Acceleration of Nucleophilic CH Activation by Strongly Basic Solvents

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- SUPPORTING INFORMATION -

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Experimental Details:

General Considerations: All air and water sensitive procedures were carried out either in a MBraun inert atmosphere glove box, or using standard Schlenk techniques under argon. Anhydrous methanol was purchased from Alfa Aesar and used without further purification. All deuterated solvents (Cambridge Isotopes) and 40% KOD/D_2O (Aldrich) were used as received. The KOD/D_2O solutions were prepared by diluting of 40% KOD/D_2O with D_2O to the desired

concentration. 2,6-Pyridinedicarbonitrile[i] and N-ethoxymethylimidazole were prepared according to literature procedure. All chemical shifts are reported in units of ppm and referenced to the residual protonated solvent. A "CombiFlash Companion"-system from Teledyne Isco Inc. was used for flash chromatography. All high-resolution mass spectra were obtained by University of Florida, Department of Chemistry - Mass Sepctrometer Services on an ESI mass spectrometer. Elemental Analysis was performed by Desert Analytics of Tucson, Arizona. X-ray Crystallography data was obtained by University of Texas at Arlington – Center for Nanostructured Materials.

Synthesis of 2,6-bis(imidazoyl)pyridine (IPI): Initial synthesis of IPI was accomplished using previously published Method A.[ii] However, inconsistent yields led us to examine and eventually prefer the use of Method B.[iii]

Method A: Synthesis was performed according to previously published procedure.[ii]

Method B: The published procedure for Method B[iii] was altered to give higher and more consistent yields: A 100-mL round-bottom flask containing 2,6-pyridinedicarbonitrile (2.0 g, 15.5 mmol), MeOH (15 mL), and a 30% solution of NaOMe in MeOH (2.4 mL, 6.3 mmol, 0.4 eq) were stirred at room temperature for 2 h. Aminoacetaldehyde diethyl acetal (4.5 mL, 30.1 mmol, 2 eq), followed by AcOH (2.1 mL, 35 mmol, 2.5 eq) were stirred at 50 °C for 1 h and cooled to room temperature. MeOH (30 mL and 6 N HCl in H_2O (7.5 mL) were added and heated to reflux for 10 h. The solution was removed on the rotary evaporator and the residue was extracted with a 1:1 mixture of H_2O:Et_2O (50 mL). The layers were separated and the aqueous layer was washed with Et_2O (2 x 50 mL). The aqueous layer was adjusted to pH = ~10 with 2 N NaOH and stirred at room temperature for 30 min. The resulting product was collected

by filtration and dried under vacuum overnight to produce a slightly yellow powder (2.7g, 83% yield). Product had spectral parameters consistent with previously published syntheses.[ii,iii]

Synthesis of Ru(IPI)Cl_3 (1): To a 50 mL Schlenk flask equipped with a reflux condenser and vacuum adapter, $RuCl_3(H_2O)_3$ (500 mg, 1.91 mmol), 2,6-bis(imidazoyl)pyridine (366 mg, 1.74 mmol), and anhydrous methanol (30 mL) were added. The mixture was heated at 85 °C with stirring for 6 h. During this time the color of the solution turned from dark red to a brownish color. After cooling, the solution was filtered in vacuo, and the brown-red precipitate was washed successively with methanol (3 x 20 mL), water (3 x 5 mL), and 1 N HCl (3 x 10 mL), and diethyl ether (3 x 20 mL). The resulting brown solid was dried under high vacuum at 100 °C overnight to yield 0.375 g (48% yield). HRMS (ESI): Calculated for $C_{11}H_9Cl_2N_5Ru$ (M-Cl) 382.9270, found 382.9280. IR (cm^{-1}) 3500-2600 (w), 1614 (m), 1557 (m), 1479 (l), 1438 (m), 1366 (m), 1312 (m), 1199 (s), 1159 (m), 1114 (m), 1083 (m), 1007 (l), 985 (l), 954 (m), 918 (m), 803 (l), 768 (l), 744 (l), 702 (l), 675 (l). Anal. Calcd. for $C_{11}H_9Cl_3N_5Ru$: C, 31.56; H, 2.17; N, 16.73. Found: C, 31.67; H, 2.47; N, 16.68. Crystals suitable for X-ray diffraction were obtained from vapor diffusion of anhydrous benzene into an anhydrous DMSO solution of the complex.

Synthesis of K[Ru(IPI)$(CN)_3$]: To a 50 mL Schlenk flask equipped with a rubber septum, Ru(IPI)Cl_3 (50 mg, 0.120 mmol), NaCN (17.6 mg, 0.359 mmol, 3 eq), and degassed D_2O (10 mL) was added. The solution was stirred for 5 min at room temperature and Zn dust (40 mg, 0.6 mmol, ~ 5eq) was added under a positive flow of argon. The reaction was stirred for 1 h at room temperature and NMR samples were prepared in a glove bag with an argon atmosphere. The crude product could be further purified by removing D_2O in vacuo and purified using flash chromatography (silica gel, gradient CH_2Cl_2 to CH_2Cl_2:MeOH, 1:3 over 20 min). ^1H NMR (400 MHz, D_2O, δ/ppm) 7.57 (t, 1H, *j* = 7.9 Hz), 7.32 (d, 2H, *j* = 7.9 Hz), 6.98 (s, 2H), 6.92 (s, 2H).

$^{13}C\{^{1}H\}$ NMR (400 MHz, D_2O, δ/ppm) 173.6 (t, 1C, *j* = 5.6 Hz), 167.0 (d, 2C, *j* = 5.6 Hz), 155.1, 151.8, 135.9, 132.3, 129.3, 112.9. MS (ESI): Calculated for $C_{14}H_9N_8Ru$ (M^-) 391.0. IR (cm^{-1}) 3500-2800 (w), 2037 (l), 1612 (m), 1554 (s), 1477 (l), 1373 (s), 1170 (s), 1116 (m), 932 (m), 804 (l), 769 (l), 746 (l), 701 (l), 667 (l). Anal. Calcd. for $K[Ru(IPI)(CN)_3]\bullet H_2O\bullet CH_3OH$, $C_{15}H_{15}KN_8O_2Ru$: C, 37.57; H, 3.15; N, 23.37. Found: C, 37.19; H, 3.23; N, 23.44. Crystals suitable for X-ray diffraction were obtained from vapor diffusion of THF into a MeOH solution of the complex.

General H/D Exchange Experiments: A typical experiment involved making stock solutions of substrate (0.90 mmol in 3 mL of 3.7M KOD/D_2O). Catalyst stock solutions were then made by adding 2 mL of substrate solution to a separate vial containing **1** (2.5 mg, 6.0 μmol). These prepared solutions (0.7 mL of two containing catalyst and one without catalyst) were added to three separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc powder (15 mg, 0.23 mmol). The reactors were sealed and the solutions were degassed by repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). **Note:** if the system is not sufficiently degassed, catalyst reproducibility is lessened. The prepared reactors were place in an aluminum block set to the desired temperature for the required reaction time. Upon reaction completion, the reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. The catalyst runs was averaged and subtracted from the background (without catalyst) to give percent deuterium incorporation. Representative NMR spectra are shown in shown in figure S1 (background), figure S2 (catalytic run), and figure S3 (^{2}H-NMR spectra of a catalytic run). Table S1 contains the data obtained from various sp^2

substrates and table S2 contains various sp^3 substrates contained in chart 1. Representative NMR spectra of background and a catalyst run are shown below.

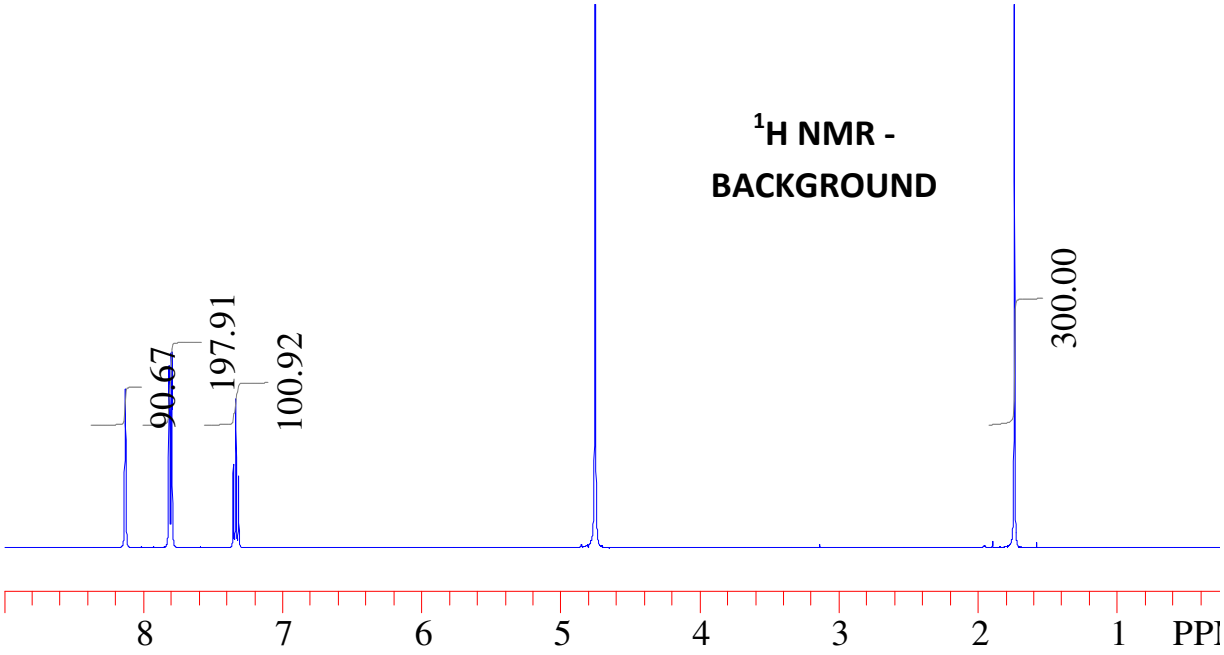


Figure S1. ^{1}H NMR Spectrum of background of **IA** with zinc dust at 90 °C for 1 h in 13% KOD

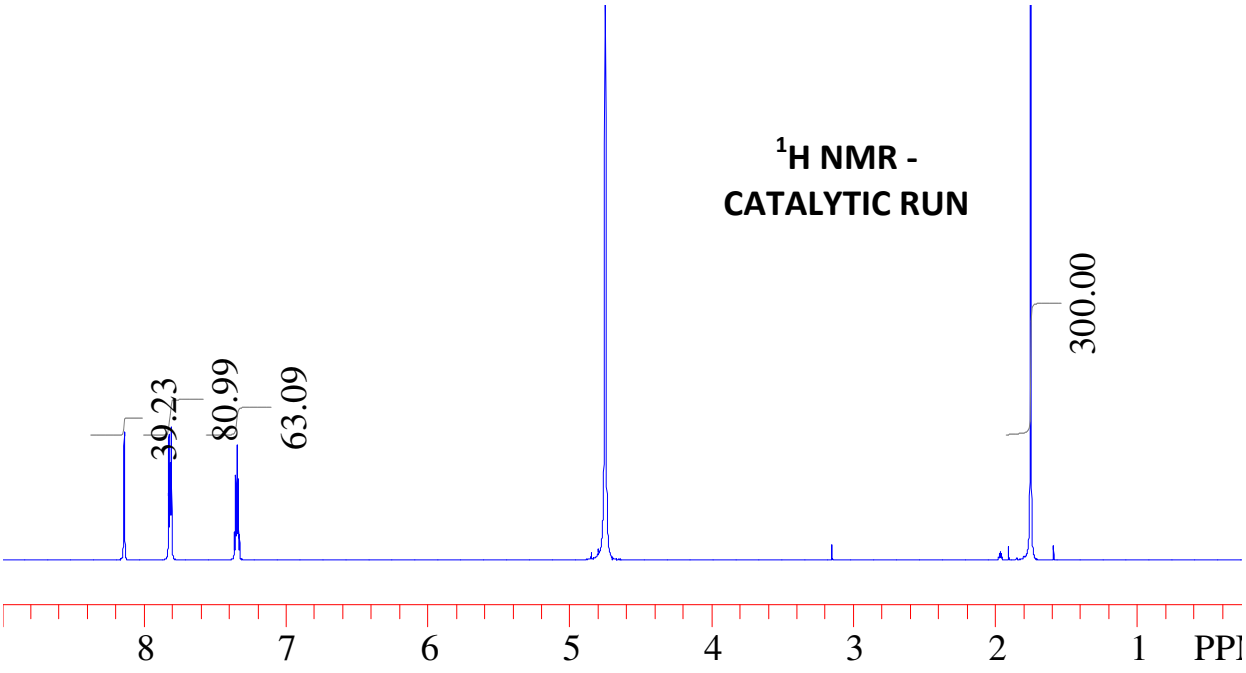


Figure S2. [1]H NMR Spectrum of **IA** at 90 °C for 1 h with **1** in 13% KOD

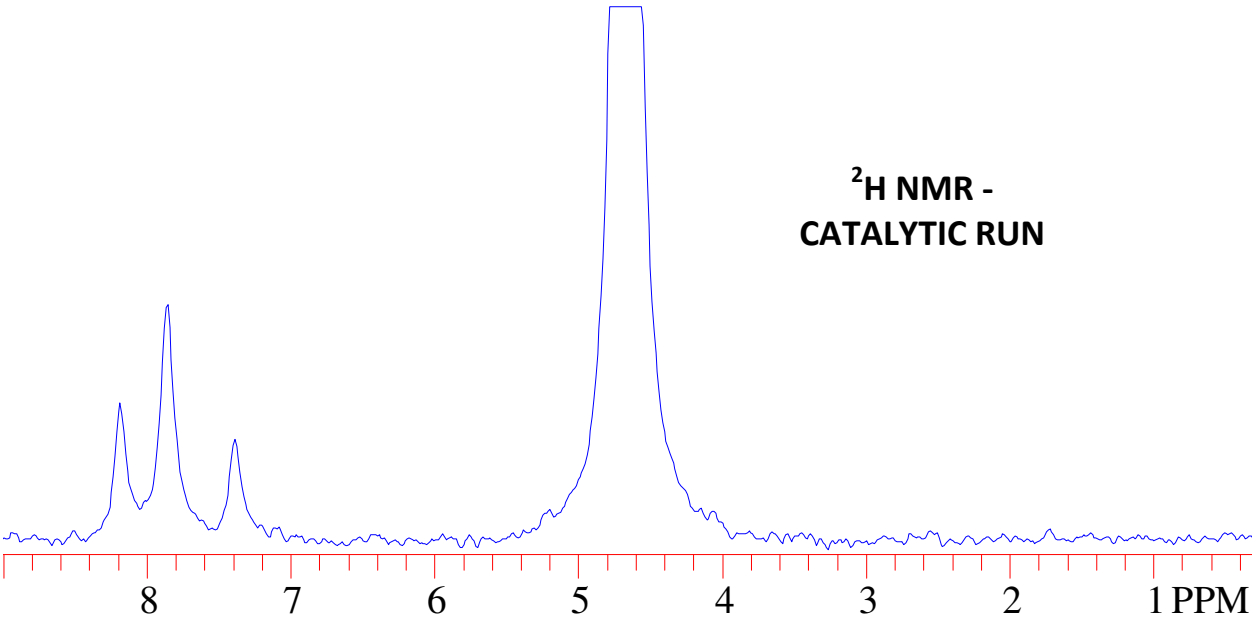
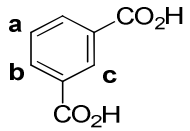
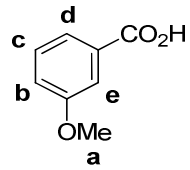
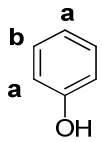
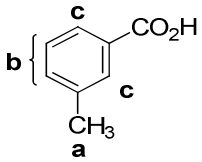
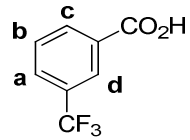


Figure S3. [2]H NMR Spectrum of **IA** at 90 °C for 1 h with **1** in 13% KOD

Table S1. H/D exchange of various substrates at 90 °C for 1 h with 1 mol% Ru(IPI)Cl_3 in 13% KOD.

