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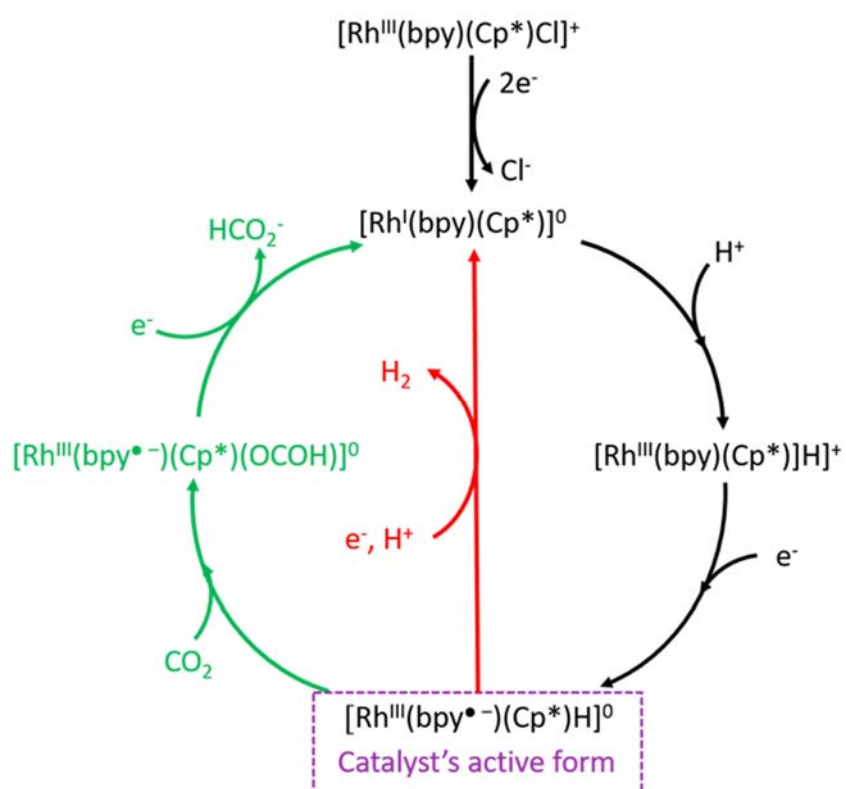
## Supporting Information

### **Electrocatalytic Conversion of CO<sub>2</sub> to Formate at Low Overpotential by Electrolyte Engineering in Model Molecular Catalysis**

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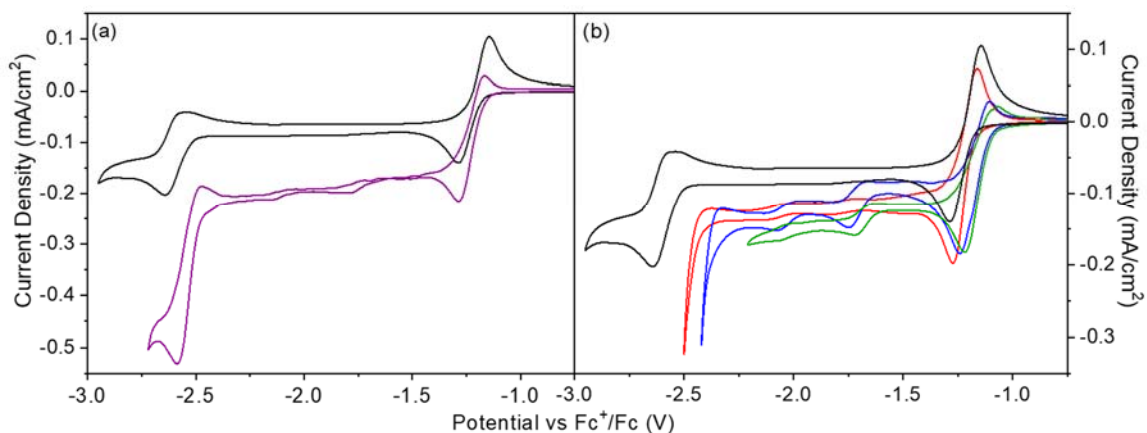
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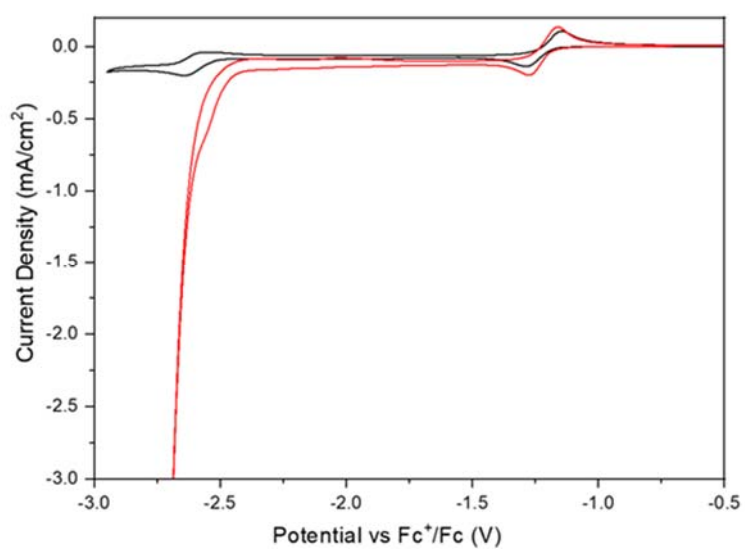


