

Electronic Supplementary Information for

Enhanced product selectivity promoted by remote metal coordination in acceptor-free alcohol dehydrogenation catalysis

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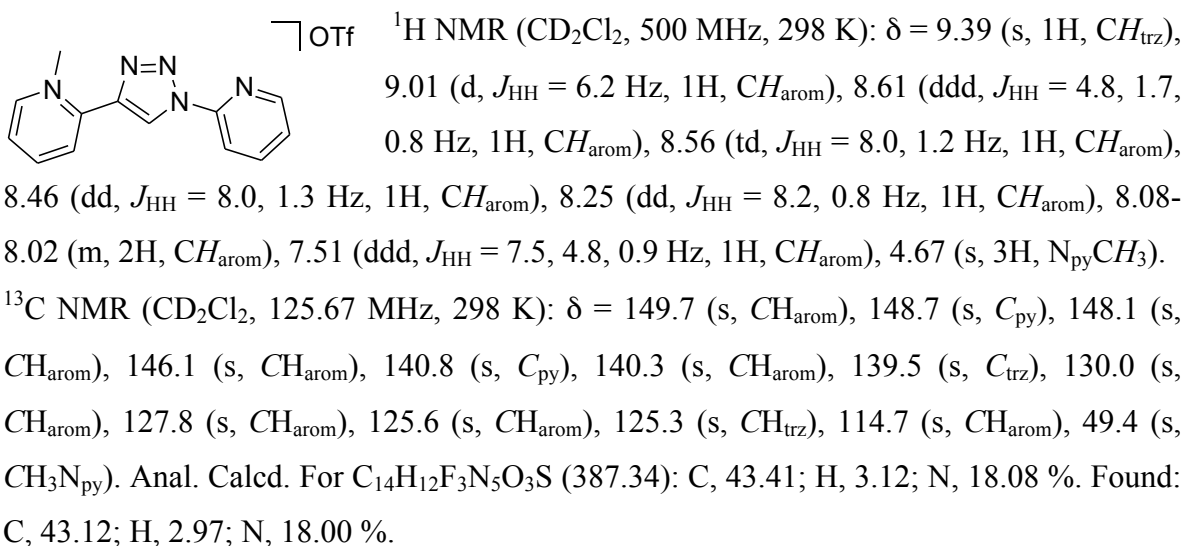
1. Synthetic procedures

General remarks. The compound 1,4-bis(2-pyridyl)triazole,^{S1} complex **3**,^{S2} and [Cp*IrCl₂]₂^{S3} were prepared according to literature procedures. Solvents were dried by passage through solvent purification columns. All other reagents were purchased from commercial sources and used without further purification. All reactions involving iridium were carried out with strict exclusion of air using Schlenk-tube techniques under a dry nitrogen atmosphere. All ¹H and ¹³C{¹H} NMR spectra were recorded on Varian spectrometers operating at 400, 500 or 600 MHz (¹H NMR). Chemical shifts (δ) are given in ppm and referenced to residual solvent signals. Signal assignments are based on heteronuclear correlation and heteronuclear multiple bond correlation experiments. Elemental analysis was performed by the microanalytical laboratory of University College Dublin. UV spectra were performed on a Shimadzu UV-1800 UV-vis spectrophotometer.

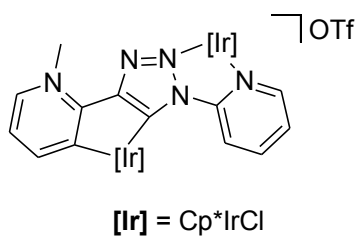
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- S1 S. Jindabot, K. Teerachanan, P. Thongkam, S. Kiatisevi, T. Khamnaen, P. Phiriyawirut, S. Charoenchaidet, T. Sooksimuang, P. Kongsaree and P. Sangtrirutnugul, *J. Organomet. Chem.*, 2014, **750**, 35.
S2 R. Lalrempuia, J. A. Woods, A. Petronilho, N. D. McDaniel, H. Müller-Bunz, M. Albrecht and S. Bernhard, *Energy Environ. Sci.*, 2014, **7**, 2316.
S3 R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyono, A. D. McMaster, B. M. Mattson and S. T. Michel, *Inorg. Chem.*, 1990, **29**, 2023.

