Electronic Supplementary Material (ESI) for Chemical Science
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Supporting Information

Selective Electrocatalytic Reduction of Carbon Dioxide to Formate by a Water-Soluble Iridium Pincer Catalyst

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I. Experimental

Materials and Methods

All the chemicals were purchased from commercial sources if not mentioned otherwise. Acetonitrile were of HPLC grade and further purified by a Pure-Solv Solvent Purification System (Innovative Technology). Distilled water was further purified by using a Milli-Q Synthesis A10 Water Purification system. Argon was purified by passing through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves. CO_2 (National Welders, research grade) was of 99.998% purity with less than 3ppm H_2O and used as received. Air-sensitive materials were prepared and manipulated using Schlenk techniques and in an argon-atmosphere glovebox (MBraun Unilab, < 1 ppm in O_2 and H_2O). Deuterated solvents CD_3CN, CD_2Cl_2, THF-d_8 (Cambridge Isotope) were dried with CaH_2 or 4Å molecular sieves and vacuum transferred into Kontes flasks. D_2O (Cambridge Isotope) was used as received. Tetrabutylammonium hexafluorophospate (^{n}Bu_4NPF_6, Fluka, electrochemical grade) was dried at 60 °C under vacuum for 12 h and stored in the glovebox. All other reagents are commercially available and were used without further purification.

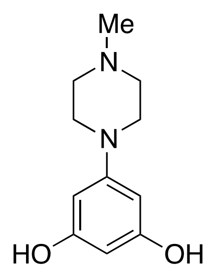
NMR spectra were recorded on Bruker NMR spectrometers (AVANCE-400, AVANCE-500, and AVANCE-600). ^{1}H and ^{13}C NMR spectra were referenced to residual solvent signals. ^{31}P chemical shifts were referenced to a H_3PO_4 external standard. ^{19}F chemical shifts were referenced to a CF_3COOH external standard. Due to a strong ^{31}P–^{31}P coupling in PCP-type ligands, some ^{1}H and ^{13}C NMR signals appear as virtual triplets and are thus reported with apparent coupling constants. Gaseous products were analyzed using a Varian 450-GC with a molecular sieve column and a PDHID detector. Electrospray ionization mass spectra (ESI-MS) were collected by using a Micromass (Milford, MA) Quattro-II triple quadrupole mass spectrometer, with a Z-spray nano-electrospray source, in combination with a NanoMate (Ithaca, NY) chip based electrospray sample introduction system and nozzle.

Electrochemistry

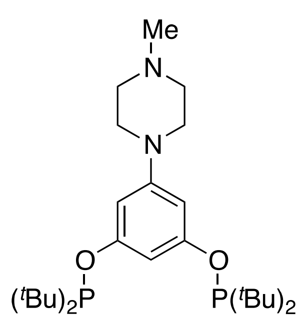
Electrochemical experiments were performed using a CHI 6012D potentiostat (CH Instruments, Inc., TX). A three-electrode setup for aqueous media consisted of a glassy carbon working electrode (BASi, 7.1 mm^{2}), a coiled Pt wire counter electrode, and a SCE reference electrode (0.244 V vs NHE) in an airtight, glass frit-separated two-compartment cell. In non-aqueous solvents, the reference electrode was Ag/$AgNO_3$ reference electrode (BASi, 10 mM $AgNO_3$, 0.1 M $^{n}Bu_4NPF_6$ in acetonitrile, 0.55 V vs NHE), and ferrocene was added at the end of the experiment and the potential was converted relative to NHE following the literature.[1] Prior to each measurement, the glassy carbon electrode was polished with 0.05-μm alumina slurry to obtain a mirror-like finish, then sonicated and thoroughly rinsed with Milli-Q water and acetone and finally dried in Ar stream. In cyclic voltammogram experiments, the working and counter electrodes were separated from the reference electrode. In controlled potential electrolyses, the reference and counter electrodes were separated from the working electrode.

Controlled potential electrolysis was carried out in 3 mL water with 0.1 M $NaHCO_3$ as the supporting electrolyte in an airtight electrochemical cell under vigorous stirring. The solution was initially degassed by bubbling Ar for 15 min and saturated with 1 atm of CO_2. At the end of electrolysis, gaseous sample (0.5 ml) was drawn from the headspace by a gas-tight syringe (Vici) and injected into the GC. Calibration curves for H_2 and CO were obtained separately. The liquid phase was carefully added with aliquots of HCl aqueous solution (15%) and DMF as internal standard under CO_2 and then diluted with CD_3CN for NMR analysis.

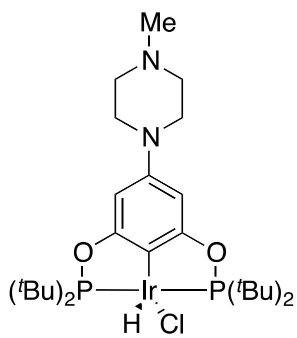
Syntheses



5-(4-Methyl-1-piperazinyl)-resorcinol: the synthesis followed a literature procedure.[2] Yield: 22.4 g, 93%. ^{1}H NMR (500 MHz, D_2O, 1% HCl): δ 6.20 (s, 2H, Ar-H), 6.06 (s, 1H, Ar-H), 3.69 (d, J = 13.9 Hz, 2H, N-CH_2), 3.60 (d, J = 13.8 Hz, 2H, N-CH_2), 3.43 (t, J = 13.2 Hz, 2H, N-CH_2), 3.27 (t, J = 12.8 Hz, 2H, N-CH_2), 2.78 (s, 3H, N-CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, D_2O, 1% HCl): δ 158.1 (C_q, s, C1 and C3), 144.6 (C_q, s, Ar-C5), 101.8 (CH, s, C4 and C6), 98.6 (CH, s, C2), 51.4 (CH_2, s, NCH_2), 49.9 (CH_2, s, NCH_2), 43.0 (CH_3, s, NMe).