**Scheme S1.** Electrocatalytic cycle of complex [1] for either  $\text{CO}_2$  to formate conversion (green pathway) or  $\text{H}_2$  production (red pathway)<sup>[1,2]</sup>

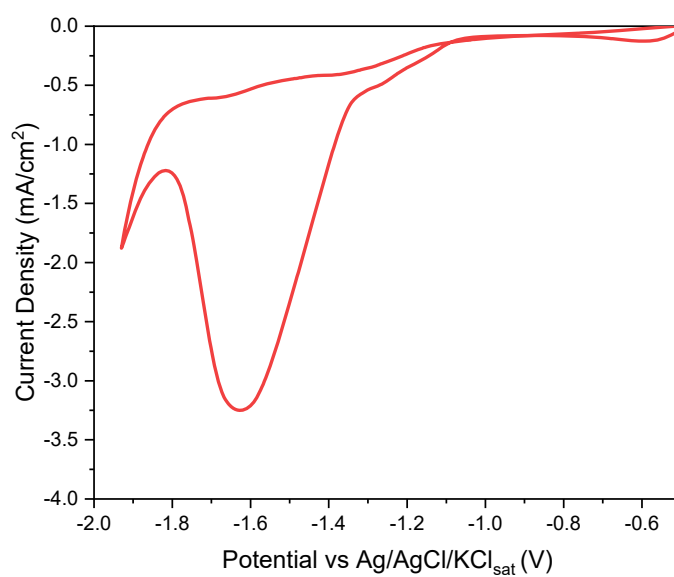
**Figure S1a** compares the benchmark electrolyte cation  $[TBA]^+$  and the pyrrolidinium cation  $[BMPyr]^+$ , by keeping  $[PF_6]^-$  as the counter anion in both cases. **Figure S1b** compares the benchmark electrolyte cation  $[TBA]^+$  and three different imidazolium-based ILs, comprising two different cations ( $[EMIM]^+$  and  $[BMIM]^+$ ) and two different counter anions ( $[PF_6]^-$  and  $[BF_4]^-$ ).



