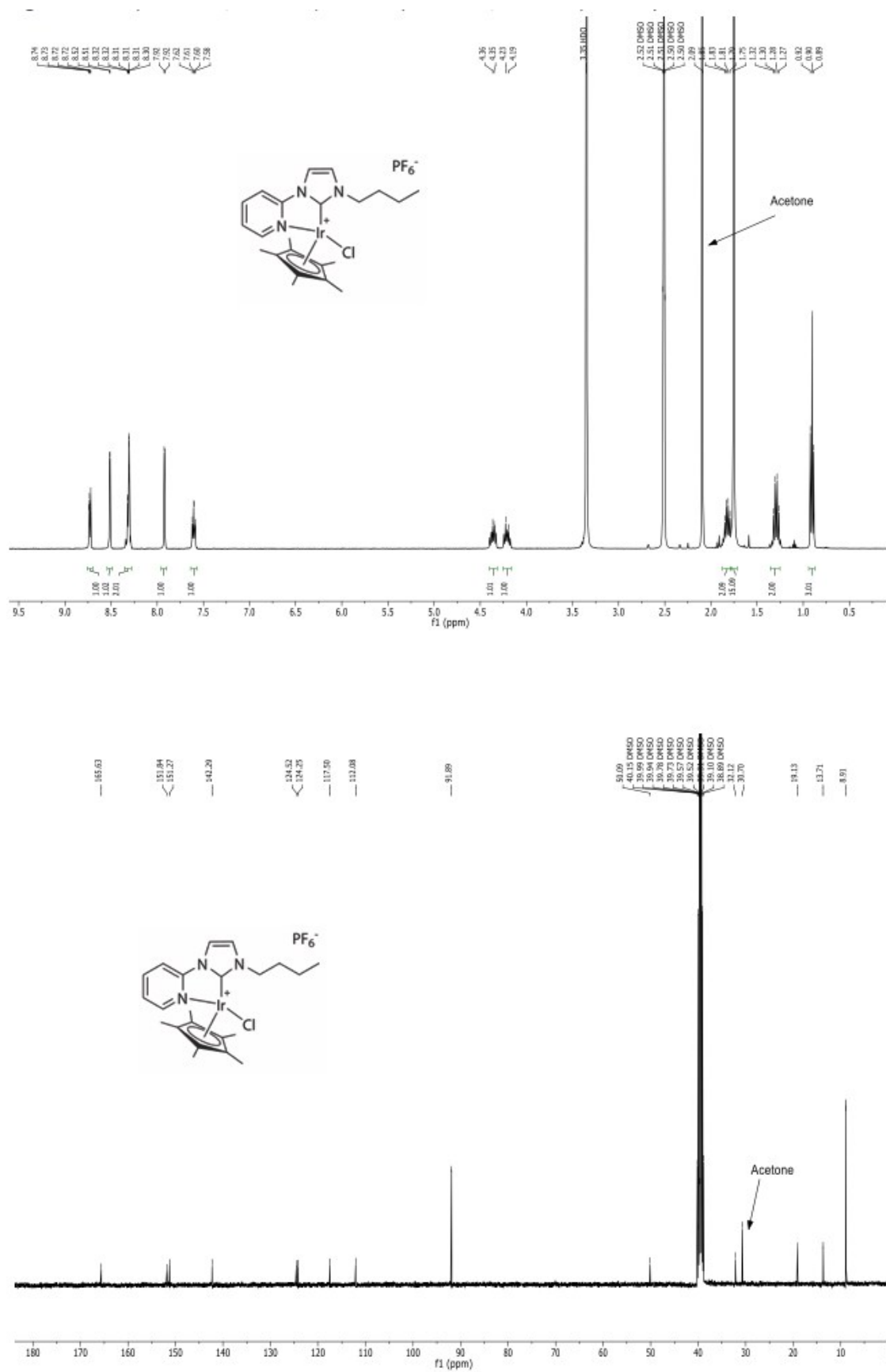
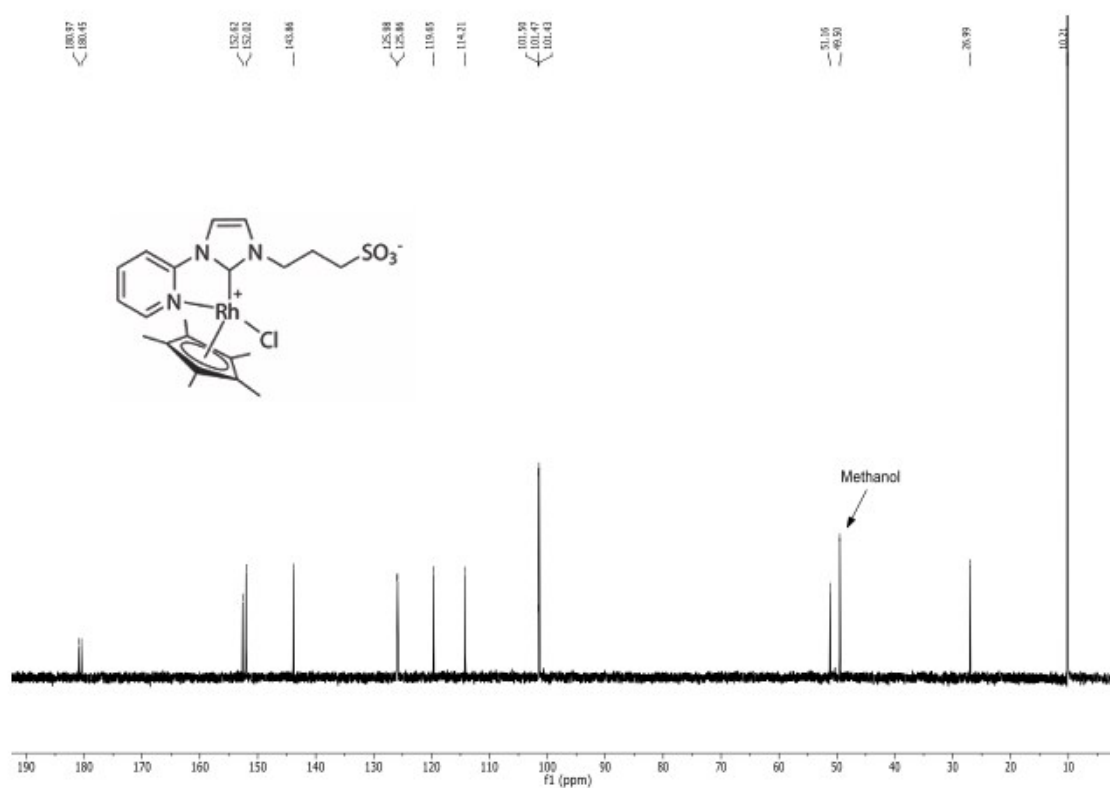
