

Cationic Dirhodium(II,II) Complexes for the Electrocatalytic Reduction of CO₂ to HCOOH

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SUPPORTING INFORMATION

Experimental

Materials. All materials were used as received unless stated otherwise. RhCl₃·3H₂O was purchased from Pressure Chemical Company, and electrochemical grade tetrabutylammonium hexafluorophosphate (≥99.0%) was purchased from Fluka Analytical. Triethyl orthoformate (98%) and formic acid (≥95.0%) were purchased from Sigma. 1,10-phenanthroline (99%), 1,10-phenanthroline-5,6-dione (97%), ethylenediamine (≥99.0%), 1,5-cyclooctadiene (≥99.0%), sodium tert-butoxide (97%), silver tetrafluoroborate (98%), *p*-toluidine (≥99.0%), D₂O (99.9%), and 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) (97%) were purchased from Aldrich Chemical Co. Acetonitrile was purchased from Fischer Scientific and distilled by refluxing over CaH₂ and stored under N₂ prior to use. Ar (99.998%), N₂ (99.998%), N₂/H₂ (95:5), He (99.999%), He/CO (95:5), and CO₂ (>99.9%) were purchased from Praxair, Inc. (Danbury, CT, USA). ¹³CO₂ (%) was purchased from Cambridge Isotopes, Inc. (location). Dipyrido[3,2-*d*:2',3'-*f*]quinoxaline (dpq),¹ [Rh₂(μ-DToIF)₂(dpq)₂][BF₄]₂² (**1**), [Rh₂(μ-DToIF)₂(phen)₂][BF₄]₂³ (**2**) and [Ru(bpy)₂(dpq)][PF₆]₂⁴ were prepared as previously reported.

Methods and Instrumentation. Electrochemical measurements were carried out on a BASi model CV-50W voltammetric analyzer (Bioanalytical Systems, Inc.; West Lafayette, IN, USA). Cyclic voltammetry (CV) was performed on solutions of 0.5 mM of the Rh₂ and Ru complexes in 0.1 M TBAPF₆/CH₃CN in a glass cell equipped with a glassy carbon disk working electrode (3 mm diameter), a platinum wire counter electrode, and a Ag/AgCl (3 M NaCl) reference electrode. The solutions were purged with either N₂ or CO₂ before recording the CV. The concentration of CO₂ in acetonitrile is approximately 0.28 M.⁵

Bulk electrolysis experiments were carried out in a custom built, air tight, two compartment bulk electrolysis cell. The working compartment contained a graphite rod working electrode (Graphtek LLC; Buffalo Grove, IL, USA) and a Ag/AgCl (3 M NaCl) reference electrode. A platinum wire counter electrode was placed in the auxiliary compartment, which was separated from the working compartment by a fine glass frit. A 3 mL solution of 0.5 mM Rh₂ complex and 3 M H₂O in 0.1 M TBAPF₆/CH₃CN was placed in the working compartment and the auxiliary compartment was filled with 0.1 M TBAPF₆/CH₃CN. Both compartments were purged with CO₂ for 20 minutes, then electrolyzed at each potential for a total of 3 hours. At the end of the electrolysis time, a 200 μL sample of the 37 mL headspace was removed from the working compartment using a Hamilton gastight syringe and injected into a Shimadzu GC-2014 equipped with a 5Å molecular sieve packed column (6 ft long x 1/8 in o.d. x 2.1 mm i.d.) and TCD-2014 thermal conductivity detector to quantify H₂ and CO evolution. The GC conditions for H₂ detection were as follows: injection temperature, 41°C; column temperature, 30 °C; detector temperature, 150 °C; detector current, 60 mA; gas flow, 25 mL/min; Ar carrier

gas. H₂ was quantified using an external calibration curve. For CO detection, the GC conditions were as follows: injection temperature, 41 °C; column temperature, 30 °C; detector temperature, 150 °C; detector current, 150 mA; gas flow, 25 mL/min; He carrier gas. The reaction mixture was then evaporated and reconstituted in D₂O to extract HCOOH. The HCOOH produced was quantified on a Bruker DPX 400 MHz NMR instrument using a DSS internal standard.

