ELECTRONIC SUPPLEMENTARY INFORMATION

Springloaded porhyrin NHC hybrid rhodium(III) complexes: carbene dissociation and oxidation catalysis

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1. Synthesis

General

Solvents were dried by passage through solvent purification columns (MeCN). Complex [Rh(TPP)Cl][S1] and imidazolium carboxylate[S2] were prepared according to published procedures. All other reagents are commercially available and were used as received. Unless otherwise stated, NMR spectra were recorded at 30 °C on Varian spectrometers operating at 300 or 500 MHz (^{1}H NMR) and 75 or 125 MHz (^{13}C{^{1}H} NMR), respectively. Chemical shifts (δ in ppm, coupling constants *J* in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the microanalytical laboratory of University College Dublin, Ireland.

Synthesis of [Rh(TPP)(MeIm)Cl] (1)

To a red solution of [Rh(TPP)Cl] (0.100 g, 0.13 mmol) in $\mathrm{CHCl_3}$ (20 mL) was added an excess of 1-methylimidazole (0.10 mL, 1.3 mmol) and the mixture was stirred overnight. A red solid was filtered and air dried resulting in the desired product as a pink solid (0.078 g, 62 %). [Rh(TPP)(MeIm)Cl]: ^{1}H NMR (500 MHz, $\mathrm{CD_2Cl_2}$): 8.88 (s, 8 H, $\mathrm{H_{pyrrol}}$), 8.11 (m, 8 H, $\mathrm{H_{ortho}}$), 7.85–7.70 (m, 12H, $\mathrm{H_{meta}}$ and $\mathrm{H_{para}}$), 7.32 (s, 1H, $\mathrm{CHCl_3}$), 4.62 (s, 1H, $\mathrm{H^{2}_{Im}}$), 2.04 (s, 3H, $\mathrm{CH_3}$-Im), 0.97 (s, 1H, $\mathrm{H^{5}_{Im}}$), 0.51 (s, 1H, $\mathrm{H^{4}_{Im}}$). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CD_2Cl_2}$) 33.23 ($\mathrm{CH_3}$–Im), 118.03 ($\mathrm{C^{2}_{Im}}$), 121.42 ($\mathrm{C^{5}_{Im}}$), 122.46 ($\mathrm{C^{4}_{Im}}$), 126.35 and 126.82 ($\mathrm{C_{meta}}$ and $\mathrm{C_{para}}$), 127.63 ($\mathrm{C_{ipso}}$), 132.10 ($\mathrm{C_{pyrrol}}$), 134.07, 134.54 ($\mathrm{C_{ortho}}$), 142.02 ($\mathrm{C_{meso}}$), 142.35 ($\mathrm{C_{pyrrol}}$). ESI-MS(+) (m/z) calcd. for $\mathrm{[Rh(C_{49}H_{36}N_6)(C_4H_6N_2)Cl]Na^+}$ 855.1720, found 855.1758. Microanalysis (%) Calcd. for $\mathrm{C_{48}H_{34}ClN_6Rh}$ (833.18) × $\mathrm{CHCl_3}$: C 61.78, H 3.70, N 8.82. Found: C 61.09, H 3.31, N 8.76.

Synthesis of [Rh(TPP)(NHC)Cl] (2)