Synthesis of the triazole pyridinium salt **L1**

A suspension of 1-(2-pyridyl)-4-(2-pyridyl)triazole (700 mg, 2.74 mmol) and MeOTf (361 μ L, 3.29 mmol) in dry CH_2Cl_2 (15 mL) was stirred at 0 $^\circ\text{C}$ for 30 min and then at r.t for 2 h. All volatiles were evaporated under reduced pressure. The residue was washed with Et_2O . Analysis of the crude product by ^1H NMR spectroscopy showed a mixture of methylation products at the triazolyl and pyridyl rings in approximately a 1:3 ratio. This crude mixture was purified by flash chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 40:1 initially with gradient to 20:1). The second fraction contained **L1** (white solid, 690mg, 65%).

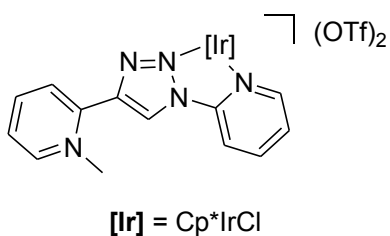


Synthesis of iridium complex **1**



A mixture of **L1** (100 mg, 0.26 mmol), NaOAc (25.41 mg, 0.30 mmol) and $[\text{IrCl}_2\text{Cp}^*]_2$ (103 mg, 0.13 mmol) in dry CH_2Cl_2 (10 mL) was stirred at room temperature for 18 h. After filtration through Celite and solvent evaporation, the reddish residue was purified by flash chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 40:1 to 20:1). The product was isolated as a red solid (60 mg, 48%). ^1H NMR (CD_2Cl_2 , 400 MHz, 298 K): δ = 9.04 (d, J_{HH} = 8.0 Hz, 1H, CH_{arom}), 8.78 (dd, J_{HH} = 5.8, 0.7 Hz, 1H, CH_{arom}), 8.53 (d, J_{HH} = 7.4 Hz, 1H, CH_{arom}), 8.26 (ddd, J_{HH} = 8.0, 7.4, 1.1 Hz, 1H, CH_{arom}), 8.08 (d, J_{HH} = 6.2 Hz, 1H, CH_{arom}), 7.76 (ddd, J_{HH} = 7.4, 5.8, 1.1 Hz, 1H, CH_{arom}), 7.25 (dd, J_{HH} = 7.4, 6.2 Hz, 1H, CH_{arom}), 4.71 (s,

3H, CH_3N_{py}), 1.83 (s, 15H, CH_3, Cp^*), 1.60 (s, 15H, CH_3, Cp^*). ^{13}C NMR (CD_2Cl_2 , 100.57 MHz, 298 K): δ = 160.7 (s, Ir- C_{py}), 160.4 (s, Ir- C_{trz}), 156.9 (s, C_{trz}), 155.3 (s, C_{py}), 151.6 (s, CH_{arom}), 150.1 (s, CH_{arom}), 149.2 (s, C_{py}), 142.1, 136.1, 127.0, 123.7, 117.5 (all s, CH_{arom}), 93.4, 90.4 (both s, C_{Cp^*}), 47.1 (s, CH_3N_{py}), 9.7, 9.4 (both s, CH_3, Cp^*). Anal. Calcd. For $C_{34}H_{40}Cl_2F_3Ir_2N_5O_3S$ (1111.11) \cdot 0.5 CH_2Cl_2 : C, 35.96; H, 3.58; N, 6.07 %. Found: C, 36.26; H, 3.30; N, 5.79 %.



Synthesis of iridium complex 2

A mixture of **L1** (200 mg, 0.52 mmol), NaOTf (88.84 mg, 0.51 mmol) and $[IrCl_2Cp^*]_2$ (206 mg, 0.26 mmol) in dry CH_2Cl_2 (10 mL) was stirred at room temperature for 18 h.

