Supplementary Information for

Electrochemical Oxidation of H_2 Catalyzed by Ruthenium Hydride Complexes Bearing P_2N_2 Ligands With Pendant Amines as Proton Relays

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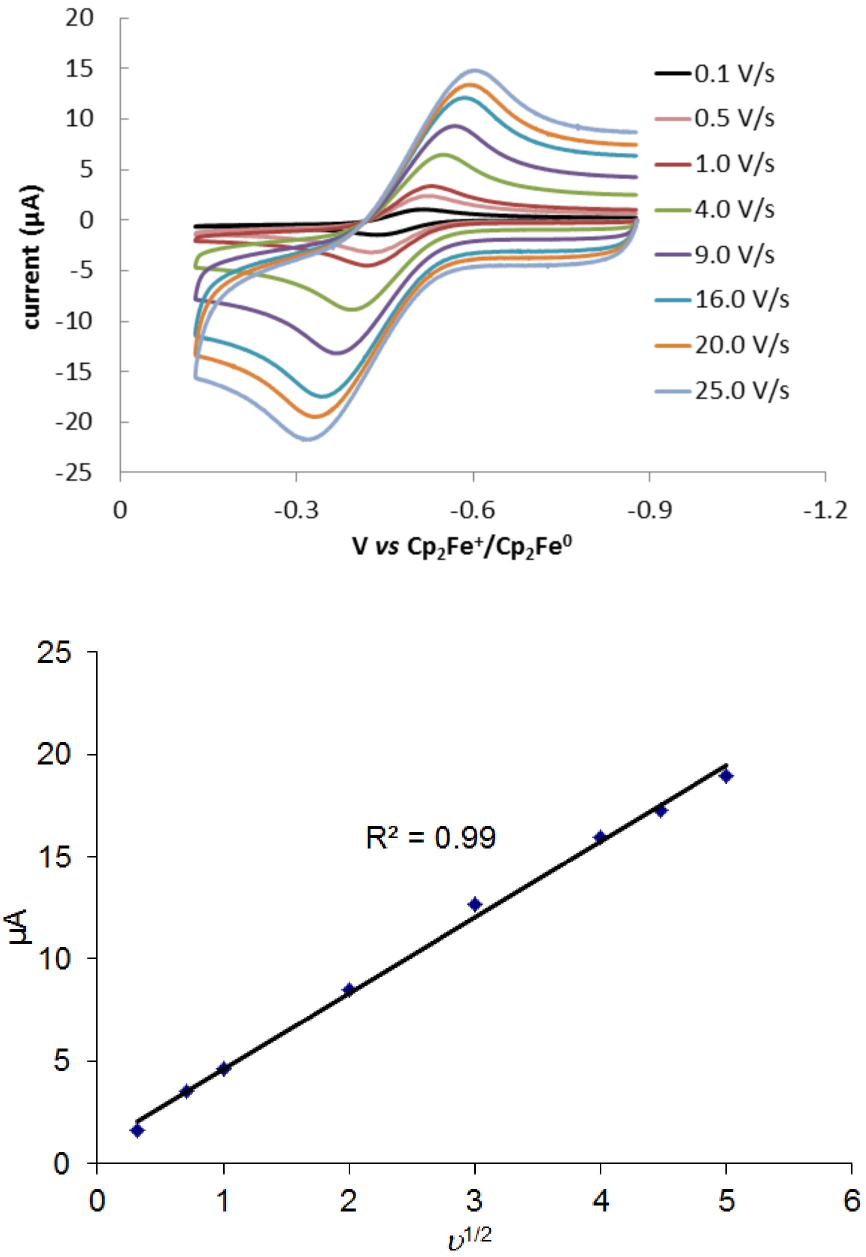


Figure S1. Cyclic voltammograms of **1-Cl** recorded at various scan rates (top), 0.1 - 25 V/s; electrolyte, 0.1 M $^{n}Bu_4NB(C_6F_5)_4$ in PhF; under Ar (1.0 atm). Plot of i_a versus the root of scan rate (bottom). A linear plot indicates the electrochemical process is under diffusion control.

