ESI: Enhanced CO$_2$ Electroreduction Efficiency through Secondary Coordination Effects on a Pincer Iridium Catalyst

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Experimental Details

General Considerations. Nitrogen (N₂, 99.999%, Corp Brothers) and carbon dioxide (CO₂, 99.995%, laser grade, Praxair) with less than 2 ppm H₂O were used as received. Acetonitrile was dried and deoxygenated using literature procedures,¹ tested via Karl Fischer titration for trace amounts of water, and stored over 4Å molecular sieves until use. 18.2 MΩ deionized water was provided by a Milli-Q water purification system and was sparged with and stored under N₂. Tetrabutylammonium hexafluorophosphate (nBu₄NPF₆, electrochemical grade, Sigma-Aldrich) was dried at 60 °C under vacuum for 24 hr and stored in a glovebox. Compounds 1,² 2,³ and H[B(ArF)₄]•(Et₂O)₂⁴ (B(ArF)₄ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) were prepared as previously described. All other reagents were purchased from Aldrich, Acros, Alpha Aesar or Strem chemicals and used as received. Manipulations of air-sensitive materials were conducted using standard vacuum, Schlenk, or glovebox techniques. ¹H and ³¹P NMR spectra were recorded on Bruker Avance DRX-400 (400 MHz) and Avance 600 (600 MHz) spectrometers. ¹H chemical shifts are referenced to residual solvent signals, and ³¹P chemical shifts are referenced to a H₃PO₄ external standard. Gaseous products were analyzed on a Buck Scientific 910 gas chromatograph (GC) in the Multiple Gas #3 configuration with automated sample loop.

Observation of [(PN³HP)IrH₂(MeCN)]⁺ (3). A J. Young NMR tube was charged with (PN³HP)IrH₃ (1) (10 mg, 0.020 mmol) in CD₃CN and treated with H[B(ArF)₄]•(Et₂O)₂ (26 mg, 0.030 mmol). The formation of 3 was monitored by NMR spectroscopy and complete conversion occurred within 30 min at ambient temperature. ¹H NMR (CD₃CN):
δ 7.71 (br s, 8H, o-Ar), 7.67 (br s, 4H, p-Ar), 3.32 (m, 2H, CH₂), 2.52 (m, 2H, CH₂), 2.19 (m, 2H, CH), 2.12 (m, 2H, CH₂), 2.06 (m, 2H, CH), 1.78 (m, 2H, CH₂), 1.24-1.29 (m, 12H, CH₃), 1.03 (dd, 6H, CH₃), 0.96 (dd, 6H, CH₃), -20.14 (t, 1H, Ir-H, J = 13 Hz), -22.27 (t, 1H, Ir-H, J = 16 Hz) (N-H resonance not located). \(^{13}\)C\(^{1}\)H NMR taken from HSQC (CD₃CN): δ 16.5 (CH₃), 17.9 (CH₃), 19.8 (CH₃), 20.6 (CH₃), 22.5 (CH), 26.5 (CH), 32.4 (CH₂), 55.2 (CH₂), 117.6 (p-Ar), 134.5 (o-Ar). \(^{31}\)P\(^{1}\)H NMR (CD₃CN): 51.37 (s, 2P).

**General Procedures for Electrochemistry Experiments**

Cyclic voltammetry and bulk electrolysis experiments were performed on a Pine Research AFCBP1 bipotentiostat. The three-electrode system included either a smaller glassy carbon (GC) working electrode (7.1 mm², BASi) or larger GC electrode (19.6 mm², Bio-Logic) and platinum (Pt) mesh counter electrode (99.9%, Alfa Aesar). The reference electrode was Ag/AgNO₃ (i.e., Ag/Ag⁺) non-aqueous electrode filled with 0.01 M AgNO₃ and 0.1 M \(^{n}\)Bu₄NPF₆ in CH₃CN (-0.08 V vs Fc/Fc⁺, BASi). Prior to each experiment, the GC electrode was polished in succession with a 1-μm, 0.3-μm, and 0.05-μm alumina slurry to obtain a mirror finish, sonicated in 50:50 acetone and Milli-Q water, rinsed in Milli-Q water and dried in vacuo. Cyclic voltammograms (CVs) were conducted in a gas-tight one-compartment cell to minimize internal resistance impacting measured potentials. For electrolysis, the counter electrode was separated from the working electrode in a gas-tight two-compartment cell with vigorous stirring in the cathode compartment. Electrolyses of 1 mM 1 were conducted under 1 atm CO₂ in 5-6 mL 12% v/v H₂O/CH₃CN (0.1 M \(^{n}\)Bu₄NPF₆, RT, no iR compensation). For control experiments, 1 was omitted and/or N₂ replaced CO₂. Ferrocene was added at the end of
each experiment and the potential was converted relative to the midpoint potential of the Fc/Fc\textsuperscript{+} CV. Electrolysis experiments lasting longer than 24 hrs required enhancements to maintain system stability and to increase turnover frequency. Of note, a salt bridge separated the Ag/Ag\textsuperscript{+} reference electrode from the cathode compartment to avoid contamination from Ag\textsuperscript{+}. A Luggin capillary was also used to reduce possible Ohmic drop between the working and reference electrodes.