To a red solution of [Rh(TPP)Cl] (0.34 g, 0.44 mmol) in dry MeCN (40 mL), was added solid imidazolium carboxylate (0.075 g, 0.54 mmol) and the mixture was refluxed under a $\mathrm{N_2}$ atmosphere for 3 h. The mixture was allowed to cool to room temperature. A bright red solid precipitated out of the solution. It was filtered off and washed with MeCN before being re-dissolved in $CHCl_3$ (20 mL) and filtered. The volume was concentrated to approximately 5 mL followed by addition of cyclohexane (200 mL). The mixture was allowed to stand at room temperature overnight. The resulting red precipitate was collected by filtration and air dried, resulting in pure [Rh(TPP)(NHC)Cl] (56.8 mg, 14 % yield). A second crop of the desired product was obtained by concentrating the filtrate to approximately a third of the initial volume and precipitation at –20 °C for 1 day (35.3 mg, overall yield 23 %). ^{1}H NMR (400 MHz, $CDCl_3$): 8.71 (s, 8 H, H_{pyrrol}), 8.05 (br, 8 H, H_{ortho}), 7.63–7.70 (m, 12H, H_{meta} and H_{para}), 4.67 (s, 2H, H_{NHC}), –0.46 (s, 6H, CH_3–NHC). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 33.32 (CH_3–NHC), 121.24 (C_{NHC}–H), 127 and 127.45 (br, C_{meta} and C_{para}), 132.36 (C_{pyrrol}), 133, 134 (br, C_{ortho} and C_{ipso}), 141.56 (C_{meso}), 142.34 (C_{pyrrol}), 142.45 (C_{NHC}–Rh, $^1J_{RhC}$ = 24.4 Hz). ESI-MS(+) (m/z) calcd. for $C_{49}H_{36}N_6Rh^+$ 811.2056, found 811.2086. Microanalysis (%) Calcd. for $C_{49}H_{36}ClN_6Rh$ (847.21) × $0.5CHCl_3$: C 65.56, H 4.06, N 9.27. Found: C 65.75, H 3.98, N 9.73.

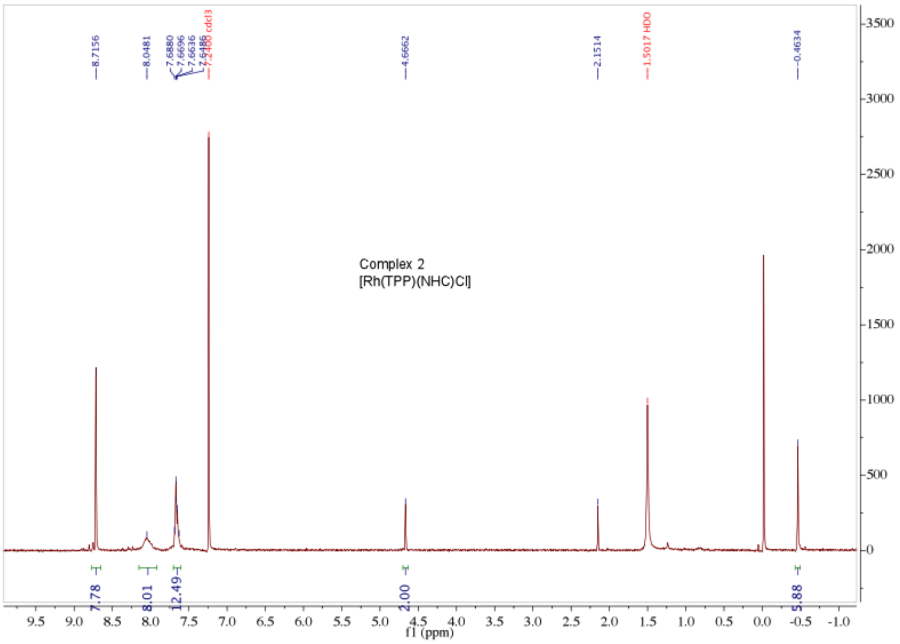

Figure S1. ^{1}H NMR spectrum of complex **2**

The *ortho* protons of the meso-phenyl groups are broad at room temperature. Variable temperature NMR spectroscopy revealed a dynamic behavior, with a fast exchange limit at >50 °C and a slow exchange limit below –10 °C (Fig. S2). From the coalescence temperature (25 °C at 500 MHz), the exchange rate for the rotation about the C_{Ph}–$C_{porphyrin}$ bond was determined to be k_{rot} = 230 (±40) s^{-1} at RT, corresponding to an activation energy $\Delta G^{\ddagger}$ = 59.5(±0.5) kJ mol^{-1}.