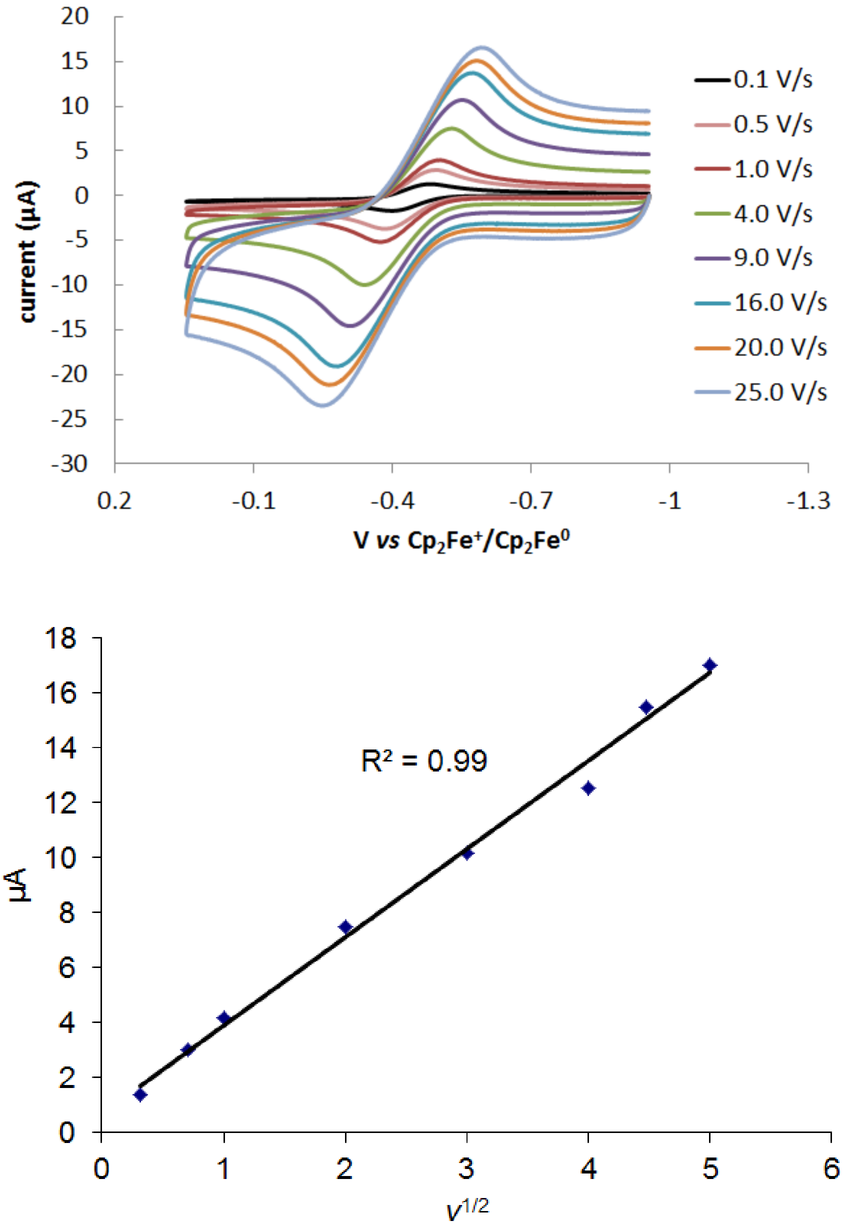


Figure S2. Cyclic voltammograms of **2-Cl** recorded at various scan rates (top), 0.1 - 25 V/s; electrolyte, 0.1 M $^{n}Bu_4NB(C_6F_5)_4$ in PhF; under Ar (1.0 atm). Plot of i_a versus the root of scan rate (bottom). A linear plot indicates the electrochemical process is under diffusion control.