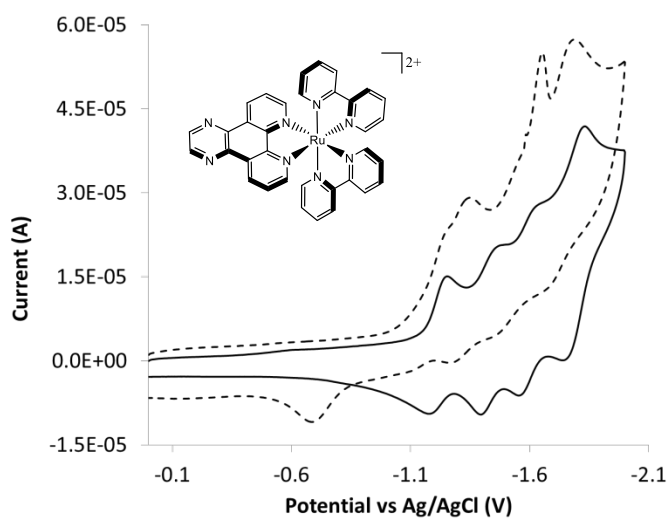


Figure S1: Cyclic voltammograms of 0.5 mM [Ru(bpy)₂(dpq)]²⁺ in 0.1 M TBAPF₆/CH₃CN deoxygenated with N₂ (solid line) or CO₂ (dashed line). Glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl reference electrode, and scan rate = 100 mV/s.

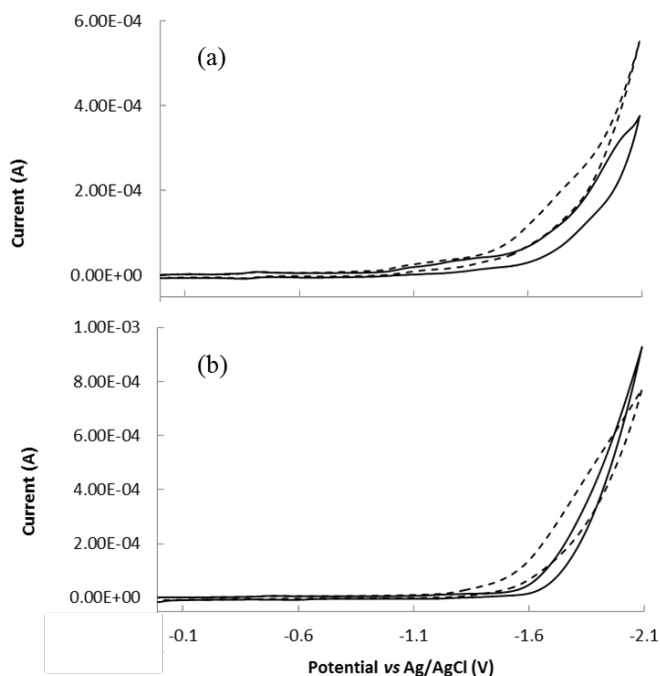


Figure S2: Cyclic voltammograms of 0.5 mM **1** (a) and **2** (b) with added 3 M H₂O in 0.1 M TBAPF₆/CH₃CN deoxygenated with N₂ (solid line) or CO₂ (dashed line). Glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl reference electrode, and scan rate = 100 mV/s.