Substrate		a	% D	b	% D	c	% D	d	% D	e	% D	Total TON	Total TOF (s^{-1})
	t=0	99.8	--	199.4	--	99.7	--	--	--	--	--	--	--
	Background	99.1	0.7	196.3	1.6	93.3	6.4	--	--	--	--	--	--
	Run #1	63.1	36.1	81.0	57.8	40.3	53.2	--	--	--	--	206.2	5.7E-02
	Run #2	64.9	34.3	84.1	56.3	42.5	51.0	--	--	--	--	199.0	5.5E-02
	Average	**64.0**	**35.2**	**82.6**	**57.0**	**41.4**	**52.1**	**--**	**--**	**--**	**--**	**202.6**	**5.6E-02**
	t=0	300.1	--	100.0	--	100.1	--	99.8	--	99.9	--	--	--
	Background	296.6	1.2	97.7	2.3	99.8	0.3	95.3	4.5	97.5	2.4	--	--
	Run #1	290.7	2.0	49.5	48.2	27.5	72.2	16.5	79.0	14.8	82.8	288.5	8.0E-02
	Run #2	294.2	0.8	57.2	40.5	34.3	65.4	21.3	74.1	19.5	78.1	260.9	7.2E-02
	Average	**292.5**	**1.4**	**53.4**	**44.4**	**30.9**	**68.8**	**18.9**	**76.6**	**17.2**	**80.4**	**274.7**	**7.6E-02**
	t=0	300.1	--	200.3	--	--	--	--	--	--	--	--	--
	Background	295.4	1.6	198.2	1.0	--	--	--	--	--	--	--	--
	Run #1	284.4	3.7	177.6	10.3	--	--	--	--	--	--	31.9	8.9E-03
	Run #2	282.8	4.2	176.8	10.7	--	--	--	--	--	--	34.3	9.5E-03
	Average	**283.6**	**3.9**	**177.2**	**10.5**	**--**	**--**	**--**	**--**	**--**	**--**	**33.1**	**9.2E-03**
	t=0	301.0	--	201.2	--	201.0	--	--	--	--	--	--	--
	Background	299.0	0.7	200.5	0.3	196.6	2.2	--	--	--	--	--	--
	Run #1	296.1	1.0	138.0	31.1	34.8	80.5	--	--	--	--	76.0	2.1E-02
	Run #2	294.3	1.6	130.6	34.7	32.9	81.4	--	--	--	--	79.7	2.2E-02
	Average	**295.2**	**1.3**	**134.3**	**32.9**	**33.9**	**81.0**	**--**	**--**	**--**	**--**	**77.8**	**2.2E-02**
	t=0	99.8		99.9	--	99.9	--	99.8	--	--	--	--	--
	Background	97.7	2.1	97.8	2.1	95.0	4.9	94.6	5.2	--	--	--	--
	Run #1	86.6	11.1	58.6	39.2	51.9	43.1	61.0	33.7	--	--	130.0	3.6E-02
	Run #2	94.0	3.7	59.4	38.4	54.2	40.8	63.2	31.5	--	--	84.9	2.4E-02
	Average	**90.3**	**7.4**	**59.0**	**38.8**	**53.1**	**42.0**	**62.1**	**32.6**	**--**	**--**	**90.2**	**2.5E-02**

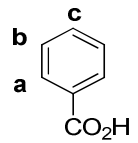
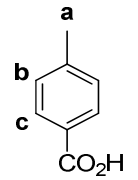
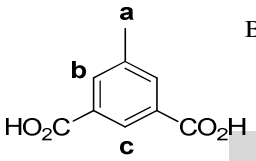
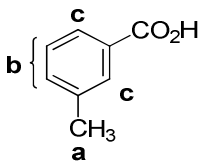
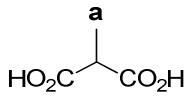
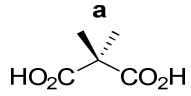
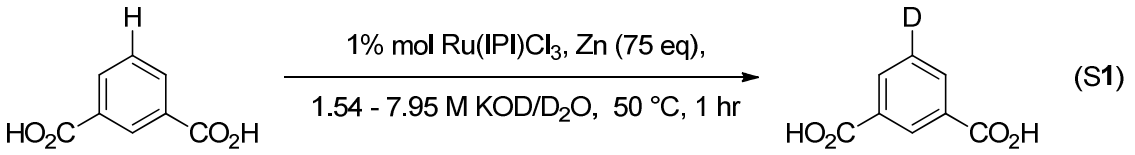
	t=0	199.8	--	200.0	--	99.9	--	--	--	--	--	--	--
	Background	191.5	4.2	198.8	0.6	96.1	3.8	--	--	--	--	--	--
	Run #1	83.3	56.5	128.3	35.5	56.7	41.0	--	--	--	--	219.4	6.1E-02
	Run #2	82.8	56.8	133.8	32.7	56.7	41.0	--	--	--	--	214.4	6.0E-02
	Average	**83.1**	**56.6**	**131.1**	**34.1**	**56.7**	**41.0**	**--**	**--**	**--**	**--**	**216.9**	**6.0E-02**

Table S2. H/D exchange of various substrates at 160 °C for 1 h with 1 mol% Ru(IPI)Cl_3 in 13% KOD.

Substrate		**a**	**% D**	**b**	**% D**	**c**	**% D**	**d**	**% D**	**e**	**% D**	**Total TON**	**Total TOF (s^{-1})**
	t=0	298.2	--	199.1	--	198.9	--	--	--	--	--	--	--
	Background	229.7	23.0	193.8	2.7	193.8	2.6	--	--	--	--	--	--
	Run #1	151.6	34.0	92.7	52.2	5.2	97.3	--	--	--	--	379.6	1.1E-01
	Run #2	155.9	32.1	98.4	49.2	4.6	97.6	--	--	--	--	369.9	1.0E-01
	Average	**153.8**	**33.1**	**95.6**	**50.7**	**4.9**	**97.5**	**--**	**--**	**--**	**--**	**374.7**	**1.0E-01**
	t=0	292.0	--	194.7	--	97.2	--	--	--	--	--	--	--
	Background	280.1	4.1	190.0	2.4	90.6	6.8	--	--	--	--	--	--
	Run #1	231.8	17.2	4.7	97.5	2.3	97.5	--	--	--	--	338.8	9.4E-02
	Run #2	236.5	15.6	4.7	97.5	2.3	97.5	--	--	--	--	333.9	9.3E-02
	Average	**234.2**	**16.4**	**4.7**	**97.5**	**2.3**	**97.5**	**--**	**--**	**--**	**--**	**336.4**	**9.3E-02**
	t=0	299.5	--	199.8	--	199.6	--	--	--	--	--	--	--
	Background	284.7	4.9	196.8	1.5	193.5	3.1	--	--	--	--	--	--
	Run #1	233.8	17.9	31.2	84.1	4.5	97.7	--	--	--	--	412.1	1.1E-01
	Run #2	220.2	22.7	56.9	71.1	4.5	97.7	--	--	--	--	399.8	1.1E-01
	Average	**227.0**	**20.3**	**44.1**	**77.6**	**4.5**	**97.7**	**--**	**--**	**--**	**--**	**405.9**	**1.1E-01**

	t=0	301.1	--					--	--	--	--	--	--
	Background	299.8	0.4	--	--	--	--	--	--	--	--	--	--
	Run #1	261.4	12.8	--	--	--	--	--	--	--	--	38.4	1.1E-02
	Run #2	260.9	13.0	--	--	--	--	--	--	--	--	38.9	1.1E-02
	Average	**261.2**	**12.9**	**--**	**--**	**--**	**--**	**--**	**--**	**--**	**--**	**38.7**	**1.1E-02**
	t=0	599.5	--					--	--	--	--	--	--
	Background	598.3	0.2	--	--	--	--	--	--	--	--	--	--
	Run #1	559.4	6.5	--	--	--	--	--	--	--	--	39.0	1.1E-02
	Run #2	564.8	5.6	--	--	--	--	--	--	--	--	33.6	9.3E-03
	Average	**562.1**	**6.1**	**--**	**--**	**--**	**--**	**--**	**--**	**--**	**--**	**36.3**	**1.0E-02**

Base Acceleration Study: A stock solution of substrate (0.90 mmol in 3 mL of 2.14-8.55 M KOD/D_2O resulting in effective concentrations of 1.54-7.95 M KOD/D_2O) which was subsequently added to a separate vial containing **1** (2.5 mg, 6.0 μmol in 2 mL of substrate solution). These prepared solutions (0.7 mL of two containing catalyst and one without catalyst) were added to three separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc powder (15 mg, 0.23 mmol). The reactors were sealed and the solutions were degassed by repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). The prepared reactors were place in an aluminum block set 50 °C for 1 h. Upon reaction completion, the reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. The catalyst runs was averaged and subtracted from the background (without catalyst) to give percent deuterium incorporation. The only position that was used for the study was *meta* to both carboxylic acid moieties to ensure no steric or chelation effect was observed. The raw data contained in table S3 for figure 4.



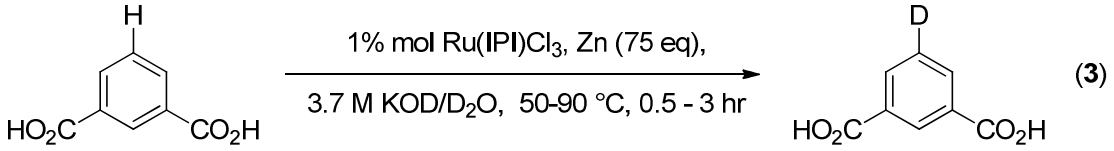
(S**1**)

Table S3. H/D exchange of IA at 50 °C for 1 mol% Ru(IPI)Cl_3 in 1.54-7.95 M KOD for 1h.

Added [KOD] (M)	Reaction [KOD] (M)		Hours	a	b	c	Total TON	Total TOF (s^{-1})	Meta TON	Meta TOF (s^{-1})	Standard Error (s^{-1})
8.55	7.95	t=0	1	99.4	198.9	99.3	--	--	--	--	--
8.55	7.95	Background	1	99.3	197.1	94.5	--	--	--	--	--
8.55	7.95	Run #1	1	87.9	161.8	79.3	62.3	1.7E-02	11.5	3.2E-03	0.0001539
8.55	7.95	Run #2	1	89	163.9	80.5	57.9	1.6E-02	10.4	2.9E-03	0.0001539
8.55	7.95	**Average**	**1**	**88.45**	**162.85**	**79.9**	**60.1**	**1.7E-02**	**10.9**	**3.0E-03**	**0.0001539**
7.60	7.00	t=0	1	98.2	197.4	98.3	--	--	--	--	--
7.60	7.00	Background	1	97.9	194.3	94.1	--	--	--	--	--
7.60	7.00	Run #1	1	90.3	169.1	81.1	46.8	1.3E-02	7.8	2.2E-03	0.0001746
7.60	7.00	Run #2	1	89.8	166.5	82.2	48.8	1.4E-02	9.0	2.5E-03	0.0001746
7.60	7.00	**Average**	**1**	**90.05**	**167.8**	**81.65**	**47.8**	**1.3E-02**	**8.0**	**2.2E-03**	**0.0001746**
6.41	5.81	t=0	1	98.4	197	98.2	--	--	--	--	--
6.41	5.81	Background	1	98.1	194.2	91.4	--	--	--	--	--
6.41	5.81	Run #1	1	93.9	179.3	86.5	24.5	6.8E-03	4.3	1.2E-03	0
6.41	5.81	Run #2	1	93.9	180	86.6	23.6	6.6E-03	4.3	1.2E-03	0
6.41	5.81	**Average**	**1**	**93.9**	**179.65**	**86.55**	**24.1**	**6.7E-03**	**4.3**	**1.2E-03**	**0.00E+00**
5.06	4.46	t=0	1	98.4	196.9	98.3	--	--	--	--	--
5.06	4.46	Background	1	98.2	195.2	91.1	--	--	--	--	--
5.06	4.46	Run #1	1	95.1	180.7	86.4	22.7	6.3E-03	3.2	8.8E-04	1.414E-05
5.06	4.46	Run #2	1	95	180.4	85.9	23.6	6.6E-03	3.3	9.1E-04	1.414E-05
5.06	4.46	**Average**	**1**	**95.05**	**180.55**	**86.15**	**23.2**	**6.4E-03**	**3.2**	**8.9E-04**	**1.414E-05**
3.71	3.11	t=0	1	98	196.1	97.8	--	--	--	--	--
3.71	3.11	Background	1	97.9	193.2	88.1	--	--	--	--	--
3.71	3.11	Run #1	1	96.1	186.5	86.9	9.9	2.8E-03	1.8	5.1E-04	1.952E-05
3.71	3.11	Run #2	1	96	184.8	85.9	12.8	3.5E-03	2.0	5.5E-04	1.952E-05
3.71	3.11	**Average**	**1**	**96.05**	**185.65**	**86.4**	**11.3**	**3.1E-03**	**1.9**	**5.2E-04**	**1.952E-05**

2.14	1.54	t=0	1	99	198.1	98.9	--	--	--	--	--
2.14	1.54	Background	1	98.8	193.4	85.3	--	--	--	--	--
2.14	1.54	Run #1	1	97.6	190.7	85	4.3	1.2E-03	1.2	3.4E-04	1.649E-05
2.14	1.54	Run #2	1	97.5	189.5	84.4	6.2	1.7E-03	1.3	3.7E-04	1.649E-05
2.14	1.54	**Average**	**1**	**97.55**	**190.1**	**84.7**	**5.2**	**1.4E-03**	**1.3**	**3.6E-04**	**1.649E-05**

Activation Parameters for IA with 2: A stock solution of substrate (0.90 mmol in 3 mL of 3.71 M KOD/D_2O resulting in effective concentrations of 3.11 M KOD/D_2O) which was subsequently added to a separate vial containing **1** (2.5 mg, 6.0 μmol in 2 mL of substrate solution). These prepared solutions (0.7 mL of two containing catalyst and one without catalyst) were added to three separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc powder (15 mg, 0.23 mmol). The reactors were sealed and the solutions were degassed by repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). The prepared reactors were place in an aluminum block set (50-80 °C) for 1 h. Upon reaction completion, the reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. The catalyst runs was averaged and subtracted from the background (without catalyst) to give percent deuterium incorporation. Figure S4 shows the eyring plot of **IA** and table S4 shows the data for the plot. The data gives a $\Delta G = 23.6 \pm 1.7$ kcal mol^{-1} at 298 K, $\Delta H = 17.8 \pm 0.9$ kcal mol^{-1}, and $\Delta S = -19.6 \pm 2.6$ kcal mol^{-1}.



(**3**)

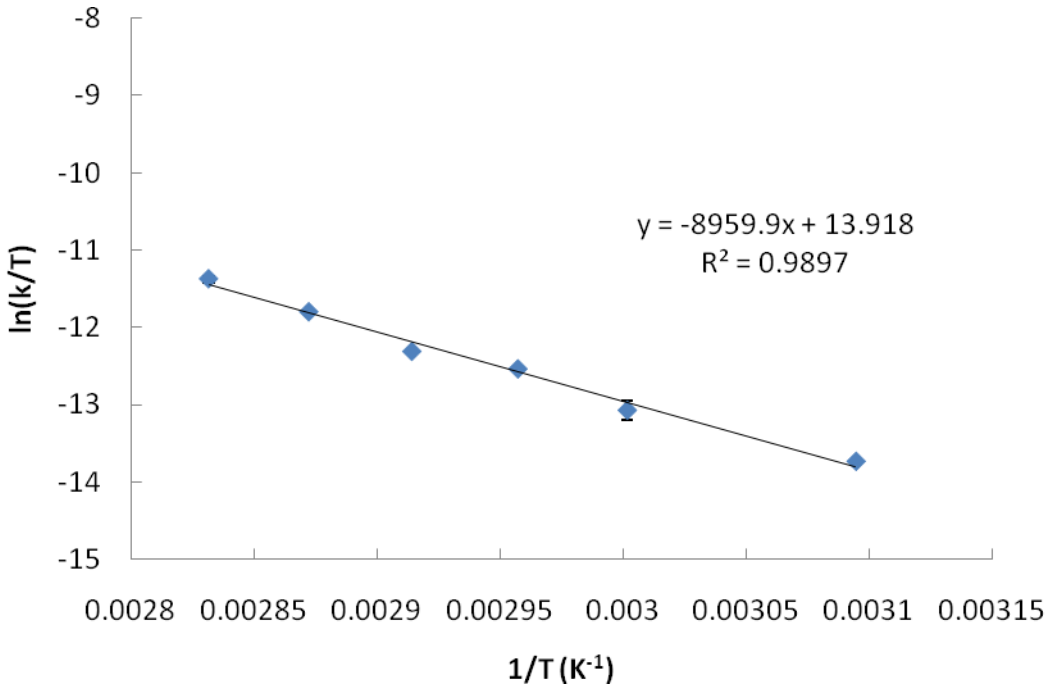


Figure S4. Eyring Plot of ln(k/T) vs 1/T

Table S4. H/D exchange of IA at 50-90 °C with 1 mol% Ru(IPI)Cl_3 in 3.11 M KOD for 0.5-3 h.