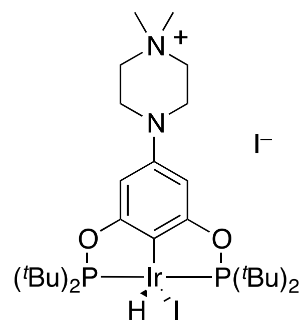


3: NaH (2.0 mmol, 48 mg) was added to a solution of 5-(4-methyl-1-piperazinyl)-resorcinol (1.0 mmol, 208 mg) in 25 mL THF (caution: hydrogen evolution). The mixture was refluxed for 1 h, and di-*tert*-butylchlorophosphine (2.0 mmol, 360 mg) in THF was then added using a syringe, and refluxed for additional 1 h. After removing the solvent under high vacuum, the residue was extracted with 50 mL pentane, and the extract was filtered through Celite. Upon removal of pentane from the filtrate under vacuum, the flask was kept under high vacuum at 55 °C for 2 h. The products were off-white pellets which exhibited high NMR purity, and used for further reactions without additional purification. Yield: 431 mg, 87%. ^{1}H NMR (500 MHz, C_6D_6): δ 7.33 (m, 1H, Ar-H), 6.85 (m, 2H, Ar-H), 3.21 (t, J_{H-H} = 4.9 Hz, 4H, CH_2), 2.31 (t, J_{H-H} = 4.9 Hz, 4H, 2CH_2), 2.14 (s, 3H, N-CH_3), 1.29 (d, J_{P-H} = 11.7 Hz, 36H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ 161.8 (C_q, d, J_{P-C} = 9.5 Hz, C1 and C3), 153.6 (Cq, s, Ar-C5), 99.8 (CH, d, J_{P-C} = 10.4 Hz, C4 and C6), 99.6 (CH, d, J_{P-C} = 13.1 Hz, C2), 55.0 (CH_2, s, NCH_2), 48.8 (CH_2, s, NCH_2), 45.9 (CH_3, s, NMe), 35.4 (C_q, d, J_{P-C} = 27.2 Hz, ^{t}Bu-C), 27.3 (CH_3, d, J_{P-C} = 15.9 Hz, ^{t}Bu-CH_3). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6): δ 149.4.

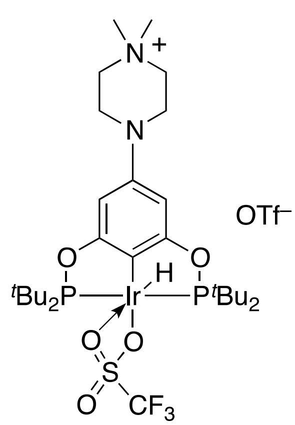


4: To an Ar-filled Schlenk flask was added with 0.5 equivalent of [(COE)$_2$IrCl]$_2$ (0.32 mmol, 283 mg, COE = cycloctene) and 0.95 equivalent of **3** (0.6 mmol, 298 mg) in 20 mL toluene. The solution was refluxed at 130 °C for 12 h and then cooled to room temperature. The solvent was removed in vacuum, and the residue was extracted with 30 mL pentane. After filtration and solvent removal, the resulting solid was dried under high vacuum to yield analytically pure product. Yield: 360 mg, 83%. ^{1}H NMR (600 MHz, C_6D_6): δ 6.50 (s, 2H, Ar-H), 2.99 (t, J_{H-H} = 4.9 Hz, 4H, NCH_2), 2.23 (t, J_{H-H} = 4.9 Hz, 4H, NCH_2), 2.07 (s, 3H, NCH_3), 1.36 (t, J_{P-H} = 7.0 Hz, 18H, C(CH_3)$_3$), 1.30 (t, J_{P-H} = 7.0 Hz, 18H, C(CH_3)$_3$), -41.1 (t, J_{P-H} = 13.5 Hz, 1H, IrH). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ

168.3 (C_q, t, $J_{P\text{-}C}$ = 6.0 Hz, C1 and C3), 152.1 (Cq, s, Ar-C5), 108.0 (C_q, m, C2), 94.6 (CH, t, $J_{P\text{-}C}$ = 5.5 Hz, C4 and C6), 55.5 (CH_2, s, NCH_2), 49.7 (CH_2, s, NCH_2), 46.2 (CH_3, s, NMe), 43.0 (C_q, t, $J_{P\text{-}C}$ = 11.6 Hz, ^{t}Bu-C), 39.5 (C_q, t, $J_{P\text{-}C}$ = 11.6 Hz, ^{t}Bu-C), 27.8 (CH_3, t, $J_{P\text{-}C}$ = 3.1 Hz, ^{t}Bu-CH_3), 27.7 (CH_3, t, $J_{P\text{-}C}$ = 3.1 Hz, ^{t}Bu-CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ 176.1.