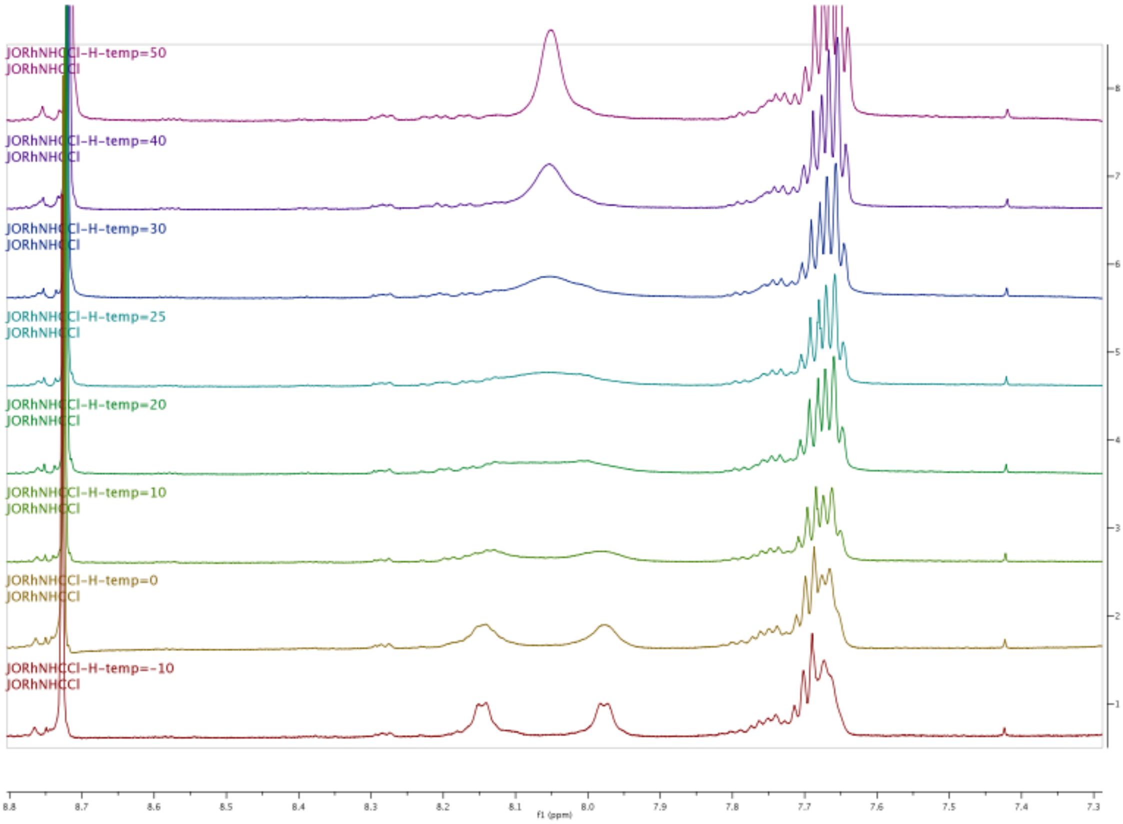

Figure S2. Aromatic section of the NMR spectrum of complex **2** at variable temperatures, indicating the dynamic nature of the *ortho* protons of the *meso*-phenyl groups in the 7.9–8.2 ppm range.

Synthesis of [Rh(TPP)(NHC)$_2$]Cl (3)