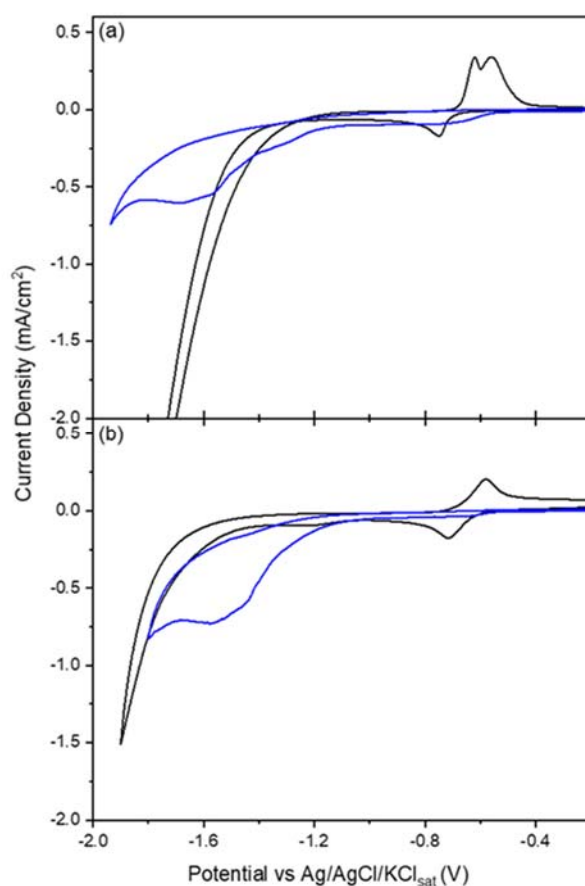
**Figure S1.** Cyclic voltammograms on GC electrode of 1 mM complex [1] and 0.5 M of different supporting electrolytes in acetonitrile solution under Ar. (a)  $[TBA][PF_6]$  (black plot) and  $[BMPyr][PF_6]$  (purple plot) and (b)  $[TBA][PF_6]$  (black plot),  $[EMIM][PF_6]$  (red plot) and  $[BMIM][PF_6]$  (blue plot) and  $[EMIM][BF_4]$  (green plot). Scan rate  $0.01 \text{ V s}^{-1}$ .



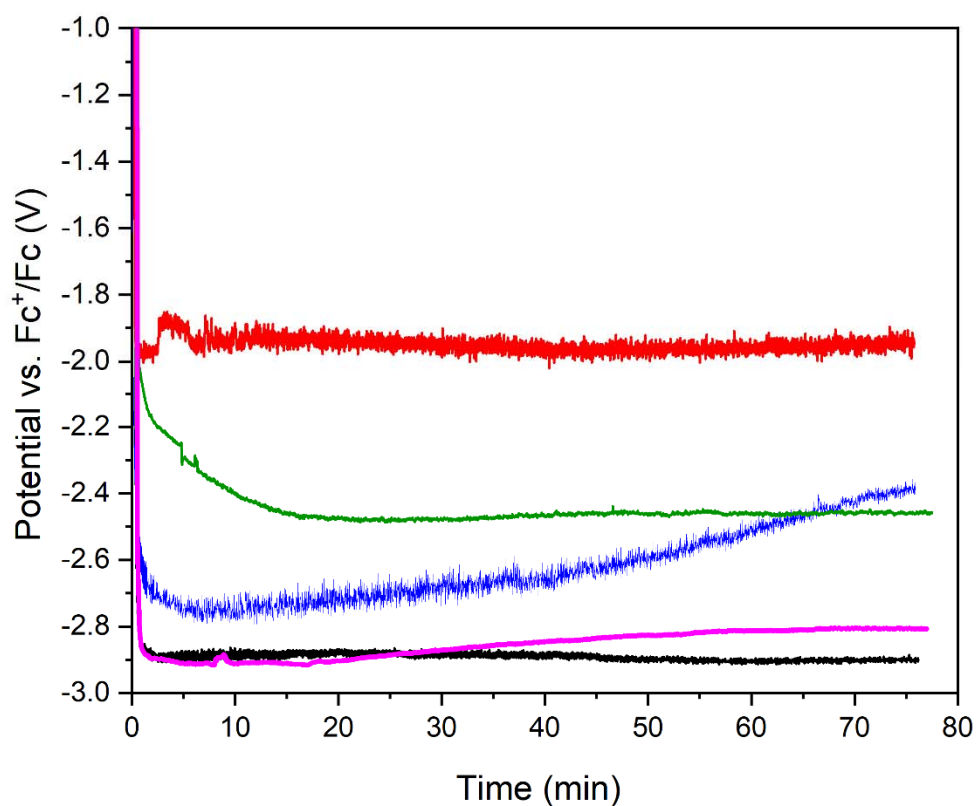
**Figure S2.** Cyclic voltammograms on GC electrode of 1 mM complex [1] and 0.5 M of different supporting electrolytes in acetonitrile solution under Ar. (a) [TBA][PF<sub>6</sub>] (black plot) and [EMIM][PF<sub>6</sub>] (red plot). Scan rate 0.01 V s<sup>-1</sup>.