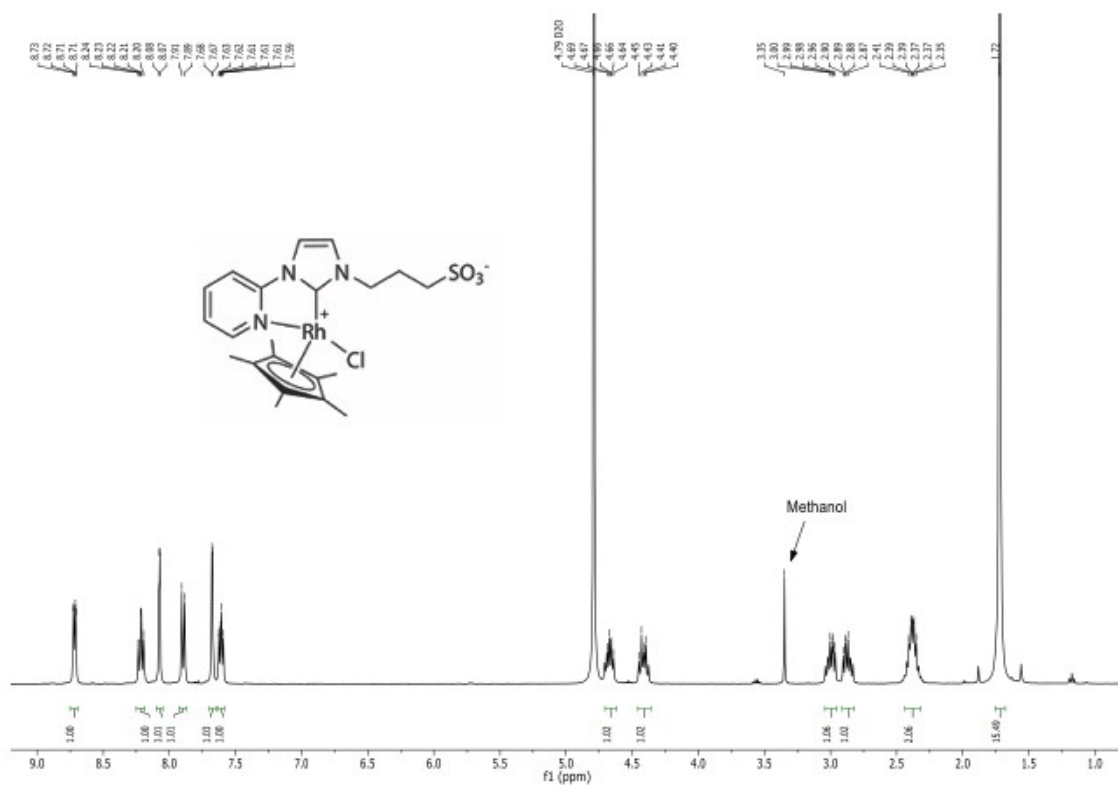


