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Supporting Information

Electrocatalytic Conversion of CO_2 to Formate at Low Overpotential by Electrolyte Engineering in Model Molecular Catalysis

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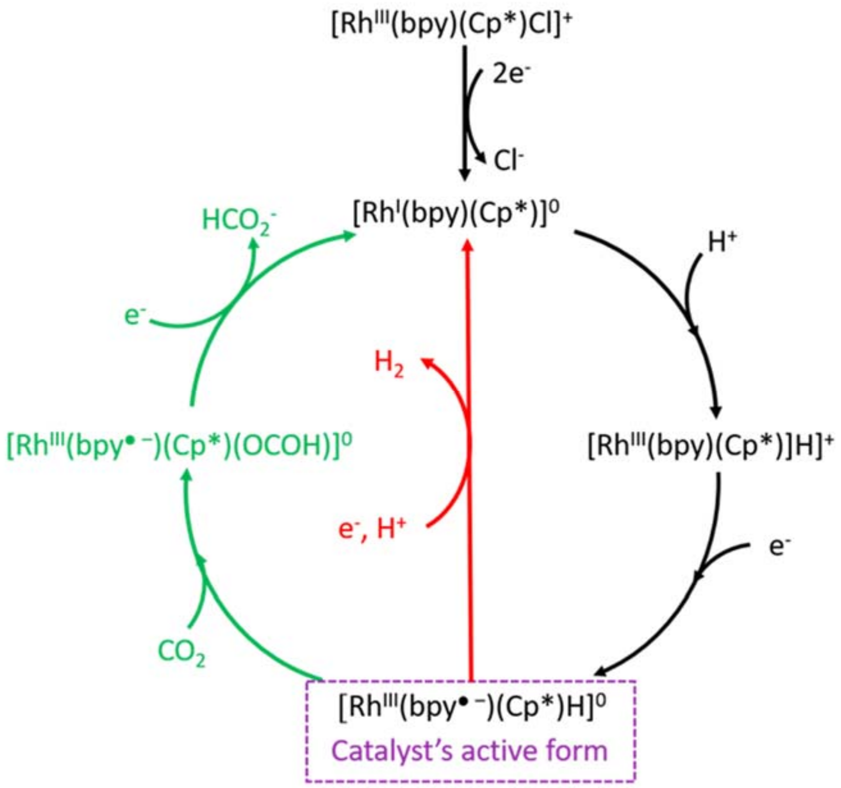

Scheme S1. Electrocatalytic cycle of complex [1] for either CO_2 to formate conversion (green pathway) or H_2 production (red pathway)[1,2]

Figure S1a compares the benchmark electrolyte cation $[TBA]^+$ and the pyrrolidinium cation $[BMPyrr]^+$, 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 $[BF_4]^-$).

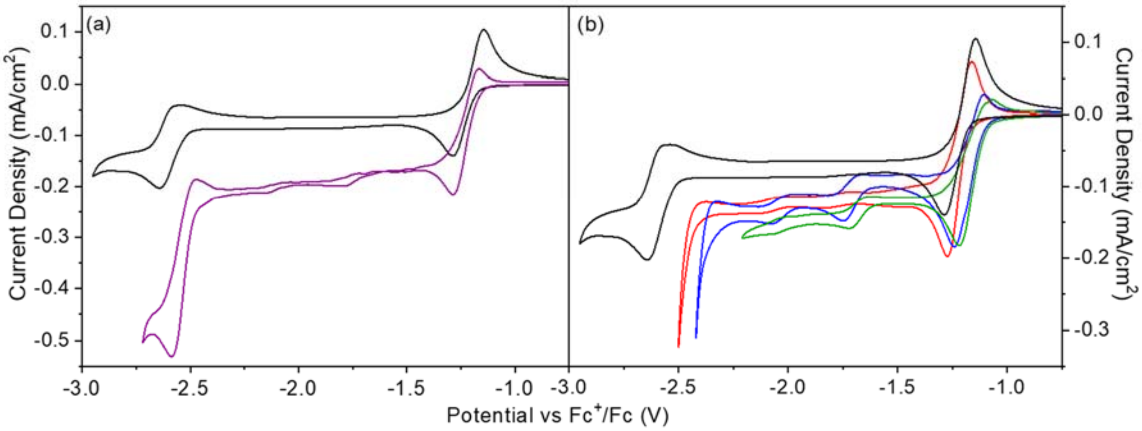

Figure S1. Cyclic voltammograms on GC electrode of 1 mM complex [1] and 0.5 M of different supporting electrolytes in acetonitrile solution under Ar. (a) $[TBA][PF_6]$ (black plot) and $[BMPyrr][PF_6]$ (purple plot) and (b) $[TBA][PF_6]$ (black plot), $[EMIM][PF_6]$ (red plot) and $[BMIM][PF_6]$ (blue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