**Figure S3.** Cyclic voltammogram on GC electrode of 1 mM complex [1] in an acetonitrile/water 50/50 v/v solution containing 0.1 M of [TBA][BF<sub>4</sub>] under CO<sub>2</sub>. Scan rate 0.01 V s<sup>-1</sup>.

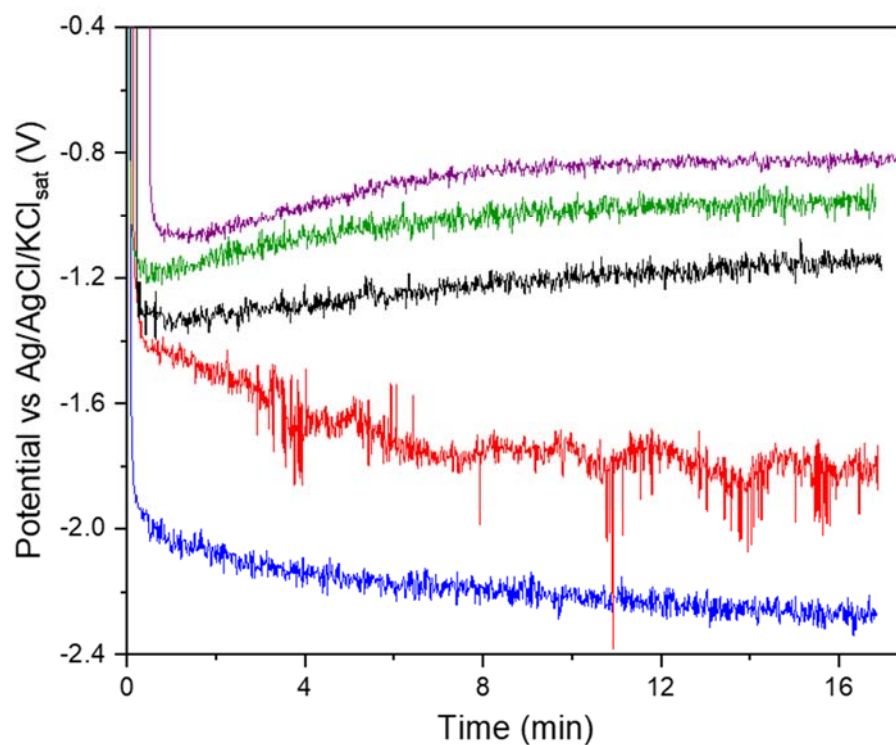


**Figure S4.** Cyclic voltammograms on GC electrode of 1 mM complex [1] in purely aqueous solution containing: (a) 0.1 M [TBA][BF<sub>4</sub>] under Argon (black plot) or under CO<sub>2</sub> (blue plot) and (b) 0.5 M [EMIM][BF<sub>4</sub>] under Argon (black plot) or under CO<sub>2</sub> (blue plot). Scan rate = 0.01 V s<sup>-1</sup>.