T (°C)		Hours	a	b	c	Total TON	Total TOF (s^{-1})	Meta TON	Meta TOF (s^{-1})	1/T	ln(k/T)
80	t=0	1	99.4	198.9	99.3	--	--	--	--	--	--
80	Background	1	99.2	196.2	91.4	--	--	--	--	--	--
80	Run #1	1	85.3	143	68.1	91.1	2.5E-02	14.0	3.9E-03	0.00283	-11.416
80	Run #2	1	84.1	139.9	66.9	96.7	2.7E-02	15.2	4.2E-03	0.00283	-11.333
80	**Average**	**1**	**84.7**	**141.45**	**67.5**	**93.9**	**2.6E-02**	**14.6**	**4.1E-03**	**0.00283**	**-11.373**
75	t=0	1	99.7	197	97.9	--	--	--	--	--	--
75	Background	1	99.5	196.2	90.3	--	--	--	--	--	--
75	Run #1	1	90.0	146.0	70.9	79.5	2.2E-02	9.5	2.7E-03	0.00287	-11.785
75	Run #2	1	90.3	165.3	77.8	52.9	1.5E-02	9.2	2.6E-03	0.00287	-11.817
75	**Average**	**1**	**90.2**	**155.7**	**74.4**	**66.2**	**1.8E-02**	**9.4**	**2.6E-03**	**0.00287**	**-11.801**
70	t=0	1	99.7	197	97.9	--	--	--	--	--	--
70	Background	1	99.5	196.2	90.3	--	--	--	--	--	--
70	Run #1	1	94.3	166.6	81.2	44.1	1.2E-02	5.2	1.5E-03	0.00291	-12.373
70	Run #2	1	94.4	166.6	81.7	43.5	1.2E-02	5.1	1.4E-03	0.00291	-12.393
70	**Average**	**1**	**94.4**	**166.6**	**81.5**	**43.8**	**1.2E-02**	**5.2**	**1.4E-03**	**0.00291**	**-12.383**
65	t=0	1	98.6	197.3	98.5	--	--	--	--	--	--
65	Background	1	99.6	197.1	89.8	--	--	--	--	--	--
65	Run #1	1	95.2	175.4	82.2	33.8	9.4E-03	4.4	1.2E-03	0.00296	-12.527
65	Run #2	1	95.3	177.5	82.9	30.9	8.6E-03	4.3	1.2E-03	0.00296	-12.55
65	**Average**	**1**	**95.25**	**176.45**	**82.55**	**32.4**	**9.0E-03**	**4.4**	**1.2E-03**	**0.00296**	**-12.538**
60	t=0	1	98.6	197.3	98.5	--	--	--	--	--	--
60	Background	1	97.8	195.1	90	--	--	--	--	--	--
60	Run #1	1	96.2	182	85.1	20.0	5.6E-03	1.6	4.5E-04	0.003	-13.505
60	Run #2	1	95.6	181.4	86	20.3	5.7E-03	2.2	6.2E-04	0.003	-13.187
60	**Average**	**1**	**95.9**	**181.7**	**85.55**	**20.2**	**5.6E-03**	**1.9**	**5.4E-04**	**0.003**	**-13.333**

50	t=0	1	98	196.1	97.8	--	--	--	--	--	--
50	Background	1	98.8	193.4	85.3	--	--	--	--	--	--
50	Run #1	1	97.6	190.7	85	4.3	1.2E-03	1.2	3.4E-04	0.00309	-13.772
50	Run #2	1	97.5	189.5	84.4	6.2	1.7E-03	1.3	3.7E-04	0.00309	-13.692
50	**Average**	**1**	**97.55**	**190.1**	**84.7**	**5.2**	**1.4E-03**	**1.3**	**3.5E-04**	**0.00309**	**-13.732**

Order in Catalyst: Four stock solutions of substrate (three containing 150 mg in 3 mL of 3.71 M KOD/D_2O and 1 containing 300 mg in 6 mL of 3.71 M KOD/D_2O) of which 2 mL of each 3 mL solution and 4 mL of the 6 mL solution was subsequently added to four separate vials containing **1** (1.25 mg, 1.88 mg, 2.5 mg, and 1.25 mg respectively). These prepared solutions (0.7 mL of two containing catalyst and one without catalyst at for 4 different time points for a total of 12 runs) were added to 12 separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc powder (15 mg, 0.23 mmol). The reactors were sealed and the solutions were degassed by repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). The prepared reactors were place in an aluminum block set at 80 °C for 1 h. Upon reaction completion, the reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. The catalyst runs was averaged and subtracted from the background (without catalyst) to give percent deuterium incorporation. Table S5 contains the raw data for Figure 3A.

Table S5. H/D exchange of 0.3 M **IA** at 80 °C with 0.25-1 mol% **1** in 3.11 M KOD for 1 h.

[Cat] (mM)	[IA] (M)		time (h)	a	b	c	Total TON	Total TOF (s^{-1})	Meta TON	Meta TOF (s^{-1})	Rate (s^{-1})	Standard Error
3.00	0.30	t=0	0	101.2	202.2	101.0	--	--	--	--	--	--
3.00	0.30	Background	1	100.6	200.8	99.2	--	--	--	--	--	--
3.00	0.30	Run #1	1	85.7	140.7	68.9	105.0	2.9E-02	14.9	4.1E-03	1.2E-03	8.3E-05
3.00	0.30	Run #2	1	83.7	136.9	68.3	111.4	3.1E-02	16.9	4.7E-03	1.4E-03	8.3E-05
3.00	0.30	**Average**	**1**	**84.7**	**138.8**	**68.6**	**108.2**	**3.0E-02**	**15.9**	**4.4E-03**	**1.3E-03**	**8.3E-05**
2.25	0.30	t=0	0	98.8	197.5	98.4	--	--	--	--	--	--
2.25	0.30	Background	1	98.5	194.3	89.4	--	--	--	--	--	--
2.25	0.30	Run #1	1	86.8	145.7	70.2	107.9	3.0E-02	15.9	4.4E-03	9.9E-04	7.6E-05
2.25	0.30	Run #2	1	88.6	152.5	73.0	92.5	2.6E-02	13.4	3.7E-03	8.4E-04	7.6E-05
2.25	0.30	**Average**	**1**	**87.7**	**149.1**	**71.6**	**100.2**	**2.8E-02**	**14.7**	**4.1E-03**	**9.2E-04**	**7.6E-05**
1.50	0.30	t=0	0	100.4	200.4	100.3	--	--	--	--	--	--
1.50	0.30	Background	1	100.0	197.9	95.6	--	--	--	--	--	--
1.50	0.30	Run #1	1	93.2	165.8	77.3	129.0	3.6E-02	13.6	3.8E-03	5.7E-04	4.6E-05
1.50	0.30	Run #2	1	92.1	167.9	78.3	125.0	3.5E-02	15.8	4.4E-03	6.6E-04	4.6E-05
1.50	0.30	**Average**	**1**	**92.7**	**166.9**	**77.8**	**127.0**	**3.5E-02**	**14.7**	**4.1E-03**	**6.1E-04**	**4.6E-05**
0.75	0.30	t=0	0	98.8	197.2	98.5	--	--	--	--	--	--
0.75	0.30	Background	1	98.4	194.9	88.9	--	--	--	--	--	--
0.75	0.30	Run #1	1	94.7	183.0	87.0	146.4	4.1E-02	15.1	4.2E-03	3.1E-04	1.3E-05
0.75	0.30	Run #2	1	95.0	178.1	81.4	188.0	5.2E-02	13.9	3.9E-03	2.9E-04	1.3E-05
0.75	0.30	**Average**	**1**	**94.9**	**166.9**	**77.8**	**249.1**	**6.9E-02**	**14.5**	**4.0E-03**	**3.0E-04**	**1.3E-05**

Order in Catalyst: Four stock solutions of substrate (75 mg, 150 mg, 225 mg, and 300 mg in 3 mL of 3.40 M, 3.71 M, 4.01 M, 4.31 M KOD/D_2O respectively) of which 2 mL of each solution was subsequently added to four separate vials containing **1** (2.5 mg, 6 μmol in 2 mL). These prepared solutions (0.7 mL of two containing catalyst and one without catalyst at for 4 different time points for a total of 12 runs) were added to 12 separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc powder (15 mg, 0.23 mmol). The reactors were sealed and the solutions were degassed by repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). The prepared reactors were place in an aluminum block set at 80 °C for 1 h. Upon reaction completion, the reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. The catalyst runs was averaged and subtracted from the background (without catalyst) to give percent deuterium incorporation. Table S6 contains the raw data for Figure 3B.

Table S6. H/D exchange of 0.15-0.60 M **IA** at 80 °C with 1 mol% **1** in 3.11 M KOD for 1 h.

[Cat] (mM)	[IA] (M)		time (h)	a	b	c	Total TON	Total TOF (s^{-1})	Meta TON	Meta TOF (s^{-1})	Rate (s^{-1})	Standard Error
3.0	0.60	t=0	0	100.1	200.2	100.0	--	--	--	--	--	--
3.0	0.60	Background	1	99.8	197.6	96.2	--	--	--	--	--	--
3.0	0.60	Run #1	1	83.2	130.5	64.6	245.8	6.8E-02	33.4	9.3E-03	2.8E-03	9.2E-05
3.0	0.60	Run #2	1	84.3	133.7	66.1	234.2	6.5E-02	31.2	8.7E-03	2.6E-03	9.2E-05
3.0	0.60	**Average**	**1**	**83.8**	**132.1**	**65.4**	**240.0**	**6.7E-02**	**32.3**	**9.0E-03**	**2.7E-03**	**9.2E-05**
3.0	0.45	t=0	0	99.5	198.8	99.4	--	--	--	--	--	--
3.0	0.45	Background	1	99.3	196.8	90.7	--	--	--	--	--	--
3.0	0.45	Run #1	1	82.5	136.0	66.9	153.2	4.3E-02	25.4	7.0E-03	2.1E-03	1.1E-04
3.0	0.45	Run #2	1	84.2	140.1	68.5	142.0	3.9E-02	22.8	6.3E-03	1.9E-03	1.1E-04
3.0	0.45	**Average**	**1**	**83.4**	**138.1**	**67.7**	**147.6**	**4.1E-02**	**24.1**	**6.7E-03**	**2.0E-03**	**1.1E-04**
3.0	0.30	t=0	0	101.2	202.2	101.0	--	--	--	--	--	--
3.0	0.30	Background	1	100.6	200.8	99.2	--	--	--	--	--	--
3.0	0.30	Run #1	1	85.7	140.7	68.9	105.0	2.9E-02	14.9	4.1E-03	1.2E-03	8.3E-05
3.0	0.30	Run #2	1	83.7	136.9	68.3	111.4	3.1E-02	16.9	4.7E-03	1.4E-03	8.3E-05
3.0	0.30	**Average**	**1**	**84.7**	**138.8**	**68.6**	**108.2**	**3.0E-02**	**15.9**	**4.4E-03**	**1.3E-03**	**8.3E-05**
3.0	0.15	t=0	0	100.8	201.3	100.7	--	--	--	--	--	--
3.0	0.15	Background	1	100.1	199.0	91.4	--	--	--	--	--	--
3.0	0.15	Run #1	1	85.0	135.3	69.9	55.3	1.5E-02	7.6	2.1E-03	6.3E-04	5.8E-05
3.0	0.15	Run #2	1	87.8	138.7	67.0	53.7	1.5E-02	6.2	1.7E-03	5.2E-04	5.8E-05
3.0	0.15	**Average**	**1**	**86.4**	**137.0**	**68.4**	**54.5**	**1.5E-02**	**6.9**	**1.9E-03**	**5.7E-04**	**5.8E-05**

Stability Study: A stock solution of substrate (400 mg in 8 mL of 3.71 M KOD/D_2O resulting in an effective concentration of 3.11 M KOD/D_2O) which 6 mL was subsequently added to a separate vial containing **1** (7.5 mg). These prepared solutions (0.7 mL of two containing catalyst and one without catalyst at for 3 different time points for a total of 9 runs) were added to 9 separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc powder (15 mg, 0.23 mmol). The reactors were sealed and the solutions were degassed by repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). The prepared reactors were place in an aluminum block set at 90 °C for 2-4 h. Upon reaction completion, the reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. The catalyst runs was averaged and subtracted from the background (without catalyst) to give percent deuterium incorporation. Figure S5 is a plot of the TOF (s^{-1}) vs time (h) of the H/D exchange reaction of IA at 70 °C with 1% of **1** and table S7 contains the data for the plot.

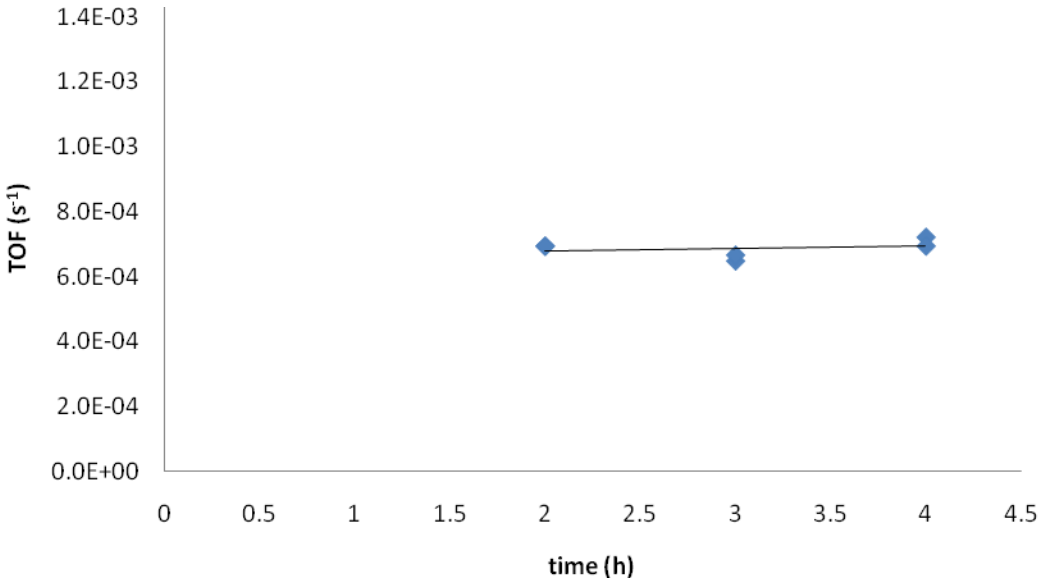


Figure S5. Plot of TOF (s^{-1}) vs time (h) at 70 °C with [**1**] = 3.0 mM and [**IA**] = 0.30 M

Table S7. H/D exchange of 0.3 M **IA** at 70 °C with 1 mol% **1** in 1.54 M KOD for 2-4 h.

[Cat] (mM)	[IA] (M)		time (h)	a	b	c	Total TON	Total TOF (s^{-1})	Meta TON	Meta TOF (s^{-1})
3.00	0.30	Background	0	100.3	197.3	87.3	--	--	--	--
3.00	0.30	Run #1	2	95.3	172.2	79.9	37.5	5.2E-03	5.0	6.9E-04
3.00	0.30	Run #2	2	95.3	172.7	80.4	36.5	5.1E-03	5.0	6.9E-04
3.00	0.30	**Average**	**2**	**95.3**	**172.45**	**80.15**	**37.0**	**5.1E-03**	**5.0**	**6.9E-04**
3.00	0.30	Background	3	100.5	197.5	87.3	--	--	--	--
3.00	0.30	Run #1	3	93.5	166.2	77.9	47.7	4.4E-03	7.0	6.5E-04
3.00	0.30	Run #2	3	93.3	164.6	76.2	51.2	4.7E-03	7.2	6.7E-04
3.00	0.30	**Average**	**3**	**93.4**	**165.4**	**77.05**	**49.5**	**4.6E-03**	**7.1**	**6.6E-04**
3.00	0.30	Background	4	99.2	195.6	88.2	--	--	--	--
3.00	0.30	Run #1	4	88.8	146.3	70	77.9	5.4E-03	10.4	7.2E-04
3.00	0.30	Run #2	4	88.5	148.8	70.3	75.4	5.2E-03	10.7	7.4E-04
3.00	0.30	**Average**	**4**	**88.65**	**147.55**	**70.15**	**76.7**	**5.3E-03**	**10.6**	**7.3E-04**

Isolation of (IPI)Ru(II) Species.: A 5mL Schlenk bomb was charged with 11.9 mg of **2**, ~20 mg Zn, and 1 mL of 3.71 M KOD/D_2O. The solution was stirred for ~10 min, then 15 mg of KCN. The solution wash then stirred 2.5 h at RT. The solution was then transferred to a J-Young tube under argon.

