Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Electronic effects on the catalytic disproportionation of formic acid to methanol by [Cp*Ir^{III}(R-bpy)Cl]Cl complexes

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General considerations

Unless otherwise noted, all chemicals were used as obtained from commercial suppliers. All ^{1}H NMR spectra were obtained on a 500 MHz Joel spectrometer, and spectral data are referenced against residual solvent signals and reported in ppm downfield of tetramethylsilane ($\delta = 0$). Elemental analyses were performed by NuMega Labs in San Diego, CA.

Preparation of reagents and standards

$[Cp^*IrCl_2]_2$ was prepared according to previously reported methods.[1] Preparation using freshly opened reagents resulted in good yield and purity and is highly recommended. 4,4'-trifluoromethane-2,2'-bipyridine was prepared according to previously reported methods, with a yield of 10%.[2] Sodium tosylate was recrystallized from vapor diffusion of diethylether into saturated methanol solutions, filtered and rinsed with pentane, and dried under vacuum and heat overnight.

Synthesis of iridium complexes

$[Cp^*Ir(CF_3\text{-bpy})Cl]Cl$ (1)

4,4'-trifluoromethane-2,2'-bipyridine (200 mg, 0.68 mmol) and $[Cp^*IrCl_2]_2$ (266 mg, 0.33 mmol) were stirred at 40°C in 20 mL MeOH in a 50 mL round bottom flask overnight. Solvent was removed *in vacuo* and the resulting orange solid was purified by liquid chromatography on neutral alumina with 5/95 MeOH/$CHCl_3$ and purified further by recrystallization from large scale vapor diffusion of diethylether into a saturated MeOH solution yielding 435 mg of **1** (0.63 mmol, 94% yield) after filtering and drying under heat and vacuum.

Calcd. for $C_{22}H_{21}Cl_2F_6IrN_2$: 38.27% C, 3.07% H, 4.06% N. Found: 37.99% C, 3.46% H, 3.90% N. ^{1}H NMR (500MHz, CD_3OD): $\delta = 9.32$ (s, ArH, 2H), 9.26 (d, J = 5 Hz, ArH, 2H), 8.20 (d, J = 5 Hz, ArH, 2H), 1.76 (s, Cp*H, 15H).

X-ray quality crystals of **1** were grown by small-scale vapor diffusion of ether into a saturated acetonitrile solution. Single crystal X-ray structural data was collected at 100K on a Kappa diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) equipped with a

Bruker APEX-II CCD detector. The structure was solved by direct methods using SHELXT and refined with full-matrix least-squares procedures using SHELXL.[3]

[Cp*Ir(H-bpy)Cl]Cl (2)

2,2'-bipyridine (206 mg, 1.32 mmol) and $[Cp^*IrCl_2]_2$ (500 mg, 0.63 mmol) were stirred at room temperature in 20 mL MeOH in a 50 mL round bottom flask overnight. Solvent was removed *in vacuo* and the resulting yellow solid was purified by liquid chromatography on neutral alumina with 5/95 MeOH/$CHCl_3$ and purified further by recrystallization from large scale vapor diffusion of diethylether into a saturated MeOH solution yielding 531 mg of **2** (0.96 mmol, 76 % yield) after filtering and drying under heat and vacuum. Spectral data matched previously reported values. [4]

Calcd. for $C_{20}H_{23}Cl_2IrN_2 \cdot H_2O$: 41.96% C, 4.40% H, 4.89% N. Found: 41.98% C, 4.78% H, 4.89% N. ^{1}H NMR (500MHz, CD_3OD): δ = 9.00 (d, J = 5.0 Hz, ArH, 2H), 8.64 (d, J = 5.0 Hz, ArH, 2H), 8.28 (t, J = 7.5 Hz, ArH, 2H), 7.85 (t, J = 7.5 Hz, ArH, 2H), 1.72 (s, Cp*H, 15H).