2^{HI}: To a benzene solution (20 mL) of **4** (0.2 mmol, 145 mg) was added 10 equivalent of methyl iodide (2 mmol, 284 mg) and stirred for 24 h under Ar at room temperature. The precipitated solid was collected, filtered, washed with pentane, and dried under vacuum. Yield: 185 mg, 97%. ^1H NMR (600 MHz, CD_2Cl_2): δ 6.30 (s, 2H, Ar-H), 3.79 (t, $J_{H\text{-}H}$ = 4.9 Hz, 4H, NCH_2), 3.47 (t, $J_{H\text{-}H}$ = 4.9 Hz, 4H, NCH_2), 3.53 (s, 6H, $N(CH_3)_2$), 1.37 (t, $J_{P\text{-}H}$ = 7.5 Hz, 36H, $C(CH_3)_3$), -41.9 (t, $J_{P\text{-}H}$ = 13.2 Hz, 1H, IrH). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2): δ 167.4 (C_q, t, $J_{P\text{-}C}$ = 6 Hz, C1 and C3), 148.4 (Cq, s, Ar-C5), 94.3 (CH, t, $J_{P\text{-}C}$ = 5.5 Hz, C4 and C6), 62.3 (CH_2, s, NCH_2), 52.0 (CH_3, s, NMe_2), 44.0 (CH_2, s, NCH_2), 43.3 (C_q, t, $J_{P\text{-}C}$ = 12 Hz, ^{t}Bu-C), 40.1 (C_q, t, $J_{P\text{-}C}$ = 12 Hz, ^{t}Bu-C), 27.8 (CH_3, t, $J_{P\text{-}C}$ = 2.7 Hz, ^{t}Bu-CH_3), 27.7 (CH_3, t, $J_{P\text{-}C}$ = 2.7 Hz, ^{t}Bu-CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2): δ 181.6. MS ESI+ *m/z* (80:20 v/v% MeOH:H_2O): calculated 831.23 (M^+); found 831.00.



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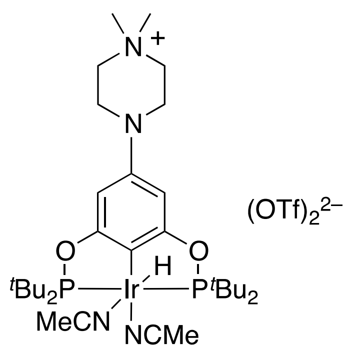
2^{OTF}: To an acetonitrile solution (20 mL) of **2^{HI}** (48 mg, 0.05 mmol) was added with 2.1 eq of thallium triflate (39 mg, 0.11 mmol) and stirred for 2 h at RT. The reaction mixture was filtered through a frit and the solvent of resulting filtrate was then removed under vacuum. The residue was extracted by CH_2Cl_2 and the extract was filtrated and evaporated to yield a brown solid. Yield: 46 mg, 93%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 6.19 (s, 2H, Ar-H), 3.68 (t, $J_{H\text{-}H}$ = 4.9 Hz, 4H, NCH_2), 3.42 (t, $J_{H\text{-}H}$ = 4.9 Hz, 4H, NCH_2), 3.36 (s, 6H, $N(CH_3)_2$), 1.31 (m, 36H, $C(CH_3)_3$), -31.8 (t, $J_{P\text{-}H}$ = 12.5 Hz, 1H, IrH). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ 165.8 (C_q, t, $J_{P\text{-}C}$ = 6 Hz, C1 and C3), 147.1 (Cq, s, Ar-C5), 97.1 (C_q, m, C2), 94.6 (CH, t, $J_{P\text{-}C}$ = 5.5 Hz, C4 and C6), 62.0 (CH_2, s, NCH_2), 51.5 (CH_3, s, NMe_2), 44.4 (CH_2, s, NCH_2), 41.4 (C_q, t, $J_{P\text{-}C}$ = 12 Hz, ^{t}Bu-C), 36.9 (C_q, t, $J_{P\text{-}C}$ = 12 Hz, ^{t}Bu-C), 28.0 (CH_3, t, $J_{P\text{-}C}$ = 3.3 Hz, ^{t}Bu-CH_3), 26.8 (CH_3, t, $J_{P\text{-}C}$ = 2.9 Hz, ^{t}Bu-CH_3). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): δ 169.6. MS ESI+ *m/z* (80:20 v/v% MeOH:H_2O): calculated 853.27 ($[M]^+$); found 853.12.



2^{MeCN}: 2^{OTF} complex (0.03 mmol, 30 mg) was dissolved in small amount of MeCN and re-precipitated by layering pentane on top. The solid was collected on a frit, and dried under a stream of Ar to give nearly colorless crystals. The solid slowly loses bound MeCN and changes to **2^{OTF}** at room temperature over time. Yield: 25 mg, 78%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 6.20 (s, 2H, Ar-H), 3.54 (t, $J_{H\text{-}H}$ = 4.7 Hz, 4H, NCH_2), 3.39 (t, $J_{H\text{-}H}$ = 4.7 Hz, 4H, NCH_2), 3.20 (s, 6H, $N(CH_3)_2$), 2.14 (br, 6H, CH_3CN), 1.45 (t, $J_{P\text{-}H}$ = 7.4 Hz, 18H, $C(CH_3)_3$), 1.27 (t, $J_{P\text{-}H}$ = 7.4 Hz, 18H, $C(CH_3)_3$), -22.2 (br, 1H, IrH). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2): δ 167.4 (C_q, t, $J_{P\text{-}C}$ = 6 Hz, C1 and C3), 148.4 (Cq, s, Ar-C5), 120.0 (C_q, br, MeCN-CN), 94.3 (CH, t, $J_{P\text{-}C}$ = 5.5 Hz, C4 and C6), 62.1 (CH_2, s, NCH_2), 51.7 (CH_3, s, NMe_2), 44.1 (CH_2, s, NCH_2), 41.8 (C_q, t, $J_{P\text{-}C}$ = 11.3 Hz, ^{t}Bu-C), 41.3 (C_q, t, $J_{P\text{-}C}$ = 11.3 Hz, ^{t}Bu-C), 28.2 (CH_3, t, $J_{P\text{-}C}$ = 2.0 Hz, ^{t}Bu-CH_3), 27.6 (CH_3, t, $J_{P\text{-}C}$ = 2.0 Hz,

^{t}Bu-CH_3), 2.6 (CH_3, br, MeCN-CH_3). $^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2): δ 164.0. MS ESI+ *m/z* (CH_3CN): calculated 372.67 ($[M - MeCN]^{2+}$); found 372.58.