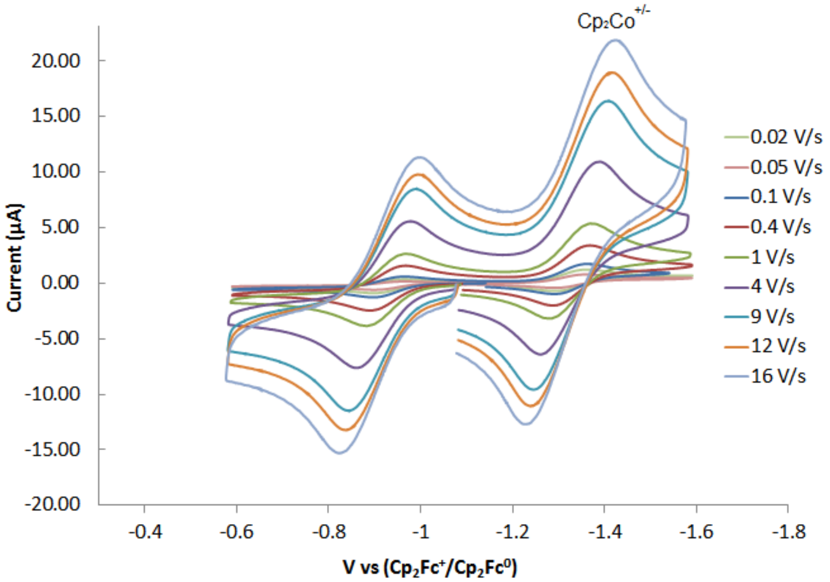


Figure S3. Cyclic voltammograms of **1-H** recorded at various scan rates (top), 0.1 - 16 V/s; electrolyte, 0.1 M ^{n}Bu$_4$NB(C$_6$F$_5$)$_4$ in PhF; under Ar (1.0 atm); Cp$_2$CoPF$_6$ (-1.33 V) as internal reference.

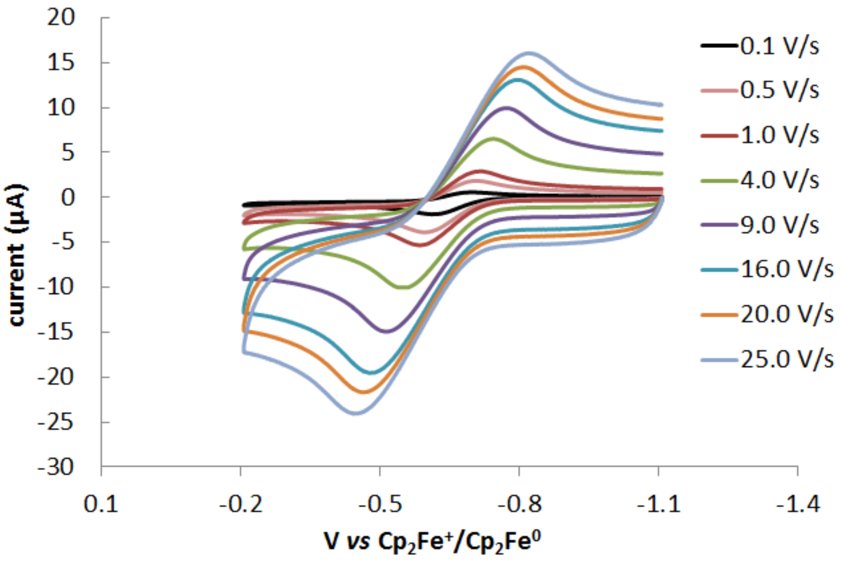


Figure S4. Cyclic voltammograms of **2-H** recorded at various scan rates (top), 0.1 - 16 V/s; electrolyte, 0.1 M ^{n}Bu$_4$NB(C$_6$F$_5$)$_4$ in PhF; under Ar (1.0 atm).