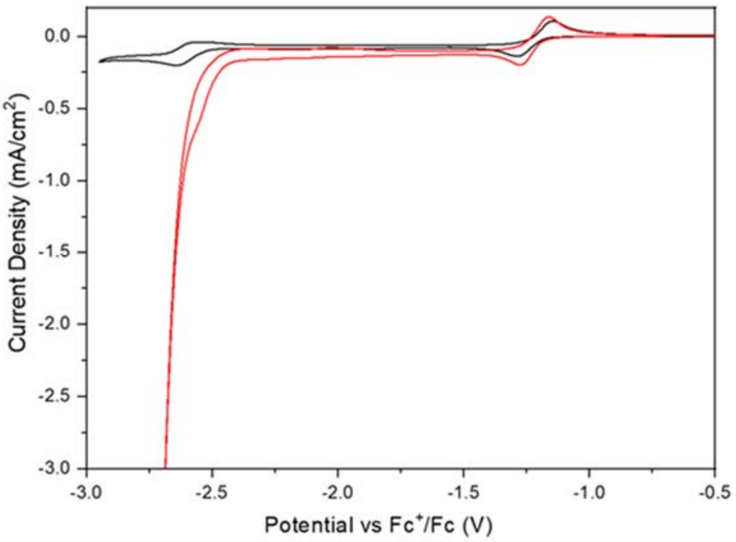

Figure S2. Cyclic voltammograms on GC electrode of 1 mM complex [1] and 0.5 M of different supporting electrolytes in acetonitrile solution under Ar. (a) [TBA][PF_6] (black plot) and [EMIM][PF_6] (red plot). Scan rate 0.01 V s^{-1}.

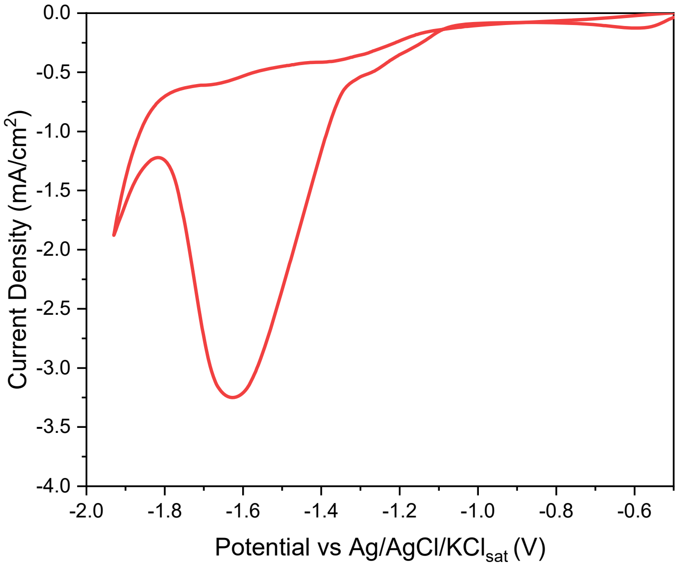

Figure S3. Cyclic voltammogram on GC electrode of 1 mM complex [1] in an acetonitrile/water 50/50 v/v solution containing 0.1 M of [TBA][BF_4] under CO_2. Scan rate 0.01 V s^{-1}.