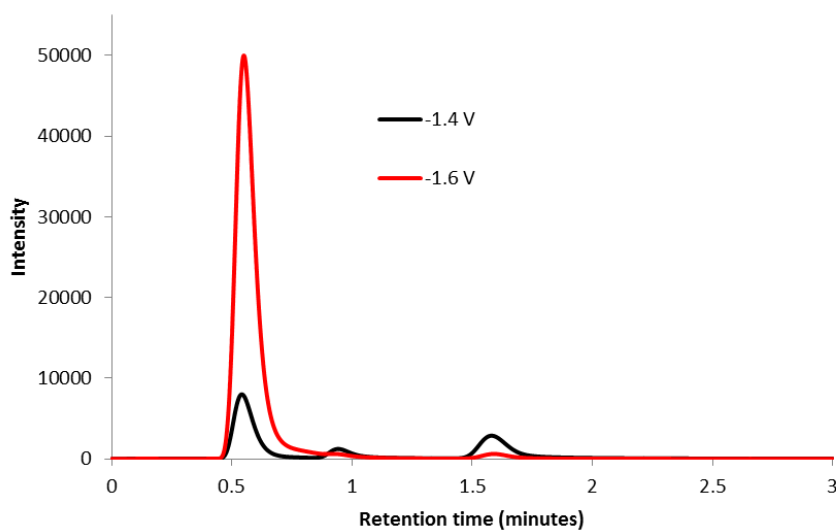


Figure S3: Gas chromatogram of a 200 µL sample of headspace after 3 hours of bulk electrolysis of **1** at -1.40 V (black) and -1.60 V (red) in 0.1 M TBAPF₆/CH₃CN in the presence of 3 M H₂O and

CO₂. H₂ appears at ~0.55 min. The smaller peaks at ~0.93 and ~1.6 min are for trace amounts of O₂ and N₂, respectively.

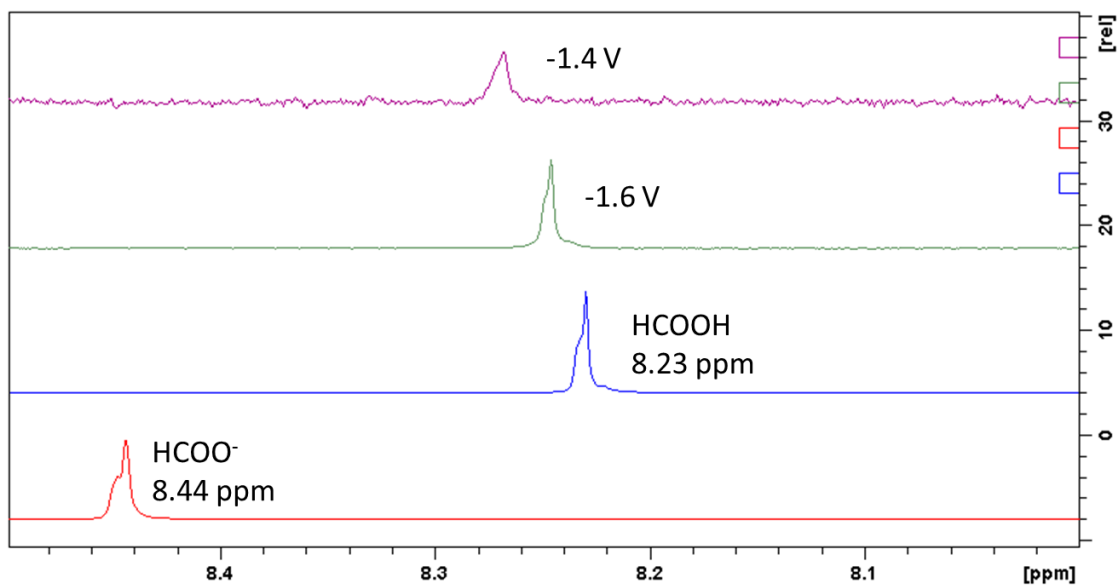


Figure S4: ¹H NMR spectra of the reaction mixture of **2** after three hours of bulk electrolysis at -1.40 V (purple) and -1.60 V (green) in 0.1 M TBAPF₆/CH₃CN with 3 M H₂O under CO₂ compared to standard samples of formic acid (blue) and potassium formate (red). The reaction mixture was evaporated and then reconstituted in D₂O to extract the product. The peak for formic acid occurs at ~8.23 ppm, while the formate anion occurs at ~8.44 ppm vs a DSS internal standard.