(POCOP)$Ir(H)_2$ complex was synthesized following a published procedure.[3]

II. Electrochemistry

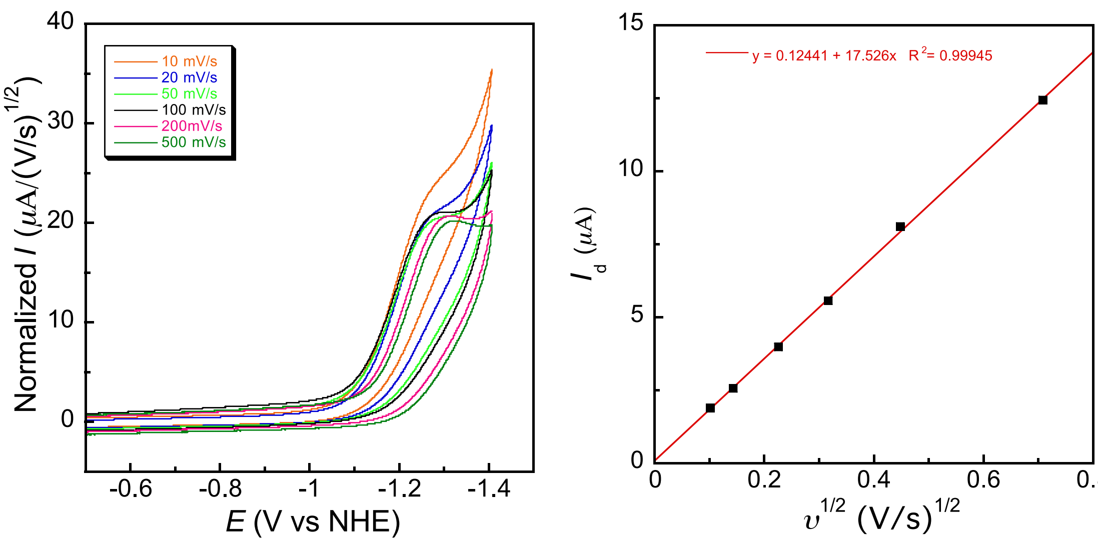


Figure S1. Left: cyclic voltammograms of $\mathbf{2}^{\mathbf{MeCN}}$ at various scan rates under Ar with currents normalized with respect to the square root of the scan rates. Right: plot of peak current i_d under Ar against the square root of the scan rate ($\upsilon^{1/2}$, υ in V/s). (glassy carbon working electrode, 7.1 mm^2, 1mM Ir, 0.1 M $NaHCO_3$, 1% v/v MeCN, room temperature)

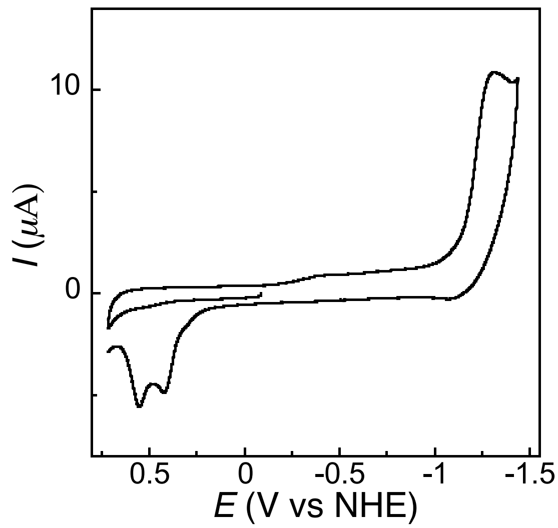


Figure S2. Cyclic voltammograms of **2**$^{\mathbf{MeCN}}$ in water under Ar. (glassy carbon working electrode, 7.1 mm^2, 0.1 M $NaHCO_3$, 200 mV/s, 1% v/v MeCN, room temperature)