The solvent was removed *in vacuo*, and the residue was dissolved in a saturated brine solution and extracted with several portions of CH_2Cl_2 until the CH_2Cl_2 fraction was colourless. The combined organic layers were concentrated, dried over $MgSO_4$, and filtered. All volatiles were removed *in vacuo*. The residue was dissolved in MeCN (1 mL) and precipitated with Et_2O (20 mL), thus affording the title product as a light yellow solid (280 mg, 61%). 1H NMR (CD_2Cl_2 , 400 MHz, 298 K): δ = 10.22 (s, 1H, CH_{Trz}), 9.02 (d, J_{HH} = 6.6 Hz, 1H, CH_{arom}), 8.72 (dd, J_{HH} = 5.7, 0.8 Hz, 1H, CH_{arom}), 8.69-8.59 (m, 3H, CH_{arom}), 8.37 (td, J_{HH} = 8.0, 1.3 Hz, 1H, CH_{arom}), 8.11 (td, J_{HH} = 6.6, 1.8 Hz, 1H, CH_{arom}), 7.82 (ddd, J_{HH} = 8.0, 5.7, 0.9 Hz, 1H, CH_{arom}), 4.72 (s, 3H, CH_3N_{py}), 1.82 (s, 15H, CH_3, Cp^*). ^{13}C NMR (CD_2Cl_2 , 100.57MHz, 298 K): δ 150.5 (s, CH_{arom}), 148.5 (s, CH_{arom}), 146.6 (s, C_{py}), 144.0 (s, C_{py}), 143.9 (s, CH_{arom}), 142.5 (s, C_{trz}), 131.1 (s, CH_{arom}), 129.4 (CH_{trz}), 129.0, 128.6, 116.6 (all s, CH_{arom}), 91.7 (s, C_{Cp^*}), 49.6 (s, CH_3N_{py}), 9.2 (s, CH_3, Cp^*). Anal. Calcd. For $C_{25}H_{27}ClF_6IrN_5O_6S_2$ (899.30): C, 33.39; H, 3.03; N, 7.70 %. Found: C, 33.34; H, 2.82; N, 7.32 %.

2. General Procedure for Catalytic Alcohol Oxidations.

A mixture of substrate alcohol (0.2 mmol) and the iridium complex (0.005 mmol **1** or 0.01 mmol **2** or **3**, final alcohol/Ir concentration always 20:1) in 1,2-dichlorobenzene (2 mL) was heated at 150 °C in a closed vial. Aliquots were taken at specific times, diluted with CDCl₃ and then analyzed by ¹H NMR spectroscopy. Hexamethylbenzene (0.033 mmol) was used in all cases as internal standard in order to accurately determine the percentage conversions and yields. Products were identified by comparison with commercially available samples (benzaldehyde, acetophenone, benzophenone, octanal, methyl ethyl ketone).

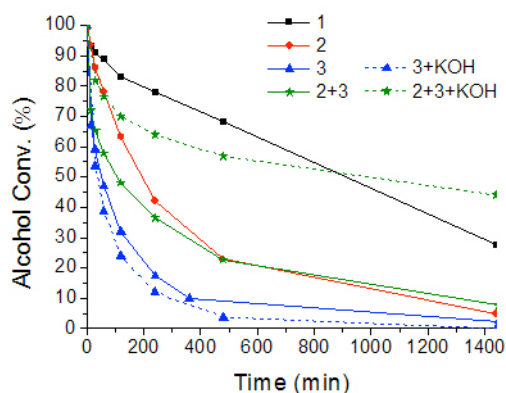


Fig. S1. Time-conversion profile for the catalytic alcohol oxidation of benzyl alcohol.