To a red solution of [Rh(TPP)Cl] (0.170 g, 0.23 mmol) in dry MeCN (40 mL), was added solid imidazolium carboxylate (0.047 g, 0.34 mmol), and the mixture was refluxed under a N_2 atmosphere for 18 h. The mixture was allowed to cool to room temperature before the solvent was removed in vacuo. The resulting purple solid was purified by gradient column chromatography (SiO_2, CH_2Cl_2, then CH_2Cl_2/acetone 9:1, then CH_2Cl_2/MeOH 9:1). The last red-green fraction was collected and identified as [Rh(TPP)(NHC)$_2$]Cl (0.060 g, 37 % yield). When using a 2:1 imidazolium carboxylate/Rh(TPP)Cl ratio, in order to increase the yield of **3**, a product was obtained that contained significant amounts of contaminations which could not be removed by precipitation or by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): 8.72 (s, 8 H, H_{pyrrol}), 7.63–7.71 (m, 20 H, H_{phenyl}), 4.97 (s, 4H, H_{NHC}), –0.70 (s, 12H, CH_3–NHC). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 31.92 (CH_3–NHC), 121.38 (C_{NHC}–H), 127.34 and 128.47 (C_{meta} and C_{para}), 133.94 (C_{pyrrol}), 134.03 (C_{ortho}) 139.80 (C_{ipso}), 141.93 (C_{pyrrol}), 142.55 (C_{meso}), 153.40 (C_{NHC}–Rh, $^1J_{RhC}$ = 34.9 Hz). ESI-MS(+) (m/z) calcd. for $C_{54}H_{44}N_8Rh^+$ 907.2744, found 907.2744. Microanalysis (%) Calcd. for $C_{54}H_{44}ClN_8Rh$ (943.34) × 0.75CH_2Cl_2: C 65.30, H 4.55, N 11.13. Found: C 65.72, H 4.31, N 10.61.

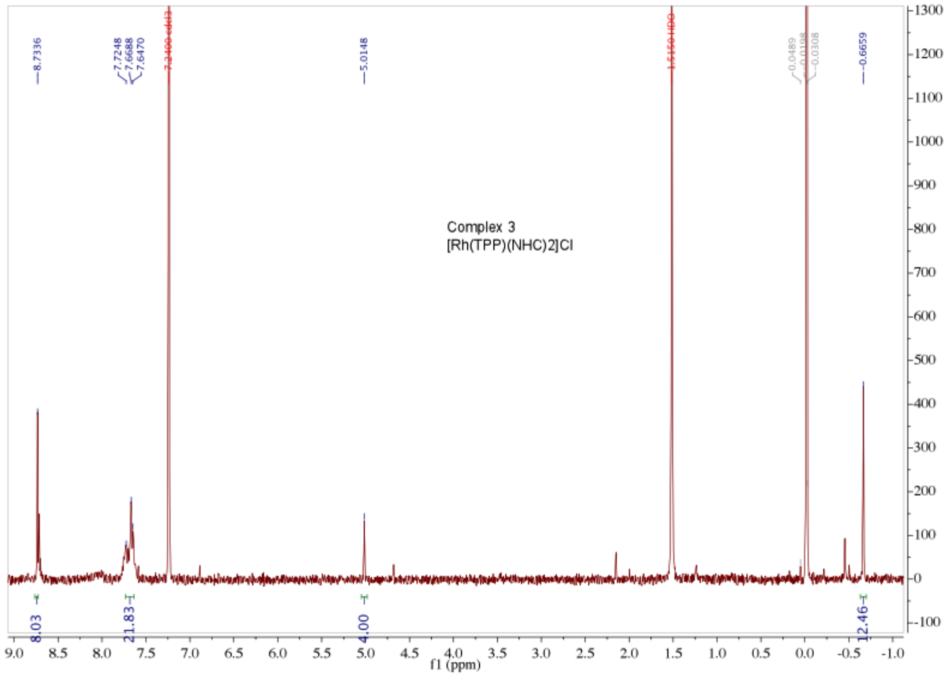

Figure S3. ^{1}H NMR spectrum of complex **3**.