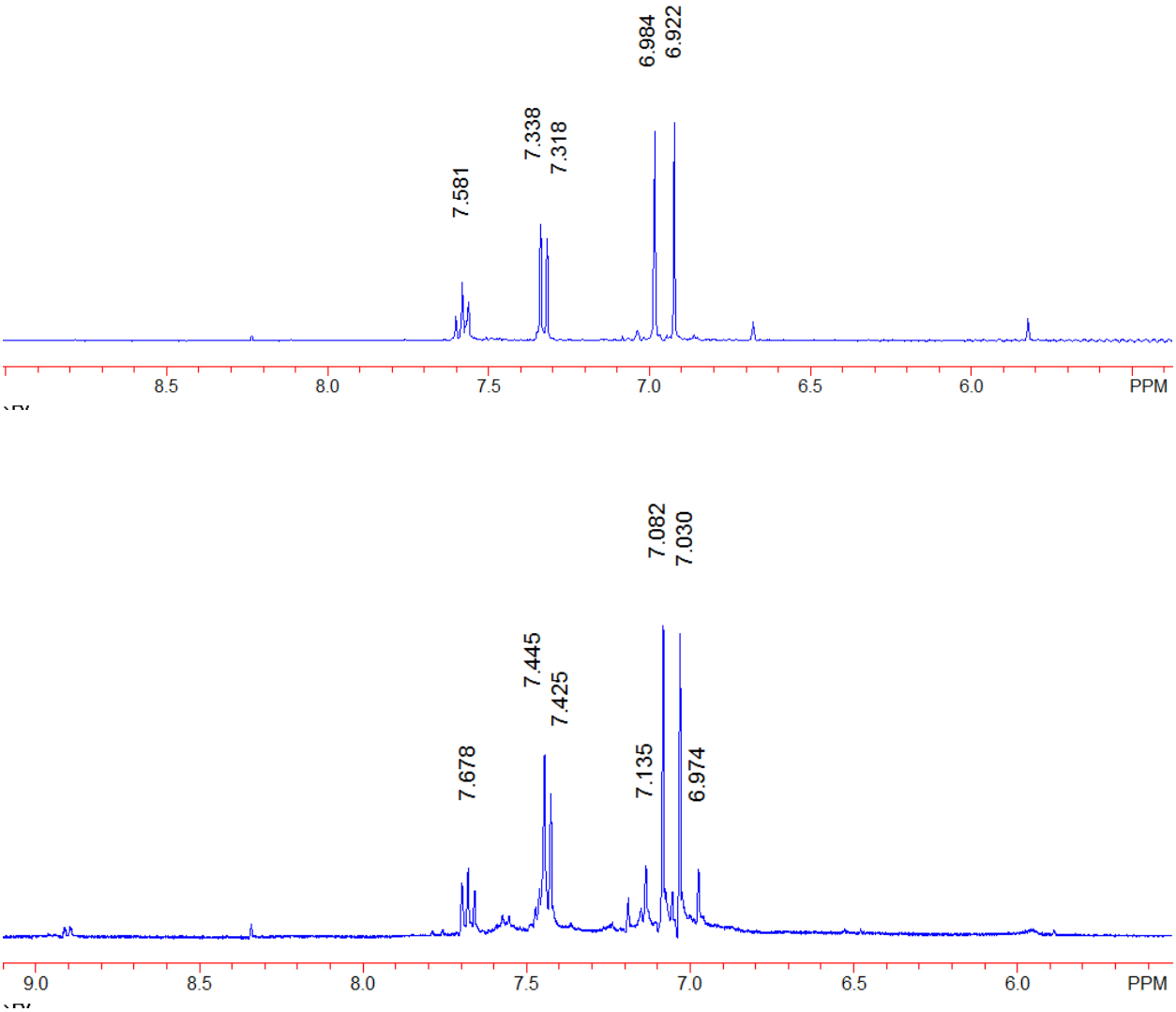
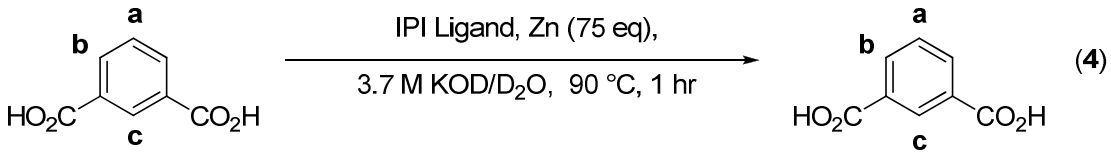


Figure S6. Top. ^{1}H NMR of (IPI)Ru(II)$(CN)_3$. Bottom. ^{1}H NMR of trapped species from the addition of KCN to a reduced solution of **2**.

H/D exchange with IPI ligand: A stock solutions of isophtahlic acid (0.90 mmol in 3 mL of 3.71 M KOD/D_2O) was made. IPI stock solution was then made by adding 2 mL of substrate solution to a separate vial containing IPI ligand (10 mg, 47.3 µmol). These prepared solutions (0.7 mL of two containing ligand and one without ligand) were added to three separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc powder (~20 mg). The reactors were sealed and the solutions were degassed by repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). The prepared reactors were place in an aluminum block set at 90°C and heated for 1h. The reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. Table S8 contains the data obtained from the free ligand study.



(**4**)

Table S8. H/D exchange of **IA** at 90 °C with 15.8 mol% IPI ligand in 3.71 M KOD for 1h.

		a	%D	b	%D	c	%D
IPI Ligand	t=0	111.2	--	222.6	--	109.3	--
IPI Ligand	Background	111.3	-0.1	222.2	0.4	105.1	3.8
IPI Ligand	Run #1	114.8	-3.1	233.8	-10.4	108.5	-3.1
IPI Ligand	Run #2	106.3	4.5	216.5	5.1	103.5	1.5
IPI Ligand	**Average**	**110.6**	**0.7**	**225.2**	**-2.7**	**106.0**	**-0.8**

H/D exchange with $RuCl_3$.: A stock solutions of isophtahlic acid (0.90 mmol in 3 mL of 3.71 M KOD/D_2O) was made. The stock solution was then added to three separate high pressure

stainless steel reactors (two with 5 mg of $RuCl_3(H2O)_3$ each, and one without $RuCl_3(H2O)_3$) each containing a PTFE insert, a stir-bar and zinc powder (~20 mg). The reactors were sealed and the solutions were degassed by repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). The prepared reactors were place in an aluminum block set at 90°C and heated for 1h. The reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. Table S9 contains the data obtained from the $RuCl_3(H2O)_3$ study.

Table S9. H/D exchange of **IA** at 90 °C with 6.4 mol% $RuCl_3$ in 3.71 M KOD for 1h.

		a	%D	b	%D	c	%D
$Ru(H_2O)_3Cl_3$	t=0	111.2	--	222.6	--	109.3	--
$Ru(H_2O)_3Cl_3$	Background	109.7	1.3	218.9	3.3	103.8	5.0
$Ru(H_2O)_3Cl_3$	Run #1	108.4	1.2	221.7	-2.5	102.0	1.6
$Ru(H_2O)_3Cl_3$	Run #2	108.7	0.9	215.1	3.4	100.9	2.7
$Ru(H_2O)_3Cl_3$	**Average**	**108.6**	**1.0**	**218.4**	**0.4**	**101.5**	**2.2**

Inhibition studies: In a typical experiment a 0.55 M stock solution of isophthalic acid in 3.71 M KOD/D_2O was made. For the KCN study 5.2 mg of catalyst was dissolved in 2 mL of the substrate stock solution. For the KCN Three separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc dust (~20 mg), were separately loaded with 0.7 mL of substrate solution, 0.7 mL catalyst solution, and 0.7mL catalyst solution and 5 equiv. KCN. For the Isonicotinic studies, 5.2 mg of catalyst was dissolved in 2 mL of the substrate stock solution. Three separate high pressure stainless steel reactors each containing a PTFE insert, a stir-bar and zinc dust (~20 mg), were separately loaded with 0.7 mL of substrate solution, 0.7 mL catalyst solution and 5 equiv. isonicatinic acid sodium salt, and 0.7mL catalyst solution and 25 equiv. isonicatinic acid sodium salt. The reactors were sealed and the solutions were degassed by

repeatedly (5x) pressurizing with Ar (500 psi) and purging and finally left under Ar (500 psi). The prepared reactors were place in an aluminum block set at 90°C and heated for 1h. Upon reaction completion, the reactors were cooled in a dry ice/acetone bath and the pressure was released. An internal standard (0.2 mL of a 1.05 M KOAc solution) was added to each reactor and NMR spectroscopy (with a 10 s relaxation delay) was used to monitor proton loss and deuterium incorporation. Table S10 contains the data obtained from the inhibition studies.

Table S10. H/D exchange of **IA** at 90 °C with 1 mol% **1** in 3.71 M KOD in the presence of L for 1h.

		a	**%D**	**b**	**%D**	**c**	**%D**
	Background	191.6	--	379.7	--	177.7	--
1 mol % **2**	w/out KCN	172.8	9.8	349.2	8.0	164.9	7.2
1 mol % **2**	5 eq KCN	190.7	0.5	376.9	0.7	179.3	-0.9

		a	**%D**	**b**	**%D**	**c**	**%D**
	t=0	139.1	--	278.2	--	137.6	--
	Background	127.1	--	254.8	--	123.2	--
1 mol % **2**	5 eq Nicotinic acid	134.5	-5.8	266.9	-4.7	131.6	-6.8
1 mol % **2**	25 eq Nicotinic acid	137.0	-7.8	274.8	-7.8	134.9	-9.5

Rate Law:

$$HLM(OH)(H_2O) + OH^- \underset{\text{Fast}}{\overset{K_1}{\rightleftharpoons}} [HLM(OH)_2]^- + H_2O \quad \textbf{(5)}$$

To account for the lack of inhibition by OH^- it is required that Eq 5 be reversible; i.e. $HLM(OH)(H_2O)$ is strongly basic and $K_1 < 1$. $HLM(OH)(H_2O)$ is representative of a ground state with the key requirement that this state still has protic ligands that can be reversibly deprotonated. In the actual systems it is likley that some of the protic ligands will be irreversibly deprotonated to generate a ground state that meets this requirement. This will only be possible with weakly acidic metals and multiple protic spectator ligands. The following equilibria (eq. 6-8) can be simplified to eq. 9 and eq 10 is proposed to be the slow step:

$$HLM(OH)(H_2O) + OH- \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} [LM(OH)(H_2O)]^- + H_2O \quad \textbf{(6)}$$

$$[LM(OH)(H_2O)]^- \underset{\text{fast}}{\overset{K_2}{\rightleftharpoons}} [LM(OH)]^- + H_2O \quad \textbf{(7)}$$

$$[LM(OH)]^- + RH \underset{\text{fast}}{\overset{K_3}{\rightleftharpoons}} [LM(OH)(RH)]^- \quad \textbf{(8)}$$

Conjugate mechanism

Simplifies

$$HLM(OH)(H_2O) + OH- + RH \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} [LM(OH)(RH)]- + 2\,H_2O \quad \textbf{(9)}$$

$$[LM(OH)(RH)]^- + H_2O \xrightarrow[\text{slow}]{k} HLM(H_2O)(R) + OH^- \quad \textbf{(10)}$$

The eq. 9 and 10 can be used to solve the rate equation (eq. 11) and the catalyst TOF can be solved from eq 11 to give eq 12.

$$r = \frac{kK[RH][HLM(OH)(H_2O)][OH^-]}{[H_2O]} \quad \textbf{(11)}$$

where $r = k[[LM(OH)(RH)]^-][H_2O]$ and $K = \frac{[[LM(OH)(RH)]^-][H_2O]^2}{[HLM(OH)(H_2O)][OH^-][RH]}$

$$TOF = \frac{kK[RH][OH^-]}{[H_2O]} \quad \textbf{(12)}$$

NMR

Data:

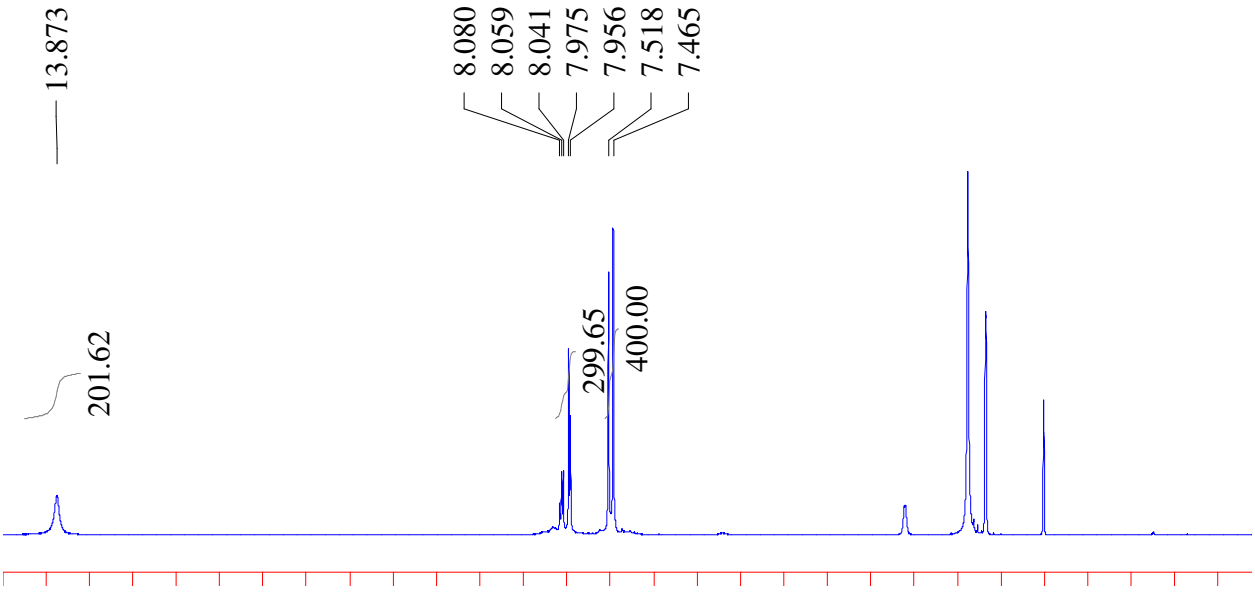


Figure S7. ^{1}H NMR Spectrum of Ru(IPI)Cl_3 with zinc dust in d^6-DMSO

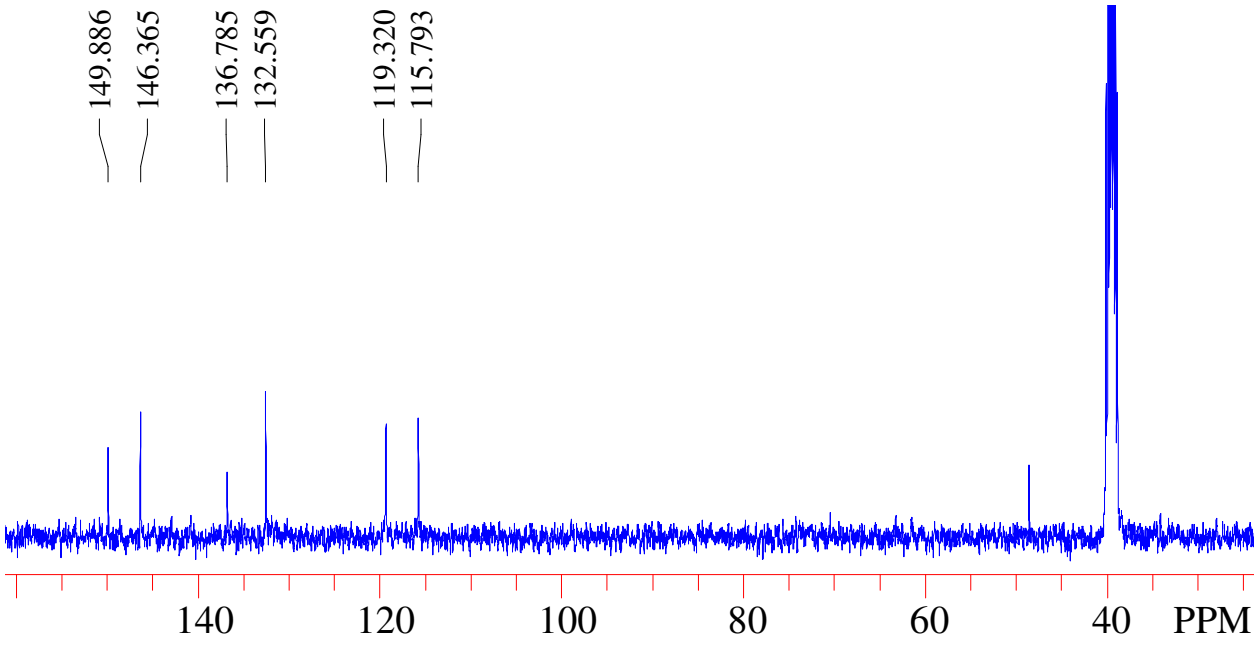


Figure S8. $^{13}C\{^{1}H\}$ NMR Spectrum of $Ru(IPI)Cl_3$ with zinc dust in d^6-DMSO