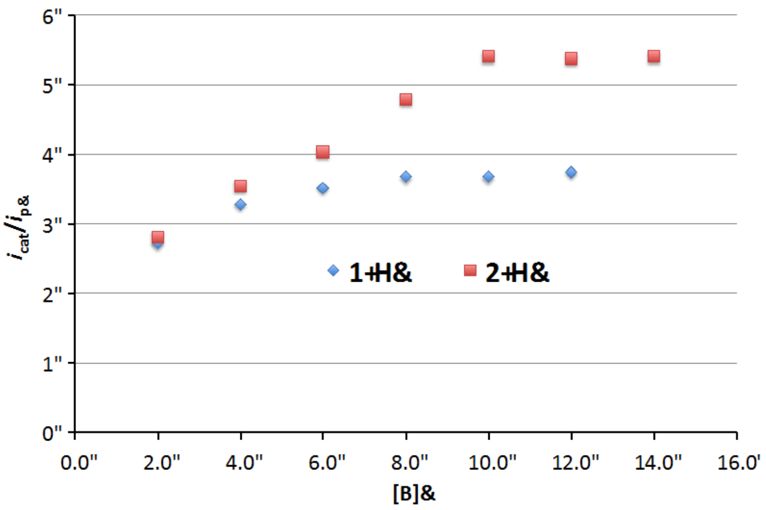


Figure S5. Plots of i_{cat}/i_p versus DBU base concentration for **1-H** and **2-H**. Conditions: 1.0 mM solution of **1-H** or **2-H** in PhF at 22 °C under 1.0 atm H_2 at 20 mV/s scan.

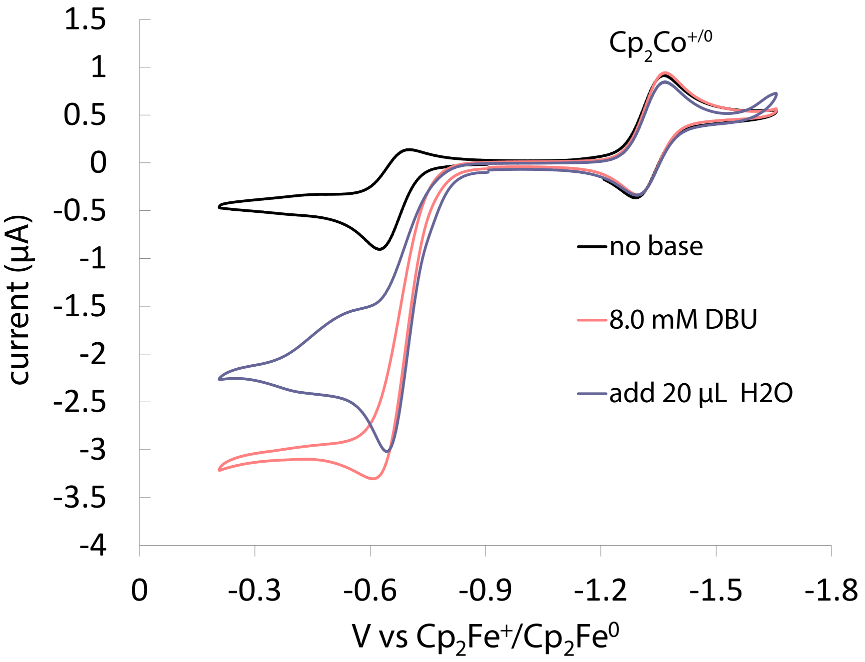


Figure S6. Electrochemical H_2 oxidation by **1-H** before and after saturation of the solution with H_2O (adding 20 μL H_2O into 1.0 mL PhF solution). Conditions: 1.0 mM **1-H**; 0.1 M $^{n}Bu_4NB(C_6F_5)_4$; 1.0 atm H_2; scan rate, 20 mV/s; 22 °C; Cp_2CoPF_6 (-1.33 V) as internal reference.