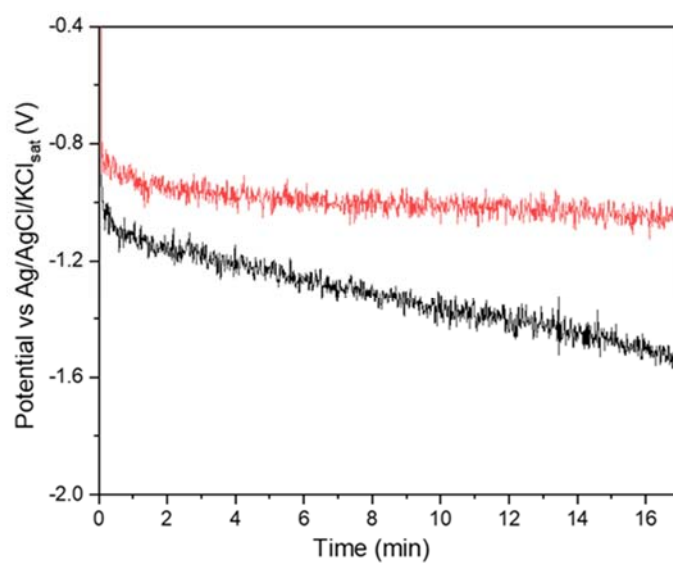


**Figure S5.** Constant current electrolysis (CCE) at  $-3.33 \text{ mA/cm}^2$  of 1 mM complex [1] in acetonitrile solution under  $\text{CO}_2$  in presence of: 5 % (vol.)  $\text{H}_2\text{O}$  and 0.5 M  $[\text{TBA}][\text{PF}_6]$  (black plot), 5 % (vol.)  $\text{H}_2\text{O}$  and 0.5 M  $[\text{TBA}][\text{BF}_4]$  (magenta plot) 5 % (vol.)  $\text{H}_2\text{O}$  and 0.5 M  $[\text{EMIM}][\text{PF}_6]$  (red plot) and 50 % (vol.)  $\text{H}_2\text{O}$  with 0.5 M  $[\text{TBA}][\text{BF}_4]$  (blue plot). Blank CCE at  $-3.33 \text{ mA/cm}^2$  in the absence of complex [1] under  $\text{CO}_2$  in presence of: 5 % (vol.)  $\text{H}_2\text{O}$  and 0.5 M  $[\text{TBA}][\text{PF}_6]$  (green plot). Room temperature:  $20 \pm 2 \text{ }^\circ\text{C}$ , stirring rate: 400 rpm.