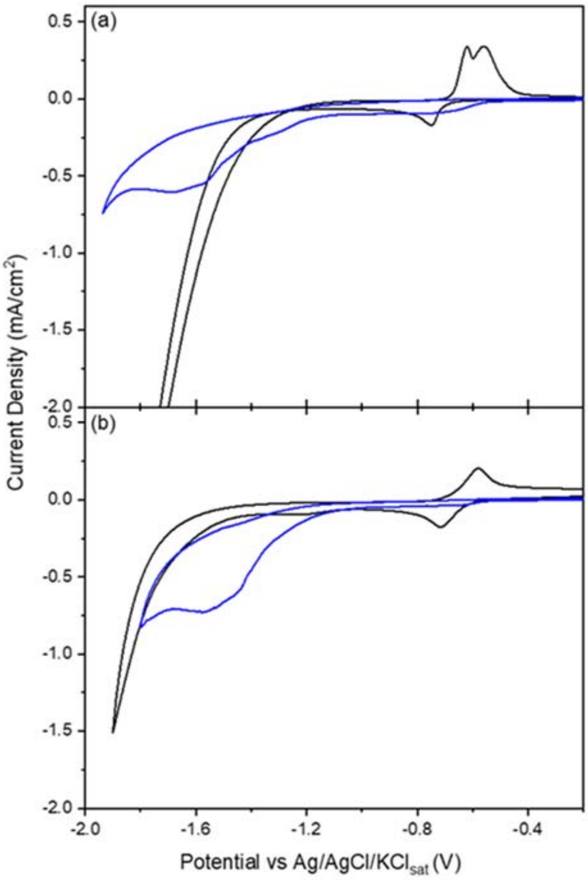

Figure S4. Cyclic voltammograms on GC electrode of 1 mM complex [1] in purely aqueous solution containing: (a) 0.1 M [TBA][BF_4] under Argon (black plot) or under CO_2 (blue plot) and (b) 0.5 M [EMIM][BF_4] under Argon (black plot) or under CO_2 (blue plot). Scan rate = 0.01 V s^{-1}.

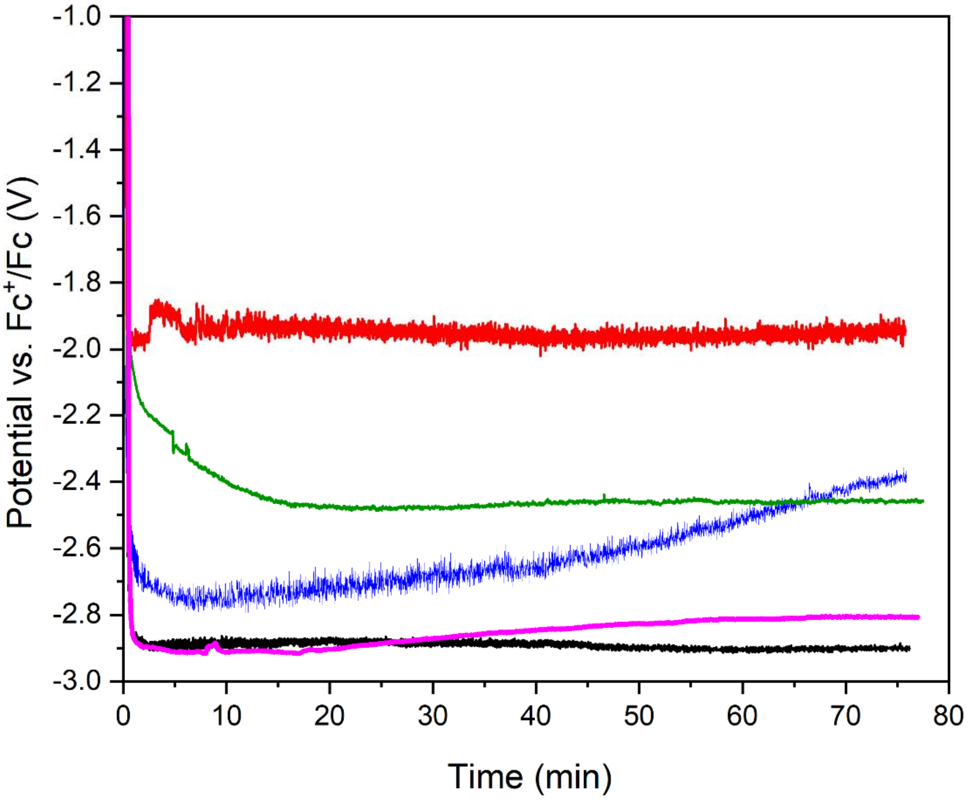

Figure S5. Constant current electrolysis (CCE) at -3.33 mA/cm^2 of 1 mM complex [1] in acetonitrile solution under CO_2 in presence of: 5 % (vol.) H_2O and 0.5 M [TBA][PF_6] (black plot), 5 % (vol.) H_2O and 0.5 M [TBA][BF_4] (magenta plot) 5 % (vol.) H_2O and 0.5 M [EMIM][PF_6] (red plot) and 50 % (vol.) H_2O with 0.5 M [TBA][BF_4] (blue plot). Blank CCE at -3.33 mA/cm^2 in the absence of complex [1] under CO_2 in presence of: 5 % (vol.) H_2O and 0.5 M [TBA][PF_6] (green plot). Room temperature: 20 ± 2 °C, stirring rate: 400 rpm.