Figure S9. ^1H (D_2O , 400MHz) and ^{13}C (D_2O , 100MHz) NMR spectra of **5b**.



2. X-Ray Crystallographic Data

Data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II, κ -CCD), a rotating anode FR591 equipped with a Montel mirror optic (**5a**, **5b**, **6a**, **6b**) or a fine focused sealed tube equipped with a graphite monochromator (**2a**, **2b**, **4b**) by using the APEXII software package.^{S1} The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals were frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarization effects, scan speed, and background using SAINT.^{S2} Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.^{S2} Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps,^{S3} and were refined against all data using the APEX 2 software^{S1} in conjunction with SHELXL-97^{S4} and SHELXLE.^{S5} Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{\text{iso(H)}} = 1.5 \cdot U_{\text{eq(C)}}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{\text{iso(H)}} = 1.2 \cdot U_{\text{eq(C)}}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme.^{S4} Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.^{S6} Images of the crystal structures were generated by Mercury.^{S7} Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.'s 1404189-1404195. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.)

Table S1. Crystallographic data for compounds **2a**, **2b**, **5a**, **6a**, **4b**, **5b** and **6b**.

	7	2b	5a	6a	4b	5b	6b
Formula	C ₃₆ H ₄₅ Ag ₂ F ₁₂ N ₉ P ₂	C ₂₃ H ₂₈ AgN ₆ NaO ₇ S ₂	C ₂₂ H ₃₀ ClF ₆ N ₃ PRh	C ₂₂ H ₃₀ ClF ₆ IrN ₃ P	C ₂₂ H ₃₀ ClN ₃ O ₄ OsS	C ₂₁ H ₃₁ ClN ₃ O _{5.1} RhS	C ₂₁ H ₃₁ ClIrN ₃ O _{5.09} S
fw	1109.49	695.51	619.82	709.13	658.24	577.55	666.72
Colour/habit	brown fragment	colourless fragment	orange fragment	yellow plate	yellow block	orange block	yellow plate
Cryst. dimensions (mm³)	0.090 x 0.120 x 0.260	0.080 x 0.250 x 0.310	0.134 x 0.232 x 0.277	0.090 x 0.179 x 0.290	0.186 x 0.230 x 0.370	0.227 x 0.231 x 0.279	0.164 x 0.378 x 0.445
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P bca</i>	<i>P bca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
a, Å	12.6948(6)	9.0008(3)	14.9552(4)	15.0548(6)	10.5278(2)	11.3895(3)	11.3664(6)
b, Å	13.5073(6)	12.2235(4)	15.0093(4)	14.9891(6)	17.4635(4)	12.1721(3)	12.2127(6)
c, Å	14.4562(7)	13.4457(5)	21.7963(6)	21.8205(9)	13.6800(3)	17.5563(5)	17.5641(9)
α, deg	94.699(2)	71.899(2)	90	90	90	90	90
β, deg	105.537(2)	82.767(2)	90	90	93.009(1)	93.134(1)	93.028(2)
γ, deg	112.654(2)	76.054(2)	90	90	90	90	90
V, Å³	2155.71(18)	1362.57(8)	4892.6(2)	4924.0(3)	2511.63(9)	2430.26(11)	2434.8(2)
Z	2	2	8	8	4	4	4
T, K	123	123	123	123	123	123	123
D_{calcd}, g cm⁻³	1.709	1.695	1.683	1.913	1.741	1.579	1.819
μ, mm⁻¹	1.074	0.964	0.935	5.658	5.299	0.936	5.716
F(000)	1112	708	2512	2768	1296	1187.3	1315