Synthesis of [Rh(TPP)(NHC)](PF$_6$)

A solution of [Rh(TPP)(NHC)Cl] (0.222 g, 0.25 mmol) in CH_2Cl_2 (30 mL) was stirred with an aqueous solution of KPF_6 (20 mL of 0.05 M) for 2 h, the phases were separated and washed with deionised water (20 mL). The organic phase was dried over Na_2SO_4 before the solvent was removed in vacuo, leaving complex [Rh(TPP)(NHC)](PF$_6$) as a red solid (0.161 g, 68 %). ^{1}H NMR (500 MHz, $CDCl_3$): 8.86 (s, 8 H, H_{pyrrol}), 8.02 (br, 8 H, H_{ortho}), 7.68–7.73 (m, 12 H, H_{meta} and H_{para}), 4.83 (s, 2H, H_{NHC}), –0.53 (s, 6H, CH_3–NHC). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 33.39 (CH_3–NHC), 122.91 (C_{NHC}–Rh, $^1J_{RhC}$ = 74.0 Hz), 127.6 (br, C_{Ph} and C_{NHC}), 128.76 (C_{Ph}), 133.78 (C_{Ph}), 134.55 (br, C_{pyrrol}), 140.73 (C_{meso}), 143.07 (C_{pyrrol}), 146.68 (C_{Ph}). ESI-MS(+) (m/z) calcd. for $C_{49}H_{36}N_6Rh^+$ 811.2056, found 811.2081. Microanalysis (%) Calcd. for $C_{49}H_{36}F_6N_6PRh$ (956.72): C 61.51, H 3.79, N 8.78. Found: C 61.72, H 4.03, N 8.18.

Synthesis of monodeuterated 4-methoxybenzylalcohol (^{MeO}BnOH–d_1)

To a solution of 4-methoxybenzaldehyde (0.33 g, 2.50 mmol) in dry THF (20 mL) at 0 °C (water/ice bath) under a N_2 atmosphere was added portionwise solid $LiAlD_4$ (0.21 g, 5.0 mmol) over a period of 10 min. The mixture was stirred at 0 °C for 2 h then allowed to warm up to room temperature. The mixture was quenched by slowly adding a saturated solution of Na_2SO_4 (5 mL) followed by dilution with water (5 mL). The mixture was extracted with CH_2Cl_2 (2 × 50 mL). The organic phase was separated and dried over $MgSO_4$. The product was isolated as a yellow oil (0.28 g, 82% yield). ^{1}H NMR (300 MHz, $CDCl_3$): 7.29 (d J = 6.6 Hz, 2H, $H_{Ph\ ortho}$), 6.88 (d J = 6.6 Hz Hz, 2$H_{Ph\ meta}$), 4.68 (s broad, 1H, C*H*D–OH), 3.80 (s, 3H, OCH_3).

2. Catalytic studies

General method for the catalytic oxidation of benzyl alcohol

A mixture of the corresponding catalyst precursor (25 µmol) and KO*t*Bu (50 µmol) and anisole (0.5 mmol, internal standard) in 1,2-dichlorobenzene (2.5 mL) was heated to 150 °C for 10 min. The benzyl alcohol (0.5 mmol) was added and the mixture was stirred at 150 °C. Aliquots (0.10 mL) were taken at relevant times (Figure S5), diluted with $CDCl_3$ and conversions determined by comparing the integrals of the pertinent substrate and product resonances in the ^1H NMR spectrum.

Blank reaction 1 (base only, no complex)

A mixture of KO*t*Bu (50 µmol) in 1,2-dichlorobenzene (2.5 mL) was heated to 150 °C for 10 min. The benzyl alcohol (0.5 mmol) was added and the mixture was stirred at 150 °C. Aliquots (0.10 mL) were taken at relevant times. Conversion was <5% after 24 h.

Blank reaction 2 (base and NHC precursor)

A mixture of KO*t*Bu (50 µmol) and dimethylimidazolium carboxylate (25 µmol) in 1,2-dichlorobenzene (2.5 mL) was heated to 150 °C for 10 min. The benzyl alcohol (0.5 mmol) was added and the mixture was stirred at 150 °C. Aliquots (0.10 mL) were taken at relevant times. Conversion was <5% after 24 h.