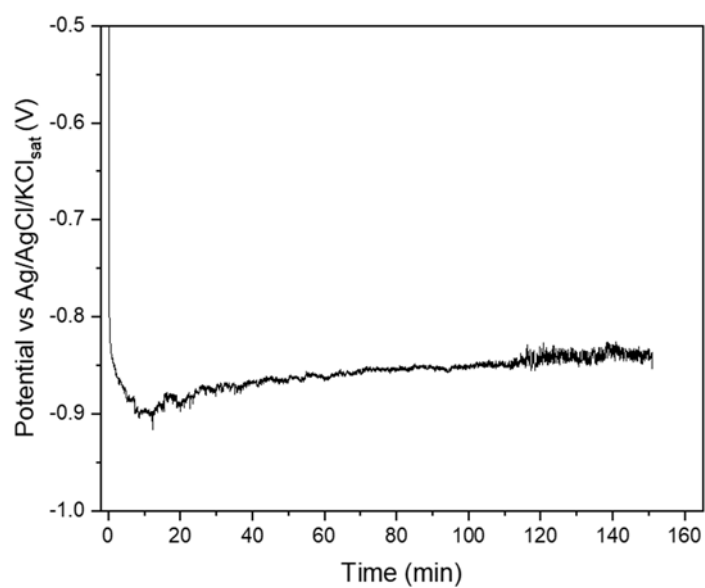




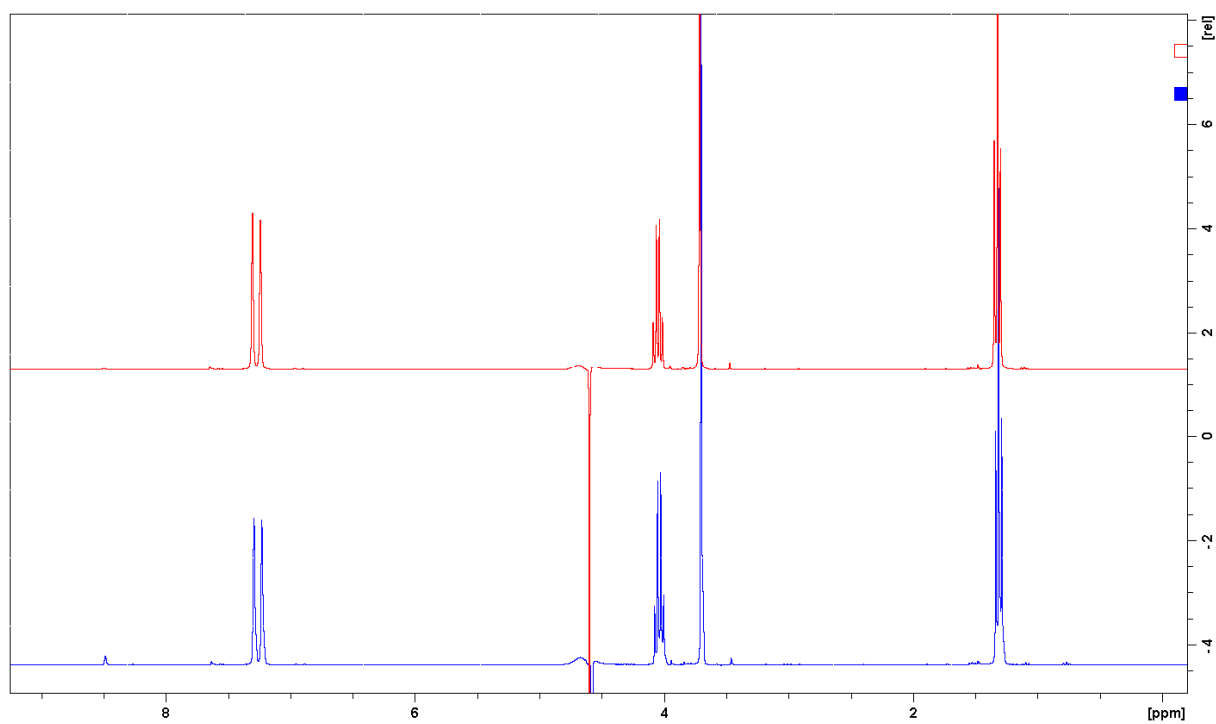
**Figure S6.** Constant current electrolysis (CCE) at  $-3.33 \text{ mA cm}^{-2}$  of 1 mM complex [1] in acidic aqueous solution under  $\text{CO}_2$  in presence of: 0.1 M [TBA][ $\text{BF}_4$ ] (blue plot), 0.5 M [EMIM][ $\text{BF}_4$ ] (red plot), 0.1 M [TBA][ $\text{BF}_4$ ] and 0.1 M acetic acid (pH=2.5) (black plot), 0.1 M [TBA][ $\text{BF}_4$ ] and 0.1 M acetate buffer (pH = 3.8) (green plot) and 0.1 M [EMIM][ $\text{BF}_4$ ] and 0.1 M acetate buffer (pH = 3.8) (purple plot). Room temperature:  $20 \pm 2 \text{ }^\circ\text{C}$ , stirring rate: 400 rpm.