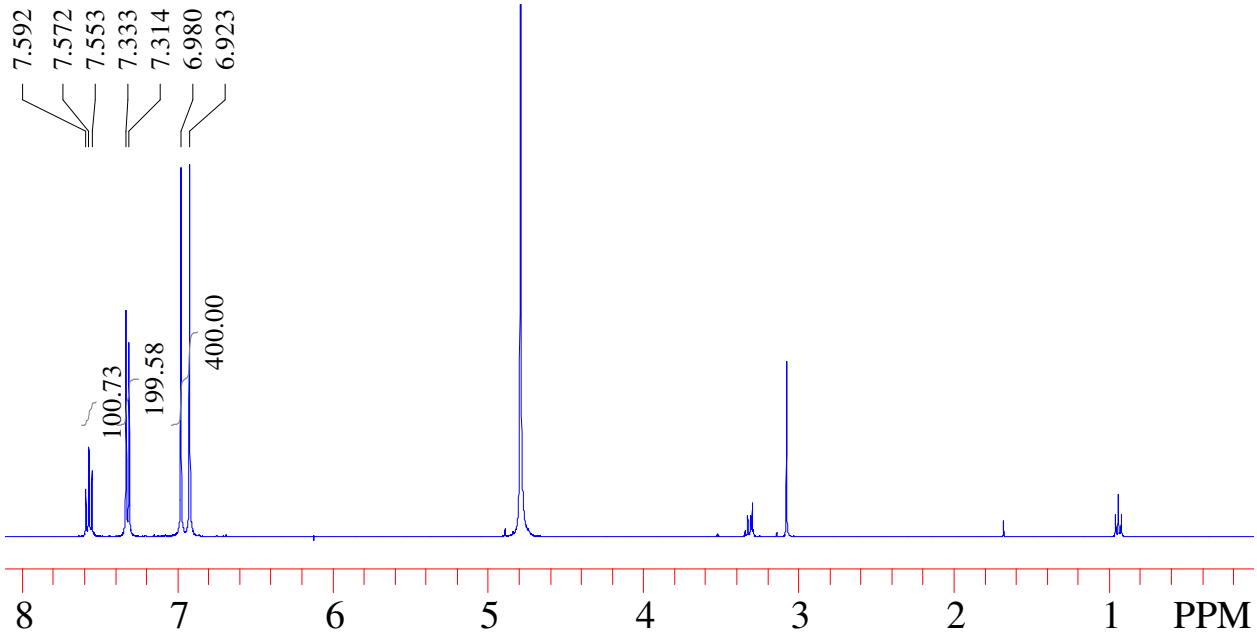


Figure S9. ^{1}H NMR Spectrum of $K[Ru(IPI)(CN)_3]$ in 13% KOD

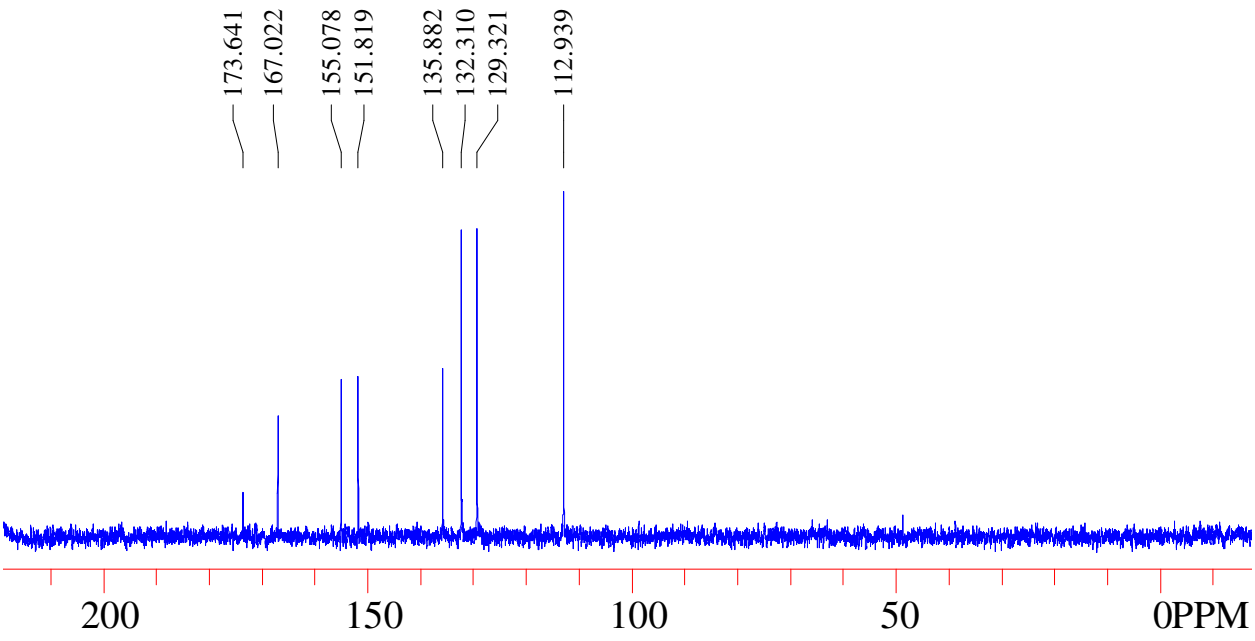


Figure S10. $^{13}C\{^{1}H\}$ NMR Spectrum of K[Ru(IPI)$(CN)_3$] in 13% KOD/D_2O

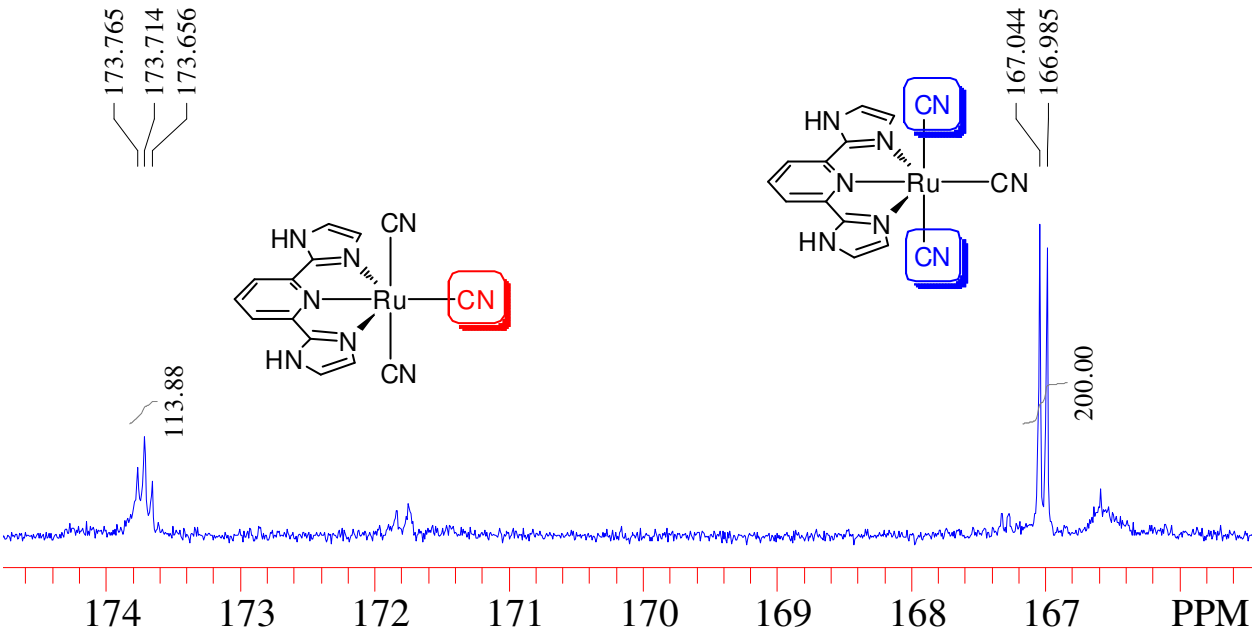


Figure S11. Selected Region of $^{13}C\{^{1}H\}$ NMR Spectrum of K[Ru(IPI)$(^{13}CN)_3$] prepared with K^{13}CN in 13% KOD

X-ray Structure Determination

Diffraction data were collected at T = 296(2) K as crystals from these compounds cracked upon cooling. The data sets were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71073 Å). The cell parameters were obtained from a least-squares refinement of the spots (from 60 collected frames) using the SMART program. Intensity data were processed using the Saint Plus program. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14).[ref] Initial atomic positions were located by direct methods using XS, and the structures of the compounds were refined by the least-squares method using XL. Absorption corrections were applied by using SADABS. Hydrogen positions were input and refined in a riding manner along with the attached carbons.

[ref]Sheldrick, G. M. *SHELXTL*, version 6.14; Bruker Analytical X-ray Systems, Inc.; Madison, WI, 2000.

Refinement details

Ru(IPI)Cl_3 (1) Crystals of **1** were deep-red prisms and desolvated upon exposure to air for an extended length of time. However, crystals cracked upon cooling under liquid nitrogen, necessitating room temperature data collection. Crystals were covered in a thin layer of mineral oil and data collection was performed for 10 hours due to the weak diffraction pattern from relatively small crystals. The compound lies on a 2-fold rotation and crystallizes with disordered DMSO. ISOR restraints were applied to address the non-positive definite errors on S1, O1 and C8.

K[Ru(IPI)$(CN)_3$] (2) Crystals of **2** were thin orange needles requiring an extended time for data collection. A crystal was layered with mineral oil and data was acquired for 17 hours. The compound crystallizes with three molecules of methanol. One methanol was treated with the ISOR restraint to address the non-positive definite error on C15.

[Ru(IPI)Cl_2-O-Cl_2(IPI)Ru]Cl (3) Crystals of **3** were prismatic and deep-red in color. Crystals cracked upon cooling again necessitating room temperature data collection in a thin layer of mineral oil. **3** crystallizes with two molecules of DMSO (one of which demonstrated partial occupancy disorder), and two molecules of benzene (one of which lies on a special position making it effectively one-half molecule). The compound is dinuclear containing an O-atom bridge. Locating attached protons to the O-atom proved problematic while in the vicinity of two heavy metals so the compound is currently formulated as an oxide. However, a search of the Crystal Structure Database reveals that the O-Ru bond distances and the Ru-O-Ru bridge angle are comparable to an OH bridge and therefore [Ru(IPI)Cl_2-OH-Cl_2(IPI)Ru]Cl is most likely the correct formulation. One benzene molecule demonstrated disorder and the angles and bond distances were fixed using the appropriate DFIX command. ISOR restraints were applied to one DMSO (C25 C25A C26 C26A) and both benzenes (C27 C28 C29 C30 C31 C31 C32 C33 C34 C35).

Crystal Structure Data for 1:

Table S11. Crystal data and structure refinement for (C11 H9 Cl3 N5 Ru) * 2(S O C2 H6).

Identification code	periana15	
Empirical formula	C15 H21 Cl3 N5 O2 Ru S2	
Formula weight	574.91	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(3)2(1)2	
Unit cell dimensions	a = 12.773(2) Å	α= 90°.
	b = 12.773(2) Å	β= 90°.
	c = 14.166(5) Å	γ = 90°.
Volume	2311.3(9) $Å^3$	
Z	4	
Density (calculated)	1.652 Mg/m^3	
Absorption coefficient	1.226 mm^{-1}	
F(000)	1156	
Crystal size	0.19 x 0.18 x 0.17 mm^3	
Theta range for data collection	2.15 to 28.32°.	
Index ranges	-17<=h<=17, -16<=k<=16, -18<=l<=18	
Reflections collected	22526	
Independent reflections	2869 [R(int) = 0.0371]	
Completeness to theta = 28.32°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.643	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2869 / 18 / 131	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1374	
R indices (all data)	R1 = 0.0672, wR2 = 0.1468	
Largest diff. peak and hole	1.308 and -0.508 $e.Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for (C11 H9 Cl3 N5 Ru) * 2(S O C2 H6). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	8552(1)	8552(1)	0	57(1)
Cl(1)	9876(1)	9876(1)	0	85(1)
Cl(2)	8830(1)	8224(1)	-1611(1)	74(1)
N(1)	9437(4)	7248(4)	334(4)	64(1)
N(2)	9431(5)	5573(4)	610(4)	73(2)
N(3)	7449(3)	7449(3)	0	57(2)
C(1)	10447(5)	6931(6)	491(5)	71(2)
C(2)	10435(6)	5898(6)	686(5)	76(2)
C(3)	8841(5)	6391(5)	423(5)	61(1)
C(4)	7716(5)	6467(5)	218(4)	61(1)
C(5)	6963(5)	5677(5)	226(5)	72(2)
C(6)	5952(5)	5952(5)	0	77(3)
S(1)	9051(3)	2611(2)	692(4)	165(2)
O(1)	8807(8)	3681(6)	1181(7)	156(3)
C(7)	10450(9)	2496(9)	857(11)	146(5)
C(8)	8729(14)	1804(15)	1540(13)	192(7)

Table S13. Bond lengths [Å] and angles [°] for (C11 H9 Cl3 N5 Ru) * 2(S O C2 H6).

Ru(1)-N(3)	1.993(6)
Ru(1)-N(1)	2.068(5)
Ru(1)-N(1)#1	2.068(5)
Ru(1)-Cl(2)	2.3480(19)
Ru(1)-Cl(2)#1	2.3480(19)
Ru(1)-Cl(1)	2.391(2)
N(1)-C(3)	1.339(8)
N(1)-C(1)	1.370(8)
N(2)-C(3)	1.316(8)
N(2)-C(2)	1.353(9)
N(2)-H(2N)	0.8600
N(3)-C(4)	1.336(7)
N(3)-C(4)#1	1.336(7)
C(1)-C(2)	1.348(10)
C(1)-H(1)	0.9300
C(2)-H(2)	0.9300
C(3)-C(4)	1.469(8)
C(4)-C(5)	1.394(9)
C(5)-C(6)	1.376(8)
C(5)-H(5)	0.9300
C(6)-C(5)#1	1.376(8)
C(6)-H(6)	0.9300
S(1)-O(1)	1.563(8)
S(1)-C(8)	1.636(18)
S(1)-C(7)	1.808(12)
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
N(3)-Ru(1)-N(1)	79.45(15)
N(3)-Ru(1)-N(1)#1	79.45(15)
N(1)-Ru(1)-N(1)#1	158.9(3)
N(3)-Ru(1)-Cl(2)	88.87(5)
N(1)-Ru(1)-Cl(2)	89.74(16)
N(1)#1-Ru(1)-Cl(2)	89.84(16)
N(3)-Ru(1)-Cl(2)#1	88.87(5)
N(1)-Ru(1)-Cl(2)#1	89.84(16)
N(1)#1-Ru(1)-Cl(2)#1	89.74(16)
Cl(2)-Ru(1)-Cl(2)#1	177.75(10)
N(3)-Ru(1)-Cl(1)	180.00(3)
N(1)-Ru(1)-Cl(1)	100.55(15)
N(1)#1-Ru(1)-Cl(1)	100.55(15)
Cl(2)-Ru(1)-Cl(1)	91.13(5)
Cl(2)#1-Ru(1)-Cl(1)	91.13(5)
C(3)-N(1)-C(1)	106.2(6)
C(3)-N(1)-Ru(1)	111.7(4)
C(1)-N(1)-Ru(1)	142.2(5)
C(3)-N(2)-C(2)	108.3(6)
C(3)-N(2)-H(2N)	125.8
C(2)-N(2)-H(2N)	125.8
C(4)-N(3)-C(4)#1	122.2(7)

C(4)-N(3)-Ru(1)	118.9(4)
C(4)#1-N(3)-Ru(1)	118.9(3)
C(2)-C(1)-N(1)	108.2(7)
C(2)-C(1)-H(1)	125.9
N(1)-C(1)-H(1)	125.9
C(1)-C(2)-N(2)	107.2(6)
C(1)-C(2)-H(2)	126.4
N(2)-C(2)-H(2)	126.4
N(2)-C(3)-N(1)	110.1(5)
N(2)-C(3)-C(4)	130.7(6)
N(1)-C(3)-C(4)	118.9(6)
N(3)-C(4)-C(5)	120.3(6)
N(3)-C(4)-C(3)	110.9(5)
C(5)-C(4)-C(3)	128.7(6)
C(6)-C(5)-C(4)	117.5(6)
C(6)-C(5)-H(5)	121.3
C(4)-C(5)-H(5)	121.3
C(5)#1-C(6)-C(5)	122.1(8)
C(5)#1-C(6)-H(6)	118.9
C(5)-C(6)-H(6)	118.9
O(1)-S(1)-C(8)	100.1(8)
O(1)-S(1)-C(7)	102.2(6)
C(8)-S(1)-C(7)	95.9(9)
S(1)-C(7)-H(7A)	109.5
S(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
S(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
S(1)-C(8)-H(8A)	109.5
S(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
S(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 y,x,-z