[Cp*Ir(Me-bpy)Cl]Cl (3)

4,4'-dimethyl-2,2'-bipyridine (243 mg, 1.32 mmol) and $[Cp^*IrCl_2]_2$ (500 mg, 0.63 mmol) were stirred at 40°C in 20 mL MeOH in a 50 mL round bottom flask overnight. Solvent was removed *in vacuo* and the resulting yellow solid was purified by liquid chromatography on neutral alumina with 5/95 MeOH/$CHCl_3$ and purified further by recrystallization from large scale vapor diffusion of diethylether into a saturated MeOH solution yielding 451 mg of **3** (0.77 mmol, 62 % yield) after filtering and drying under heat and vacuum. Spectral data matched previously reported values.[5]

Calcd. for $C_{22}H_{27}Cl_2IrN_2 \cdot H_2O$: 44.00% C, 4.87% H, 4.66% N. Found: 43.78% C, 5.20% H, 4.64% N. ^{1}H NMR (500MHz, CD_3OD): δ = 8.79 (d, J = 5.0 Hz, ArH, 2H), 8.48 (s, ArH, 2H), 7.66 (d, J = 5 Hz, ArH, 2H), 2.68 (s, MeH, 6H), 1.70 (s, Cp*H, 15H).

[Cp*Ir(tBu-bpy)Cl]Cl (4)

4,4'-di-*tert*-butyl-2,2'-bipyridine (354 mg, 1.32 mmol) and $[Cp^*IrCl_2]_2$ (500 mg, 0.63 mmol) were stirred at 40°C in 20 mL MeOH in a 50 mL round bottom flask

overnight. Solvent was removed *in vacuo* and the resulting yellow solid was purified by liquid chromatography on neutral alumina with 5/95 MeOH/$CHCl_3$ and purified further by recrystallization from large scale vapor diffusion of diethylether into a saturated MeOH solution yielding 718 mg of **4** (1.08 mmol, 86 % yield) after filtering and drying under heat and vacuum.

Calcd. for $C_{28}H_{39}Cl_2IrN_2 \cdot H_2O \cdot CH_3OH$: 48.59% C, 6.33% H, 3.91% N. Found: 48.87% C, 6.61% H, 3.92% N. ^{1}H NMR (500MHz, CD_3OD): δ = 8.86 (d, J = 5.0 Hz, ArH, 2H), 8.68 (d, J = 5 Hz, ArH, 2H), 7.86 (dd, J = 5 Hz, J = 5 Hz, ArH, 2H), 1.71 (s, Cp*H, 15H), 1.51 (s, tBuH, 18H).

X-ray quality crystals of **4** were grown by small-scale vapor diffusion of pentane into a saturated dichloromethane solution. Single crystal X-ray structural data was collected at 100K on a Kappa diffractometer using Mo Kα radiation (λ = 0.71073 Å) equipped with a Bruker APEX-II CCD detector. The structure was solved by direct methods using SHELXT and refined with full-matrix least-squares procedures using SHELXL.[3]

[Cp*Ir(OMe-bpy)Cl]Cl (5)

4,4'-dimethoxy-2,2'-bipyridine (285 mg, 1.32 mmol) and $[Cp^*IrCl_2]_2$ (500 mg, 0.63 mmol) were stirred at RT in 20 mL MeOH in a 50 mL round bottom flask overnight. Solvent was removed *in vacuo* and the resulting yellow solid was purified by liquid chromatography on neutral alumina with 5/95 MeOH/$CHCl_3$ and purified further by recrystallization from large scale vapor diffusion of diethylether into a saturated MeOH solution yielding 655 mg of **5** (1.07 mmol, 85 % yield) after filtering and drying under heat and vacuum. Spectral data matched previously reported values.[5]

Calcd. for $C_{22}H_{27}Cl_2IrN_2O_2$: 42.99% C, 4.43% H, 5.21% N. Found: 42.60% C, 4.60% H, 4.61% N. ^{1}H NMR (500MHz, CD_3OD): δ = 8.68 (d, J = 10 Hz, ArH, 2H), 8.13 (s, ArH, 2H), 7.34 (d, J = 10 Hz, ArH, 2H), 4.08 (s, OMeH, 6H), 1.66 (s, Cp*H, 15H).