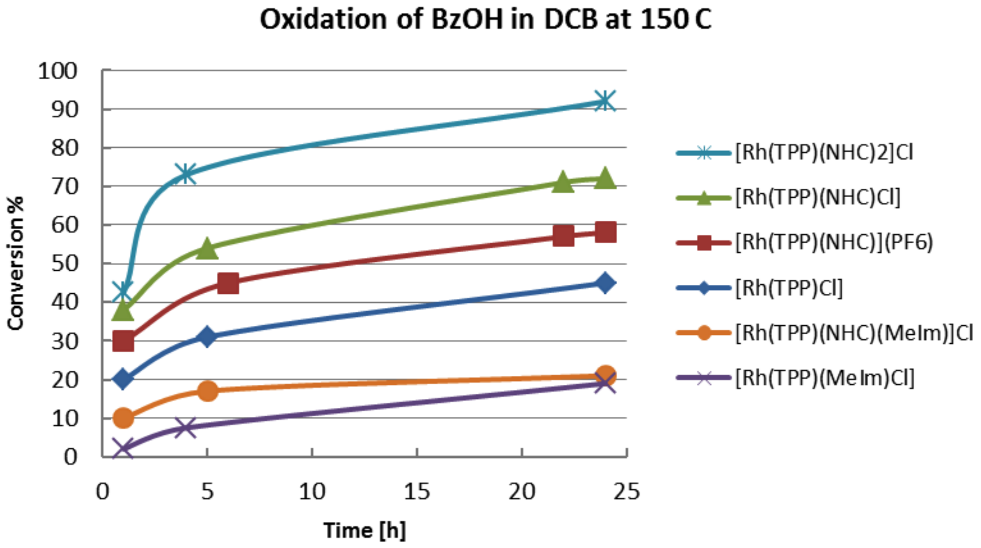

Figure S4. Conversion profile for the catalytic oxidation of BnOH with different rhodium porphyrin complexes.

Effect of $AgPF_6$ and irradiation

In an attempt to improve the catalytic activity of $[Rh(TPP)(NHC)_2]Cl$, one equivalent of $AgPF_6$ was added to the catalytic mixture, as it is known that silver is a good carbene-transfer agent. However, in this case addition of the silver additive did not result in any improvement on the catalytic activity as shown in Figure S6.

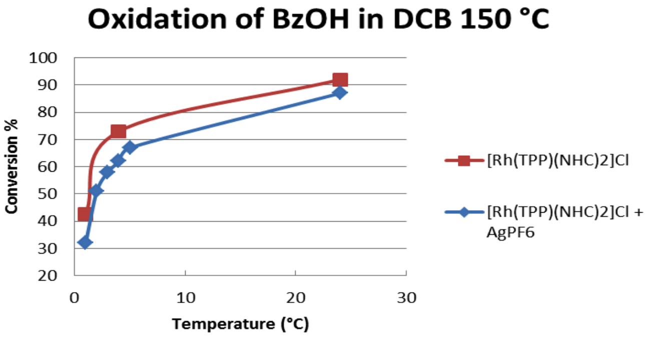

Figure S5. Time-conversion profile for the catalytic oxidation of BnOH with complex **3** in the presence (blue) and absence (red) of $AgPF_6$.

Irradiation with a Xe lamp during the reaction improved the catalytic activity by a factor of 2 (around 40% conversion after 0.5 h instead of 1 h, 75% conversion reached after 2 h instead of 4 h), see Fig. S4.