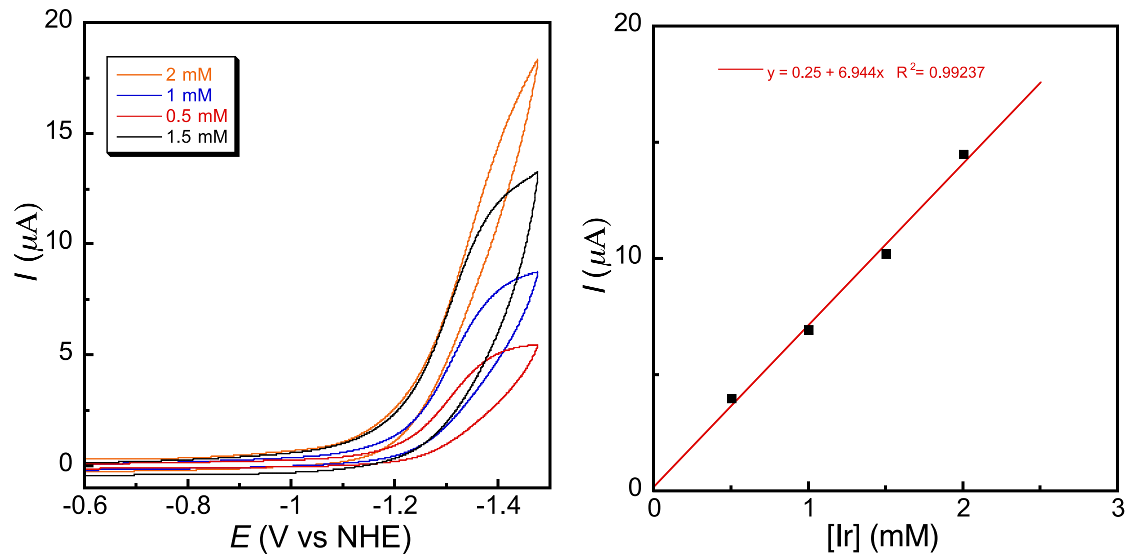


Figure S3. Left: cyclic voltammograms of 0.5–2 mM **2**$^{\mathbf{MeCN}}$ in water under 1 atm CO_2; Right: plot of catalytic current i_{cat} at the catalytic peak potential vs. Ir concentration. (glassy carbon working electrode, 7.1 mm^2, 0.1 M $NaHCO_3$, scan rate 100 mV/s, 1% v/v MeCN, room temperature)

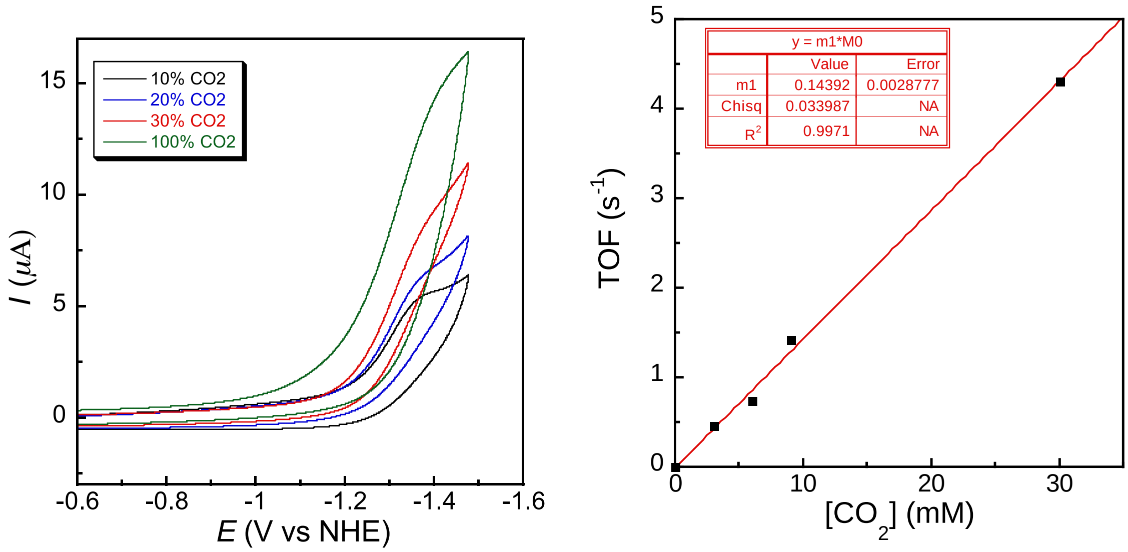


Figure S4. Left: cyclic voltammograms of **2**$^{\mathbf{MeCN}}$ in water under 0.1–1 atm CO_2; Right: plot of catalytic TOF vs. CO_2 concentration in water. (glassy carbon working electrode, 7.1 mm^2, 0.1 M $NaHCO_3$, scan rate 50 mV/s, 1% v/v MeCN, room temperature, 1 atm total pressured balanced with Ar)

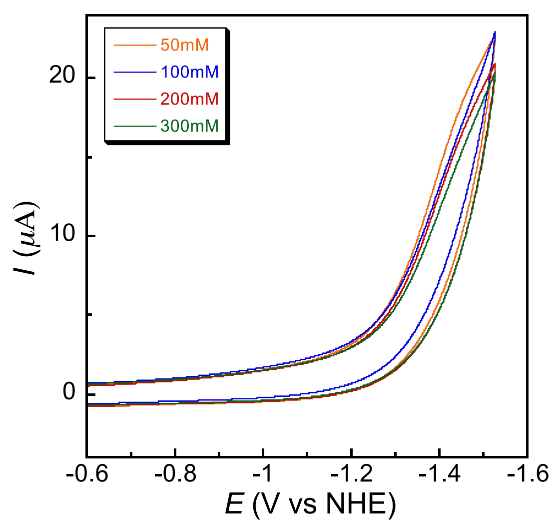


Figure S5. Cyclic voltammograms of **2**$^{\mathbf{MeCN}}$ in water with 50–300 mM $NaHCO_3$ under 1 atm CO_2. (glassy carbon working electrode, 7.1 mm^2, 0.3 M ionic strength balanced with $NaNO_3$, scan rate 100 mV/s, 1% v/v MeCN, room temperature)

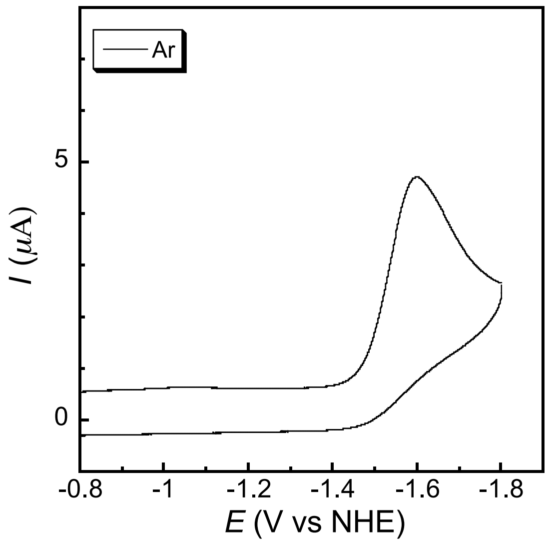


Figure S6. Cyclic voltammograms of $\mathbf{2}^{\mathbf{OTf}}$ in THF under 1 atm Ar. (glassy carbon working electrode, 7.1 mm^2, 0.1 M $^{n}Bu_4NPF_6$, scan rate 100 mV/s, room temperature)