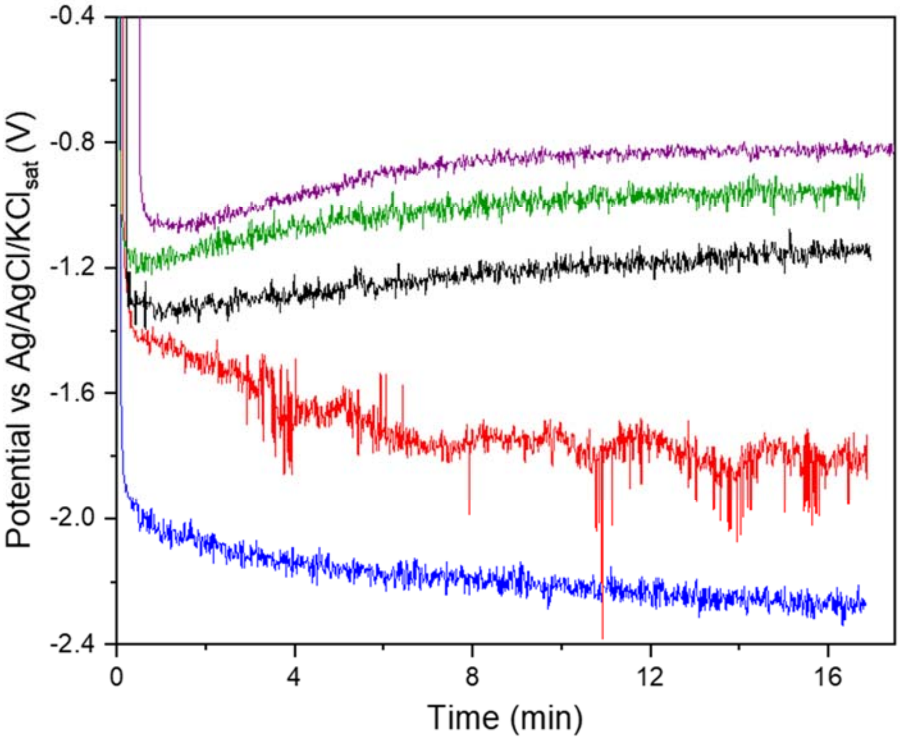

Figure S6. Constant current electrolysis (CCE) at -3.33 mA cm^{-2} of 1 mM complex [1] in acidic aqueous solution under CO_2 in presence of: 0.1 M [TBA][BF_4] (blue plot), 0.5 M [EMIM][BF_4] (red plot), 0.1 M [TBA][BF_4] and 0.1 M acetic acid (pH=2.5) (black plot), 0.1 M [TBA][BF_4] and 0.1 M acetate buffer (pH = 3.8) (green plot) and 0.1 M [EMIM][BF_4] and 0.1 M acetate buffer (pH = 3.8) (purple plot). Room temperature: 20 ± 2 °C, stirring rate: 400 rpm.

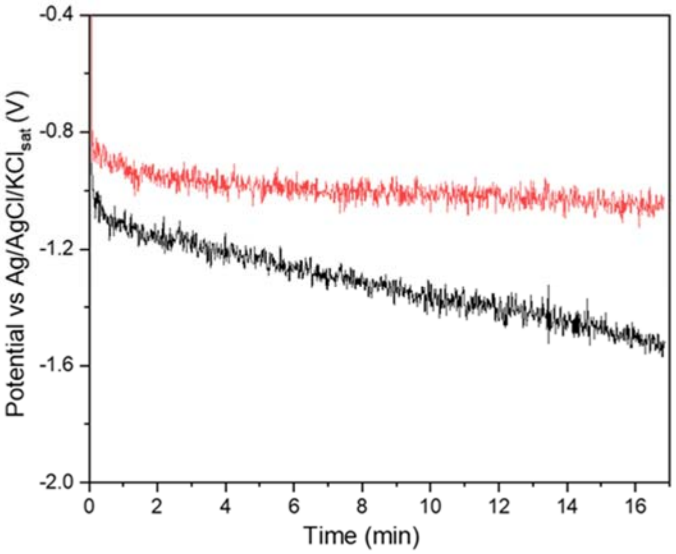

Figure S7. Control experiments: Constant current electrolysis (CCE) at -3.33 mA cm^{-2} in 0.1 M [TBA][BF_4] + 0.1 M acetate buffer (pH = 3.8) aqueous solution in the presence of only CO_2 (black plot) or 1 mM complex [1] and Ar (red plot). Room temperature: 20 ± 2 °C, stirring rate: 400 rpm