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (C11 H9 Cl3 N5 Ru) * 2(S O C2 H6). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	44(1)	44(1)	82(1)	-2(1)	2(1)	-2(1)
Cl(1)	61(1)	61(1)	134(2)	-7(1)	7(1)	-18(1)
Cl(2)	79(1)	60(1)	82(1)	0(1)	10(1)	2(1)
N(1)	52(3)	48(3)	92(4)	-4(2)	-5(2)	3(2)
N(2)	65(3)	53(3)	102(4)	-3(3)	0(3)	10(2)
N(3)	47(2)	47(2)	76(4)	-6(3)	6(3)	0(3)
C(1)	50(3)	72(4)	90(4)	-10(3)	-5(3)	8(3)
C(2)	63(4)	68(4)	98(5)	-7(4)	-5(4)	15(3)
C(3)	56(3)	51(3)	76(4)	-3(3)	4(3)	1(3)
C(4)	55(3)	48(3)	80(4)	0(3)	4(3)	-2(3)
C(5)	65(4)	46(3)	105(5)	-4(3)	7(4)	-10(3)
C(6)	57(3)	57(3)	117(8)	-3(5)	3(5)	-16(4)
S(1)	126(2)	66(1)	302(4)	-5(2)	17(3)	1(1)
O(1)	157(6)	89(4)	224(7)	6(5)	47(5)	-1(5)
C(7)	107(9)	91(7)	239(14)	-20(9)	6(9)	-8(6)
C(8)	201(10)	190(10)	185(9)	-10(7)	28(7)	10(8)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for (C11 H9 Cl3 N5 Ru) * 2(S O C2 H6).

	x	y	z	U(eq)
H(2N)	9215	4939	673	88
H(1)	11038	7355	467	85
H(2)	11010	5487	843	91
H(5)	7137	4991	378	87
H(6)	5437	5437	0	92
H(7A)	10802	3003	471	219
H(7B)	10672	1805	680	219
H(7C)	10620	2617	1508	219
H(8A)	8861	2128	2140	288
H(8B)	9137	1175	1488	288
H(8C)	7999	1634	1491	288

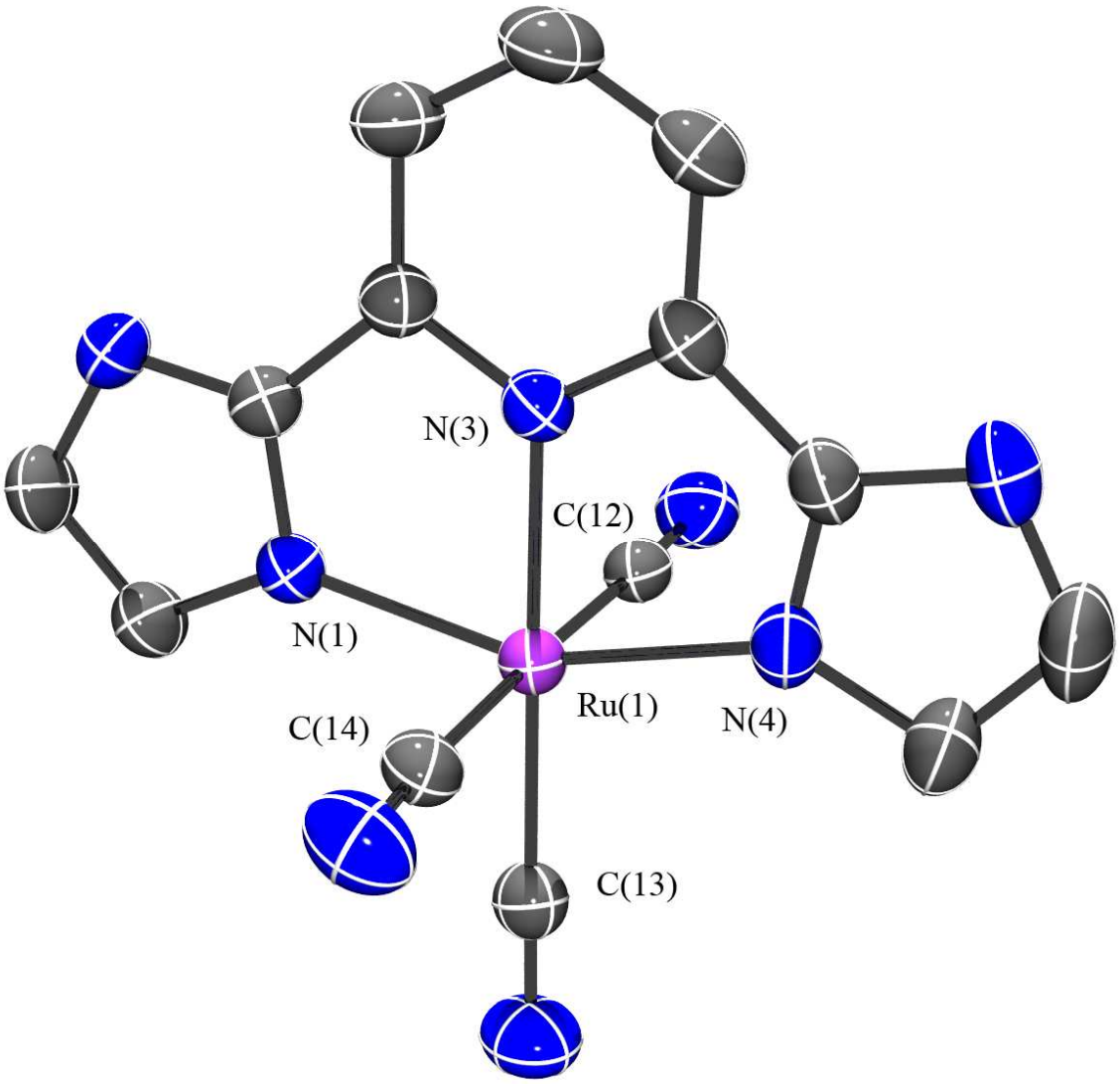


Figure S12. ORTEP drawing of **2** with ellipsoids shown at 50% probability. Hydrogens, Outersphere Potassium counter ion and Methanol co-solvent are removed for clarity.

Crystal Structure Data for K[Ru(IPI)(CN)$_3$]:

Table S16. Crystal data and structure refinement for (C14 H9 K N8 Ru) * 3(C H4 O).

Identification code	periana16	
Empirical formula	C17 H21 K N8 O3 Ru	
Formula weight	525.59	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.000(5) Å	α= 90°.
	b = 9.424(5) Å	β= 99.104(6)°.
	c = 24.093(13) Å	γ = 90°.
Volume	2242(2) Å^3	

Z	4
Density (calculated)	1.557 Mg/m^3
Absorption coefficient	0.919 mm^{-1}
F(000)	1064
Crystal size	0.53 x 0.06 x 0.06 mm^3
Theta range for data collection	1.71 to 28.35°.
Index ranges	-13<=h<=13, -12<=k<=12, -32<=l<=32
Reflections collected	21209
Independent reflections	5587 [R(int) = 0.0355]
Completeness to theta = 28.35°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.636
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5587 / 12 / 277
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.0968
R indices (all data)	R1 = 0.0558, wR2 = 0.1051
Largest diff. peak and hole	1.035 and -0.483 $e.Å^{-3}$

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (C14 H9 K N8 Ru) * 3(C H4 O). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	3336(1)	2901(1)	3698(1)	32(1)
N(1)	2652(2)	4065(3)	4338(1)	35(1)
N(2)	2924(3)	4592(3)	5240(1)	42(1)
N(3)	4614(2)	2242(3)	4392(1)	33(1)
N(4)	4567(3)	1458(3)	3360(1)	39(1)
N(5)	6343(3)	39(3)	3503(1)	51(1)
N(6)	1114(3)	502(4)	3752(2)	59(1)
N(7)	1401(3)	3944(4)	2613(1)	59(1)
N(8)	5616(3)	5208(3)	3602(1)	48(1)
C(1)	1684(3)	5030(4)	4428(1)	44(1)
C(2)	1843(3)	5356(4)	4982(2)	48(1)
C(3)	3386(3)	3817(3)	4842(1)	35(1)
C(4)	4507(3)	2812(3)	4898(1)	35(1)
C(5)	5390(4)	2432(4)	5376(2)	46(1)
C(6)	6405(4)	1460(4)	5315(2)	53(1)
C(7)	6529(3)	906(4)	4801(2)	48(1)
C(8)	5603(3)	1309(3)	4335(1)	37(1)
C(9)	5530(3)	911(3)	3747(1)	39(1)
C(10)	5870(4)	42(5)	2944(2)	62(1)
C(11)	4783(4)	902(4)	2855(2)	51(1)
C(12)	1927(3)	1365(3)	3752(1)	38(1)
C(13)	2113(3)	3585(3)	3013(1)	39(1)
C(14)	4742(3)	4426(3)	3616(1)	35(1)
K	470(1)	1057(1)	2441(1)	70(1)
O(1)	8840(3)	9286(4)	4102(2)	81(1)
C(15)	9348(7)	8168(7)	4442(3)	121(2)
O(2)	1713(3)	-185(4)	1634(2)	92(1)
C(16)	1504(5)	-1631(6)	1524(2)	87(2)
O(3)	-1419(5)	2799(6)	1850(2)	137(2)
C(17)	-2764(6)	2611(7)	1853(2)	99(2)

Table S18. Bond lengths [Å] and angles [°] for (C14 H9 K N8 Ru) * 3(C H4 O).

Ru(1)-C(13)	1.999(3)
Ru(1)-N(3)	2.035(3)
Ru(1)-C(12)	2.039(3)
Ru(1)-C(14)	2.042(3)
Ru(1)-N(4)	2.084(3)
Ru(1)-N(1)	2.094(2)
N(1)-C(3)	1.335(4)
N(1)-C(1)	1.370(4)
N(2)-C(3)	1.343(4)
N(2)-C(2)	1.364(4)
N(2)-H(2N)	0.8600
N(3)-C(8)	1.347(4)
N(3)-C(4)	1.352(4)
N(4)-C(9)	1.334(4)
N(4)-C(11)	1.373(4)
N(5)-C(9)	1.353(4)
N(5)-C(10)	1.356(5)
N(5)-H(5N)	0.8600
N(6)-C(12)	1.150(4)
N(7)-C(13)	1.154(4)
N(7)-K#1	2.721(4)
N(8)-C(14)	1.148(4)
C(1)-C(2)	1.355(5)
C(1)-H(1)	0.9300
C(2)-H(2)	0.9300
C(3)-C(4)	1.457(4)
C(4)-C(5)	1.382(4)
C(5)-C(6)	1.391(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.368(5)
C(6)-H(6)	0.9300
C(7)-C(8)	1.391(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.455(5)
C(10)-C(11)	1.346(5)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300
C(13)-K#1	3.522(4)
K-N(7)#2	2.721(4)
K-C(13)#2	3.522(4)
K-K#1	4.822(3)
K-K#2	4.822(3)
O(1)-C(15)	1.381(7)
O(1)-H(1A)	0.8200
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
O(2)-C(16)	1.398(6)
O(2)-H(2A)	0.8200
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
O(3)-C(17)	1.357(7)
O(3)-H(3)	0.8200

C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600

C(13)-Ru(1)-N(3)	178.64(11)
C(13)-Ru(1)-C(12)	86.68(13)
N(3)-Ru(1)-C(12)	94.68(11)
C(13)-Ru(1)-C(14)	91.94(12)
N(3)-Ru(1)-C(14)	86.70(11)
C(12)-Ru(1)-C(14)	178.03(12)
C(13)-Ru(1)-N(4)	102.11(12)
N(3)-Ru(1)-N(4)	77.83(11)
C(12)-Ru(1)-N(4)	91.04(12)
C(14)-Ru(1)-N(4)	87.87(12)
C(13)-Ru(1)-N(1)	102.16(12)
N(3)-Ru(1)-N(1)	77.89(10)
C(12)-Ru(1)-N(1)	90.91(12)
C(14)-Ru(1)-N(1)	90.76(11)
N(4)-Ru(1)-N(1)	155.72(10)
C(3)-N(1)-C(1)	105.9(3)
C(3)-N(1)-Ru(1)	112.41(19)
C(1)-N(1)-Ru(1)	141.7(2)
C(3)-N(2)-C(2)	107.4(3)
C(3)-N(2)-H(2N)	126.3
C(2)-N(2)-H(2N)	126.3
C(8)-N(3)-C(4)	121.1(3)
C(8)-N(3)-Ru(1)	119.4(2)
C(4)-N(3)-Ru(1)	119.4(2)
C(9)-N(4)-C(11)	105.9(3)
C(9)-N(4)-Ru(1)	112.6(2)
C(11)-N(4)-Ru(1)	141.3(2)
C(9)-N(5)-C(10)	106.9(3)
C(9)-N(5)-H(5N)	126.5
C(10)-N(5)-H(5N)	126.5
C(13)-N(7)-K#1	125.7(3)
C(2)-C(1)-N(1)	109.2(3)
C(2)-C(1)-H(1)	125.4
N(1)-C(1)-H(1)	125.4
C(1)-C(2)-N(2)	106.9(3)
C(1)-C(2)-H(2)	126.6
N(2)-C(2)-H(2)	126.6
N(1)-C(3)-N(2)	110.6(3)
N(1)-C(3)-C(4)	120.1(3)
N(2)-C(3)-C(4)	129.3(3)
N(3)-C(4)-C(5)	121.1(3)
N(3)-C(4)-C(3)	110.1(3)
C(5)-C(4)-C(3)	128.8(3)
C(4)-C(5)-C(6)	117.6(3)
C(4)-C(5)-H(5)	121.2
C(6)-C(5)-H(5)	121.2
C(7)-C(6)-C(5)	121.3(3)
C(7)-C(6)-H(6)	119.4
C(5)-C(6)-H(6)	119.4
C(6)-C(7)-C(8)	118.8(3)
C(6)-C(7)-H(7)	120.6
C(8)-C(7)-H(7)	120.6

N(3)-C(8)-C(7)	120.1(3)
N(3)-C(8)-C(9)	110.1(3)
C(7)-C(8)-C(9)	129.8(3)
N(4)-C(9)-N(5)	110.4(3)
N(4)-C(9)-C(8)	120.0(3)
N(5)-C(9)-C(8)	129.6(3)
C(11)-C(10)-N(5)	107.8(3)
C(11)-C(10)-H(10)	126.1
N(5)-C(10)-H(10)	126.1
C(10)-C(11)-N(4)	108.9(3)
C(10)-C(11)-H(11)	125.5
N(4)-C(11)-H(11)	125.5
N(6)-C(12)-Ru(1)	176.4(3)
N(7)-C(13)-Ru(1)	178.2(3)
N(7)-C(13)-K#1	38.9(2)
Ru(1)-C(13)-K#1	142.46(14)
N(8)-C(14)-Ru(1)	173.7(3)
N(7)#2-K-C(13)#2	15.44(9)
N(7)#2-K-K#1	125.40(9)
C(13)#2-K-K#1	121.65(7)
N(7)#2-K-K#2	31.66(7)
C(13)#2-K-K#2	39.79(6)
K#1-K-K#2	155.50(5)
C(15)-O(1)-H(1A)	109.5
O(1)-C(15)-H(15A)	109.5
O(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
O(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(16)-O(2)-H(2A)	109.5
O(2)-C(16)-H(16A)	109.5
O(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
O(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(17)-O(3)-H(3)	109.5
O(3)-C(17)-H(17A)	109.5
O(3)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(3)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,y+1/2,-z+1/2 #2 -x,y-1/2,-z+1/2