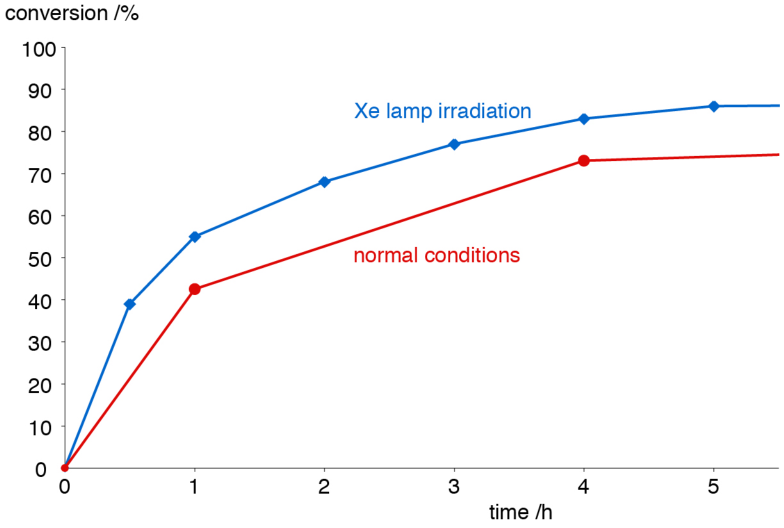

Figure S6. Time-conversion profile for the catalytic oxidation of BnOH with complex **3** in the presence (blue) and absence (red) of Xe light.

Substoichiometric experiment

Three equivalents of BnOH (34 mg, 0.30 mmol), one equivalent of $[Rh(TPP)(NHC)_2]Cl$ **3** (80 mg, 0.08 mmol) and two equivalents of KO*t*Bu (17 mg, 0.16 mmol) were heated in 1,2-dichlorbenzene (5 mL) for 24 h to 150 °C (Scheme S1) After this time the catalyst was precipitated by addition of Et_2O and the mixture was filtered. The residue was collected, dried, and analyzed by ^1H NMR spectroscopy. Signals were identical to those of [Rh(TPP)(NHC)(Cl)] **2**.

Determination of kinetic isotope effect (KIE)

$[Rh(TPP)(NHC)_2]Cl$ (24 mg, 0.025 mmol), KO*t*Bu (6.0 mg, 0.05 mmol) and $^{MeO}BnOH\text{–}d_1$ (70 mg, 0.5 mmol) were heated at 150 °C in 1,2-dichlorobenzene (2.5 mL) under standard conditions (see above). The total conversion was calculated from the ratio between the integral of the resonances corresponding to the methoxy groups in the *para*-positions of the phenyl ring of the product and starting material by ^1H NMR spectroscopy. The oxidation of this substrate occurred faster than in the parent benzyl alcohol, due to the electrodonating group in the *para*-position of the phenyl ring (Table S1). The D/H ratio in the aldehyde product was constant over time, as calculated from the ratios between the integral of the resonances for the aldehyde proton (product) and the methyl group in the methoxy substituent in the starting material (Table S1)

Table S1. Conversion and hydrogen:deuterium ratio found in the product of oxidation of (4-methoxyphenyl)methanol–d_1.

Time (h)	Conversion (%)	D/H ratio
1	65	2.5:1
2	81	2.5:1
3	85	2.5:1
4	88	2.5:1
5	91	2.5:1

3. Crystallographic details

Crystal data for complexes **1**, **2**, and **3** were collected by using an Agilent Technologies SuperNova A diffractometer fitted with an Atlas detector and using monochromated Mo–K_α radiation (0.71073 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical numeric absorption correction was performed.[S3] The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares fitting on F^2 for all data using SHELXL-97.[S4] Hydrogen atoms were added at calculated positions and refined by using a riding model. Anisotropic thermal displacement parameters were used for all nonhydrogen atoms. The solvents in **2** and **3** could not be modeled in terms of atomic sites. The SQUEEZE option as incorporated in PLATON[S5] was used to compensate for the spread electron density. Despite being achiral, complex **1** crystallizes in the non-centrosymmetric space group $P2_12_12_1$. It is known that rigid achiral molecules with non-flexible torsion angles and fixed conformation could crystallize in non-centrosymmetric space groups. However $P2_12_12_1$ is the rarest.[S6] Crystallographic details are compiled in the supporting information (Tables S2–S4). CCDC numbers 958621–958623 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S2. Crystal data and structure refinement for complex **1.**