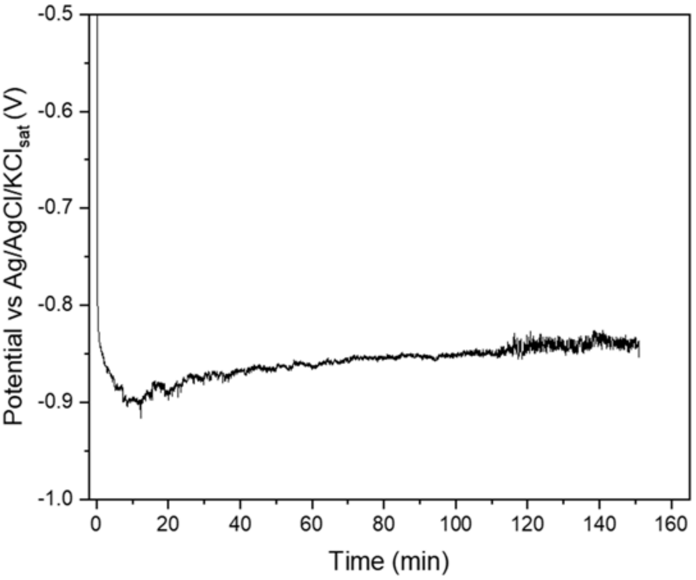

Figure S8. Long term constant current electrolysis (CCE) at -3.33 mA cm^{-2} of 1 mM complex [1] in aqueous solution under CO_2 in presence of: 0.1 M [TBA][BF_4] + 0.1 M acetate buffer (pH = 3.8). Room temperature: 20 ± 2 °C, stirring rate: 400 rpm