Table S19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (C14 H9 K N8 Ru) * 3(C H4 O). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	30(1)	35(1)	29(1)	0(1)	5(1)	3(1)
N(1)	32(1)	39(1)	33(1)	0(1)	5(1)	5(1)
N(2)	44(2)	50(2)	31(1)	-4(1)	7(1)	4(1)
N(3)	30(1)	35(1)	34(1)	1(1)	4(1)	2(1)
N(4)	36(1)	43(1)	41(1)	-7(1)	12(1)	0(1)
N(5)	45(2)	49(2)	63(2)	-5(1)	19(1)	11(1)
N(6)	45(2)	55(2)	74(2)	9(2)	5(2)	-8(2)
N(7)	54(2)	69(2)	49(2)	15(2)	-1(2)	3(2)
N(8)	45(2)	53(2)	44(2)	-1(1)	6(1)	-6(1)
C(1)	38(2)	48(2)	43(2)	-4(2)	4(1)	12(1)
C(2)	44(2)	53(2)	49(2)	-9(2)	12(2)	13(2)
C(3)	34(2)	36(2)	34(2)	-1(1)	5(1)	0(1)
C(4)	35(2)	34(2)	35(2)	1(1)	4(1)	1(1)
C(5)	47(2)	49(2)	38(2)	2(2)	-2(2)	3(2)
C(6)	47(2)	58(2)	50(2)	10(2)	-7(2)	12(2)
C(7)	38(2)	47(2)	58(2)	6(2)	2(2)	10(1)
C(8)	33(2)	33(2)	44(2)	1(1)	7(1)	2(1)
C(9)	33(2)	39(2)	47(2)	-4(1)	10(1)	3(1)
C(10)	64(2)	65(3)	63(2)	-17(2)	30(2)	6(2)
C(11)	55(2)	60(2)	43(2)	-8(2)	17(2)	3(2)
C(12)	34(2)	42(2)	37(2)	4(1)	3(1)	7(1)
C(13)	37(2)	41(2)	38(2)	1(1)	7(1)	-1(1)
C(14)	34(2)	40(2)	29(1)	0(1)	3(1)	5(1)
K	64(1)	74(1)	71(1)	-11(1)	8(1)	-11(1)
O(1)	44(2)	82(2)	120(3)	34(2)	24(2)	10(2)
C(15)	108(4)	104(4)	155(4)	39(3)	36(3)	16(3)
O(2)	70(2)	88(3)	126(3)	-8(2)	42(2)	-3(2)
C(16)	83(4)	90(4)	91(4)	6(3)	26(3)	-6(3)
O(3)	103(3)	134(3)	165(4)	48(3)	-8(3)	-14(3)
C(17)	81(4)	127(5)	83(4)	25(4)	-13(3)	-35(3)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for (C14 H9 K N8 Ru) * 3(C H4 O).

	x	y	z	U(eq)
H(2N)	3250	4605	5592	50
H(5N)	7029	-428	3671	62
H(1)	1022	5402	4151	52
H(2)	1315	5980	5153	58
H(5)	5309	2812	5725	55
H(6)	7010	1183	5630	64
H(7)	7221	270	4764	58
H(10)	6233	-461	2671	74
H(11)	4262	1090	2507	62
H(1A)	9450	9638	3957	121
H(15A)	8987	7292	4279	181
H(15B)	9093	8280	4808	181
H(15C)	10318	8154	4477	181
H(2A)	2515	5	1641	138
H(16A)	2076	-2176	1804	130
H(16B)	1720	-1849	1159	130
H(16C)	573	-1863	1534	130
H(3)	-1085	3227	2135	205
H(17A)	-3005	1647	1755	149
H(17B)	-3270	3239	1584	149
H(17C)	-2968	2815	2220	149

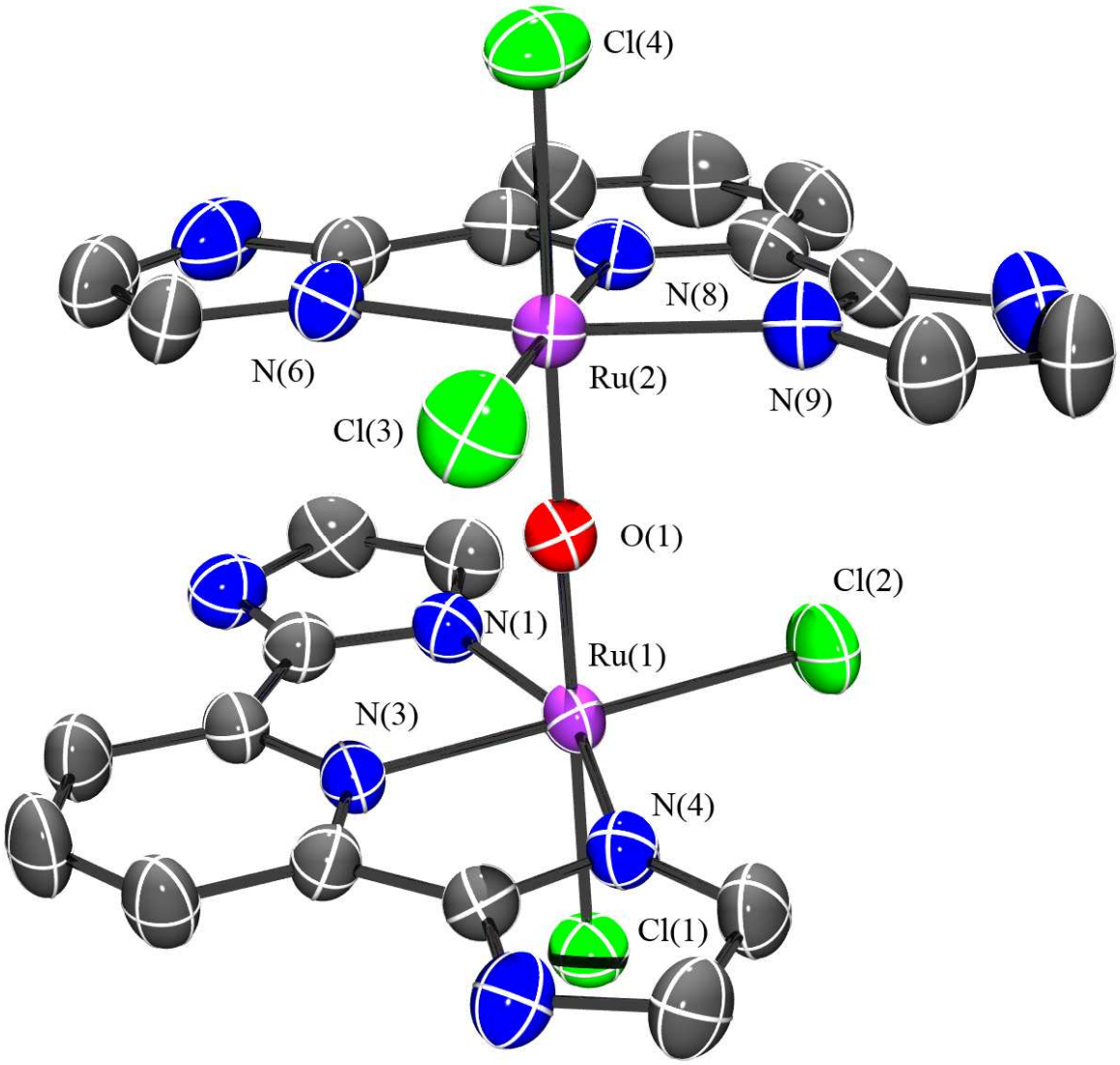


Figure S13. ORTEP drawing of $[Ru(IPI)Cl_2\text{-}O\text{-}Cl_2(IPI)Ru]Cl$ with ellipsoids shown at 50% probability. Hydrogens, Outersphere Chloride counter ion, DMSO, and Benzene co-solvent are removed for clarity.

Crystal Structure Data for $[Ru(IPI)Cl_2\text{-}O\text{-}Cl_2(IPI)Ru]Cl$:

Table S21. Crystal data and structure refinement for (C22 H18 Cl5 N10 O Ru2) * (C6 H6) * 2(S O C2 H6) * 0.5(C6 H6).

Identification code	periana7	
Empirical formula	C35 H39 Cl5 N10 O3 Ru2 S2	
Formula weight	1091.27	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.060(8) Å	α= 90°.
	b = 27.232(16) Å	β= 114.476(10)°.
	c = 13.899(8) Å	γ = 90°.

Volume	4499(4) $Å^3$
Z	4
Density (calculated)	1.611 Mg/m^3
Absorption coefficient	1.107 mm^{-1}
F(000)	2192
Crystal size	0.65 x 0.20 x 0.02 mm^3
Theta range for data collection	1.50 to 28.41°.
Index ranges	-17<=h<=17, -33<=k<=34, -18<=l<=16
Reflections collected	29461
Independent reflections	10643 [R(int) = 0.0380]
Completeness to theta = 28.41°	94.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.614
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10643 / 105 / 559
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1463
R indices (all data)	R1 = 0.0823, wR2 = 0.1729
Largest diff. peak and hole	1.974 and -0.663 $e.Å^{-3}$

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (C22 H18 Cl5 N10 O Ru2) * (C6 H6) * 2(S O C2 H6) * 0.5(C6 H6). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	7406(1)	4051(1)	4776(1)	38(1)
Ru(2)	5461(1)	3761(1)	2101(1)	38(1)
Cl(1)	8636(1)	4258(1)	6519(1)	50(1)
Cl(2)	5993(1)	3819(1)	5371(1)	66(1)
Cl(3)	6746(1)	3240(1)	1758(1)	71(1)
Cl(4)	4053(1)	3640(1)	384(1)	62(1)
Cl(5)	2160(2)	3168(1)	4733(2)	92(1)
O(1)	6501(2)	3878(1)	3434(2)	43(1)
N(1)	6972(3)	4789(1)	4470(3)	44(1)
N(2)	7332(3)	5495(2)	3904(3)	51(1)
N(3)	8573(3)	4281(1)	4287(3)	37(1)
N(4)	8346(3)	3407(1)	4948(3)	42(1)
N(5)	9765(3)	3062(1)	4749(3)	48(1)
N(6)	5783(3)	4448(1)	1612(3)	44(1)
N(7)	5349(4)	5235(2)	1452(4)	62(1)
N(8)	4354(3)	4173(1)	2385(3)	41(1)
N(9)	4707(3)	3236(1)	2659(3)	46(1)
N(10)	3613(4)	3085(2)	3463(4)	68(1)
C(1)	6224(4)	5139(2)	4513(4)	54(1)
C(2)	6441(4)	5571(2)	4153(5)	59(1)
C(3)	7633(4)	5022(2)	4096(4)	43(1)
C(4)	8532(4)	4753(2)	3963(4)	41(1)
C(5)	9287(4)	4919(2)	3570(4)	51(1)
C(6)	10082(4)	4588(2)	3533(5)	60(1)
C(7)	10122(4)	4103(2)	3868(4)	52(1)
C(8)	9332(4)	3955(2)	4250(4)	39(1)
C(9)	9174(4)	3476(2)	4627(3)	38(1)
C(10)	9316(4)	2713(2)	5165(4)	54(1)
C(11)	8423(4)	2931(2)	5282(4)	53(1)
C(12)	6449(4)	4676(2)	1219(4)	54(1)
C(13)	6191(5)	5169(2)	1122(4)	63(2)
C(14)	5117(4)	4790(2)	1751(4)	47(1)
C(15)	4302(4)	4664(2)	2191(4)	46(1)
C(16)	3572(5)	4953(2)	2425(5)	66(2)
C(17)	2929(5)	4736(2)	2885(5)	76(2)
C(18)	2982(5)	4239(2)	3091(5)	65(2)
C(19)	3732(4)	3957(2)	2844(4)	48(1)
C(20)	3977(4)	3432(2)	2995(4)	50(1)
C(21)	4116(6)	2660(2)	3441(5)	76(2)
C(22)	4802(5)	2748(2)	2927(5)	67(2)
S(1)	1335(2)	3481(1)	7234(1)	82(1)
O(2)	1749(5)	3979(2)	7152(6)	122(2)
C(23)	2507(8)	3097(3)	7643(6)	103(3)
C(24)	1161(7)	3515(3)	8399(6)	94(2)
S(2)	5940(3)	3529(1)	8036(3)	72(1)
O(3)	5561(17)	3986(8)	8177(16)	135(9)
C(25)	7060(20)	3371(10)	7970(20)	118(9)
C(26)	5670(20)	3220(11)	8820(20)	148(11)
S(2A)	6584(6)	3657(2)	9015(5)	125(2)
O(3A)	6143(14)	4039(5)	8673(16)	105(6)

C(25A)	7415(18)	3513(9)	8246(19)	98(6)
C(26A)	6087(18)	3085(6)	9078(16)	86(5)
C(27)	10480(14)	5352(5)	692(11)	178(5)
C(28)	9509(13)	5155(5)	661(10)	154(4)
C(29)	9018(13)	4826(6)	-59(12)	179(5)
C(30)	671(12)	3496(4)	1099(11)	193(6)
C(31)	1227(9)	3109(5)	980(9)	158(4)
C(32)	878(10)	2664(4)	1058(9)	157(4)
C(33)	-65(12)	2602(4)	1209(11)	190(6)
C(34)	-592(9)	2991(6)	1360(10)	163(5)
C(35)	-197(13)	3433(5)	1340(11)	200(7)

Table S23. Bond lengths [Å] and angles [°] for (C22 H18 Cl5 N10 O Ru2) * (C6 H6) * 2(S O C2 H6) * 0.5(C6 H6).

Ru(1)-O(1)	1.808(3)
Ru(1)-N(3)	2.008(3)
Ru(1)-N(1)	2.084(4)
Ru(1)-N(4)	2.095(4)
Ru(1)-Cl(1)	2.3544(16)
Ru(1)-Cl(2)	2.3987(16)
Ru(2)-O(1)	1.815(3)
Ru(2)-N(8)	1.995(4)
Ru(2)-N(9)	2.060(4)
Ru(2)-N(6)	2.093(4)
Ru(2)-Cl(4)	2.3560(17)
Ru(2)-Cl(3)	2.3911(16)
N(1)-C(3)	1.339(6)
N(1)-C(1)	1.383(6)
N(2)-C(3)	1.340(6)
N(2)-C(2)	1.361(7)
N(2)-H(2N)	0.8600
N(3)-C(8)	1.347(6)
N(3)-C(4)	1.355(6)
N(4)-C(9)	1.342(5)
N(4)-C(11)	1.369(6)
N(5)-C(9)	1.336(6)
N(5)-C(10)	1.364(6)
N(5)-H(5N)	0.8600
N(6)-C(14)	1.341(6)
N(6)-C(12)	1.355(6)
N(7)-C(14)	1.356(6)
N(7)-C(13)	1.367(8)
N(7)-H(7N)	0.8600
N(8)-C(15)	1.359(6)
N(8)-C(19)	1.359(6)
N(9)-C(20)	1.334(6)
N(9)-C(22)	1.372(6)
N(10)-C(21)	1.337(8)
N(10)-C(20)	1.341(7)
N(10)-H(10N)	0.8600
C(1)-C(2)	1.353(7)
C(1)-H(1)	0.9300
C(2)-H(2)	0.9300
C(3)-C(4)	1.459(6)
C(4)-C(5)	1.387(6)
C(5)-C(6)	1.392(7)
C(5)-H(5)	0.9300
C(6)-C(7)	1.394(7)
C(6)-H(6)	0.9300
C(7)-C(8)	1.401(6)
C(7)-H(7)	0.9300
C(8)-C(9)	1.453(6)
C(10)-C(11)	1.376(7)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300
C(12)-C(13)	1.377(8)
C(12)-H(12)	0.9300

C(13)-H(13)	0.9300
C(14)-C(15)	1.471(7)
C(15)-C(16)	1.375(7)
C(16)-C(17)	1.381(9)
C(16)-H(16)	0.9300
C(17)-C(18)	1.381(8)
C(17)-H(17)	0.9300
C(18)-C(19)	1.394(7)
C(18)-H(18)	0.9300
C(19)-C(20)	1.463(7)
C(21)-C(22)	1.379(8)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
S(1)-O(2)	1.484(5)
S(1)-C(24)	1.728(7)
S(1)-C(23)	1.743(8)
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
S(2)-O(3)	1.38(2)
S(2)-C(26)	1.53(3)
S(2)-C(25)	1.56(3)
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
S(2A)-O(3A)	1.188(13)
S(2A)-C(26A)	1.704(19)
S(2A)-C(25A)	1.85(2)
C(25A)-H(25D)	0.9600
C(25A)-H(25E)	0.9600
C(25A)-H(25F)	0.9600
C(26A)-H(26D)	0.9600
C(26A)-H(26E)	0.9600
C(26A)-H(26F)	0.9600
C(27)-C(28)	1.361(17)
C(27)-C(29)#1	1.385(17)
C(27)-H(27)	0.9300
C(28)-C(29)	1.297(16)
C(28)-H(28)	0.9300
C(29)-C(27)#1	1.385(17)
C(29)-H(29)	0.9300
C(30)-C(35)	1.320(9)
C(30)-C(31)	1.328(8)
C(30)-H(30)	0.9300
C(31)-C(32)	1.315(8)
C(31)-H(31)	0.9300
C(32)-C(33)	1.343(8)
C(32)-H(32)	0.9300
C(33)-C(34)	1.327(9)
C(33)-H(33)	0.9300