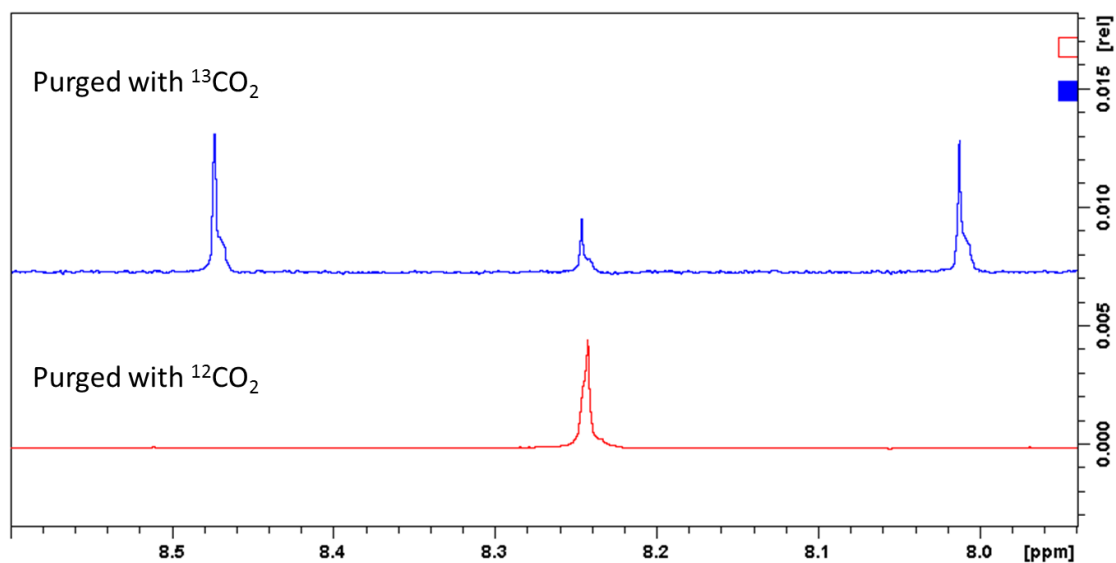


Figure S5: ^1H NMR spectra of the reaction mixture of **2** after three hours of bulk electrolysis at -1.6 V in 0.1 M TBAPF₆/ACN with 3 M H₂O under CO₂ (red) or $^{13}\text{CO}_2$ (blue). The singlet for HCOOH occurs at ~ 8.23 ppm, and the doublet for H $^{13}\text{COOH}$ occurs at the same chemical shift with a J coupling constant of ~ 185 Hz. Chemical shifts are reported vs a DSS internal standard.