CCDC No	958622	
Empirical formula	$C_{48.75}H_{35.50}N_6Cl_{2.50}Rh$	
Molecular formula	$C_{48}H_{34}N_6ClRh \times 0.75\ (CH_2Cl_2)$	
Formula weight	896.87	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$ (#19)	
Unit cell dimensions	a = 9.6618(1) Å	α = 90°
	b = 17.3989(2) Å	β = 90°
	c = 25.1987(3) Å	γ = 90°
Volume	4236.02(8) $Å^3$	
Z	4	
Density (calculated)	1.406 Mg m^{-3}	
Absorption coefficient	0.603 mm^{-1}	
F(000)	1830	
Crystal size	0.1818 × 0.1708 × 0.1033 mm^3	
Theta range for data collection	2.85 to 29.53°	
Index ranges	–12<=h<=13, –23<=k<=22, –30<=l<=34	
Reflections collected	43286	
Independent reflections	10592 [R(int) = 0.0308]	
Completeness to theta = 28.00°	98.8 %	

Absorption correction	Analytical
Max. and min. transmission	0.949 and 0.909
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	10592 / 0 / 534
Goodness–of–fit on F^2	1.077
Final R indices [I>2σ(I)]	R1 = 0.0323, wR2 = 0.0801
R indices (all data)	R1 = 0.0363, wR2 = 0.0829
Absolute structure parameter	0.056(19)
Largest diff. peak and hole	0.930 and –0.532 e Å^{-3}

Table S3. Crystal data and structure refinement for complex **2**.

CCDC No	958621	
Empirical formula	$C_{50}H_{38}N_6Cl_3Rh$	
Molecular formula	$C_{49}H_{36}N_6ClRh \times CH_2Cl_2$	
Formula weight	932.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$ (#14)	
Unit cell dimensions	a = 13.2973(2) Å	α = 90°
	b = 23.3659(3) Å	β = 103.471(1)°
	c = 14.0359(2) Å	γ = 90°
Volume	4241.02(10) Å^3	
Z	4	
Density (calculated)	1.460 Mg m^{-3}	
Absorption coefficient	0.636 mm^{-1}	
F(000)	1904	
Crystal size	0.2893 × 0.2364 × 0.0784 mm^3	
Theta range for data collection	2.97 to 31.03°	
Index ranges	–18<=h<=19, –33<=k<=33, –20<=l<=20	
Reflections collected	111975	
Independent reflections	12852 [R(int) = 0.0539]	
Completeness to theta = 30.00°	99.0 %	
Absorption correction	Analytical	
Max. and min. transmission	0.958 and 0.861	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	12852 / 0 / 516	
Goodness–of–fit on F^2	1.073	

Final R indices [I>2σ(I)]	R1 = 0.0377, wR2 = 0.1002
R indices (all data)	R1 = 0.0436, wR2 = 0.1036
Largest diff. peak and hole	2.453 and –1.175 e Å^{-3}

Table S4. Crystal data and structure refinement for complex **3**.

CCDC No	958623	
Empirical formula	$C_{221}H_{181}N_{32}Cl_{19}Rh_4$	
Molecular formula	$\{[C_{54}H_{44}N_8Rh]Cl\}_4 \times 5\ CHCl_3$	
Formula weight	4370.17	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$ (#14)	
Unit cell dimensions	a = 15.1167(2) Å	α = 90°
	b = 19.9147(2) Å	β = 90.679(1)°
	c = 17.2364(2) Å	γ = 90°
Volume	5188.56(11) Å^3	
Z	1	
Density (calculated)	1.399 Mg m^{-3}	
Absorption coefficient	0.619 mm^{-1}	
F(000)	2234	
Crystal size	0.2299 × 0.1583 × 0.1183 mm^3	
Theta range for data collection	2.88 to 29.53°	
Index ranges	–17<=h<=20, –27<=k<=25, –23<=l<=22	
Reflections collected	53398	
Independent reflections	12825 [R(int) = 0.0325]	
Completeness to theta = 27.00°	98.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.962 and 0.934	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	12825 / 0 / 581	
Goodness–of–fit on F^2	1.069	
Final R indices [I>2σ(I)]	R1 = 0.0380, wR2 = 0.1032	
R indices (all data)	R1 = 0.0461, wR2 = 0.1086	
Largest diff. peak and hole	0.584 and –0.580 e Å^{-3}	

4. References

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