C(34)-C(35)	1.313(8)
C(34)-H(34)	0.9300
C(35)-H(35)	0.9300
O(1)-Ru(1)-N(3)	89.74(14)
O(1)-Ru(1)-N(1)	91.93(14)
N(3)-Ru(1)-N(1)	79.08(14)
O(1)-Ru(1)-N(4)	90.10(14)
N(3)-Ru(1)-N(4)	78.96(14)
N(1)-Ru(1)-N(4)	157.93(14)
O(1)-Ru(1)-Cl(1)	177.97(10)
N(3)-Ru(1)-Cl(1)	89.05(11)
N(1)-Ru(1)-Cl(1)	89.44(11)
N(4)-Ru(1)-Cl(1)	88.07(11)
O(1)-Ru(1)-Cl(2)	91.10(11)
N(3)-Ru(1)-Cl(2)	177.07(11)
N(1)-Ru(1)-Cl(2)	98.08(11)
N(4)-Ru(1)-Cl(2)	103.84(11)
Cl(1)-Ru(1)-Cl(2)	90.19(6)
O(1)-Ru(2)-N(8)	89.81(15)
O(1)-Ru(2)-N(9)	90.56(15)
N(8)-Ru(2)-N(9)	79.48(16)
O(1)-Ru(2)-N(6)	90.50(14)
N(8)-Ru(2)-N(6)	79.64(16)
N(9)-Ru(2)-N(6)	159.09(15)
O(1)-Ru(2)-Cl(4)	177.09(10)
N(8)-Ru(2)-Cl(4)	87.32(12)
N(9)-Ru(2)-Cl(4)	89.41(12)
N(6)-Ru(2)-Cl(4)	88.50(12)
O(1)-Ru(2)-Cl(3)	91.00(11)
N(8)-Ru(2)-Cl(3)	177.85(12)
N(9)-Ru(2)-Cl(3)	98.52(12)
N(6)-Ru(2)-Cl(3)	102.35(12)
Cl(4)-Ru(2)-Cl(3)	91.88(7)
Ru(1)-O(1)-Ru(2)	172.51(19)
C(3)-N(1)-C(1)	105.7(4)
C(3)-N(1)-Ru(1)	111.9(3)
C(1)-N(1)-Ru(1)	142.5(3)
C(3)-N(2)-C(2)	107.8(4)
C(3)-N(2)-H(2N)	126.1
C(2)-N(2)-H(2N)	126.1
C(8)-N(3)-C(4)	122.6(4)
C(8)-N(3)-Ru(1)	118.8(3)
C(4)-N(3)-Ru(1)	118.5(3)
C(9)-N(4)-C(11)	106.8(4)
C(9)-N(4)-Ru(1)	111.2(3)
C(11)-N(4)-Ru(1)	142.1(3)
C(9)-N(5)-C(10)	108.3(4)
C(9)-N(5)-H(5N)	125.8
C(10)-N(5)-H(5N)	125.8
C(14)-N(6)-C(12)	107.7(4)
C(14)-N(6)-Ru(2)	110.1(3)
C(12)-N(6)-Ru(2)	142.2(3)
C(14)-N(7)-C(13)	107.3(5)
C(14)-N(7)-H(7N)	126.3
C(13)-N(7)-H(7N)	126.3

C(15)-N(8)-C(19)	122.0(4)
C(15)-N(8)-Ru(2)	119.6(3)
C(19)-N(8)-Ru(2)	118.2(3)
C(20)-N(9)-C(22)	106.7(4)
C(20)-N(9)-Ru(2)	112.2(3)
C(22)-N(9)-Ru(2)	140.4(4)
C(21)-N(10)-C(20)	108.8(5)
C(21)-N(10)-H(10N)	125.6
C(20)-N(10)-H(10N)	125.6
C(2)-C(1)-N(1)	108.9(5)
C(2)-C(1)-H(1)	125.5
N(1)-C(1)-H(1)	125.5
C(1)-C(2)-N(2)	107.1(4)
C(1)-C(2)-H(2)	126.5
N(2)-C(2)-H(2)	126.5
N(1)-C(3)-N(2)	110.5(4)
N(1)-C(3)-C(4)	119.4(4)
N(2)-C(3)-C(4)	130.1(4)
N(3)-C(4)-C(5)	120.3(4)
N(3)-C(4)-C(3)	111.0(4)
C(5)-C(4)-C(3)	128.7(4)
C(4)-C(5)-C(6)	117.8(4)
C(4)-C(5)-H(5)	121.1
C(6)-C(5)-H(5)	121.1
C(5)-C(6)-C(7)	121.7(4)
C(5)-C(6)-H(6)	119.1
C(7)-C(6)-H(6)	119.1
C(6)-C(7)-C(8)	117.9(4)
C(6)-C(7)-H(7)	121.0
C(8)-C(7)-H(7)	121.0
N(3)-C(8)-C(7)	119.7(4)
N(3)-C(8)-C(9)	111.2(4)
C(7)-C(8)-C(9)	129.2(4)
N(5)-C(9)-N(4)	110.1(4)
N(5)-C(9)-C(8)	130.0(4)
N(4)-C(9)-C(8)	119.9(4)
N(5)-C(10)-C(11)	106.5(4)
N(5)-C(10)-H(10)	126.7
C(11)-C(10)-H(10)	126.7
N(4)-C(11)-C(10)	108.4(4)
N(4)-C(11)-H(11)	125.8
C(10)-C(11)-H(11)	125.8
N(6)-C(12)-C(13)	108.3(5)
N(6)-C(12)-H(12)	125.9
C(13)-C(12)-H(12)	125.9
N(7)-C(13)-C(12)	107.1(5)
N(7)-C(13)-H(13)	126.4
C(12)-C(13)-H(13)	126.4
N(6)-C(14)-N(7)	109.6(5)
N(6)-C(14)-C(15)	121.4(4)
N(7)-C(14)-C(15)	128.9(5)
N(8)-C(15)-C(16)	119.9(5)
N(8)-C(15)-C(14)	109.1(4)
C(16)-C(15)-C(14)	131.0(5)
C(15)-C(16)-C(17)	118.7(5)
C(15)-C(16)-H(16)	120.6

C(17)-C(16)-H(16)	120.6
C(18)-C(17)-C(16)	121.7(5)
C(18)-C(17)-H(17)	119.1
C(16)-C(17)-H(17)	119.1
C(17)-C(18)-C(19)	118.0(5)
C(17)-C(18)-H(18)	121.0
C(19)-C(18)-H(18)	121.0
N(8)-C(19)-C(18)	119.6(5)
N(8)-C(19)-C(20)	110.7(4)
C(18)-C(19)-C(20)	129.7(5)
N(9)-C(20)-N(10)	109.7(5)
N(9)-C(20)-C(19)	119.1(4)
N(10)-C(20)-C(19)	131.1(5)
N(10)-C(21)-C(22)	106.9(5)
N(10)-C(21)-H(21)	126.5
C(22)-C(21)-H(21)	126.5
N(9)-C(22)-C(21)	107.8(5)
N(9)-C(22)-H(22)	126.1
C(21)-C(22)-H(22)	126.1
O(2)-S(1)-C(24)	102.6(4)
O(2)-S(1)-C(23)	106.0(4)
C(24)-S(1)-C(23)	99.5(4)
S(1)-C(23)-H(23A)	109.5
S(1)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
S(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
S(1)-C(24)-H(24A)	109.5
S(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
S(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
O(3)-S(2)-C(26)	101.1(15)
O(3)-S(2)-C(25)	131.0(15)
C(26)-S(2)-C(25)	112.9(14)
O(3A)-S(2A)-C(26A)	133.5(12)
O(3A)-S(2A)-C(25A)	104.9(12)
C(26A)-S(2A)-C(25A)	99.4(11)
S(2A)-C(25A)-H(25D)	109.5
S(2A)-C(25A)-H(25E)	109.5
H(25D)-C(25A)-H(25E)	109.5
S(2A)-C(25A)-H(25F)	109.5
H(25D)-C(25A)-H(25F)	109.5
H(25E)-C(25A)-H(25F)	109.5
S(2A)-C(26A)-H(26D)	109.5
S(2A)-C(26A)-H(26E)	109.5
H(26D)-C(26A)-H(26E)	109.5
S(2A)-C(26A)-H(26F)	109.5
H(26D)-C(26A)-H(26F)	109.5
H(26E)-C(26A)-H(26F)	109.5
C(28)-C(27)-C(29)#1	121.5(14)
C(28)-C(27)-H(27)	119.2
C(29)#1-C(27)-H(27)	119.2
C(29)-C(28)-C(27)	116.9(14)

C(29)-C(28)-H(28)	121.5
C(27)-C(28)-H(28)	121.5
C(28)-C(29)-C(27)#1	121.2(15)
C(28)-C(29)-H(29)	119.4
C(27)#1-C(29)-H(29)	119.4
C(35)-C(30)-C(31)	120.0(6)
C(35)-C(30)-H(30)	120.0
C(31)-C(30)-H(30)	120.0
C(32)-C(31)-C(30)	119.6(5)
C(32)-C(31)-H(31)	120.2
C(30)-C(31)-H(31)	120.2
C(31)-C(32)-C(33)	120.0(5)
C(31)-C(32)-H(32)	120.0
C(33)-C(32)-H(32)	120.0
C(34)-C(33)-C(32)	119.6(5)
C(34)-C(33)-H(33)	120.2
C(32)-C(33)-H(33)	120.2
C(35)-C(34)-C(33)	119.6(5)
C(35)-C(34)-H(34)	120.2
C(33)-C(34)-H(34)	120.2
C(34)-C(35)-C(30)	120.7(6)
C(34)-C(35)-H(35)	119.6
C(30)-C(35)-H(35)	119.6

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z

Table S24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (C22 H18 Cl5 N10 O Ru2) * (C6 H6) * 2(S O C2 H6) * 0.5(C6 H6). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	34(1)	42(1)	41(1)	2(1)	19(1)	-2(1)
Ru(2)	39(1)	35(1)	41(1)	-1(1)	18(1)	3(1)
Cl(1)	49(1)	54(1)	44(1)	-4(1)	17(1)	-2(1)
Cl(2)	51(1)	92(1)	67(1)	5(1)	36(1)	-12(1)
Cl(3)	77(1)	67(1)	84(1)	3(1)	50(1)	24(1)
Cl(4)	70(1)	55(1)	47(1)	-7(1)	10(1)	-1(1)
Cl(5)	77(1)	93(1)	134(2)	37(1)	72(1)	28(1)
O(1)	40(2)	46(2)	43(2)	2(1)	17(2)	-2(1)
N(1)	39(2)	46(2)	48(2)	4(2)	18(2)	2(2)
N(2)	54(2)	42(2)	56(3)	7(2)	22(2)	3(2)
N(3)	35(2)	38(2)	42(2)	1(2)	18(2)	-3(2)
N(4)	41(2)	38(2)	46(2)	3(2)	18(2)	-2(2)
N(5)	58(2)	41(2)	54(2)	-1(2)	31(2)	1(2)
N(6)	50(2)	38(2)	46(2)	3(2)	21(2)	2(2)
N(7)	77(3)	40(2)	57(3)	5(2)	17(2)	6(2)
N(8)	38(2)	42(2)	43(2)	-3(2)	16(2)	5(2)
N(9)	51(2)	43(2)	50(2)	-1(2)	26(2)	0(2)
N(10)	66(3)	73(3)	81(4)	-2(3)	47(3)	-15(3)
C(1)	53(3)	54(3)	63(3)	-1(2)	33(3)	9(2)
C(2)	58(3)	50(3)	74(4)	-3(3)	31(3)	15(2)
C(3)	43(2)	41(2)	45(3)	2(2)	18(2)	3(2)
C(4)	37(2)	46(3)	41(2)	2(2)	18(2)	-3(2)
C(5)	51(3)	44(3)	66(3)	13(2)	31(3)	1(2)
C(6)	56(3)	60(3)	83(4)	10(3)	49(3)	0(3)
C(7)	46(3)	49(3)	73(4)	8(2)	36(3)	7(2)
C(8)	41(2)	38(2)	41(2)	4(2)	20(2)	3(2)
C(9)	39(2)	38(2)	38(2)	-2(2)	16(2)	2(2)
C(10)	68(3)	36(3)	63(3)	8(2)	31(3)	2(2)
C(11)	53(3)	42(3)	64(3)	8(2)	26(3)	-6(2)
C(12)	59(3)	58(3)	50(3)	6(2)	27(3)	-6(2)
C(13)	76(4)	54(3)	58(3)	7(3)	26(3)	-13(3)
C(14)	55(3)	36(2)	44(3)	1(2)	13(2)	-3(2)
C(15)	48(3)	41(3)	48(3)	-4(2)	19(2)	5(2)
C(16)	60(3)	54(3)	84(4)	3(3)	28(3)	18(3)
C(17)	73(4)	72(4)	90(5)	-8(3)	42(4)	26(3)
C(18)	51(3)	79(4)	74(4)	-11(3)	34(3)	3(3)
C(19)	39(2)	53(3)	50(3)	-6(2)	16(2)	0(2)
C(20)	38(2)	52(3)	57(3)	-4(2)	18(2)	-7(2)
C(21)	95(5)	52(4)	100(5)	11(3)	60(4)	-7(3)
C(22)	75(4)	46(3)	85(4)	5(3)	40(3)	0(3)
S(1)	94(1)	77(1)	63(1)	7(1)	20(1)	-15(1)
O(2)	149(5)	78(3)	177(5)	38(3)	107(4)	5(3)
C(23)	130(7)	77(5)	93(6)	5(4)	39(5)	15(5)
C(24)	117(6)	86(5)	85(5)	1(4)	46(5)	-24(4)
S(2)	85(2)	62(2)	71(2)	15(2)	34(2)	16(2)
O(3)	180(20)	104(11)	128(16)	26(10)	67(13)	93(13)
C(25)	124(12)	116(12)	110(11)	6(8)	43(8)	10(8)
C(26)	132(13)	166(14)	152(14)	-15(9)	64(9)	18(9)
S(2A)	172(5)	101(4)	125(4)	-1(3)	85(4)	4(4)
O(3A)	131(13)	42(6)	171(19)	54(9)	90(13)	55(8)

C(25A)	87(9)	102(10)	111(10)	6(8)	46(8)	15(7)
C(26A)	114(9)	69(7)	84(8)	23(6)	50(7)	16(7)
C(27)	194(9)	179(9)	161(8)	-54(7)	74(7)	-5(7)
C(28)	187(9)	155(8)	125(7)	-21(6)	68(6)	4(7)
C(29)	183(9)	182(9)	170(9)	-24(7)	70(7)	-6(7)
C(30)	196(9)	190(9)	150(8)	-1(7)	28(7)	20(8)
C(31)	152(7)	179(7)	136(7)	10(6)	51(5)	-16(6)
C(32)	153(8)	162(8)	156(8)	10(7)	64(6)	36(7)
C(33)	179(9)	202(10)	188(9)	8(8)	75(8)	-7(8)
C(34)	141(7)	207(9)	146(8)	10(7)	65(6)	17(7)
C(35)	215(10)	198(10)	163(9)	15(8)	53(8)	12(8)

Table S25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for (C22 H18 Cl5 N10 O Ru2) * (C6 H6) * 2(S O C2 H6) * 0.5(C6 H6).

	x	y	z	U(eq)
H(2N)	7647	5712	3667	61
H(5N)	10330	3022	4591	58
H(7N)	5026	5509	1468	74
H(10N)	3134	3128	3733	82
H(1)	5664	5086	4750	64
H(2)	6053	5864	4089	71
H(5)	9263	5241	3339	61
H(6)	10601	4693	3278	72
H(7)	10656	3885	3838	63
H(10)	9565	2391	5337	65
H(11)	7953	2779	5544	63
H(12)	6988	4526	1044	65
H(13)	6526	5412	879	76
H(16)	3512	5287	2275	80
H(17)	2447	4931	3062	91
H(18)	2531	4096	3385	78
H(21)	4022	2361	3719	91
H(22)	5249	2518	2786	80
H(23A)	2753	3065	7084	154
H(23B)	2311	2779	7814	154
H(23C)	3102	3235	8255	154
H(24A)	1785	3687	8921	142
H(24B)	1124	3189	8648	142
H(24C)	476	3687	8276	142
H(25A)	7006	3032	7764	178
H(25B)	7674	3415	8643	178
H(25C)	7172	3569	7449	178
H(26A)	6346	3069	9315	222
H(26B)	5135	2971	8441	222
H(26C)	5358	3427	9188	222
H(25D)	6924	3498	7508	148
H(25E)	7784	3203	8471	148
H(25F)	7969	3765	8362	148
H(26D)	5387	3112	9146	129
H(26E)	6624	2913	9678	129
H(26F)	5970	2907	8444	129
H(27)	10815	5612	1149	214
H(28)	9211	5253	1133	185
H(29)	8315	4708	-151	215
H(30)	894	3811	1012	232
H(31)	1860	3152	842	190
H(32)	1285	2392	1009	189
H(33)	-348	2288	1207	228
H(34)	-1237	2952	1480	195
H(35)	-532	3704	1497	240

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