III. DFT Computations

Density functional theory (DFT) calculations were performed using a Gaussian 09 program[4] (revision B.01) on a Linux cluster. Unrestricted wave function was used. The level of theory for geometry optimizations is B3LYP[5] hybrid functional with a pseudo relativistic effective core potential LANL2DZ basis set[6] on Ir/Ru and a double-ζ 6-31G(d) basis set on all other atoms. The geometry optimizations were performed in the gas phase and frequency calculations on the optimized structure confirmed the absence of imaginary frequencies in all geometries. Single point energy was evaluated using B3LYP functional and a ECP LANL2DZ basis set on Ir/Ru and a triple-ζ 6-311+G(d,p) basis set on all other atoms. CPCM polarizable conductor solvation model[7] was used to calculate the solvation energy in aqueous phase. Thermal corrections with zero-point energy, enthalpy and entropy contributions were done at 298.15 K under 1 atm. The total free energy and pK_a were calculated as follows.

$$\Delta G_{\mathrm{sol}} = \Delta G_{\mathrm{gas}} + \Delta\Delta G_{\mathrm{sol}}$$

$$\Delta G_{\mathrm{gas}} = \Delta E_{\mathrm{ZPE}} + \Delta H - \mathrm{T}\Delta S$$

$$[(\mathrm{POCOP})\mathrm{IrH}(\eta^2\text{-}\mathrm{H_2})(\mathrm{MeCN})]^+ \rightleftharpoons [(\mathrm{POCOP})\mathrm{Ir(H)_2(MeCN)}] + \mathrm{H}^+ \qquad \Delta G$$

$$\Delta G = 2.303RT\mathrm{p}K_{\mathrm{a}}$$

The value of –6.28 kcal/mol was used as the free energy ΔG_{gas}^{H+} of proton for 1 M gas and –264.41 kcal/mol for the aqueous solvation free energy $\Delta\Delta G_{sol}^{H+}$ of proton.[8] The pK_a value of $[(tpy)(bpy)Ru(OH_2)]^{2+}$ was used as a calibration of the computation method.

Complex	Computed pK_a	Experimental pK_a
$[(tpy)(bpy)Ru(OH_2)]^{2+}$	9.2	10
$[(POCOP)IrH(\eta^2\text{-}H_2)(MeCN)]^+$	4.5	n/a

Cartesian Coordinates of Optimized Geometry

$[(POCOP)IrH(\eta^2\text{-}H_2)(MeCN)]^+$

Ir	-0.00002400	-0.30324700	0.10091900
P	2.35706800	0.11954400	-0.00497100
P	-2.35713000	0.11935500	-0.00496900
O	2.40622200	1.77869700	-0.15554500
C	1.18975100	2.45927200	-0.16533900
C	1.21557900	3.84603300	-0.29849100
H	2.16382900	4.36832600	-0.36526200
C	-0.00021200	4.53070500	-0.35616500
H	-0.00025400	5.61131200	-0.46001700
C	-1.21594800	3.84593700	-0.29848900
H	-2.16423900	4.36815600	-0.36525900
C	-1.19001200	2.45917800	-0.16533900
C	-0.00010100	1.73054000	-0.06309300
O	-2.40642700	1.77850500	-0.15555000
C	3.35299000	-0.15845900	1.59943500
C	2.82742600	0.84455200	2.65214200
H	1.75973100	0.73869100	2.85874800
H	3.01520900	1.87813600	2.35105000
H	3.35768700	0.66473600	3.59474000
C	4.86633200	0.09518800	1.44344600
H	5.33377000	0.01908800	2.43272900
H	5.07575200	1.09718200	1.05818400
H	5.35414700	-0.64056600	0.79954300
C	3.11755900	-1.60306700	2.08819300
H	3.50066400	-2.34886500	1.38476300
H	2.05731900	-1.81308600	2.26178900
H	3.64451400	-1.74902500	3.03860800
C	3.30405900	-0.41915500	-1.56585400