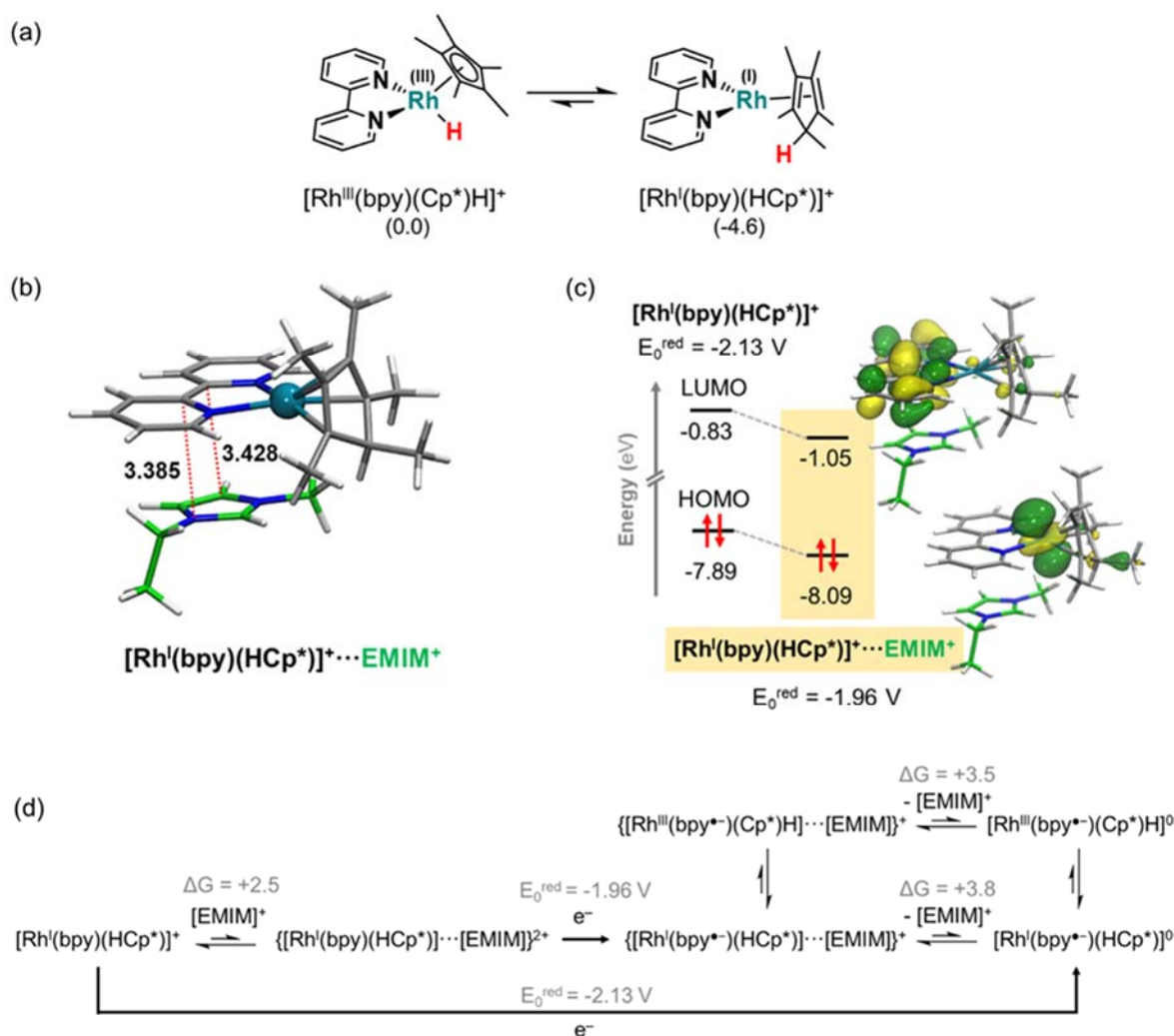
**Figure S7.** Control experiments: Constant current electrolysis (CCE) at  $-3.33 \text{ mA cm}^{-2}$  in  $0.1 \text{ M [TBA][BF}_4\text{]}$  +  $0.1 \text{ M}$  acetate buffer ( $\text{pH} = 3.8$ ) aqueous solution in the presence of only  $\text{CO}_2$  (black plot) or  $1 \text{ mM}$  complex [1] and Ar (red plot). Room temperature:  $20 \pm 2 \text{ }^\circ\text{C}$ , stirring rate:  $400 \text{ rpm}$