**Product Analysis**

The liquid products of electroreduction were analyzed by \textsuperscript{1}H NMR spectrometry. The liquid phase was acidified with an aqueous solution of HCl (18%), spiked with a benzene internal standard and then diluted with CD\textsubscript{3}CN. Gaseous products of electroreduction were analyzed by gas chromatography using both a FID and a TCD. The headspace of the electrochemical cell was connected to the GC sample loop. A bubbler was then connected to the back end of the loop to confirm a gas-tight system. Gaseous products were analyzed at random points during electrolysis, at least thrice in a 24-hr period and after at least 1 hr from the start of experiment to ensure adequate degassing of connections.
**Fig. S1** GC traces from FID channel *in situ* during bulk electrolysis with potential held at -1.73 V vs Fc/Fc$^+$ (red) juxtaposed with calibration standards (blue and black). All traces were taken at least 1 hr after the start of electrolysis. Asterisk (*) indicates valve switching.
**Fig. S2** GC trace from TCD channel *in situ* during bulk electrolysis with potential held at -1.73 V vs Fc/Fc⁺ (red) juxtaposed with calibration standard (black). All traces were taken at least 1 hr after the start of electrolysis. Asterisk (*) indicates valve switching.

**Fig. S3** $^1$H NMR spectrum of formate electrolysis product following acidification (*vide supra*) and addition of a benzene internal standard in acetonitrile-$d_3$. Spectrum taken post-electrolysis with potential held at -1.73 V vs Fc/Fc⁺. Insert corresponds to a spectral region between 7.0 and 8.4 ppm.
Selected Electrochemical Data

**Fig. S4** Electrolysis current in the absence of catalyst (black) and in the presence of 1 mM 1 (red) under CO$_2$ in 12% H$_2$O/CH$_3$CN with potential held at -1.73 V vs Fc/Fc$^+$ and vigorous stirring. Additional conditions: glassy carbon electrode, 0.1 M $^{\text{a}}$Bu$_4$NPF$_6$ electrolyte, 1 atm CO$_2$, RT, no $iR$ compensation.

**Fig. S5** CVs of 1 mM 1 in CH$_3$CN under CO$_2$ with 0-14% added H$_2$O from +0.2 V to -1.4 V vs Fc/Fc$^+$. 
Fig. S6 CVs of electrolyte solution (0.1 M $n$-Bu$_4$NPF$_6$) with 0-14% added H$_2$O under N$_2$ at (a) 10 mV/s and (b) 100 mV/s scan rates.

Fig. S7 CVs of 1 mM 1 and 10 mM (i.e., 10 equiv.) NaPF$_6$ under N$_2$ (black) and 1 atm CO$_2$ (red). Additional conditions: glassy carbon electrode (7.1 mm$^2$), 12% H$_2$O/CH$_3$CN solvent, 0.1 M $n$-Bu$_4$NPF$_6$ electrolyte, 10 mV/s scan rate.
Fig. S8  $^{31}$P $^1$H NMR (top) and $^1$H NMR (bottom) spectra of 3 generated from H[B(ArF)$_4$]•(Et$_2$O)$_2$ addition to 1 in acetonitrile-$d_3$. An insert for the upfield region of the $^1$H NMR spectrum is provided. The * denotes residual THF, diethyl ether, and acetonitrile solvents.
References