C	4.53005100	0.48351100	-1.83178200
H	5.31551300	0.37269800	-1.08451400
H	4.24726400	1.53810500	-1.88329200
H	4.95819600	0.20212800	-2.80129000
C	3.72792600	-1.89652700	-1.44546900
H	4.15636200	-2.22151900	-2.40114700
H	2.87511500	-2.55086700	-1.23031100
H	4.49019900	-2.05659000	-0.67767000
C	2.34475800	-0.27065400	-2.76806900
H	2.90932700	-0.46346300	-3.68792100
H	1.92671300	0.73852500	-2.84141300
H	1.51956700	-0.98632800	-2.72541500
C	-3.35304300	-0.15873200	1.59941900
C	-2.82751100	0.84425600	2.65216700
H	-3.35780100	0.66441600	3.59474200
H	-3.01529100	1.87784900	2.35109900
H	-1.75982300	0.73838400	2.85879700
C	-3.11757600	-1.60335000	2.08812900
H	-2.05732300	-1.81334100	2.26169400
H	-3.50067100	-2.34913800	1.38468600
H	-3.64450400	-1.74934000	3.03855300
C	-4.86638900	0.09487500	1.44340400
H	-5.35414800	-0.64084400	0.79941700
H	-5.07583400	1.09689500	1.05822400
H	-5.33385900	0.01866900	2.43266400
C	-3.30406300	-0.41944100	-1.56585000
C	-3.72782300	-1.89684100	-1.44542200
H	-4.15618600	-2.22190500	-2.40111000
H	-4.49013400	-2.05692000	-0.67766300
H	-2.87499000	-2.55111800	-1.23016200
C	-4.53012300	0.48312200	-1.83180800
H	-4.24741800	1.53773600	-1.88335700
H	-5.31557700	0.37227200	-1.08453600
H	-4.95824800	0.20167100	-2.80130600
C	-2.34477400	-0.27089200	-2.76807000
H	-1.51955200	-0.98653000	-2.72543000
H	-1.92677000	0.73830300	-2.84141400
H	-2.90934300	-0.46371900	-3.68791800
H	-0.00003200	-0.24795500	-1.45941600
N	0.00011700	-2.43539500	0.04426600
C	0.00038000	-3.58997200	-0.04279600
C	0.00097900	-5.04468300	-0.15125200
H	0.90162500	-5.45661000	0.31506700
H	-0.87870500	-5.45996600	0.35075100
H	-0.01956200	-5.34113400	-1.20490300
H	0.00026300	0.07666200	2.00829900

H	-0.00023000	-0.70678900	2.02558000

trans-[(POCOP)Ir(H)$_2$(MeCN)]

Ir	-0.00000100	-0.31576000	-0.05694300
P	2.30240500	0.10793500	-0.01106100
P	-2.30241200	0.10788900	-0.01106700
O	2.40017400	1.77531400	-0.15192500
C	1.18458000	2.45897500	-0.16178400
C	1.21339900	3.85176200	-0.22341000
H	2.16467700	4.37393800	-0.25138300
C	-0.00005000	4.54365900	-0.25226200
H	-0.00006100	5.62911700	-0.29992400
C	-1.21348400	3.85173500	-0.22345600
H	-2.16477300	4.37389100	-0.25146300
C	-1.18463800	2.45894900	-0.16182900
C	-0.00002100	1.71622900	-0.12019200
O	-2.40021700	1.77526100	-0.15200700
C	3.17391400	-0.18036600	1.66996800
C	2.54909300	0.82221600	2.66641900
H	1.45962600	0.74405700	2.68617400
H	2.82090700	1.85248200	2.41897200
H	2.93110900	0.59986700	3.67151800
C	4.69725300	0.04511300	1.67594600
H	5.05577600	-0.02749000	2.71140700
H	4.96625900	1.03857200	1.30494700
H	5.24012900	-0.70701300	1.09594700
C	2.86272400	-1.61687900	2.13889100
H	3.29852800	-2.37470000	1.47750200
H	1.78344700	-1.78218700	2.19771600
H	3.29107400	-1.76962100	3.13849200
C	3.43139600	-0.38977600	-1.47135500
C	4.71564500	0.46363900	-1.56064600
H	5.43845500	0.24016200	-0.77580500
H	4.48234100	1.53140400	-1.52412100
H	5.20580500	0.25943000	-2.52166200
C	3.77644500	-1.88838100	-1.37291900
H	4.31189000	-2.19801100	-2.28000000
H	2.87318400	-2.50487500	-1.29746100
H	4.42287400	-2.11575600	-0.51900600
C	2.63304000	-0.14939900	-2.77117200
H	3.27794400	-0.39350400	-3.62594000
H	2.32446500	0.89649900	-2.86730200
H	1.73271300	-0.76382800	-2.81807600
C	-3.17389200	-0.18033000	1.66999200
C	-2.54935900	0.82259700	2.66627400
H	-2.93137300	0.60035500	3.67139700

H	-2.82140900	1.85274900	2.41860900
H	-1.45987400	0.74470400	2.68609900
C	-2.86233700	-1.61667300	2.13919900
H	-1.78301800	-1.78166900	2.19813400
H	-3.29788200	-2.37473700	1.47792000
H	-3.29071500	-1.76935000	3.13879800
C	-4.69728800	0.04476600	1.67589800
H	-5.23994800	-0.70753100	1.09591700
H	-4.96653800	1.03813600	1.30483700
H	-5.05583400	-0.02787000	2.71134800
C	-3.43140300	-0.38990200	-1.47134000
C	-3.77638500	-1.88852100	-1.37289600
H	-4.31172600	-2.19820200	-2.28002200
H	-4.42289100	-2.11590700	-0.51904500
H	-2.87309900	-2.50496500	-1.29733100
C	-4.71569700	0.46344300	-1.56062600
H	-4.48246200	1.53122000	-1.52402100
H	-5.43852000	0.23986300	-0.77582800
H	-5.20580700	0.25926400	-2.52167400
C	-2.63308700	-0.14949800	-2.77117700
H	-1.73273200	-0.76388500	-2.81809800
H	-2.32456700	0.89641500	-2.86732500
H	-3.27800000	-0.39364100	-3.62592900
H	-0.00001600	-0.30357300	-1.72430500
H	0.00001800	-0.33954900	1.62872100
N	0.00002700	-2.40932200	-0.06947200
C	0.00005300	-3.56881700	-0.07922800
C	0.00010200	-5.02801400	-0.08694100
H	0.88888500	-5.41035500	0.42598500
H	-0.88846700	-5.41041300	0.42632600
H	-0.00008300	-5.40586400	-1.11484900