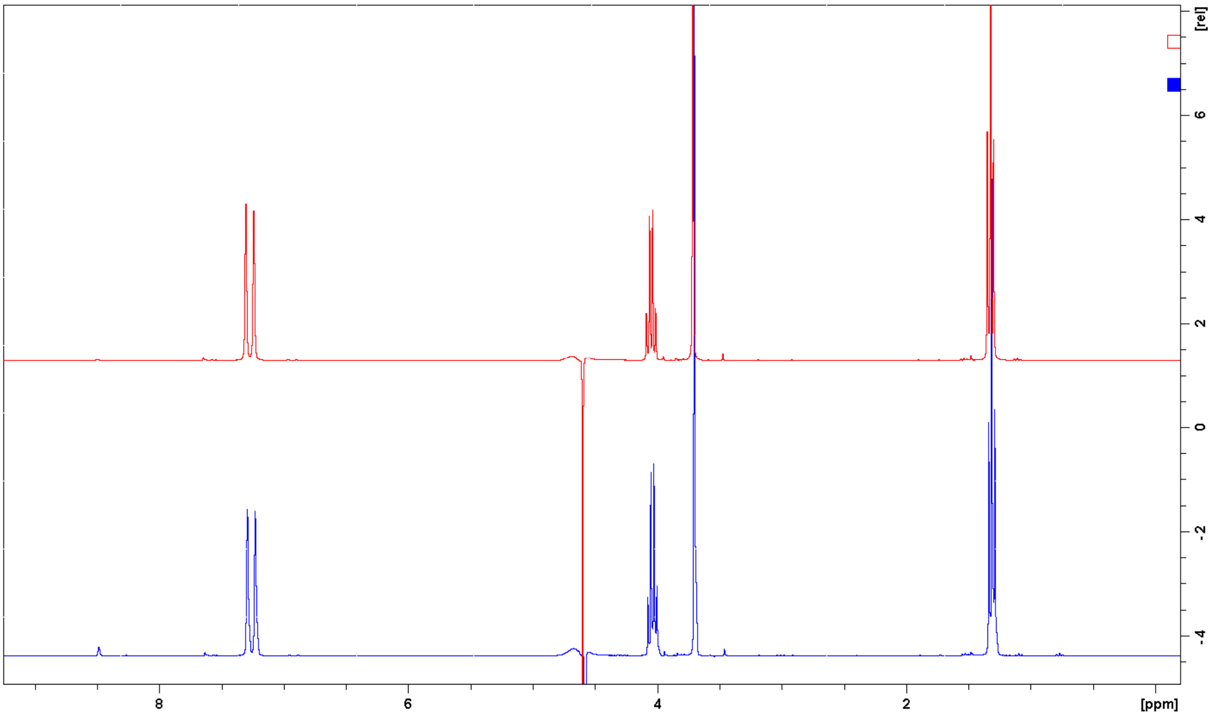

Figure S9. ^{1}H NMR (300 MHz, D_2O) of Entry 1 in Table 3 (1 mM complex [1] and 0.5 M $EMIMBF_4$ in H_2O under CO_2) before (red plot) and after CCE (blue plot) for a total charge of 10 C.