θ range, deg	1.84 – 26.87	2.02 – 25.35	1.87 – 25.35	1.87 – 26.02	1.89 – 26.37	2.04 – 33.14	2.32 – 25.35
Index ranges (<i>h</i>, <i>k</i>, <i>l</i>)	±16, ±17, ±18	±10, ±14, ±16	±18, ±18, ±26	±18, -16 – 18, ±26	±13, ±21, ±17	-17 – 16, ±18, -24 – 27	±13, ±14, ±21
No. of rflns collected	65786	50061	82866	92223	92387	51535	24095
No. of independent rflns/R_{int}	9239/0.0717	4965/0.0748	4466/0.0649	4859/0.0476	5125/0.0589	9255/0.0494	4452/0.0461
No. of observed rflns ($I > 2\sigma(I)$)	6537	3948	3634	4133	4445	8308	4266
No. of data/restraints/parameters	9239/0/ 553	4965/0/363	4466/0/313	4859/0/313	5125/0/294	9255/6/311	4452/6/320
R1/wR2 ($I > 2\sigma(I)$)^a	0.0390/ 0.0819	0.0303/0.0546	0.0336/0.0669	0.0179/0.0360	0.0227/0.0491	0.0237/0.0595	0.0201/0.0501
R1/wR2 (all data)^a	0.0729/ 0.0927	0.0492/0.0593	0.0497/0.0751	0.0251/0.0384	0.0306/0.0515	0.0281/0.0617	0.0210/0.0506
GOF (on F^2)^a	1.007	1.022	1.113	1.026	1.040	1.071	1.208
Largest diff peak and hole (e \AA^{-3})	1.054/ -0.959	0.435/-0.403	0.094/-0.646	0.797/-0.515	1.368/-0.745	0.708/-0.878	1.803/-0.745

^[a] $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$; $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$

Table S2. Selected bond lengths (Å) and bond angles (°) for rhodium and iridium complexes.

Complex		5a ^a	5b ^b	6a ^a	6b ^b	
Bond lengths (Å)	M(1)–C(1)	2.023(3)	2.0263(11)	2.018(3)	2.021(2)	
	M(1)–N(3)	2.128(3)	2.118(10)	2.122(2)	2.107(2)	
	M(1)–Cl(1)	2.4065(8)	2.4053(3)	2.4090(7)	2.4088(6)	
	M(1)–C(12) ^b or M(1)–C(13) ^a	2.155(3)	2.1992(11)	2.165(3)	2.173(2)	
	M(1)–C(13) ^b or M(1)–C(14) ^a	2.213(3)	2.1566(12)	2.232(3)	2.227(3)	
	M(1)–C(14) ^b or M(1)–C(15) ^a	2.236(3)	2.2264(12)	2.250(3)	2.233(2)	
	M(1)–C(15) ^b or M(1)–C(16) ^a	2.154(3)	2.2159(11)	2.163(2)	2.166(3)	
	M(1)–C(16) ^b or M(1)–C(17) ^a	2.181(3)	2.1673(11)	2.180(3)	2.198(2)	
	Bond angles (°)	C(1)–M(1)–N(3)	76.78(12)	76.82(4)	76.33(10)	76.22(9)
		C(1)–M(1)–Cl(1)	85.53(9)	86.28(3)	85.20(7)	86.12(7)
		N(3)–M(1)–Cl(1)	89.03(8)	87.99(3)	86.78(6)	86.02(5)
		C(1)–M(1)–C(12) ^a or C(1)–M(1)–C(13) ^b	117.04(13)	102.54(4)	117.33(11)	124.35(10)
		C(1)–M(1)–C(13) ^a or C(1)–M(1)–C(14) ^b	155.12(13)	113.39(4)	155.12(11)	163.12(10)
C(1)–M(1)–C(14) ^a or C(1)–M(1)–C(15) ^b		154.84(13)	149.56(4)	156.47(10)	150.05(10)	
C(1)–M(1)–C(15) ^a or C(1)–M(1)–C(16) ^b		117.07(13)	162.11(5)	118.51(10)	114.26(9)	
C(1)–M(1)–C(16) ^a or C(1)–M(1)–C(17) ^b		100.50(13)	123.12(5)	101.47(10)	103.85(10)	
Torsion angles (°)		C(1)–N(2)–C(4)–N(3)	-2.2(4)	-0.04(15)	-2.0(3)	-0.05(3)

3. References

- S1 APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
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- S7 Mercury: visualization and analysis of crystal structures C.F. Macrae, P.R. Edgington, P McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Cryst.* (2006), 39-3, 453-457.