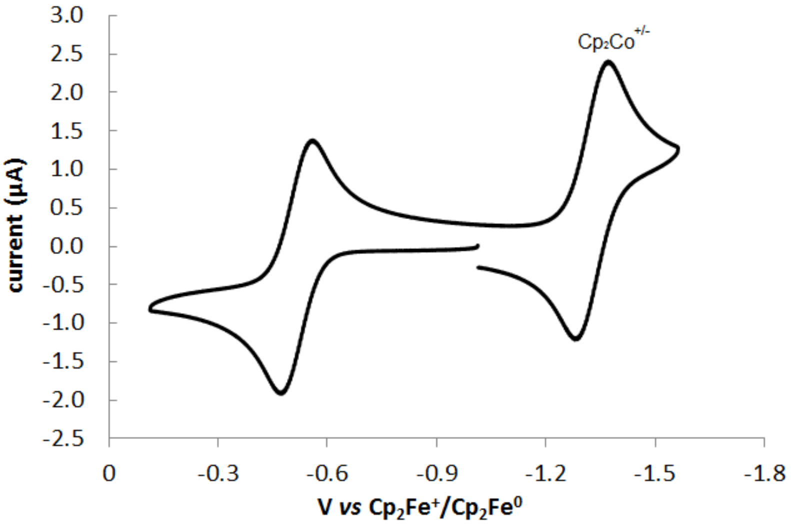
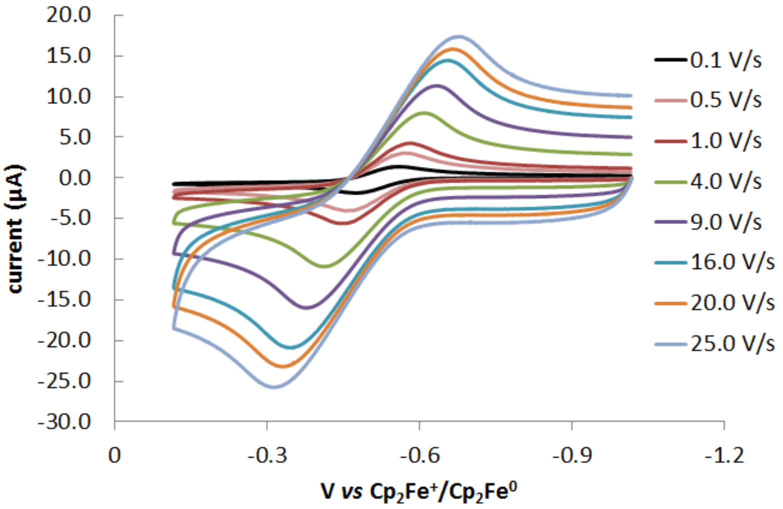


Figure S7. Cyclic voltammograms of Cp*Ru(dmpm)Cl. Conditions: 1.0 mM; 0.1 M $^nBu_4NB(C_6F_5)_4$; under 1.0 atm Ar; scan rate, 100 mV/s; Cp_2CoPF_6 (-1.33 V) as internal reference.



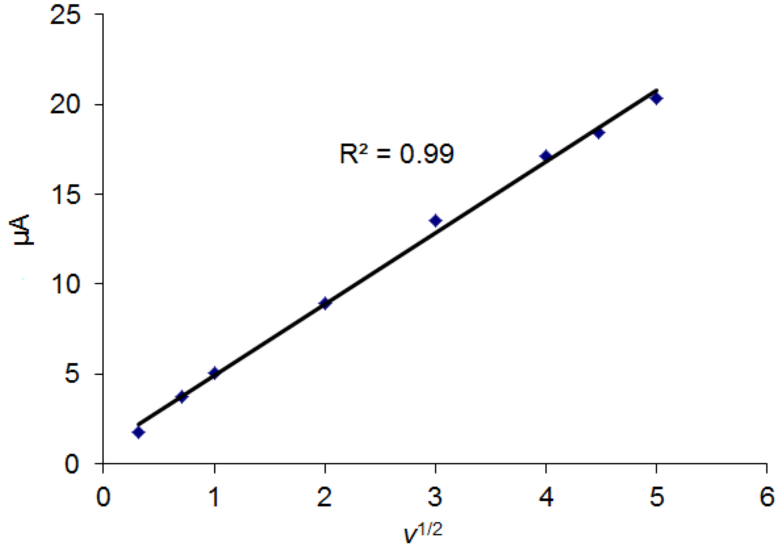


Figure S8. Cyclic voltammograms of Cp*Ru(dmpm)Cl recorded at various scan rates (top), 0.1 - 25 V/s; electrolyte, 0.1 M $^{n}Bu_4NB(C_6F_5)_4$ in PhF; under Ar (1.0 atm). Plot of i_a versus the root of scan rate (bottom). A linear plot indicates the electrochemical process is under diffusion control.