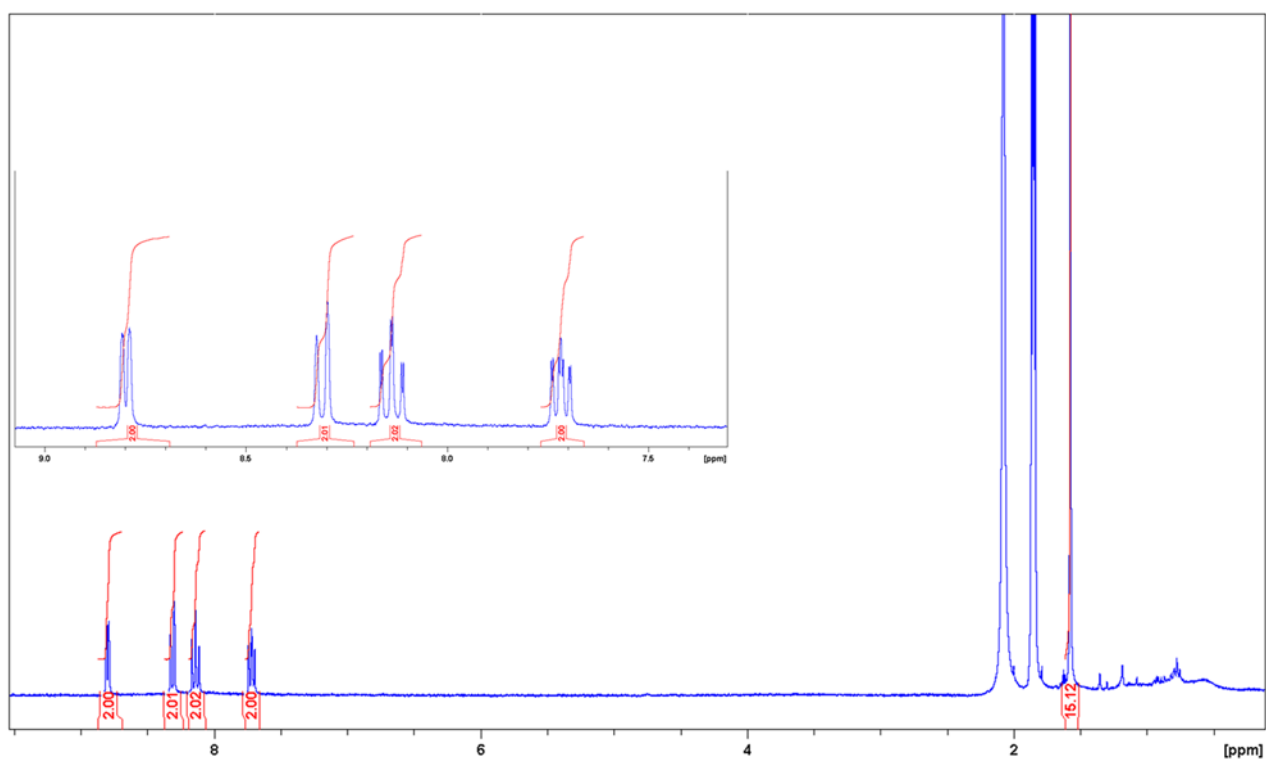
**Figure S8.** Long term constant current electrolysis (CCE) at  $-3.33 \text{ mA cm}^{-2}$  of 1 mM complex [1] in aqueous solution under  $\text{CO}_2$  in presence of: 0.1 M [TBA][BF<sub>4</sub>] + 0.1 M acetate buffer (pH = 3.8). Room temperature:  $20 \pm 2 \text{ }^\circ\text{C}$ , stirring rate: 400 rpm



**Figure S9.**  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ) of Entry 1 in Table 3 (1 mM complex [1] and 0.5 M EMIMBF $_4$  in  $\text{H}_2\text{O}$  under  $\text{CO}_2$ ) before (red plot) and after CCE (blue plot) for a total charge of 10 C.



**Figure S10.** a) Proton/hydride tautomerism in the protonated form of the catalyst. Relative Gibbs free energies in parenthesis are given in kcal mol<sup>-1</sup>. b) Optimized geometry for the non-bonding interaction between the [Rh<sup>I</sup>(bpy)(HCp<sup>\*</sup>)]<sup>+</sup> catalyst and [EMIM]<sup>+</sup>. Key distances are shown in Å and carbon atoms of [EMIM]<sup>+</sup> are colored in green for clarity. c) Schematic frontier MO diagram showing the impact of the interaction with [EMIM]<sup>+</sup> on the energy levels and reduction potential of the [Rh<sup>I</sup>(bpy)(HCp<sup>\*</sup>)]<sup>+</sup> species. Orbital energies computed at the ωB97X-D level are given in eV and reduction potentials are referred to the Fc<sup>+</sup>/Fc reference electrode. d) Possible relevant equilibria established in solution before and after the third reduction of the catalyst and in the presence of [EMIM]<sup>+</sup> cations. Gibbs free energies are given in kcal mol<sup>-1</sup>. Reduction potentials are referred to the Fc<sup>+</sup>/Fc reference electrode.



**Figure S11.**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ) of synthesized  $[\text{Rh}(\text{bpy})(\text{Cp}^*)\text{Cl}]$ :  $\delta/\text{ppm}$ , 1.61 (s, 15H), 7.71 ( $\psi\text{t}$ ,  $J = 7.2$  Hz, 2H), 8.13 (dt,  $J = 7.7$  Hz, 2H), 8.30 (d,  $J = 8.0$  Hz, 2H), 8.78 (d,  $J = 5.5$  Hz, 2H).

## REFERENCES

- [1] C. Caix, S. Chardon-Noblat, A. Deronzier, *J. Electroanal. Chem.* **1997**, 434, 163–170.
- [2] C. Caix, S. Chardon-Noblat, A. Deronzier, J.-C. Moutet, S. Tingry, *J. Organomet. Chem.* **1997**, 540, 105–111.