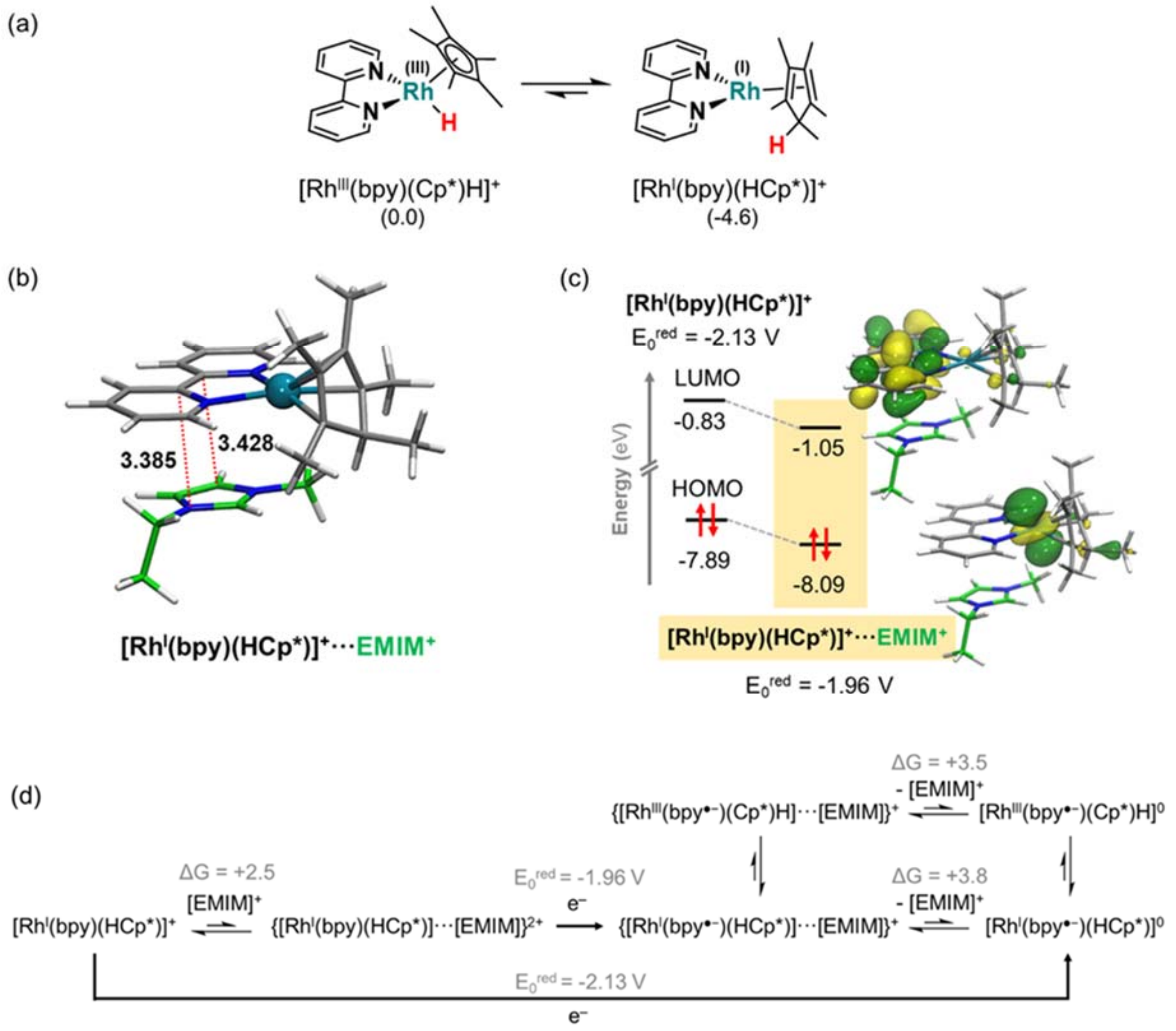

Figure S10. a) Proton/hydride tautomerism in the protonated form of the catalyst. Relative Gibbs free energies in parenthesis are given in kcal mol^{-1}. b) Optimized geometry for the non-bonding interaction between the [Rh^{I}(bpy)(HCp*)]$^{+}$ catalyst and [EMIM]$^{+}$. Key distances are shown in Å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

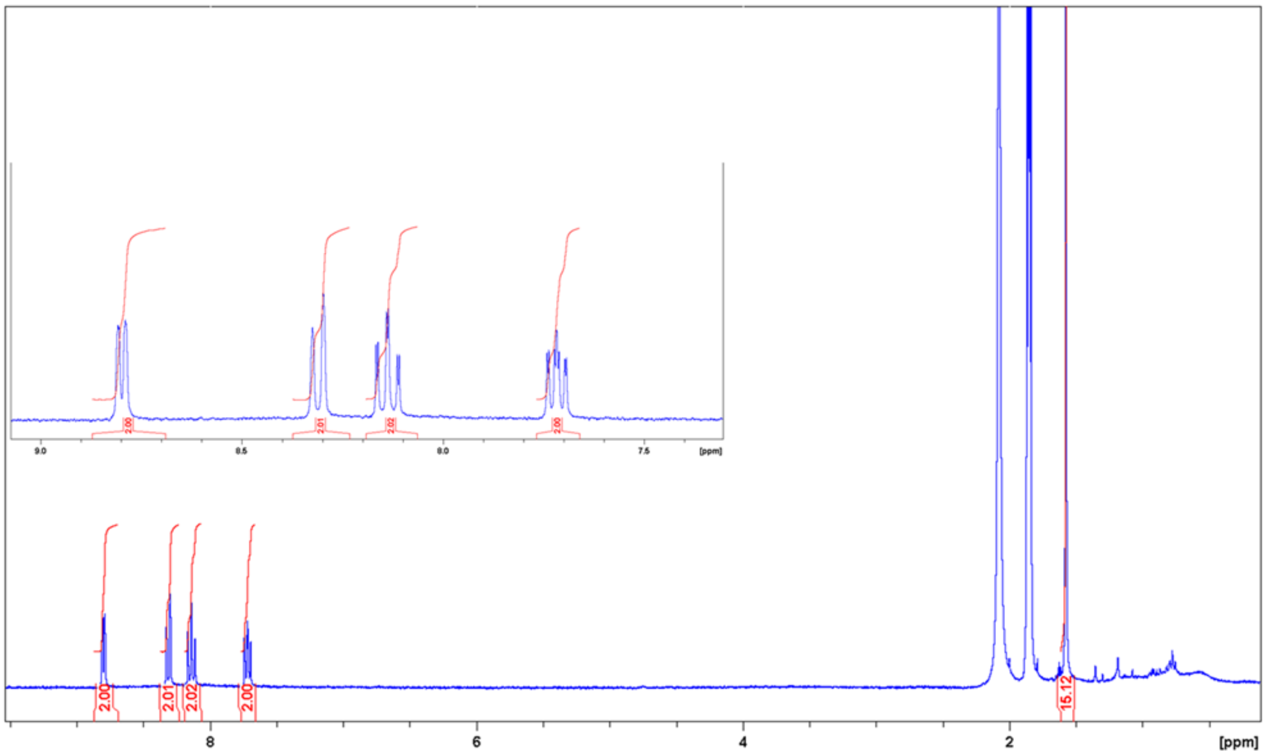

Figure S11. ^{1}H NMR (300 MHz, CD_3CN) of synthesized [Rh(bpy)(Cp*)Cl]: δ/ppm, 1.61 (s, 15H), 7.71 (ψt, J = 7.2 Hz, 2H), 8.13 (dt, J = 7.7 Hz, 2H), 8.30 (d, J = 8.0 Hz, 2H), 8.78 (d, J = 5.5 Hz, 2H).

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.