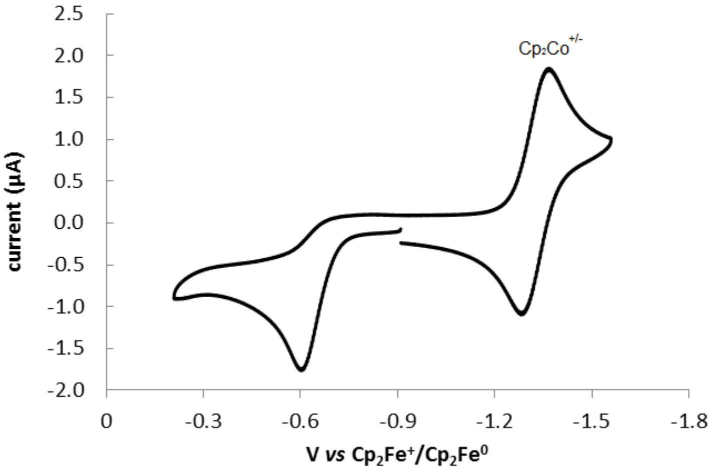


Figure S9. Cyclic voltammograms of Cp*Ru(dmpm)H recorded at various scan rates (top), 0.1 - 25 V/s; electrolyte, 0.1 M $^{n}Bu_4NB(C_6F_5)_4$ in PhF; Cp_2CoPF_6 (-1.33 V) as internal reference; under Ar (1.0 atm).

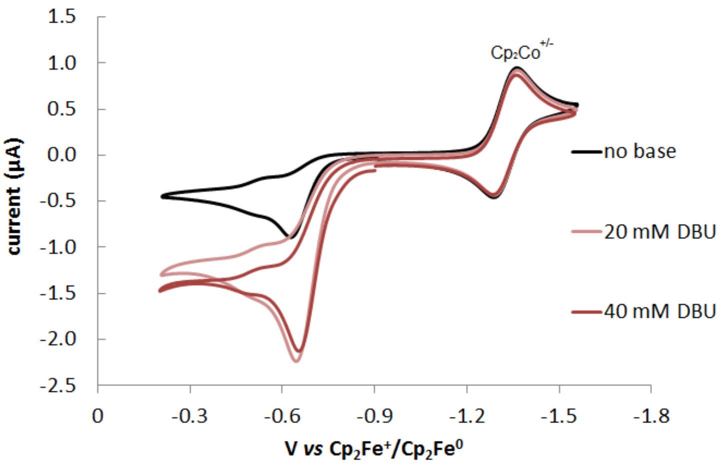
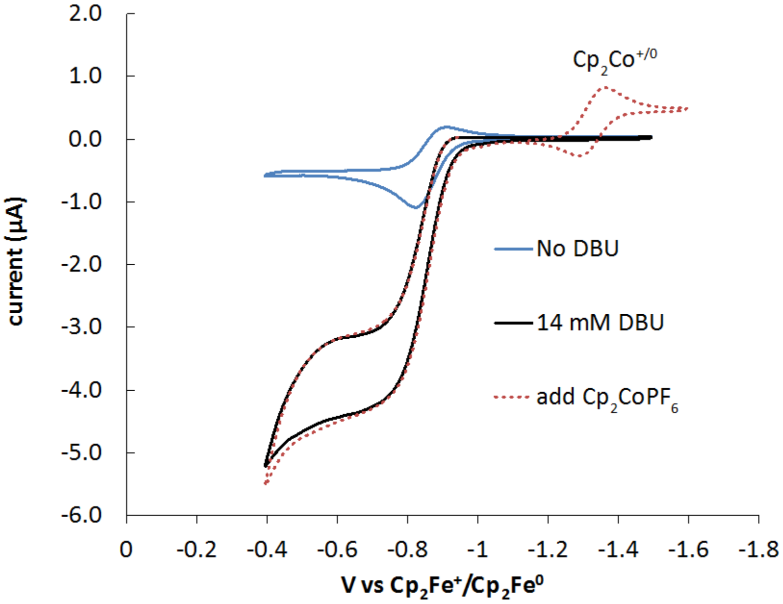