Table S1. BnOH oxidation catalyzed by iridium complexes **1–3** in the presence of a base.^a

entry	[Ir]	time (h)	conv'n (%) ^b	BnCHO / Bn ₂ O (%) ^c
1	2	96	93	96 / 4
2	3	24	99	50 / 50
3	2+3 ^d	24	56	95 / 5
4	2+3 ^d	96	69	93 / 7

^a Conditions: alcohol (0.2 mmol), [Ir] (0.01 mmol, 5 mol% based on Ir), KOH (5 mol%) 1,2-dichlorobenzene (2 mL), 150 °C; ^b Determined by ¹H NMR spectroscopic analysis in CDCl₃ with hexamethylbenzene as internal standard; ^c Ratio of products given in percent; ^d 5 μmol of **2** plus 5 μmol of **3**.

It should be noted that complex **2** is not stable in the presence of a base and undergoes N_{trz}-Ir dissociation and C_{trz}-H bond activation to form a new chelate structure with a C_{trz},N_{pyr}-bidentate bonding ligand.

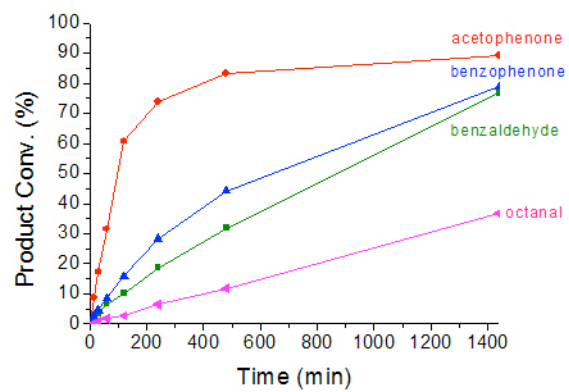


Fig. S2. Time conversion profiles for the catalytic oxidation of selected alcohols.

3. Electrochemical data

Electrochemical studies were carried out using an Metrohm Autolab Potentiostat Model PGSTAT101 employing a gas-tight three electrode cell under an argon atmosphere. A platinum disk with 7.0 mm² surface area was used as the working electrode and was polished before each measurement. The reference electrode was Ag/AgCl; the counter electrode was a Pt foil. In all experiments, Bu₄NPF₆ (0.1 M) was used as supporting electrolyte with analyte concentrations of approximately 1 mM. Measurements were performed at between 250 and 20 mV s⁻¹ scan rates. The redox potentials were referenced to ferrocenium/ferrocene (Fc⁺/Fc; $E_{1/2} = +0.46$ V vs. SCE in CH₂Cl₂)^{S4} as internal standard and are compiled in Table S2.

Table S2. Electrochemical data for complex **2**.^a

entry	scan rate (mV s ⁻¹)	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	I_a (μA)	I_c (μA)	I_c/I_a
1	250	1.12	0.98	1.05	21.69	23.69	1.09
2	100	1.09	0.97	1.03	14.14	14.72	1.04
3	50	1.08	0.97	1.03	9.07	9.85	1.09
4	20	1.08	0.97	1.02	6.03	6.50	1.08

[a] in CH₂Cl₂ (ca. 10⁻³M) with Ag/AgCl (3M) as reference and ferrocene as internal standard ($E_{1/2}$ (Fc/Fc⁺) = 0.46 V vs SCE).

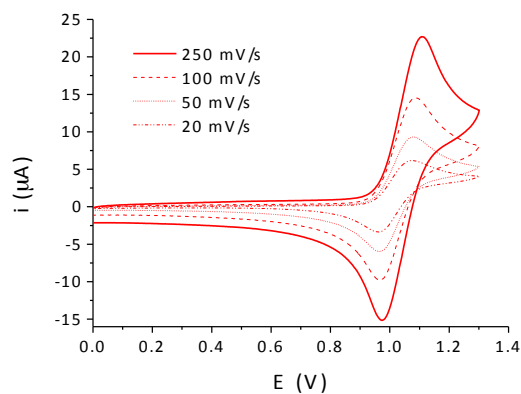


Fig. S3. Cyclic voltammogram of complex **2** in CH₂Cl₂ (ca. 10⁻³M) with Ag/AgCl (3M) as reference and ferrocene as internal standard ($E_{1/2}$ (Fc/Fc⁺) = 0.46 V vs. SCE).