$[(tpy)(bpy)Ru(OH_2)]^{2+}$

Ru	-0.04493800	0.00007600	-0.51533800
N	-0.76039000	-0.00069300	1.42648300
N	-2.14215000	-0.00034800	-0.83104000
N	0.36891300	-2.09098900	-0.44746000
N	1.92900800	0.00059600	-0.11208700
N	0.36765100	2.09139600	-0.44681800
C	-2.12026900	-0.00112100	1.56378500
C	-2.70693600	-0.00193900	2.83314500
C	-1.90617500	-0.00228600	3.97168100
C	-0.52042100	-0.00179500	3.81817000
C	0.00892500	-0.00100000	2.53301000
C	-2.89254300	-0.00073200	0.30636900
C	-4.28997000	-0.00070700	0.24578600

C	-4.92555500	-0.00034500	-0.99365700
C	-4.14797700	-0.00002900	-2.15218900
C	-2.76225200	-0.00003800	-2.02744300
C	1.68543700	-2.36598200	-0.17335800
C	2.13580600	-3.68324800	-0.07155200
C	1.23980800	-4.73753000	-0.24905200
C	-0.09467500	-4.44904400	-0.52694700
C	-0.48630000	-3.11472800	-0.61650700
C	2.56950300	-1.18824800	-0.00181600
C	3.94497000	-1.21027900	0.24806400
C	4.62719700	0.00132800	0.37474000
C	3.94423400	1.21256800	0.24844700
C	2.56878500	1.18979400	-0.00142400
C	1.68401000	2.36705700	-0.17254100
C	2.13358500	3.68454700	-0.07011200
C	1.23697000	4.73838000	-0.24715400
C	-0.09733100	4.44922500	-0.52524000
C	-0.48815500	3.11472200	-0.61542600
H	-3.78535100	-0.00233600	2.93496400
H	-2.35747300	-0.00293800	4.95857700
H	0.14577800	-0.00203000	4.67398300
H	1.07928700	-0.00058800	2.36913500
H	-4.88191200	-0.00093200	1.15312200
H	-6.00928600	-0.00029800	-1.05169000
H	-4.60076100	0.00023600	-3.13780800
H	-2.11199900	0.00019600	-2.89549900
H	3.17727700	-3.89014700	0.14642100
H	1.58220200	-5.76441300	-0.17066900
H	-0.82608100	-5.23656200	-0.67287300
H	-1.51377800	-2.84230600	-0.83057200
H	4.48231500	-2.14682700	0.34011800
H	5.69495300	0.00162700	0.56813800
H	4.48103800	2.14939700	0.34079600
H	3.17491900	3.89196300	0.14801900
H	1.57874500	5.76543100	-0.16826500
H	-0.82920300	5.23637300	-0.67082600
H	-1.51546600	2.84178700	-0.82963800
O	0.36862100	0.00061000	-2.71523900
H	0.83767400	0.77901600	-3.06214500
H	0.84016200	-0.77603400	-3.06271400

[(tpy)(bpy)Ru(OH)]$^+$

Ru	-0.01741000	0.03329300	-0.45204000
N	0.91849000	-0.12510400	1.48243200
N	2.05611700	0.07043300	-0.89064600
N	-0.39207200	2.09690000	-0.28668900

N	-1.94385400	0.01968200	-0.01509500
N	-0.43520200	-2.03981600	-0.51404900
C	2.28194700	-0.14656900	1.48142000
C	3.00034900	-0.27381200	2.67614800
C	2.32072900	-0.37978200	3.88527500
C	0.92555500	-0.35575700	3.87646600
C	0.27009300	-0.22730600	2.65751700
C	2.92050600	-0.02690200	0.15403400
C	4.30361400	-0.00424800	-0.06017900
C	4.79348500	0.12388900	-1.35752000
C	3.89123200	0.23092000	-2.41802700
C	2.52727000	0.20039800	-2.14559600
C	-1.70995600	2.38002200	-0.04492000
C	-2.15464000	3.70240700	0.04645100
C	-1.25312300	4.74822200	-0.12354400
C	0.08450400	4.44886300	-0.38435400
C	0.46835300	3.11421800	-0.45866800
C	-2.59243300	1.21013700	0.10286100
C	-3.96925700	1.22981700	0.33594400
C	-4.66580000	0.02349200	0.41925900
C	-3.98852500	-1.18482700	0.24697800
C	-2.61198900	-1.16558500	0.01504400
C	-1.74769500	-2.33102800	-0.24226000
C	-2.20093100	-3.65401900	-0.23021400
C	-1.31552300	-4.69172600	-0.50426700
C	0.01651100	-4.38522400	-0.78726400
C	0.41058600	-3.05170000	-0.78180000
H	4.08377200	-0.29121600	2.66270300
H	2.87038400	-0.47855100	4.81596000
H	0.35108100	-0.43338200	4.79335700
H	-0.81269000	-0.20197400	2.60036600
H	4.99296900	-0.08157400	0.77250000
H	5.86424800	0.14321800	-1.53545000
H	4.23427200	0.33785700	-3.44171000
H	1.74383800	0.28122700	-2.89699800
H	-3.20024400	3.91204100	0.24134200
H	-1.59041400	5.77782600	-0.05929100
H	0.82098700	5.23090000	-0.53450200
H	1.49362800	2.83281300	-0.66977400
H	-4.49860800	2.17009800	0.43872900
H	-5.73580800	0.02554200	0.59803500
H	-4.53229200	-2.12211500	0.27846200
H	-3.24048900	-3.86915500	-0.01035300
H	-1.66010200	-5.72092300	-0.49918000
H	0.74072500	-5.16096000	-1.01152200
H	1.43278200	-2.76279300	-0.99961700

O	-0.41056900	0.26893200	-2.43119700
H	-0.76096900	-0.56329100	-2.78809800

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