Figure S10. Attempted electrochemical H_2 oxidation by Cp*Ru(dmpm)H under 1.0 atm H_2 with increasing concentrations of DBU as indicated in the legend. Conditions: 1.0 mM analyt of Ru-complexes; 0.1 M $^{n}Bu_4NB(C_6F_5)_4$; 1.0 atm H_2; scan rate, 20 mV/s; 22 °C; Cp_2CoPF_6 (-1.33 V) as internal reference.



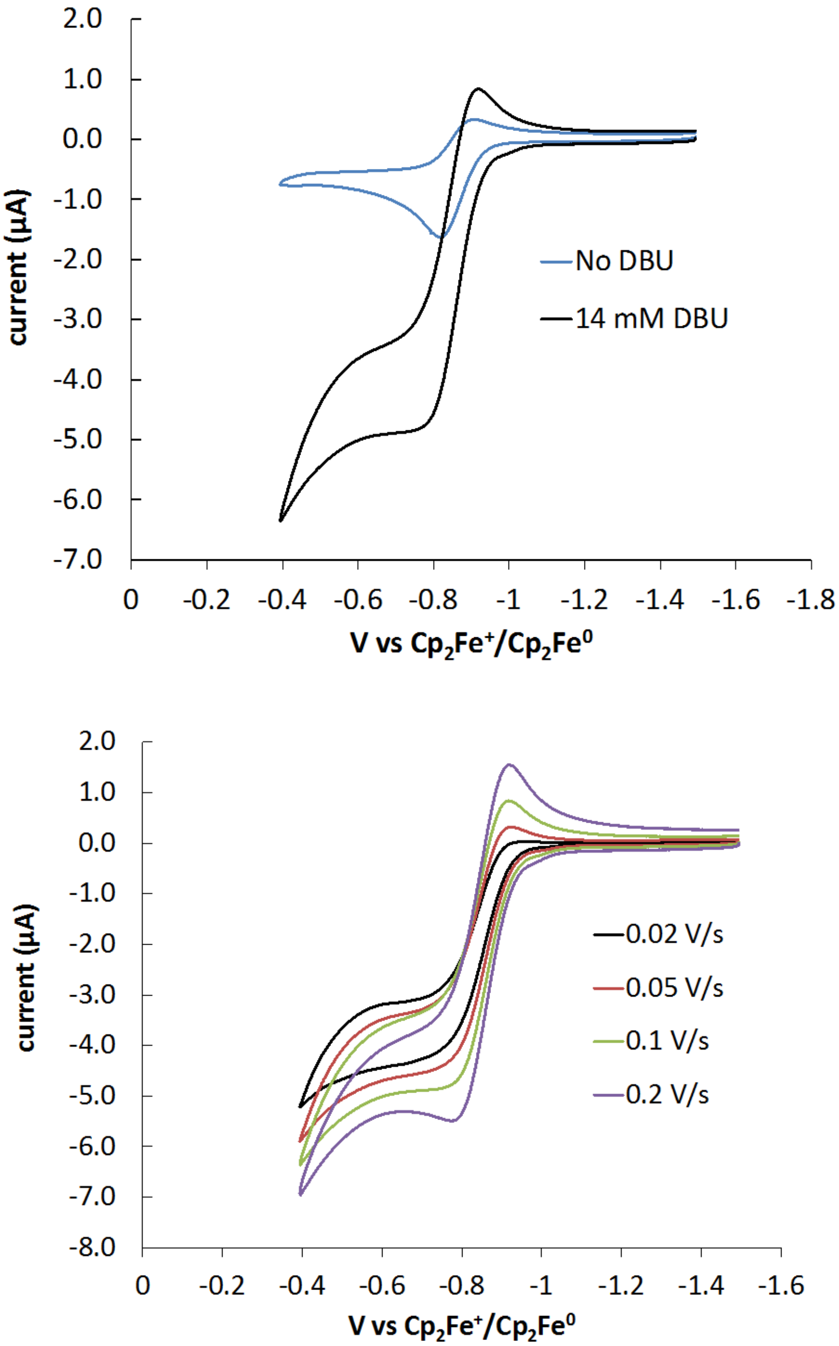


Figure S11. Electrochemical H_2 oxidation by **2-H** under 1.0 atm H_2 in the presence of 14 mM DBU. (top) Cyclic voltammograms recorded at 0.02 V/s: the overlapped catalytic waves (black trace and red dot trace) confirmed the presence of the internal reference, Cp_2CoPF_6 (-1.33 V), has no influence on the catalytic current for the oxidation of H_2. (middle) Cyclic voltammograms recorded at 0.1 V/s. (bottom) Cyclic voltammograms for the oxidation of H_2 by **2-H** recorded at 0.02 V/s, 0.05 V/s, 0.1 V/s and 0.2 V/s for a same solution under catalytic conditions (1.0 atm H_2

in the presence of 14 mM DBU). Conditions: 1.0 mM **2-H**; 0.1 M $^{n}Bu_4NB(C_6F_5)_4$; 1.0 atm H_2; scan rate, 20 mV/s; 22 °C; Cp_2CoPF_6 (-1.33 V) as internal reference.

Calculation of thermodynamic equilibrium potential of $[DBU\text{-}H]^+/DBU$ for H_2 oxidation. The poor solubility of $[DBU\text{-}H]^+$ precludes direct experimental measurement of the thermodynamic equilibrium potential by the open circuit potential method developed by our group.[1-3] Therefore, the thermodynamic equilibrium potential of $[DBU\text{-}H]^+/DBU$ was estimated.[2] The relationship of thermodynamic dynamic equlibrium potential for diferent $[B\text{-}H]^+/B$ can be expressed as equation S2.