S4 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.

4. Crystallographic analyses

Crystallographic details. Crystal data for complexes **1** and **2** were collected by using an Agilent Technologies (now Rigaku) SuperNova A diffractometer fitted with an Atlas detector using 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.^{S5} The structure was solved by direct methods using SHELXS-97^{S6} and refined by full-matrix least-squares fitting on F² for all data using SHELXL-97.^{S6} Hydrogen atoms were added at calculated positions and refined by using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. Anisotropic thermal displacement parameters were used for all nonhydrogen atoms. Crystallographic details are compiled in Tables S3 and S4. CCDC 1434920 and 1434921 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.

S5 R. C. Clark and J. S. Reid, *Acta Crystallogr.*, 1995, **A51**, 887.

S6 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

Table S3. Crystal data and structure refinement for complex 1.

CCDC number	1434920
Empirical formula	C ₃₄ H ₄₀ N ₅ O ₃ F ₃ SCl ₂ Ir ₂
Molecular formula	[C ₃₃ H ₄₀ N ₅ Cl ₂ Ir ₂] ⁺ [CF ₃ SO ₃] ⁻
Formula weight	1111.07
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n (#14)
Unit cell dimensions	a = 14.4786(2) Å b = 11.9118(1) Å β = 98.8187(8)° c = 21.7475(2) Å
Volume	3706.37(7) Å ³
Z	4
Density (calculated)	1.991 Mg m ⁻³
Absorption coefficient	7.431 mm ⁻¹
F(000)	2136
Crystal size	0.4358 × 0.2364 × 0.1655 mm ³
Theta range for data collection	2.78 to 32.96°
Index ranges	-21 ≤ h ≤ 22, -18 ≤ k ≤ 17, -32 ≤ l ≤ 32
Reflections collected	116141
Independent reflections	13215 [R(int) = 0.0531]
Completeness to theta = 32.00°	99.3 %
Absorption correction	Analytical
Max. and min. transmission	0.388 and 0.139
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13215 / 0 / 462
Goodness-of-fit on F ²	1.081
Final R indices [I > 2σ(I)]	R1 = 0.0219, wR2 = 0.0463
R indices (all data)	R1 = 0.0253, wR2 = 0.0477
Largest diff. peak and hole	1.304 and -0.821 e Å ⁻³

Table S4. Crystal data and structure refinement for complex **2**.

CCDCnumber	1434921
Empirical formula	C ₂₅ H ₂₇ N ₅ O ₆ F ₆ S ₂ ClIr
Molecular formula	[C ₂₃ H ₂₇ N ₅ ClIr] ⁺ {[CF ₃ SO ₃] ⁻ } ₂
Formula weight	899.29
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n (#14)
Unit cell dimensions	a = 14.4611(7) Å b = 8.8412(5) Å β = 94.954(4)° c = 24.209(1) Å
Volume	3083.6(3) Å ³
Z	4
Density (calculated)	1.937 Mg m ⁻³
Absorption coefficient	11.223 mm ⁻¹
F(000)	1760
Crystal size	0.1879 × 0.0295 × 0.0172 mm ³
Theta range for data collection	3.43 to 77.05°
Index ranges	-11 ≤ h ≤ 17, -11 ≤ k ≤ 10, -26 ≤ l ≤ 30
Reflections collected	15463
Independent reflections	6356 [R(int) = 0.0606]
Completeness to theta = 75.00°	98.9 %
Absorption correction	Analytical
Max. and min. transmission	0.858 and 0.288
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6356 / 0 / 422
Goodness-of-fit on F ²	1.025
Final R indices [I > 2σ(I)]	R1 = 0.0487, wR2 = 0.1208
R indices (all data)	R1 = 0.0635, wR2 = 0.1318
Extinction coefficient	0.00034(4)
Largest diff. peak and hole	2.234 and -2.322 e Å ⁻³