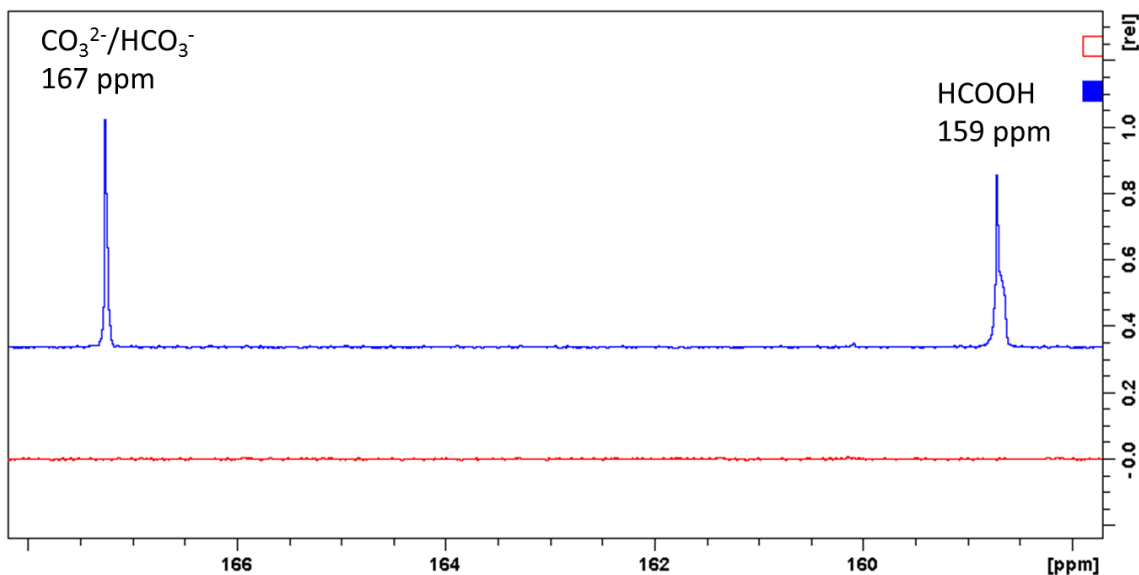


Figure S6: ^{13}C NMR spectra of the reaction mixture of **2** before (red) and after (blue) three hours of bulk electrolysis at -1.6 V in 0.1 M TBAPF₆/ACN with 3 M H₂O under $^{13}\text{CO}_2$. The peak for carbonate appears at ~ 167 ppm and the peak for HCOOH appears at ~ 159 ppm. Chemical shifts are reported vs a C₆D₆ internal standard.

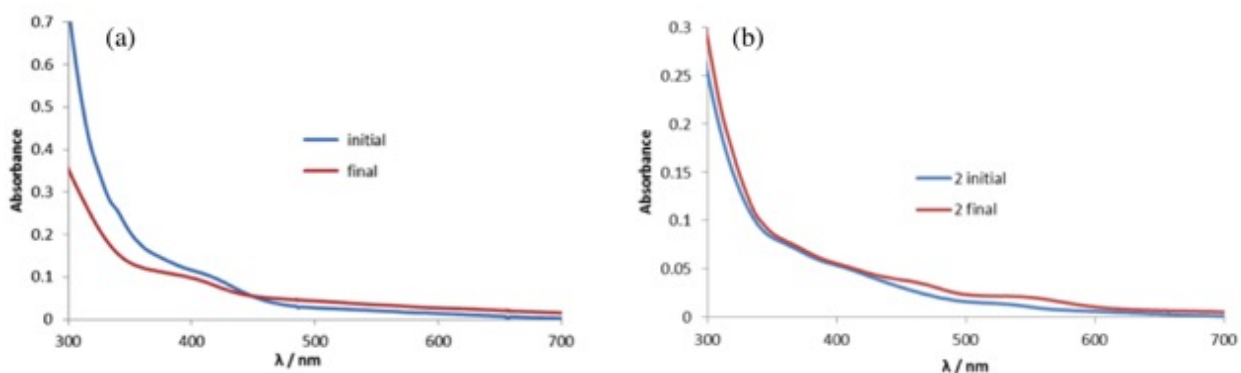


Figure S7: UV-Vis absorption spectra of (a) **1** and (b) **2** before (blue) and after (red) bulk electrolysis at -1.6 V in 0.1 M TBAPF₆/ACN with 3 M H₂O under CO₂.

Details of control experiments

Bulk electrolyses under identical conditions in the absence of catalyst were conducted as control experiments. At -1.4 V, 1.86 C of charge was passed, generating small amounts of H_2 (5.04 μmol) and HCOOH (0.302 μmol), respectively. Similarly, 7.98 C of charge was passed at -1.6 V, generating and 24.3 μmol of H_2 and 2.31 μmol of HCOOH. These values were subtracted from those obtained from bulk electrolysis in the presence of catalyst in order to calculate TON values and %FE.

Bulk electrolysis at -1.6 V under N_2 in the presence of catalyst was performed to confirm CO_2 as the source of carbon for HCOOH formation. In these experiments, 25.5 C of charge was passed and 93.4 μmol of H_2 and 0.387 μmol of HCOOH were detected when **1** was used as the catalyst. For **2**, 48.9 C of charge was passed and 197 μmol of H_2 and 2.19 μmol of HCOOH were detected.

References

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