$$E^{\circ}_{([B-H]^{+}/B)} = E^{\circ}_{H^{+}} - \left(\frac{2.303RT}{F}\right) pK_{a,\,([B-H]^{+})} \qquad (equation\ S1)$$

$$E^{\circ}_{([B'-H]^{+}/B')} = E^{\circ}_{([B-H]^{+}/B)} - \left(\frac{2.303RT}{F}\right) \Delta pK_{a} \qquad (equation\ S2)$$

Since $E^{\circ}_{[Et_3N\text{-}H]^{+}/Et_3N}$ in PhF was determined as -1.01 V *vs* $Cp_2Fe^{+/0}$, $E^{\circ}_{[DBU\text{-}H]^{+}/DBU}$ in PhF can be calculated using ΔpK_a ($[DBU\text{-}H]^+$ - $[Et_3N\text{-}H]^+$), 5.52, in CH_3CN:

$$E^{\circ}_{([DBU-H]^{+}/DBU)}$$
$$= E^{\circ}_{([Et_3N-H]^{+}/Et_3N)} - \left(\frac{2.303RT}{F}\right) \Delta pK_{a} = -1.31\ V$$

Overpotential (η) calculations for 1-H and 2-H.

$$\eta = Operating\ potential - E^{\circ}_{([DBU-H]^{+}/DBU)} \qquad (equation\ S3)$$

The operating potential is defined as the middle point of the catalytic wave for the H_2 oxidation, -0.82 V and -0.85 *vs* $Cp_2Fe^{+/0}$ for **1-H** and **2-H** respectively.

For **1-H**,

$$\eta(DBU) = -0.71 - (-1.31) = 0.60\ V$$

For **2-H**,

$$\eta(DBU) = -0.85 - (-1.31) = 0.46\ V$$

References

(1) Pool, D. H.; Stewart, M. P.; O'Hagan, M.; Shaw, W. J.; Roberts, J. A. S.; Bullock, R. M.; DuBois, D. L. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15634-15639.
(2) Liu, T.; DuBois, D. L.; Bullock, R. M. *Nat. Chem.* **2013**, *5*, 228-233.
(3) Roberts, J. A. S.; Bullock, R. M. *Inorg. Chem.* **2013**, *52*, 3823-3835.