Crystal data

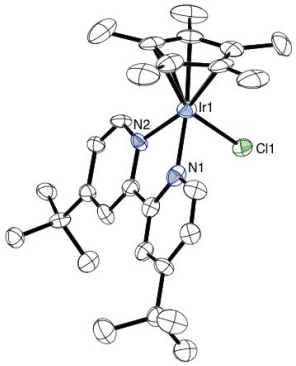
Table S1 Crystal data and structure refinement for **1**

Identification code	KubASCF3	
Empirical formula	C22 H22 Cl2 F6 Ir N2 O0.50	
Molecular formula	C22 H21 Cl F6 Ir N2, Cl, 0.5(H2 O)	
Formula weight	699.51	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2/c 1	
Unit cell dimensions	a = 16.2237(5) Å	α= 90°.
	b = 15.7371(4) Å	β= 109.000(2)°.
	c = 21.8522(7) Å	γ = 90°.
Volume	5275.2(3) $Å^3$	
Z	8	
Density (calculated)	1.762 Mg/m^3	
Absorption coefficient	5.321 mm^{-1}	
F(000)	2696	
Crystal size	0.109 x 0.085 x 0.067 mm^3	
Crystal color, habit	Yellow Orange Block	
Theta range for data collection	1.627 to 26.403°.	
Index ranges	-20<=h<=20, -18<=k<=19, -26<=l<=27	
Reflections collected	68790	
Independent reflections	10796 [R(int) = 0.0779]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0452 and 0.0239	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10796 / 3 / 621	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0712	
R indices (all data)	R1 = 0.0509, wR2 = 0.0788	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.159 and -0.893 $e.Å^{-3}$	

Table S2 Crystal data and structure refinement for **4**

Identification code	Tbut	
Empirical formula	C28 H39 Cl2 Ir N2	
Molecular formula	C28 H39 Cl Ir N2, 1(Cl)	
Formula weight	666.71	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = 16.6890(11) Å	α= 90°.
	b = 16.6890(11) Å	β= 90°.
	c = 21.5798(16) Å	γ = 120°.
Volume	5205.2(8) $Å^3$	
Z	6	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	4.016 mm^{-1}	
F(000)	1992	
Crystal size	0.253 x 0.217 x 0.215 mm^3	
Crystal color, habit	Yellow Orange Block	
Theta range for data collection	1.409 to 26.408°.	
Index ranges	-19<=h<=20, -20<=k<=20, -26<=l<=26	
Reflections collected	73836	
Independent reflections	7113 [R(int) = 0.0727]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0932 and 0.0530	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7113 / 1 / 324	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0579	
R indices (all data)	R1 = 0.0340, wR2 = 0.0600	
Absolute structure parameter	?	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.570 and -0.524 $e.Å^{-3}$	

Figure S1 Thermal ellipsoid plot of the crystal structure of **4** shown at the 50% probability level. Hydrogen atoms, uncoordinated counterions, and solvent molecules are omitted for clarity.



Catalytic testing

The general procedure for NMR scale catalytic testing closely follows that of Miller, *et al*.[6] 3 M aqueous HCOOH stock solutions were prepared by dilution of 88% HCOOH with Nanopure® H_2O and degassed by freeze-pump-thaw. 1 M sodium tosylate solution prepared in a volumetric flask was used as an internal standard for NMR quantification. 1 mM solutions of each iridium complex in 3 M HCOOH were prepared freshly before each catalytic test.

Catalytic tests were carried out in J. Young tubes. To each tube was added 120 μL of iridium complex solution, 16 μL of sodium tosylate solution, 264 μL of HCOOH stock solution, and a sealed capillary containing D_2O for locking. This results in tests of 0.3 mM iridium complex in 3M HCOOH. Reaction solutions were sparged with Ar prior to reaction.

Catalytic testing was carried out in the same 60°C bath for 21 hr in order to screen the iridium complexes against each other in a consistent manner. MeOH, methyl formate, and HCOOH concentrations before and after reaction were quantified by integration of ^{1}H NMR peaks in comparison to calibration curves of known concentrations with respect to a standard concentration of NaOTs. Total MeOH consisted of MeOH and methyl formate, since methyl formate is formed from MeOH and HCOOH. TOF, MeOH selectivities, and HCOOH conversion were calculated as in Miller, *et al*.[6]

References

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